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IONIC VOLUMES, COMPRESSIBILITIES AND ELECTROSTRICTION OF ELECTROLYTE SOLUTIONS

by

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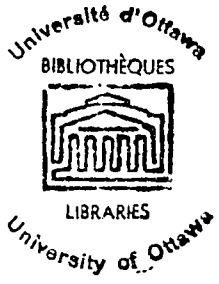

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PREFACE

Since the beginning of quantitative physical chemistry, the study of electrolyte solutions has occupied a central position in that subject and constituted the early basis of electrochemistry. Early views on the electrical nature of salts were somewhat clarified by understanding of the nature of dissociation, conductance and ionic migration. Later studies indicated that electrolytic solutions possessed a high-degree of non-ideality and these results led to the first satisfactory ideas about ionic interaction effects and non-ideal solutions as discussed by Ostwald, Sutherland and Bjerrum, and more quantitatively by Milner, and in a more useful form by Debye and Hückel.

Brønsted, in an early paper, stressed the specificity of ionic behaviour in electrolyte solutions and although this view was not readily accepted at that time, it is now well known that electrolytes in solution exhibit a surprisingly high degree of specific behaviour at moderate and higher concentrations, a situation which is principally associated with the ion-solvent interactions.

One of the best means of observing the specific nature of ion-solvent interaction is by measuring the volumes of salts in solution. Partial molal volumes of ions $\bar{V}_i$ reflect (a) the extent of electrostriction of solvent when the infinite dilution value $\bar{V}_i^o$ is compared with the intrinsic volume of the ion in the salt lattice or in the gas phase; and (b) at finite concentration, the pressure dependence of the non-ideal

chemical potential of the ions. The volume studies may be carried out in a related manner by examining the compressibility properties of electrolyte solutions. The coefficient of compressibility indicates the relative volume change of solution with pressure and consequently provides complementary information on the extent and nature of ion-solvent interaction.

The theoretical problem of volume change associated with the process of solution of an ion has been developed along two distinct lines; firstly, the volume of the ion itself may change, e.g., if it enters the solution from the gas phase or from another phase in which the internal pressure is different from that in the solution considered; secondly the ion may influence the local volume of the solvent by polarisation forces. Effects of the second type are more fully discussed in the treatment described in the present thesis. The particular model chosen avoids the difficulties of previous calculations by eliminating integration of the electrostatic volume change all the way up to the ion where the continuum model on which earlier theories have been based is least applicable. Using the above results, the compressional entropy associated with the electrostricted solvent volume is calculated in a more sophisticated manner than that in a related treatment by Latimer and Kasper in 1929.

The principal part of the original work described in this thesis is experimental in nature and is concerned with the measurement of partial molal volumes and partial molar adiabatic compressibilities of tetraalkylammonium halide and alkylamine hydrogen halide salts. The former salts are of special interest

with regard to the structure promoting effects which their cations exhibit in water while the latter salts are of interest with regard to ionisation equilibria of bases and steric effects in hydration. The results obtained show that effects associated with structure promotion of solvent are important in aqueous solutions of these salts and the anomalously large negative linear concentration dependence of $\bar{V}$ of these salts is discussed in terms of mutual salting-in of the ions and other structural influences. The results of the volume studies for the tetraalkylammonium halide salts enable a new principle to be proposed for obtaining individual $\bar{V}_i^o$ values, based on a reasonably satisfactory experimental procedure with minimal à priori theoretical assumptions.

Solvation in ionisation processes of methylammonium ions is also discussed and it is shown that ΔS^o, ΔC_p and $\Delta \bar{V}^o$ of ionisation show unexpected behaviour. A more detailed summary of the original contributions is given in the section "Claims to Original Research".

Most of the work described in this thesis has been either published or is in course of publication, as indicated in the following list of papers:

1) Electrostriction in Aqueous Solutions of Electrolytes, J.E. Desnoyers, R.E. Verrall and B.E. Conway, J. Chem. Phys., 43, 243(1965).

2) Specificity in Ionic Hydration and the Evaluation of Individual Ionic Properties, B.E. Conway, R.E. Verrall and J.E. Desnoyers, Zeit.F. physik. Chem., (Leipzig), 230,157(1966) (paper prepared in honour of the 70th birthday of Professor H. Falkenhagen).

3) Ion: Solvent Size Ratio as a Factor in the Thermodynamics of Electrolytes, B.E. Conway and R.E.Verrall, J. Phys. Chem., in course of publication (1966); now accepted.

4) Partial Molal Volumes of Tetraalkylammonium Halides and the Assignment of Individual Ionic Contributions, B.E. Conway, R.E. Verrall and J.E. Desnoyers, Trans. Faraday Soc., in course of publication.

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ABSTRACT

A theory of electrostriction of solvent water near ions is developed. The treatment is based on a calculation of the effective pressure which would, in the absence of the field, cause the same change in volume as does the field. It is shown that when the dissolution process is from the crystalline phase, the electrostriction at small ions arises mainly on account of changes of effective volume of the solvent rather than from compression of the ion cavity in the dielectric. The change in solvent volume near ions can be related, using an appropriate molecular model, to the apparent change in the volume of the salt upon dissolution. This treatment avoids the difficulties of previous calculations where use of the Born equation involves an integration over a distance from the ion. Explicit approximate solutions for high-and low-field conditions, and a complete numerical solution for the effective pressure-field and field-volume relations are given.

A method for calculation of the compressional entropy associated with hydration of ions is proposed on the basis of the above electrostriction calculations, taking into account dielectric saturation and pressure dependence of dielectric constant. Relations of the electrostatic contributions to the entropy of hydration of ions to corresponding volume changes are investigated and it is shown that the statistical mechanical method of Eley and Evans and the method of Laidler and Pegis, allowing for dielectric saturation, give entropies of hydration that are in better agreement with experimental values.

The partial molal volumes $\bar{V}$ of a series of homologous tetraalkylammonium chlorides, bromides and iodides have been precisely measured by means of a differential buoyancy technique. The extrapolated values of $\bar{V}$ to infinite dilution give $\bar{V}^o$ data which are almost additive for successive homologues and enable the absolute individual partial g. ionic volumes of the halide ions to be estimated by a new principle to an accuracy of about 0.5 ml. $(g.ion)^{-1}$. The anomalously large negative concentration dependence of $\bar{V}$ is discussed in terms of mutual salting-in by the large cations and also salting-out due to the anion. Estimates of $\mathring{a}$ and $d \ln \mathring{a}/dP$ are also made. Non-electrostatic effects arising from the large differences in size between the cations and the solvent molecules are suggested as one of the reasons for the anomalous activity coefficient and partial molal volume behaviour. It is concluded that the hydrophobic character of these ions exerts a strong structural influence on the solvent water, as indicated in other ways in previous publications.

The partial molal volumes of some alkylamine hydrogen halides series have been studied with special reference to the role of solvation in the process of ionisation of methylammonium bases. It is shown that the change in volume associated with the ionisation is almost invariant as the degree of hydrophobic character of the cation is increased. The unexpected behaviour of ΔS^o, ΔC_p and $\Delta \bar{V}^o$ is discussed in terms of structural influences upon the solvent by the different species.

Partial molal adiabatic compressibility studies have been carried out on the homologous series of tetraalkylammonium bromides and iodides, methylammonium chlorides and methylamines.

The extrapolated values of $\phi_{K(s)}$ to infinite dilution give $\phi^{o}_{K(s)}$ data which confirm the suspected structure promoting effect of these salts upon solvent water structure; these results complement those obtained from the partial molal volume studies.

CHAPTER I

INTRODUCTION

1. The Importance of Solvation in Ionic Processes in Solution

i) General

The realisation of the exceptional importance of solvation in ionic processes in solution during the past half-century has led to such a large volume of research being carried out on ionised and non-ionised solutes in both polar and non-polar solvents that this subject must be regarded as one of the major fields of physical chemistry. In direct contrast to the case of unstable ions that are found in the gas phase when, for example, gaseous molecules are subjected to the influence of x-rays, certain molecules can dissociate into stable ions under the influence of or through reaction with a polar solvent. Similarly, most inorganic crystalline substances dissolve to a greater or lesser extent in such solvents although in most cases the free ions already exist in the crystal lattice. With few exceptions, e.g., the absorption of heat attending the dissolution of a number of salts in water, the visual and thermal effects that occur when a solute is dissolved in an ionising solvent seldom reflect the profound changes locally taking place.

More particularly, solvation effects are primarily involved in the following processes:

a) the solubility of salts in solvents;

b) the ionisation of acids and bases;

c) the electrode potentials of the elements;

d) the kinetics of reactions proceeding via polar or ionic transition states;

e) the salting-out of non-electrolytes by ions of salts;

f) the volume changes accompanying dissolution of salts;

g) the mobilities of ions at infinite dilution;

and are secondarily involved in the thermodynamics of ionic solutions where such solvation effects determine, in part, the activity and osmotic coefficients of electrolytes in solutions particularly at high concentrations (>1M), and influence the partial molal entropies, heat contents, heat capacities, and compressibilities of salts in solution. The effects noted in (a), (b), (c), (d), (e), (f), and (g) arise from ion-solvent interaction behaviour characteristic of infinite dilution conditions while in the cases of those properties of electrolytes depending on non-ideality at finite concentrations, solvation effects only influence these properties at moderate or high concentrations, e.g., in the activity coefficient-concentration relations.

Some of the following abnormal thermodynamic properties attending dissolution of strong electrolytes in water had interested many of the early chemists conducting work in this particular field. The abnormally low molar heat content change, as compared with the lattice energy, on dissolution of many strong electrolytes in water was one indication of the energetics

of the changes occurring in the dissolution process. A more significant factor is the anomalously small or negative volume change which occurs when a strong electrolyte, e.g., NaCl, is dissolved in water. The fundamental significance of this observation, if the contraction is attributed to the solvent alone, is that, effectively, high pressures of the order of 1000 atmospheres would be required to produce such effects. Historically, the starting point of the physical chemistry of ionic processes in solution may be traced to the discovery that a solution containing ions possesses, in contrast usually to the properties of its pure components, the ability to conduct electricity.

The factors mentioned above have been considered in a large number of papers in which the properties and behaviour of ions in solution have been discussed. The interpretation of the results has led to the proposal of conflicting models for the nature of the solvation process. The difficulties generally arise in the assessment of the effect of the ions on the solvent and in particular with regard to the solvent arrangement or, more specifically, the local structural changes occurring in the solvent as a result of the presence of the ions. In the following introduction, a brief critical review will be given in order to outline the relevance of solvation in ionic processes with particular regard to the theories which have been advanced to describe the more important properties of aqueous ionic solutions.

Most work on solvation relates to aqueous solutions.

This is perhaps unfortunate from a theoretical viewpoint, because, as will be considered later, the nature of liquid water itself is by no means fully understood. However, the importance of the problem is obvious, since ionic hydration* influences all equilibria and transport problems involving ions, and thus has a bearing on a wide variety of chemical and biochemical processes. It is immediately obvious that when a solute is put into a solvent medium, many of the properties of the solution will depend upon the forces of solute - solvent interaction that arise when the dissolution takes place. Only rarely can the solute-solvent interactions be ignored and they are, in fact, of great importance when the solute is ionic. The liquid state is much less well understood than either of the two other normal states of aggregation of matter, because they possess neither the well-defined molecular geometrical arrangement characteristic of solids nor the relative molecular freedom characteristic of gases; it might therefore be thought that consideration of liquid solutions presents intractable problems. However, certain properties of solutions exist (namely the so-called 'colligative' properties which depend only upon the number of molecules per unit volume and not on their nature) which can be treated limitingly without any assumptions concerning the interactions between the solute and solvent. The laws of dilute solutions are well known and although they are not always obeyed exactly, even at high dilutions, they can be modified to take into account interaction

* The word 'hydration' will be used synonymously with the word solvation when the solvent in question is water.

effects, e.g., the electrostatic forces operating between ions. Although the theory of interionic attraction is regarded as one of the great successes in the field of solution physical chemistry, it sometimes can obscure (1) our ignorance of other aspects of solution chemistry.

Since the conception of the theory of ionic interactions in solution (2, 3, 14), it has been suggested that in polar solvents, solute ions are solvated. With particular regard to water, it can be seen from a molecular point of view that the charge distribution is such that a water molecule can become electrostatically associated with a positive or negative ion. Similarly, for any dipolar solvent, e.g., methanol, ethanol, etc., the same idea can be applied without obvious difficulties.

Early concepts of solvation were deficient, however, in one very important point insofar as little attempt was made to define clearly what was implied. Hydration was often used as a convenient means of accounting for discrepancies between observed properties and those predicted by some theory of solution, rather as 'association' was used to explain discrepancies in the behaviour of binary solutions of non-electrolytes and in early treatments of strong electrolytes. It was not surprising that a general discussion of solvation in 1907 (4) left the concept in a state of disrepute. In 1949, Bockris (5) pointed out that different authors and methods had led to the following figures for the hydration number of the sodium ion: 1,2,4,17,71

and clarified this situation by directing attention to the fact that various methods would be expected to give different kinds of results depending on the nature of the effects measured. In particular, primary hydration effects associated with nearest neighbour interactions between ions and the solvent were distinguished from less well characterised secondary effects.

The success of the interionic attraction theory of Debye and Hückel (3) in accounting for the properties of very dilute solutions of electrolytes produced a trend in favour of 'physical' rather than 'chemical' theories of solution. However, it became increasingly apparent that the consideration of the immediate surroundings of ions in terms of electrostatic interaction theories would also be necessary, particularly in regard to the thermodynamic properties of strong solutions of electrolytes. Thus, one of the earliest treatments of ion-solvent interaction was made by Born (6) in terms of a continuous dielectric model, in which the difference of electrostatic charging free energy for the ion in a vacuum ("gas phase") and in solution was deduced as

$$\Delta G = \frac{-(z_i e)^2}{2r_i}\left(1 - \frac{1}{\epsilon}\right) \qquad \text{I·1}$$

for an ion of charge $z_i e$, having a radius r_i solvated in a medium of dielectric constant ϵ. Various difficulties arise with this treatment, e.g., the evaluation of the relevant

radii to be used in the equation and the appropriate dielectric constant. Various improvements were considered empirically with regard to the ionic radius by Latimer, Pitzer and Slansky (7) and in a theoretical way by Laidler and Pegis (8), who also took into account the effect of dielectric saturation first considered by Webb (9). However, equation I.1 and its various modified forms (7,8,9) give the correct order of magnitude for the free energies of ionic solvation.

Since the solvent in the immediate vicinity of an ion is subjected to very large electrostatic fields and effective hydrostatic pressures, both of which modify the effective value of ϵ and no exact theory of these effects is available, the tendency has been to regard the dielectric constant as an adjustable parameter. Consequently, no advantage was gained in the early work by a 'physical' treatment rather than a 'chemical' one. It must be pointed out, however, that in the treatment of very dilute solutions ($< 10^{-3}$M) this problem does not arise, since the application of the interionic attraction theory is quantitatively successful. However, it is involved indirectly in theoretical treatments for observed properties of electrolyte solutions at higher concentrations and in the evaluation of individual energies of ionic solvation in relation to values deduced experimentally for pairs of ions.

ii) Relevance of Solvation in the Theory of Activity Coefficients

The nature of the deviations from ideal behaviour in very dilute electrolyte solutions are now reasonably well understood. Statistical mechanical studies (10) have confirmed the limiting theory of Debye and Hückel (3) for activity coefficients and the limit of the validity of the point-charge model has been set by Frank and Thompson (11) at about 10^{-3}M. Fuoss and Onsager (12) have recently shown that the necessity for using an adjustable parameter $\mathring{a}$ to allow for finite ion size effects in the Debye-Hückel theory can be eliminated. In their treatment, they showed that the integration of the Poisson-Boltzmann equation at small and large distances from the ion, using Bjerrum's parameter (13) for the critical distance of closest approach, gives an activity coefficient $\gamma_{\pm}$ for a 1:1 electrolyte in dilute solution which is limitingly independent of ion size. However, at concentrations greater than 10^{-3} molal, it becomes difficult to predict activity coefficients with a high degree of precision and specific effects begin to become significant.

At these higher concentrations, the effects of long-range coulombic forces become additively supplemented (in the chemical potential of the salt) by those associated

with the shorter range interactions characterising solvation. Many of the early estimates of hydration of solutes were based on observed deviations from Raoult's Law. In a concentrated solution, hydration of solute particles can appreciably decrease the effective molar fraction of free water, thus leading to such deviations. However, the earlier treatments of this problem neglected all other reasons for departure from ideal behaviour, in particular the interionic forces. Bjerrum (14) was the first to relate interionic forces and hydration effects and the same idea has since been pursued by many other workers.

The relation between hydration parameters and activity coefficients has been dealt with principally by Robinson and Stokes (15,16) and Glueckauf (17) using mole fraction and volume fraction statistics, respectively. It can be seen intuitively, in a qualitative way, that the net effect of interionic attractions and repulsions will be to decrease the free energy of the solute as compared with that of an assembly of non-interacting uncharged particles at the same concentration. This will tend to lead to an activity coefficient less than unity; on the other hand, the forces between ions and solvent dipoles will tend preferentially to hold the solvent in the solution, with a consequent decrease in the solvent vapour pressure from the ideal value and a corresponding increase in

the activity coefficient of the solute. Both of the treatments mentioned above allow for the effect of interionic attraction by the well known expression first derived * by Debye and Hückel (3) in 1923. Deviations from this expression are attributed at high concentrations to effective removal of free solvent water by hydration of the ions. In both treatments (15,16,17), the hydration numbers **and radii of the hydrated ions were treated as adjustable parameters and it was found possible to reproduce the observed activity coefficients by assuming that the adjustable hydration parameter was concentration independent, and (in Glueckauf's treatment) also independent of the ion of opposite charge which it is stoichiometrically associated. The main criticism of this treatment is that the hydration term depends upon a number of other factors, such

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* It is to be noted that the first treatment of interionic attraction effects was given by Milner (2) but the mathematical expression of his ideas was complex and received less attention than was due. Similarly, in 1915, Chapman used a one-dimensional Poisson-Boltzmann expression for dealing with the ionic atmosphere (diffuse - double layer) at an electrode. Debye and Hückel's treatment for ions is similar except that the three dimensional problem is involved.

**That is the number of water molecules associated with each ion. For a more detailed discussion of this parameter, see p. 52.

as local variation of the dielectric constant and any specific effects of the gegenion at high concentration; furthermore, the above treatments are based on the assumption that the coulombic contribution to the activity is given correctly by the Debye-Hückel theory for concentrations up to 4M which is certainly questionable (11). The values of hydration parameters evaluated from known experimental activity coefficients are in considerable disagreement with such data evaluated by other methods. Conway and Desnoyers (18) have shown that the contribution of the hydration term to the activity coefficient is more rational when mole fraction statistics are used. Similarly, Hildebrand (19) in a study of solutions of the very large non-polar and nearly spherical molecule octamethyl-cyclotetrasiloxane $(CH_3)_8Si_4O_4$ has shown that mole fraction statistics are, surprisingly enough, preferable to volume fraction ones in describing the entropy of solution of this large molecule. Since there is a considerable difference in the volumes of the solute and solvent molecules in this case a reversal of the preference indicated above would be expected. The implication, however, would appear to be that in considering the entropy of solution based on a quasi-crystalline solution lattice, the configuration of the solute and solvent molecules in the lattice is more important than their relative molecular size.

More recent studies on the prediction of activity coefficients at intermediate concentrations have been based on a rejection of the continuous ionic cloud model. Thus Frank and Thompson (20) have suggested that the spatial distribution

of ions varies with concentration and that a disordered lattice model would be more satisfactory at intermediate and high concentrations. This would lead to a cube-root law in salt concentration for $\ln \gamma_{\pm}$ and this relation was demonstrated by these workers (11, 20) for the concentration range of 0.001 to 0.1M. Such a quasi-lattice model would seem to be inadequate since it takes no account of thermal disturbance in the lattice and assumes that the forces are sufficiently large to maintain a regular pseudo-structure. This is equivalent to assuming that the principal average forces between ions are determined by the time average interionic distance. At moderate concentrations, any failure of such an assumption seems to be no more serious than the failure of the model of the ionic atmosphere under these conditions. Conway and Desnoyers (18) extended the treatment of Frank and Thompson (11, 20) and showed that the logarithms of the experimental molal activity coefficients of a large number of salts, corrected for hydration and cavity salting-out effects could be expressed as a linear function of $C^{1/3}$ up to 1M. They regarded this corrected activity coefficient as representing the coulombic contribution associated with the ionic interaction effects. The latter effect would then be expected to be linear in $C^{1/3}$. The results therefore demonstrate the applicability of Frank and Thompson's (11,20) disordered lattice model to higher concentrations than were originally considered.

The importance of ion-solvent interactions in contributing to the non-ideal free energy of electrolyte solutions and

hence in modifying the activity coefficients of concentrated solutions, has been recognised for some time but unfortunately an exact theory which can lead to quantitative agreement with experiment for any salt at intermediate and high concentrations has not yet been formulated. The main reasons for this are the lack of any final satisfactory model for ions in water solutions and the difficulty of interpreting thermodynamic properties of ions in solution in terms of hydration effects.

iii) Relevance of Solvation in the Theory of Conductance

The relevance of solvation to transport phenomena in electrolytes is pertinent to theories describing the movement of molecules or ions in a solvent whether the motion be due to diffusion, or electrical or centrifugal forces. Thermodynamic methods have the advantage that the underlying theory is, in some ways, better understood than that for transport phenomena. However, for any detailed interpretation, statistical mechanical approaches are necessary which are of limited value for the liquid state. Nevertheless, transport properties may give information about the interactions in the immediate neighbourhood of an ion, whereas study of any thermodynamic quantity necessarily gives an overall measure of the mutual interactions between particles of the components of the system.

Conductance measurements are perhaps the best experimental means available for studying the interaction of free ions with polar molecules. There is an abundance of accurate experimental data, at least for low concentrations, in a considerable number of solvents. The equivalent conductivity of strong

electrolytes at low concentrations is found to be accurately a linear function of the square root of concentration, decreasing as the concentration increases. Extrapolation to zero concentration yields the limiting equivalent conductivity Λ^o, (and hence with transference numbers, the ionic equivalent conductivities λ^o) and the equivalent conductivity Λ, at very low concentrations, can be represented by the expression $\Lambda = \Lambda^o - A\sqrt{c}$. According to Kohlrausch's (21) law of the independent migration of ions, each species of ion present contributes at infinite dilution a characteristic fraction to the total equivalent conductivity, regardless of the nature of the other ions present. The limiting mobilities are determined by measurements of transport numbers. It is in the interpretation of these limiting mobilities that solvation effects are found to be important. In general, the mobilities of polyvalent ions are less (on an equivalence basis) than the mobilities of monovalent ions and for ions of a given charge, the smaller ions often have a lower mobility than that of larger ions. Intuitively it would be expected that the polyvalent ions, of much smaller crystallographic size than the monovalent ions, would have greater mobilities. However, their mobilities are some 10-20 equivalent conductivity units less in the case of bivalent ions than in the case of monovalent ones. The mobilities of bivalent cations furthermore cover only a small range of values and this is probably because they all have a relatively firmly attached *layer

*I.e., the water molecules in the first layer are bound with quite large electrostatic energies. They are, however, not strongly bound in a kinetic sense since H_2O exchange is relatively rapid except at certain transition metal ions such as $Cr(H_2O)_6^{+++}$(22).

of solvent molecules and more weakly coordinated ones in a second layer.

Similarly the mobilities of the alkali-metal cations are in the inverse order of their crystallographic radii, which is of course in accordance with the general expectation that ions of the greatest effective surface charge density will be most strongly hydrated. Generally it may be noted that specific solvent effects strongly influence the conductance of small ions.

At infinite dilution, the steady velocity of ions in a unit field is usually calculated by applying Stokes' Law so that the ionic velocity v is related to the charge $z_i e$ and the field E by

$$z_i eE = (6\pi\eta r_s)v \qquad \text{I·2}$$

where v is the ionic mobility, (E = 1V $cm.^{-1}$) and r_s can be deduced from the measured λ^o for the ions. Various interpretations are then possible in terms of the Stokes' volume $\frac{4}{3}\pi r_s^3$ in relation to the crystallographic ionic volume $\frac{4}{3}\pi r_i^3$. The difference of volume $\frac{4}{3}\pi(r_s^3 - r_i^3)$ is usually attributed to the hydrodynamically significant volume of solvent solvating the ion and carried with it in the conductance process. Several problems arise in this kind of interpretation:

a) the relevant viscosity to be used in the Stokes' Law expression (since the local viscosity may not be identical with that of the bulk);

b) the validity of the factor 6π

and c) the conceptual validity of a law for macroscopic spheres applied to a microscopic situation. Nevertheless, the law seems suprisingly enough to apply semi-quantitatively to ions in solution (cf. Walden's Rule) and the hydration numbers which can be deduced from ionic mobilities are usually in moderate agreement with the values obtained by those other methods which may be expected to give the primary hydration number (23).

Similar factors determine the role of solvation in ionic diffusion coefficients D since, in general the limiting λ^o and D^o are related by the Nernst-Einstein relation

$$D^o = \frac{RT}{10^7 |z| F^2} \lambda^o \qquad \text{I•3}$$

iv) Relevance of Solvation in the Theory of Salting-Out and Solubility

A direct thermodynamic method of relating the effect of solvation to the equilibrium properties of ionic solutions is concerned with the interpretation of salting-out of non-electrolytes by added electrolytes. If solvent is associated with the ions, there will be a diminished activity of the free solvent and hence less effectively available to dissolve the non-electrolyte so that the extent of solvation can be calculated from the observed solubility decrease.

An electrostatic theory of salting-out was given by Debye and McAulay (24) and Debye (25) in which the self-energy

of the ion was considered in terms of Born's equation. The salting-out was deduced in terms of the difference in the Born charging energy for the ion brought about by the change of dielectric constant resulting from the presence of the non-electrolyte solute. Salting-out was predicted if the dielectric increment for the non-electrolyte solute was negative. A continuum model for the dielectric is involved in this theory.

A more molecular approach was given by Butler (26) who calculated the distribution of solvent and non-electrolyte about the ion in terms of the difference of electrostatic polarisation energy of the solvent and solute. However, an oversimplified model for calculation of the polarisation effects was used, and the local structure of the hydrated ion, which can be important, was not considered. Basically, however, the approach was a good one and led to further developments of the theory by similar approaches.

A more general thermodynamic approach was given by McDevit and Long (27) but none of these theories including various improvements to these approaches (28,29,30) are completely acceptable. Conway, Desnoyers and Smith (31) added some improvements to the original Debye (25) theory, of which the most important were (a) the quantitative introduction of dielectric saturation effects and (b) the allowance for the existence of a discrete primary solvation shell about the ions. Improved agreement between the theoretical and

experimental results was obtained, and one of the new conclusions drawn in this paper was that salting-out may also be associated with some non-electrostatic structural effects.

Correspondingly, the solubility of an electrolyte itself is determined by the standard free energy of the process $M^+ A^-$(lattice) + solvent $\rightleftharpoons$ M^+(solution) + A^-(solution) and the free energies of solvation of the ions will determine, amongst other factors, the equilibrium solubility. In fact, the difference of solubility of a given salt in various solvents is a direct measure of the relative solvating powers of the solvent for the ions, except in cases where the solution species are to a substantial extent present as ion pairs.

v) Relevance of Solvation in Kinetic Processes in Solution

Solvation is involved in kinetic processes in solution particularly in cases of ion producing or removing reactions, or in reactions involving polar transition states and if the solvent participates in a reaction by combining with the "reactant solute", e.g., a solvolysis reaction (32,33,34). The rate of any process depends in part upon the energy of the transition state in relation to that of the initial state so that the way in which the initial reactants and the transition state are affected by interaction with the solvent will be one of the factors determining the velocity with which the process can occur (35,36,37,38). When the species are ionic, the

solvent-solute interactions and the ionic charge govern the rate of a reaction more rigidly than in the case of reactions between uncharged species. It can readily be seen that the magnitude of the ionic charge existing in the initial and the transition states can determine (a) the degree of local electrostriction in the solvent and (b) in part, the free energy (and associated entropy and enthalpy (37,38)) change associated with formation of the transition state from the reactants. Since an increase in electrostriction is usually accompanied by a loss of entropy, any kinetic process that involves an activation step from a situation of low electrostriction (little or no charge) to one of higher electrostriction (greater charge) will tend (on this account) to be relatively retarded. The converse statement also neccessarily follows. However, electrostatic <u>energy</u> effects will operate in the opposite direction.

Solvation is of similar importance with regard to activation controlled processes occurring at the electrode-solution interface in electrochemical kinetic processes. The energy of association of solvent molecules with the ions being discharged will determine, in part, the velocity of ion transfer and neutralisation at the electrode and will also govern the distance of closest approach of the ion to the electrode surface. This latter point is important with regard to the charge transfer step in the mechanisms postulated for many electrode processes and in the theories of the configuration of the double-layer (39,40).

vi) Relevance of Solvation in Acid-Base Ionisation Reactions

Finally, it should be mentioned that the thermodynamics of acid-base ionisation equilibria are closely involved with solvation effects which are most important when the solvent enters directly into the equilibrium, as in the case for acid ionisation of the type $AH^+ + B \rightleftharpoons A + BH^+$, where the base B is, in this case, the solvent.

If values of ionisation equilibrium constants of sufficient accuracy are available over a range of temperatures, the enthalpy change ΔH_o, the standard entropy change ΔS_o^o, and the change in molar specific heat ΔC_p can be obtained from such data. The assumption that ΔC_p remains constant over the temperature range studied (based on experimental evidence) allows the following three-constant equations to be derived

$$\ln K = \frac{\Delta H_o}{RT} + \frac{\Delta C_p}{R} \ln T + \frac{(\Delta S_o^o - \Delta C_p)}{R} \qquad I\cdot4$$

The best method of treating experimental data and the application of this method to carboxylic acid and amine cation systems in water, of the type

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \qquad I\cdot5$$

and

$$R_3NH^+ + H_2O \rightleftharpoons R_3N + H_3O^+ \qquad I\cdot6$$

has been discussed by Everett and Wynne-Jones (41).

It has been suggested by Harned and Robinson (42) that an equation of the type

$$\ln K = A/T + B + CT \qquad \text{I•7}$$

is more convenient than equation I•4 for numerical computation. This last equation corresponds to the assumption that ΔC_p is directly proportional to the absolute temperature, and over the range of accessible temperatures this is usually experimentally indistinguishable from a constant ΔC_p, as assumed in equation I•4. However, Ives and Feates (43) have deduced a temperature variation in ΔC_p (with a minimum near 25°C) on the basis of very precise conductivity measurements with cyanoacetic acid. This demands high accuracy in the determinations of ionisation equilibria constants K, which does not appear to have been obtained by many workers previously. Generally, either of the assumptions (a) ΔC_p = constant or (b) ΔC_p is proportional to T, appear adequate to reproduce most experimental data.

Direct determination of ΔH and ΔC_p from calorimetric measurements did not prove successful in early studies due to insufficient accuracy. The difficulties that arise in extrapolation of data to infinite dilution from those obtained in higher concentration ranges studied give rise to inaccurate extrapolated values. However, Laidler, Papée, and Canady (44), employing an accurate microcalometric technique, were able to study directly the heats of ionisation of some weak acids down

to extremely low concentrations. The use of this technique eliminates the necessity of employing heat of dilution data, and permits the value at infinite dilution to be obtained by a procedure involving only a short extrapolation.

The interpretation of the absolute values of thermodynamic functions for systems of the type I·5 or I·6 is not easy. It appears in most cases that the term $T\Delta S^{o}$ is just as important as, if not more important than ΔH in determining the value of ΔG^{o}, and hence the equilibrium constant. The erratic behaviour and unexpected magnitude of ΔS^{o} and ΔC_{p} values, in carboxylic acid (45) and amine cation ionisation equilibria (46), strongly suggest that there is specific interaction of the ions (and perhaps also the uncharged molecules) with the highly polar and associated aqueous medium. The interpretation of the values of these thermodynamic functions necessarily involves a specific picture of local molecular interactions. The alkyl functional character and asymmetry of the acid-base species further complicate the problem. However, a few individual explanations do emerge, particularly in the case of the amine cation ionisation equilibria in an aqueous medium.

From general considerations of the inductive effect, it would be anticipated that successive alkyl groups would cause a steady rise in base strengths of the aliphatic amines in water in the series NH_3 to Me_3N. However, the following results are obtained: $pK(NH_4^+)=9.25$ (47), $pK(MeNH_3^+)=10.62$, $pK(Me_2NH_2^+)=10.77$, and $pK(Me_3NH^+)=9.80$ (46). It seems likely that the main

explanation of this anomaly (and others) lies in the interaction of the cations with water, which will vary considerably in a series NH_4^+, $MeNH_3^+$, $Me_2NH_2^+$, and Me_3NH^+ due to the diminishing accessibility of the N^+ charged centre in the conjugate acid aminiumion (49). Trotman-Dickenson (48), however, explained this effect by proposing that the degree of hydrogen bonding with the solvent depends upon the number of hydrogen atoms in the cation. The work of Hamann and Strauss (50) on the effect of pressure on the ionisation constants of weak electrolytes such as $(CH_3)_3NHOH$, $(CH_3)_2NH_2OH$, and $(CH_3)NH_3OH$ shows that pressure effect on the hydration of the un-ionised amines is important. This effect is somewhat less apparent in weak acid electrolyte ionisation equilibria e.g., HCOOH, CH_3COOH, and C_2H_5COOH, due to the related diffuseness of charge in the carboxylate group. The effect of alkyl substitution in the series NH_3 to Me_3N is to decrease the stabilisation of the cation which arises from interaction with the solvent; this effect acts in an opposite direction to that of the inductive effect. This view is supported by the observed entropy changes in the reaction (46)

$$\geqslant N^+H + H_2O \rightleftharpoons \geqslant N + H_3O^+ \qquad \text{I·8}$$

which become more negative with increasing alkyl substitution, corresponding to a decreasing number of oriented water molecules around the cation. An observation supporting this suggestion is that when base strengths of the alkylamines are investigated

by indicator measurements (51,52,53) in solvents with little or no power of hydrogen bonding, the expected order of basic strength is found. Steric effects both in the solvation of the $\geqslant N^{+}H$ entity and in the solvation of the conjugate base $\geqslant N$ are to be expected. The results obtained by indicator measurements tend to disprove the suggestion by Brown and co-workers (54) that steric strain between the alkyl groups in the cation causes the anomaly, since this effect should be independent of solvent. Further studies regarding electrostriction associated with these alkyl aminium ions are presented in this thesis.

2. Relation to Problems of the Constitution and Properties of Liquid Water.

The behaviour of ions and the chemistry of ionisation processes in water cannot be discussed without due attention to the constitution and structure of the pure liquid solvent. Hence a brief review of some of the important features of previous and more modern views on this topic is given.

In 1933 when Bernal and Fowler (55) published their paper on the special structure of water, it appeared that a new factor was introduced into the discussion of aqueous solutions. Their theory suggested that water was made up of regions of extensively hydrogen-bonded molecules approaching on the one hand a tridymite - like structure and on the other a quartz-like structure and that there was a gradual breakdown of hydrogen bonding with increasing temperature. It soon became clear that the water structure is also altered in a similar way to that caused by increasing temperature, by the addition of electrolytes in a manner that produces characteristic behaviour for various types of salts in solution.

Many peculiarities existed with regard to the trends in various properties for many strong electrolyte solutions. Properties such as the viscosity, heat capacity, and entropy of electrolyte solutions gave unusual results in some cases. These properties give considerable insight into the condition of ions in solution and the effects the ions have on the structure of water. For example, the viscosities of dilute aqueous KF and KI solutions were greater and less, respectively, than that of pure water. Similarly the entropies of solutions of ions

showed peculiarities that could not simply be explained by consideration of the direct action of the ionic charge on water as a dielectric medium. Similarly, the effect of ions on the temperature of maximum density of water are unexpectedly specific. Bernal and Fowler pointed out that the viscosity results indicated that some ions had the effect of tightening up the existing water structure and others the effect of loosening it. This early terminology is thus analogous to that used in more recent work where "structure promotion" and "structure breaking" properties are attributed to ions.

There is a semi-quantitative relationship between the heat of hydration and the entropy change during the process, viz, the greater the heat the more negative is the hydration entropy (the so-called "compensation effect"). This relation was first observed for ionic solutions by Eley and Evans (56) who carried out a statistical-mechanical calculation of entropies of hydration. The entropy change for the process of taking an ion from the gas phase and transferring it into the solution phase was calculated taking into account changes in translational freedom and modification to the rotational and vibrational behaviour of water molecules in the coordination shell about the ion. The agreement between the calculated and experimental values was quite satisfactory.

Frank and Evans (57), and Gurney (58), independently considered the problem of ionic entropies using a model in which three solvent zones were postulated around the ion. The

inner zone consisted of water molecules strongly oriented by the electrostatic field of the charged ion, surrounded at intermediate distances by a solvent region where some disorder tends to exist because of the incompatible ordering effects of the ion and water molecules further out towards the bulk. "Structure-breaking" results from the approximate balance in the intermediate solvent region between the effects mentioned above. There is no doubt that a 'normal' structural orienting influence of neighbouring water molecules predominates locally in the outer bulk solvent and that the orienting influence upon the dipoles by the spherically symmetrical ionic field predominates in the inner region; the problem is to what extent the respective regions actually contribute to the entropy loss upon dissolution of an ion. However, it is possible at least to use entropy data as a basis for assigning an orderly gradation of net structure-altering effects to a number of ions. Additional support for the essential correctness of the structural picture has been provided by independent data from experimental work on heat capacity (58), dielectric relaxation (60), the temperature of maximum density (61), ionic mobility and its temperature coefficient (62), the temperature coefficient of relative viscosity (63), and infra-red (64,65,66,67), Raman (68,69), and n.m.r. spectroscopic studies (70,71).

The entropies of solution for many uncharged solute molecules indicate that these molecules help to stabilise the open structure of water (57). The inference of a structure -

promoting influence of non-polar solutes, e.g. argon, or of non-polar groups in solute molecules made by Frank and Evans (57), was substantiated by the observation of an excessively large partial molar heat capacity for the salt $(\underline{n}\text{-}C_4H_9)_4$ NBr. Whereas the low values of heat capacity of strong alkali halides were explained by assuming a breakdown in water structure by the cation, the converse phenomenon was regarded as occurring in the case of tetraalkyl-ammonium bromide solutions. The extra ice-like nature of the water is caused by the cation and it effectively melts or breaks down as the temperature is raised, thus causing extra heat to be absorbed.

These results led Frank and Wen (72) to suggest that the formation of H-bonds in the liquid is a cooperative phenomenon, i.e., the bonds are not made or broken singly, but several at a time, thus producing short lived "clusters" of highly H-bonded regions surrounded by non-H-bonded molecules. In this picture the statistical degree of "ice-like-ness" of the system is proportional to the average size and to the average half-life of the clusters. A cluster will come into existence when a volume element of suitable size and shape suffers a negative energy fluctuation of such magnitude as to outweigh the disruptive influences at the boundaries of the patch, and will dissolve when these disruptive influences -torques and displacements - succeed in transmitting into the cluster the necessary energy of local melting. A non-polar solute particle or group should be relatively incapable of

producing or of transmitting such disruptive influences, on account of the relative feebleness of the electrostatic interactions into which it can enter. An ice-like patch should therefore be able to form more readily in a volume element bounded by a non-polar solute particle and, once formed, should have a longer half-life than "normal" by reason of having a part of its boundary protected from attack. This would, on the average, produce extra "ice-like-ness" in the solution. This concept qualitatively accounted for the excess apparent molal heat capacity of the tetrabutylammonium bromide solution.

This model was further discussed by Némethy and Scheraga (73) in a statistical mechanical formulation of the thermodynamic properties of aqueous solutions containing hydrophobic solute molecules. The solvent clusters were considered as consisting of mono, di, tri, and tetra-bonded molecules (cf. the earlier ideas of Eucken (74).) embedded in and in equilibrium with monomeric "unbonded" water molecules. The "unbonded" water was postulated as having "broken" hydrogen bonds but each molecule was regarded as participating in strong dipole-dipole* and London interactions with neighbouring molecules.

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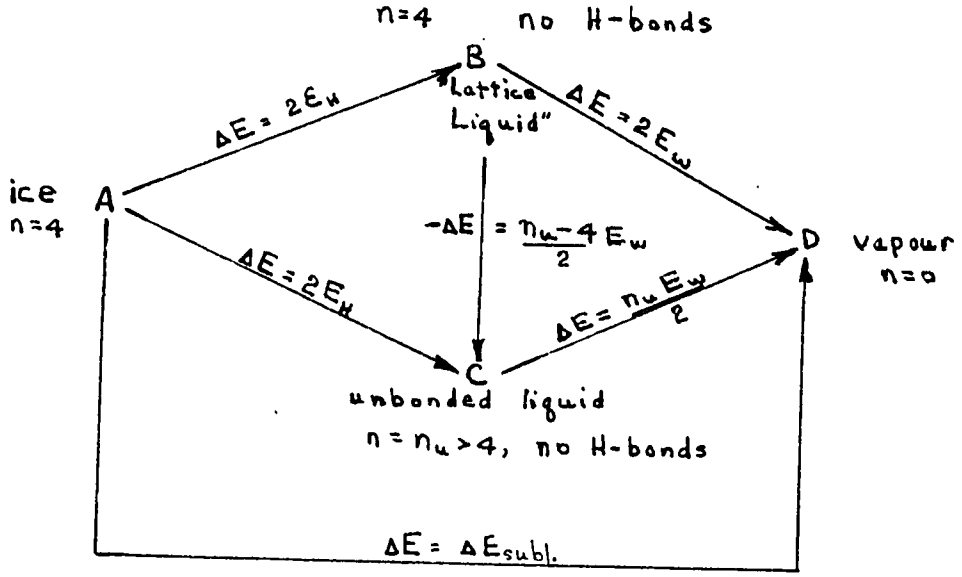
* The distinction was made (73) between hydrogen-bonded water molecules and non-bonded ones which interacted through dipole-dipole interactions. Since the H-bond is a special type of dipole-dipole interaction and has appreciable energy in non-linear configurations, this distinction is difficult to accept.

The interior of the clusters were regarded as containing molecules with all four H-bonds unbroken. At the perimeter of the clusters, molecules with three, two, and one H-bond can be found, while the molecules occupying the space between the clusters have all four bonds broken. The clusters grow by attachment of unbonded molecules and locally melt to give the latter. At a given temperature, the total number of hydrogen bonds existing in the liquid and the equilibrium between clusters and unbonded water are determined by the requirement that the free energy of the system should be a minimum. Another condition is that the clusters should be compact, i.e., they should have as many tetra-functionally bonded molecules as possible, and without extended chains of molecules bonded bifunctionally. Némethy and Scheraga introduced constraints relating the partial concentrations of the respective bonded and unbonded species to the size of cluster units by means of semiempirical equations obtained by considering models of small compact clusters. They determined weighting factors by assigning observed infrared and Raman frequencies in the range 60-800 $cm.^{-1}$ to their five species of water molecules.

The energetics of processes involved in breaking the hydrogen bonds of ice and in the interactions of molecules in water are represented by the following scheme:



I·9

where n is the coordination number, E_W is the energy of removing "non-bonded" water to a state in vacuum, E_H is the actual energy of breaking the hydrogen bond corresponding to the actual process of transferring one mole of water from ice to the unbonded liquid state and ϵ_H the energy corresponding to the same process as that determining E_H but only allowing for a coordination number of 4 for the non-H-bonded liquid. C represents those molecules of the actual liquid which are not H-bonded, but have dipole-dipole (see above) and London forces acting between them. B is a theoretical intermediate state representing a "lattice liquid" in which all four H-bonds of a given molecule are broken and the molecules allowed to interact as in C but with a coordination number of 4.

The statistical mechanical formulation of Némethy and Scheraga depends upon the energy term $2E_H$ for the process in going from A⟶C I·9. This is the energy required to

break two hydrogen bonds per mole of water in going from ice to the unbonded liquid, i.e., $\Delta E_{A \longrightarrow B} = \frac{4\varepsilon_H}{2}$, less the gain in van der Waals energy due to an increase in coordination number in the process $B \longrightarrow C$ given by $\Delta E_{B \longrightarrow C} = - \frac{(n_u - 4)}{2} E_w$.

It should be noted that the value of the H-bond energy derived from the energy parameter $2E_H$ will be less than those values deduced from quantum mechanical considerations which properly refer to the processes $\Delta E_{A \longrightarrow B}$ or $\Delta E_{A \longrightarrow D}$, depending on the reference states used. An energy level was assigned to each species, depending on the number of its hydrogen bonds, by assuming that the energy $2E_H$ required to bring a molecule from ground state level (ice) to level u (unbonded molecules) could be divided equally * between the 4 bonds.

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* The assumption of equal spacing for the energy levels may be incorrect for two reasons; (a) a charge separation effect discussed by Frank and Wen (72) may cause the energy levels of the singly and doubly bonded species (and possibily that of the triply bonded ones) to rise above the equally spaced positions, due to the unfavourable energy contribution entering through ε_H and (b) a non-linear increase in nearest neighbours for each step from ground state level to level u, may cause unequal energy contribution from the factor E_w.

The model underlying the work of Némethy and Scheraga is based on a physically reasonable picture which takes into account the properties required of hydrogen bonded systems and includes features which can account for both the liquid state and ice-like features of liquid water. Although the theoretical values of the thermodynamic free energy, enthalpy and entropy functions derived from the model are in satisfactory agreement with experimental data, weaknesses of the model are: (a) that there is a discrepancy of the calculated heat capacity from the observed values; (b) that it is unable to account for the transition that occurs in liquid water in the neighbourhood of 30-40°C, e.g. the minima in the heat capacity and compressibility relations, and the discontinuity in the rate of change of the viscosity with temperature; and (c) that it is very much less satisfactory in the case of D_2O (75) than in the case of water.

Recently, Vand and Senior (76) have shown that the concentration of the respective species derived by Némethy and Scheraga do not show a satisfactory correlation with the experimental results of Buijs and Choppin (77) determined by infrared techniques. They concluded that the way in which Némethy and Scheraga introduced the constraints due to cluster formation was incorrect. The model consists of cluster cores, composed of tetra-, tri-, and dibonded molecules. Topologically, therefore, the cluster cores contain only rings and cages, but no straight or branched chains, since ends of chains imply the presence of singly bonded molecules. On the cluster core

there are surface sites available for bonding by a singly bonded molecule.

The fallacy in the Némethy and Scheraga model is that an "adsorbed" layer of singly bonded molecules on such cores adequately describes the clusters and that outside such clusters monomer species only are to be found. Vand and Senior argue that each "adsorbed", singly-bonded molecule provides three additional sites to which further singly-bonded molecules can attach themselves, and this process can be repeated indefinitely. In addition, the clusters are not immersed in pure monomer, but also in a proportion of a dimer and straight- or branched-chain polymer units, which do not possess ring or cage cores and are therefore not counted as clusters. The concentrations of those bonded species, calculated by neglecting chains, will not include species to which such chains contribute but will include an overestimated amount of highly bonded and non-bonded species. Vand and Senior were able to compare the five species model of Némethy and Scheraga with the three species model of Buijs and Choppin (unbonded with one and two-bonded species) by introducing a more elaborate model of hydrogen bonding. Their results confirmed that the contribution from highly bonded and non-bonded species was overestimated.

Vand and Senior (78) further developed a partition function for liquid water, based on the three types of water molecules postulated by Buijs and Choppin (77). The main feature of this approach is that the concept of discrete energy levels (corresponding to zero, one, and two hydrogen bonds) is abandoned and replaced by the idea of energy "bands". This was done after

it was shown by Vand and Senior (79) that the experimental results of Buijs and Choppin could not be reconciled with a model for liquid water based on three sharp levels of positive energy. To overcome the problem of requiring reliable experimental spectroscopic data for the frequency assignment in the partition functions, the authors adopted an alternative procedure: to seek a relationship between band width Δ_i and the mean energy $\bar{E}_i$. It is also assumed that for a given type of interaction (e.g., dipole-dipole), both the number and distance of neighbouring molecules may vary so that all molecules participating in a certain type of interaction do not have the same energy. A model is therefore postulated in which the hydrogen bond in water is assumed to have a mean effective length $\bar{l}$, with some regular distribution of hydrogen bond lengths about the mean $\bar{l}$ (in this case the distribution was assumed to be Gaussian). A distribution of OHO angles should also probably be considered. As a result, the energies of the molecules in a given energy band will also have some regular distribution about a mean value $\bar{E}_i$. The calculated thermodynamic functions over the range 0° to $100^{\circ}C$ were in very good agreement with the experimental observations, the agreement for the C_v function being generally better than 0.2%.

In a recent publication, Hornig (80) has argued that the absorption peaks observed by Buijs and Choppin (77) in the near infra-red may not be due simply to the combination of frequencies assigned by these authors, but that other combinations may also lie in this region. Of the many models proposed for water, the band

model has given the best comparison between calculated and experimental values of thermodynamic functions. Why a model is considered with 0, 1 and 2 bonded species only is questioned. It seems logical that in liquids where H-bonds can be formed, it becomes advantageous for a molecule to form H-bonds, since this will lower the Helmholtz free energy at the expense of the entropy. When a water molecule forms four H-bonds, there is a large increase in the internal energy, enough to compensate for the entropy loss. Very little is gained if one or two of these H-bonds are broken since the rotational or librational motion is still rather constrained and yet there has been a loss in energy equivalent to the breaking of one or two H-bonds. Vand and Senior have carried out a partial investigation of a simplified model based on one species (in course of publication). It also appears to predict satisfactorily the thermodynamic properties of liquid water. The form of the energy distribution is also open to criticism. The Gaussian distribution of energy has the limits $\pm \infty$ for a zero value of the energy function. As a result of this choice, the authors allowed for some negative energies in their system. A <u>beta</u> function could have overcome this difficulty since the function can be made zero outside prescribed limits and can also be skewed if necessary. The authors stated preference for the Gaussian formof the energy distribution arose from their desire to keep adjustable parameters to a minimum. Finally, the model depends in part upon the results of Buijs and Choppin and Stevenson (61) which however, have been criticised by Hornig (60)

Recently, Stevenson (81) has described three independent lines of evidence which indicate that the concentration of nonhydrogen-bonded water molecules in liquid water estimated by Némethy and Scheraga (73) and Marchi and Eyring (82) in the temperature range 0° to $100^{\circ}C$, are at least two orders of magnitude too high. The latter authors proposed a two species model of freely rotating monomers (unbonded) and tetra-functionally bonded water molecules. The existence of freely rotating monomers in liquid water is disputable although neutron scattering results by Hughes (83) and low frequency Raman scattering by Stoicheff (84) seem to confirm their presence. If rotation exists, it would be expected to be of a hindered type. The results of the calculated thermodynamic functions showed that the enthalpy and entropy were in good agreement with experimental values while the calculated values of molar volume, specific heat capacity and compressibility agreed poorly with experimental results.

Stevenson concluded from the results of (a) the vacuum ultraviolet absorption spectra of water vapour and liquid, (b) semiempirical calculations of heat and entropy of solution of water monomer (unbonded) in liquid water, and (c) the lack of structure at 1.85-1.90 μ of the broad 1.90 μ band of the near infrared absorption spectrum of very dilute liquid water in CCl_4 or $CHCl_3$ solutions, that the concentration of nonhydrogen-bonded water monomer in liquid water at $0-100^{\circ}C$ is less than 1% of the molecules of the liquid. The high monomer concentration considered by Marchi and Eyring (82) is due perhaps to the overestimation of the entropy increase accompanying mono-

mer formation while Stevenson suggests that the high value obtained by Némethy and Scheraga is due to a low value of the energy, E_H, required for the dissociation of a hydrogen bond, as compared with the normally expected values. The results of Buijs and Choppin (77) are also incompatible with those of Stevenson and the latter author feels that the assumption of Buijs and Choppin of a significant concentration of water molecules with neither hydrogen atom involved in hydrogen bonds is an untenable one, particularly in view of the broadening of the liquid water absorption bands which would normally be expected to be sharp and relatively narrow if the vibrational modes of the terminal OH were unhindered.

Recently a two-state theory of the structure of water was proposed by Litovitz and Davis (85). The model is based on the existence in water of puckered hexagonal rings similar to those of more regular structure in ice. The presence of such rings in water is attributed to the highly directional cooperative forces suggested by Frank (72) which favour the formation of hydrogen bonds. However, in water these authors postulate the rings to be coexisting in two structures: (a) an open-packed, ice-like structure in an optimum configuration for forming hydrogen bonds between rings and (b) a close-packed structure in which the molecules tend to occupy a nearly complete body-centred cubic structure. In a two-state model, the close-packed structure (b) is generally assumed to consist of molecules which are no longer hydrogen bonded. For most previous two state models, this would require that a fraction in excess

of one-half the hydrogen bonds be broken. Litovitz and Davis proposed that in the "broken-down" form, water is a nearly complete body-centred cubic structure in which each molecule is hydrogen bonded to two others. The model consequently requires only 18% of the hydrogen bonds to be broken on melting.

In ice, the oxygen atoms are connected in puckered hexagonal layers with alternate atoms raised and lowered. The layers above and below are mirror images of one another with each oxygen atom tetrahedrally coordinated to three others in the same layer and one other in an adjacent layer. This tetrahedrally coordinated structure can be represented as a body-centred cubic form with the central molecule surrounded by four others situated at alternate corners of the cube. The close-packed structure (b) arises by considering that the three hydrogen bonds that exist between two adjacent puckered hexagonal rings are broken and that one of the rings rotates one-sixth of a revolution. In this orientation, the molecules fit more closely together and one-half of the molecules have two neighbours in the adjacent ring at a distance equal to the cube edge.

The tendency of pairs of rings to join as in structure (b) is explained as follows. If one of the rings in such a pair suffers a collision which twists it with respect to the other, the highly directional covalent forces between rings disappear at small angles of distortion and the ring is relatively free to rotate to another potential minimum, i.e., if one ring rotates 120° with respect to the other. Between

these two positions, however (at 60°), there exists another potential minimum corresponding to structure (b). This minimum is due to (a) the increased van der Waals forces; (b) the persistence of dipole forces even though the O-H···O angles differ appreciably from 180°; (c) the greater number of near neighbours and (d) the increased entropy.

The basic assumption with regard to their model is that water contains a mixture of such double rings, some connected by means of hydrogen bonds to adjacent rings (structure (a)), and others connected by non-hydrogen bond interaction (van der Waals interactions) between rings (structure (b)). The authors chose a non-hydrogen-bonded nearest-neighbour distance, such as to give the correct position for the "extra" X-ray diffraction peak observed by Morgan and Warren (66) and Brady and Romanow (67) between 3.5 and 3.6Å, and a hydrogen-bonded nearest neighbour distance to give the best fit to the area under the radial distribution curve observed in references (86) and (87).

The mole fraction content and specific volume of structures (a) and (b) were calculated. From these properties, thermodynamic functions such as specific heat, thermal expansion and compressibility of water were obtained. The theoretical results are in good agreement with experimental data and about half of the values of the compressibility and specific heat were regarded as due to structural effects over the temperature range 0 to 100°C.

In summarising, it may be said that the band theory model of Vand and Senior (78) and the two-state theory of Litovitz and Davis (85) have given the best agreement between calculated and observed properties of water. The results of Buijs and Choppin (77), which in part have contributed to the theory of Vand and Senior, have, however, been criticised by some workers (80, 81). The argument has not yet been completely resolved and the rather good agreement between theory and experiment obtained by Litovitz and Davis (85) for compressibility and specific heat capacity, the two properties that have not been theoretically described precisely by previous models(with the exception of the heat capacity work by Vand and Senior), would appear to favour this model at the present time.

As can be seen, the study of the constitutive properties of water has originated in important ways from consideration of models which have been developed for interpretation of ion-solvent (water) interaction. The results have not been quantitatively successful but have at least provided a rather active phase of endeavour which undoubtedly will bear fruitful results in the future. There is no doubt that studies of the dissolution of non-polar or hydrophobic solutes has stimulated this increased interest. The study of tetraalkylammonium halides is now actively being carried out and as Frank (83) points out, structural questions seem here to be of primary interest. The interaction of the solvent water molecules with these salts is rather unique and gives rise to anomalous

behaviour in the thermodynamic and transport properties of aqueous solutions of the salts.

Consideration of the partial molal volume and compressibility behaviour of these salts in aqueous solution constitutes an important part of the work described in the present thesis.

3. Nature and Characterisation of Solvation

(i) General

For characterisation of ions, it has been common to consider ions as binding a certain number of solvent molecules of the solution, the so-called "solvation numbers". It is obvious that the energy of interaction between an ion and a solvent dipole must be greater than the energy of interaction between two solvent dipoles if a solvent molecule is to spend more than an average mean half-life (characteristic of its interaction in the bulk solvent) with the ion.

In a 'uniform' field a dipole experiences only a torque, but the field near an ion is subject, in general, to both orienting and attractive forces. The mutual potential energy of a point charge e and a dipole of moment μ, in vacuo is given by the expression

$$U = \frac{\mu e \cos\theta}{r^2} \qquad \text{I·10}$$

where θ is the angle between the axis of the dipole and the radius vector passing through the ion, and r the magnitude of the radius vector. In the completely oriented position ($\cos\theta = 1$), this energy would be greater than RT (≈ 0.6 kcal./mole) up to about 14 Å for the appropriate values of μ and e. For an ion in liquid water, however, no such simple calculation is possible. For water molecules remote from the ion, a fair approximation could no doubt be made by inserting the dielectric constant ($\epsilon \approx 80$) for the intervening water in the denominator of expression I·10. The energy is then reduced to a value $<$ RT

for all r which could conceivably be regarded as remote. However, dielectric saturation does occur near ions due to the large fields produced and although it has not been clear whether the energy should be calculated with $\epsilon=1$, as for the charges in vacuo, or with $1<\epsilon<10$, the lowering of the dielectric constant does give rise to substantially larger interaction energies. It seems likely that all the water molecules in the first layer around all monatomic ions should have energies of interaction with it which are large compared with either the thermal energy or the H_2O-H_2O hydrogen bond energy. Second layer water molecules will suffer slight orienting effects only, due to increased distance of separation between them and the ion as well astoalarger dielectric constant. Both of these factors have the effect of decreasing the interaction energy. It is probably only with polyvalent ions that second layer molecules have interaction energies greater than the thermal energy or the intermolecular energy for water.

In looking at the forces which enter into the interaction between an ion and solvent molecule it can generally be said that the leading term is undoubtedly due to the coulombic interaction of an ion-dipole. However, Buckingham (89) has shown that ion-quadrupole, induction, dispersion, and repulsive effects at low 'r' values play a role in determining the overall extent of the ion-solvent interaction. It can be seen generally that conditions exist whereby the electrostatic nature of the solvent and ion favours an interaction. Properties will now be discussed which enable the characterisation of the degree of such mutual interaction.

(ii) Solvation Energies

By means of a Born-Haber cycle, the energy of the process of solution of the electrolyte (i.e., the heat content change in passing from the hypothetical gas state to the standard state in solution) can be expressed in terms of equivalent energy contributions arising from the sublimation and dissociation of the solid crystal lattice with redissolution of the ions in the solvent at infinite dilution (i.e., in the absence of ionic interaction effects). If the lattice energy is U kcal./mole and the heat of solvation for cations and anions is ΔH_s^+ and ΔH_s^- respectively, then the heat of solution $\Delta H_{soln.}$ is,

$$\Delta H_{soln.} = -U + \Delta H_s^+ + \Delta H_s^- \qquad \text{I·11}$$

In the solution of a covalent substance, e.g., hydrogen chloride, U in equation I·11 is replaced by D, the dissociation energy for the formation of gaseous ions from the molecules. The lattice energy U should not be the normal lattice energy but the corresponding heat content term for the finite temperature in question, calculated from

$$U = U_o + \int_o^T C_p \text{ salt} \, dT - \sum^{\text{ions}} \int_o^T C_p \text{ gas ions} \, dT \qquad \text{I·12}$$

One very interesting point arising out of such a calculation and determination of solvation energies is that the initial heats of solution are comparatively small, which indicates that a great deal of energy is evolved in the solution process to counterbalance the high energy requirements of the heat of crystallisation. A corollary to this statement is that the ions in solution are subjected to very nearly the same interaction energies as they are in the crystal ionic lattice. In general, the heats of solvation are greatest for the salts

possessing ions of high charge density, which is in accord with the fact that stronger ion-dipole interactions would arise. Eucken (90) showed that the individual heats of hydration are additive but the problem persisted as to how individual ionic heats of solvation could be evaluated from experimental data.

All estimates of individual solvation energies must, of course, be based on some non-thermodynamic principle for division of the observed thermodynamic function for a pair of ions. The methods used usually involve division of the observed thermodynamic energy quantity into ionic components by application of a theoretical approach in which the dependence of the energy quantity on a reciprocal function of the ionic radii is considered.

One of the earliest attempts to arrive at a set of individual ionic solvation energies was that of Bernal and Fowler (55) in which the total heat of solvation of K^+F^- (-191 kcal. mole^{-1} (55)) was divided by two, giving a value of $\Delta H^o_{K^+} = \Delta H^o_{F^-} = -95.5$ kcal. mole^{-1}. This value was somewhat modified by taking into account the different spatial distribution of water molecules around cations and anions which arises owing to the non-central position of the electric dipole in the water molecule. The corrected values were then $\Delta H^o_{K^+} = -94$ and $\Delta H^o_{F^-} = -97$ kcal. mole^{-1}. The basis of Bernal and Fowler's division of the K^+F^- heat of solvation must be regarded as over simplified and not entirely consistent with their own complex expression for à priori calculation of

of the heats and free energies of hydration.

The method of Latimer, Pitzer, and Slansky (7) is probably even less satisfactory as they used the Born equation with empirically corrected radii* to represent the free energies of solvated ions.

Verwey's (92) method is essentially similar to the method of Latimer et al. (7) except that differences of heats of hydration in a lithium halide series and in an alkali metal fluoride series are plotted against $1/r_i$ (where r_i is the crystallographic radii) and the lines extrapolated to $1/r_i = 0$ where the electrostatic contribution to hydration energy is zero. Consequently individual values for the heat of hydration of lithium and fluoride were obtained. The criticisms of the Latimer method are directly applicable to this method as well.

The calculations of Eley and Evans (56) appear to be less objectionable from the view point of their formulation, but the numerical values are discrepant by some 10-30 kcal. $mole^{-1}$ when compared with experimental values. Some theories suffer from the mixing of heat and free energy terms which may introduce an ambiguity of some 3 - 30 kcal. $g\ ion^{-1}$.

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* These empirical corrections are certainly erroneous in principle: they amount to correction of the radii of the ions in the gaseous state, since the main energy term in the Born equation for free energy of solvation (equation I·1) is that for loss of the energy of the ion in the medium where $\epsilon = 1$, as pointed out by Laidler (8). Strehlow's theoretical explanation (91) of the difference between the empirical corrections for cation and anion radii proposed by Latimer, Pitzer and Slansky (7) is therefore unjustified. In the final analysis, it seems that both gas phase and solution phase corrections to the radii are really required but not by the same amounts nor for the same reasons.

Their claims to validity rest upon comparisons with 'experimental' values which have been obtained by procedures in which the validity of the theory under test is implicitly assumed.

Glueckauf (93) has calculated heats of hydration of single ions from a modified form of the Born equation

$$\Delta G_i = \int_{E=0}^{ze} \int_{r=\infty}^{r_i} -\frac{E}{\epsilon r^2}\, dr dE - \frac{(ze)^2}{2r_i} \qquad \text{I·13}$$

where r_i is the crystallographic ionic radii, E the field, ϵ the dielectric constant, and e the electric charge. The dependence of the dielectric constant on charge and the distance from the ion was taken into account according to the equation of Booth (94). The treatment also visualises spaces free of electronic matter, in which the dielectric constant would fall to unity between the ion and the dielectric. These empty spaces arise from the spherical nature of the ions and solvent. The empty spaces (considered of importance for the regions close to the ions only) were smeared out into an annular space of thickness Δr around the ion. The value of Δr was chosen so as to give constant differences for ΔH_i with the measured values for the alkali chlorides. The values of heats of hydration for the individual ions lie between those calculated by Bernal and Fowler (55) and those of Latimer (7) and of Verwey (92). This method partially allows for the field dependence of the dielectric constant but is still semi-empirical due to the ionic radius correction factor Δr.

(iii) Solvation Numbers

Methods for the measurement of solvation numbers give rather discrepant results, as was mentioned before. The main problem is that the concept of a 'hydration number' is not a very well defined one, and that different methods give different kinds of average values. However, there is fair agreement if properties are used that are expected to depend mainly on primary solvation. Bockris (5) suggested that the term 'primary solvation' be used to refer to the number of solvent molecules near to an ion which have lost their degrees of translational freedom and move as one entity with the ion during its Brownian motion. Conway and Desnoyers (in course of publication) and Glueckauf (95) have defined hydration number as that parameter representing the number of surrounding water molecules (coordination number) multiplied by a factor indicating their fractional loss of "solvent properties".

There has been some critical discussion with regard to the entity that is to be called "the ion", whether it is the bare ion or an ion with a solvent sheath about it. Nevertheless despite the realisation of the problem, no concrete evidence has been found to indicate what the exact molecular picture is with regard to a water molecule bound to an ion. Hunt and Taube (22) have shown by an ingenious tracer technique that the ion $\left[Cr(H_2O)_6\right]^{+++}$ exchanges its water molecules very slowly with the solvent. Of course, the binding of the water molecules

in this compound is perhaps of a coordinate type. Experimental methods have not been devised which can measure the half-life of a water molecule bound to an ion through the normal ion-dipole interaction. With regard to the question of the permanence of solvated species, it can safely be said that the permanence implied is rather relative to the time-scale of the Brownian motion.

Bockris (5) also defined 'secondary' solvation as referring to solvent molecules not included in the primary solvation but which undergo some electrostatic interaction with the primary solvated ion sufficient to affect solvation dependent quantities. This is where the discrepancy obviously arises with regard to different methods of measuring hydration numbers. Some methods will give essentially primary solvation numbers whereas others possibly measure the total number of water molecules affected in any small way.

One of the oldest methods of estimating ionic hydration is based on the transport of water that occurs when a current passes through a solution. A classical method of detecting this transference (96) is to add to the solution a non-electrolyte, which is assumed not to be transported by the current. The change in concentration of this reference substance then gives a measure of the net transport, i.e., the difference between the amounts of water transported by the anions and cations. Unfortunately, there is now a good deal of evidence (97, 98) that non-electrolytes of the type employed are also transported

with the ions. It seems likely that any suitable non-electrolyte will owe its solubility to the presence of polar groups, and will therefore become attached in the same way as water itself. Furthermore, the method has the inherent disadvantage of giving only the difference between the hydration numbers of cation and anion and not absolute values. Hydration numbers have also been calculated from ionic mobilities (99). There is an inherent disadvantage in this method because of the use of Stokes' law (see p. 18). The values so obtained refer to individual cations and anions, rather than to the sums or differences.

Darmois (23) has applied density measurements to the calculation of primary solvation numbers utilising the Stokes' volume for the hydrated ion. A better method (100) is to express the Stokes' volume in terms of the crystallographic volumes of the ion and of the compressed water molecules and this procedure is developed further in this thesis. Passynskii (101) has derived primary solvation numbers from compressibility measurements utilising ultrasonic velocity techniques. The assumption is made that the solvent molecules in the primary solvation sheath are incompressible. It will be pointed out later in this thesis that the assumption of negligible compression in the first solvent sheath is a poor approximation, except in the cases of multivalent ions or very small monovalent ions.

Other procedures for deriving primary solvation numbers are; (a) the entropy method (102), in which the

entropy of hydration is regarded as arising entirely from the loss of the translational degrees of freedom of water molecules which enter the primary hydration sheath; (b) the measurement of molar dielectric decrement in aqueous solutions of monovalent ions (103); here the results were interpreted in terms of a number of water molecules attached to the ion which are unable to rotate freely in the oscillatory electric field used in dielectric constant measurements; and (c) the ultrasonic e.m.f. method (104) based on the fact that a potential difference should be produced in an electrolytic solution subjected to ultrasonic radiation and that the effect should be proportional to the difference of effective masses of the cations and anions. The methods discussed above give some idea as to the extent of primary solvation. Numerous other methods based on cryoscopic, vapour pressure, salting-out, activity, diffusion and partial molar heat capacity measurements give much higher results than those of the other methods and are mutually discrepant. They undoubtedly include varying amounts of secondary solvation. It is not surprising that there is little concordance between the results of the many ingenious experimental methods which have been devised to measure the 'solvation number' of an ion; each method measures an average of the primary and secondary solvation but there can be a number of ways in which the average is weighted.

(iv) Electrostriction

The most useful approach to the determination of the extent of solvation is through the consideration of the effect

of ions on the volume of solvent. The electrical influence of the ions on the solvent creates an effective hydrostatic pressure (in fact, a tension) of considerable magnitude near the charged particles. The first attempt to relate the volume of electrostriction of a solvent to the size and charge of the dissolved solute was by Nernst and Drude (105).

They derived an expression of the form

$$\Delta V = \frac{e^2}{2kr_i} \frac{1}{\epsilon^2} \left(\frac{\partial \epsilon}{\partial V}\right) \qquad \text{I·14}$$

where e is the electric charge, r_i the ionic radius, ϵ the dielectric constant, and k the compressional resistance. The term $\frac{1}{\epsilon}\left(\frac{\partial \epsilon}{\partial V}\right)$ was further considered to be independent of radius. Electrostriction is usually defined in terms of the apparent decrease in the volume of ions when dissolved. Mathematically it may be expressed as $\Delta V = V_{int.} - \bar{V}$, where $V_{int.}$ is the intrinsic or actual volume occupied by the salt in solution (31,106). Two useful properties which give experimental values of the extent of electrostriction are the apparent molal volumes of ions in solution - derived from density measurements - and the compressibilities of solutions - either obtainable from direct isothermal P-V observations or indirectly from ultrasonic velocity studies.

In water, electrostriction arises from the fact that normal water is a tetrahedrally coordinated liquid having a large structural free volume (55). Cubically packed water molecules would have a volume of 12.5 $ml.mole^{-1}$ compared with the observed value of 18.07 $ml.mole^{-1}$ at 25°C and 1 atm. The

main contribution to volume change associated with the presence of ions will be that arising from local collapse of the solvent structure, as pointed out by Bernal and Fowler (55). Thus, in an ion-solvent complex, the actual size of the water molecules themselves hardly changes, but the spatial arrangement is modified. Although other solvents do not have a particularly open structure similar to water, their spatial arrangements are similarly modified and changes in volumes readily observed.

(v) Solvation Entropies

The most significant fact concerning the standard entropies of hydration of ions, is that they are negative, attaining values of the order of -100 cal.$^{\circ}C^{-1}$g. ion^{-1} at 25°C for polyvalent ions. This cannot be attributed to changes in the ions since they are not themselves altered when they enter into solution and the effect must hence reflect the lowering of the entropy of water when the water molecules become ordered around the ion and the diminished free volume available to the ion in the liquid phase (56,57).

The simplest approach to the calculation of entropies of hydration is by differentiation of the free energy of hydration (as expressed by the Born equation) with respect to temperature. The expression yields the correct sign and order of the entropy of hydration, but poor detailed agreement with experimental values. Better agreement is obtained when dielectric saturation effects are considered (8), but the fit with regard to the experimental data is not good with anions.

The factors which lower the entropy of a solvent molecule around an ion are precisely those that cause a local compression of the solvent around the ions. Consequently two of the early approaches to the calculations of entropies of hydration involved the contribution expressed thermodynamically (107) in terms of the compression of the water and a statistical-mechanical method used to examine the change in order of water molecules during the hydration process (56). In both of these methods, fair agreement between the theoretical and experimental results was found as will be discussed in more detail in Chapter VI of this thesis: however, it should be mentioned here that the method of Latimer and Kasper (107) for calculating the entropy change associated with compression of the solvent contains two questionable assumptions; also the agreement of their results with experiment seems to be largely fortuitous. The statistical-mechanical calculation of Eley and Evans, on the other hand, still stands as the best and most comprehensive study of the entropy changes associated with the process of solution of an ion.

Powell and Latimer (108) have pointed out the curious fact that the electrostatic contribution to the entropy of aqueous ions is apparently proportional to the first power of the valency of the ion, rather than to its square as would be expected from Born's equation. This relationship is questionable (109, 110) from a fundamental point of view and in part could be due to the semi-empirical relationship from which it was formulated.

Padova (111) has calculated the partial molar volume

of electrolytes in aqueous solutions at infinite dilution by applying a thermodynamic treatment of a fluid in an electrostatic field. Extension of this treatment to the free energy and entropy of solvation gives reasonable agreement with literature data. Glueckauf (93) has also determined entropies of solvation from the differential of equation I·13 with respect to temperature. The cationic values obtained are in reasonable agreement with experimental data.

(vi) The Problem of Individual Ionic Solvation Properties

It can be seen that ion-solvent interactions exhibit a high degree of specific behaviour and that an assessment of the properties characterising solvation on an individual c. ionic basis is of considerable importance. This situation requires first a departure from classical thermodynamic approaches to the behaviour of salt solutions in so far as methods are required for separation of thermodynamic properties measured for the whole salt into individual ionic contributions. While the separation of kinetic properties, e.g., mobilities, diffusivities, into ionic contributions rests on a sound experimental basis, the derivation of individual ionic thermodynamic properties presents well-known problems.

It should be recognised in any ã priori calculation of the heats, free energies, and the entropies of solvation that there exists a non-radial distribution of solvent dipoles at both cations. This was, in fact, considered by Verwey (92) and is supported by more recent and complete computations of Vaslow (112). The result is a substantial inequality between heats of hydration of cations and anions of the same crystal

ionic radius. At anions, a non-radial orientation of the mean vector dipole of the solvent is anticipated owing to the tendency for the OH bonds in water to be hydrogen-bonded to the electronegative anion centre.

The most satisfactory estimate of enthalpies of hydration of single ions is that of Halliwell and Nyburg (113) who based their calculation on interpolated differences of conventional ($\Delta H^{o}_{s,H^+} = 0$) ionic enthalpies for cations and anions of the 'same radius', rather than on some rationalised, but somewhat arbitrary, method of division of the total enthalpy of hydration for a pair of ions into ionic component values (7,55,92). Using this approach, a value for the absolute heat of hydration of the proton of -260.7±2.5kcal. $mole^{-1}$ was given. The uncertainty in this value must be increased somewhat since these authors assumed that the difference between the heats of hydration of cations and anions of the same radius originated only from the ion-water quadrupole interaction, which could be incorrect (114) if the water dipole orientation is not exactly opposite at cations and anions as seems to be indicated (92,112).

The individual entropies associated with ion hydration seem to rest on a relatively satisfactory basis taking the value for the proton (100,115) as -5 ± 2 cal.$^{o}C^{-1}$ $mole^{-1}$ or correspondingly that for the Cl^-ion (116) as 18.5± 1 cal.$^{o}C^{-1}$ $mole^{-1}$.

Various empirical or semiempirical relations (109,117,118) have been proposed in an attempt to correlate the crystalline ionic radii, r_c, with the partial molal volume $\bar{V}^{o}$. They are

of the general form (117, 118) $\bar{V}^o = Ar_c^3 + B/r_c$ assuming either that constants A and B are different for anions and cations (117) or that they are the same (118). Some of these empirical approaches are reasonable; however, Mukerjee (118) has assumed that cations and anions of the same radius, and hence polarising power, will affect the solvent with regard to its local effective volume and packing, in the same way. This is rather doubtful since the orientation of water at cations and anions is probably not simply a mirror image one.

4. Previous Work on the Specific Topics Examined in the Present Research

i) Partial Molal Volumes

Studies of partial molal volumes have been carried out on a considerable number of strong and weak electrolytes. Accurate knowledge of the molal volumes of electrolytes at low concentrations is of fundamental interest in connection with the understanding of ion-solvent interactions. Many of the recent studies of molal volumes of electrolytes have been concerned with improved methods of obtaining accurate data at low concentrations; these procedures are necessary for accurate extrapolation of the experimental data to infinite dilution.

Since a principal part of the studies on ionic volumes described in this thesis is concerned with tetraalkylammonium salts, a brief resumé of the previous work on these salts will be given. Gilkerson and Stewart (119) utilised a pycnometric method to study the concentration dependence of volume for the bromide series. Similarly Wen and Saito (120) have carried out an apparent and partial molal volume study of five symmetrical tetraalkylammonium bromides in aqueous solutionsat relatively high concentrations. Recently (121), very precise dilatometric measurements of apparent molar volumes of some dilute aqueous electrolytes, one of which was tetramethylammonium bromide, have been carried out. Since the apparent molal volume increases roughly linearly with the square root of the concentration, precise apparent molal volumes require a high degree

of accuracy in the density measurements. Direct pycnometry at concentrations below 0.1 M presents serious difficulties in reproducibility of weighings and consequently cannot be relied upon for obtaining precise extrapolated data or for evaluating the limiting law behaviour. It is felt that the experimental method utilised in the work described in this thesis is of sufficient accuracy to allow reasonable interpretation of extrapolated data and discussion of the results near the limiting law region.

(ii) Electrostriction

The usual method of calculating the electrostriction is based on the use of the Born equation (or some modified form of this relation (8)) which gives the free energy of charging of ions in aqueous solution; thus, by differentiation of this quantity with respect to pressure, the change in volume associated with the presence of the ion is obtained. The most detailed treatment of this problem by such an approach is that of Padova (111). The method, which was also followed in principle by several other authors (6, 106, 122), involves at some stage an integration from the periphery of the ion to infinity. This implies that spherical symmetry around the ion and a dimensionless continuum for the solvent must be assumed as a basis for the model. A more detailed discussion follows in the presentation of a new theory of electrostriction in Chapter III.

(iii) Compressibilities

The problem of calculating the compressibility coefficient

at one atmosphere from direct measurement of the pressure-volume relationships is a difficult one. The pressure dependence of the coefficient of compressibility is such that it decreases most rapidly at low pressures, where it is most difficult to obtain experimental results of high accuracy. The usual measurement involves determining the contraction in volume attending an increase in pressure of the order of 200 to 1000 atmospheres. There has been much work carried out on both electrolyte and non-electrolyte solutions that has utilised such a method (125). However, the most accurate method of determining compressibilities at atmospheric pressure and low concentrations depends upon measurements of the velocity of sound through the solutions. This gives the coefficient of adiabatic compressibility which is related to the coefficient of isothermal compressibility through the ratio of the specific heats at constant pressure and constant volume. Rassymskii (101) carried out some of the earliest studies utilising the measurement of the velocity of sound in aqueous solutions of electrolytes and non-electrolytes. By assuming (a) the solute species were incompressible (b) the primary hydration sphere of solvent molecules around the ions was incompressible and (c) the I^- ion was not solvated and consequently any decrease in compressibility of a solution containing this anion could be attributed to the co-cation, he was able to deduce hydration number parameters that agreed with values determined from other methods. Some of the most recent work on the compressibility of aqueous solutions of strong electrolytes, using the above technique,

has been carried out by Owen, Simons, and Aronick (124,125). Compressibilities of some electrolyte solutions (126), using a phase-comparison pulse method (127) similar to that used in the determination of compressibilities in this present work, have also been determined recently.

5. Description and Aims of the Present Work

The work described in the present thesis has consisted of experimental determinations of apparent molal volumes and adiabatic compressibilities of some symmetrical tetraalkylammonium halides and hydrogen halide salts of neutral alkylamines. The aims of this research work are to develop a theory of electrostriction based on the local specific volume change near an ion and to compare the theoretical results with experimental electrostriction data (obtained from partial molal volume and compressibility measurements), with a view to determining more information, at a molecular level, on the specific interactions between solute and solvent species. The results will be further discussed in terms of the relation between compressibility and partial molal volumes and the problem of evaluation of individual ionic values of these properties will be examined. An experimental method for the determination of individual ionic volumes will be suggested.

The relation between the entropy and volume changes associated with electrostriction at ions will also be discussed. The effect of solvation in the ionisation of bases will be considered from the complementary viewpoints of volume and compressibility changes which occur in their aqueous solutions.

Chapter II

General Formulation of Partial Molal Volumes and Compressibilities.

1. Partial Molal Volumes

Extensive properties of a system, e.g. volume, free energy, etc., are functions of physical variables such as pressure and temperature and also of the quantities of the different components. In the case of a solution at constant temperature and pressure, the total volume V of the system may be written differentially in terms of the contributions from different constituents as

$$dV = \left(\frac{\partial V}{\partial n_1}\right) dn_1 + \left(\frac{\partial V}{\partial n_2}\right) dn_2 + \left(\frac{\partial V}{\partial n_3}\right) dn_3 + \ldots \left(\frac{\partial V}{\partial n_i}\right) dn_i + \ldots \qquad \text{II·1}$$

where n_i is number of moles of constituent i. The term $\partial V / \partial n_i$, when all the other variables are held constant (viz. $P, T, n_1, n_2 \ldots$), is called the partial specific or molar volume depending on the units in which n is expressed, and is usually denoted by the symbol $\bar{V}_i$. The partial molar volume $\bar{V}_i$ may be considered as the increase in volume of the solution when one mole of constituent i is added to such a large volume of solution that the composition of the solution remains effectively unchanged.

Partial molal and apparent molal volumes of solutes are derived from the densities of their solutions. The apparent molal volume is given by the equation

$$\phi_v = \frac{V - n_1 \bar{V}_1^{\,o}}{n_2} \qquad \text{II·2}$$

where ϕ_v is the apparent molal volume of the salt, n_1 is the

number of moles of solvent of partial molar volume $\bar{V}_1^o$ and n_2 is the number of moles of solute. If the concentration n_2/V is expressed in terms of molarity, i.e., the number of moles of solute in V=1000 cc. of solution, then equation II·2 can be written

$$\phi_v = \frac{1000}{cd_o}(d_o - d) + \frac{M_2}{d_o} \qquad \text{II·3}$$

If, on the other hand, concentration is expressed as the number of moles of solute per 1000 grams of solvent then equation II·2 becomes

$$\phi_v = \frac{1000}{mdd_o}(d_o - d) + \frac{M_2}{d} \qquad \text{II·4}$$

where d_o is the density of the solvent, M is the molecular weight of the solute, and d the density of the solution.

From equation II·2 it may be shown that $V = n_2\phi_v + n_1\bar{V}_1^o$ and the partial molal volume may be expressed as

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1,T,P} = \phi_v + n_2\left(\frac{\partial \phi_v}{\partial n_2}\right) \qquad \text{II·5}$$

This shows that at infinite dilution, i.e., as $n_2 \rightarrow 0$ the partial molal volume becomes identical with the apparent molal volume. Because of the linear relationship that exists between ϕ_v and $c^{\frac{1}{2}}$ in dilute solutions (as theoretically expected from the Debye-Hückel limiting law) i.e.,

$$\phi_v = \phi_v^o + S_v c^{\frac{1}{2}} \qquad \text{II·6}$$

the most convenient calculation of partial molal volume of

solute makes use of the c-scale. The equation is

$$\bar{V}_2 = \phi_V + \left[\frac{1000 - c\phi_V}{2000 + c^{3/2}\left(d\phi_V/dc^{\frac{1}{2}}\right)}\right] c^{\frac{1}{2}} \frac{d\phi_V}{dc^{\frac{1}{2}}} \qquad \text{II•7}$$

which is derived from equations II•4 and II•5.

2. Partial Molal Compressibilities

The partial molal compressibilities of the components of a binary solution are defined by

$$-\bar{K}_1 \equiv \left(\frac{\partial \bar{V}_1}{\partial P}\right)_T \qquad \text{II•8}$$

and

$$-\bar{K}_2 \equiv \left(\frac{\partial \bar{V}_2}{\partial P}\right)_T \qquad \text{II•9}$$

The apparent molal compressibility is similarly defined as

$$-\phi_k \equiv \left(\frac{\partial \phi_V}{\partial P}\right)_T \qquad \text{II•10}$$

which, in combination with equation II•2, becomes

$$-\phi_k = \frac{\left(\frac{\partial V}{\partial P}\right)_T - n_1\left(\frac{\partial \bar{V}_1^\circ}{\partial P}\right)_T}{n_2} = \frac{-V\beta + n_1 \bar{V}_1^\circ \beta_o}{n_2} \qquad \text{II•11}$$

The coefficients of specific compressibility in II•11 are defined by

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{d}\left(\frac{\partial d}{\partial P}\right)_T = \frac{1}{c}\left(\frac{\partial c}{\partial P}\right)_T \qquad \text{II•12}$$

and $$\beta_o = -\frac{1}{\bar{V}_1^o}\left(\frac{\partial \bar{V}_1^o}{\partial P}\right)_T = \frac{1}{d_o}\left(\frac{\partial d_o}{\partial P}\right)_T \qquad \text{II·13}$$

for the solution and pure solvent respectively.

In practice the apparent molal compressibility may be calculated from compressibility and density data as follows. Suppose $n_2 = m$, the number of moles of solute in 1000 grams of solvent, then

$$V = \frac{n_1M_1+n_2M_2}{d} \quad \text{becomes} \quad V = \frac{1000+mM_2}{d} \qquad \text{II·14}$$

where n_1M_1 is weight of solvent, M_2 the molecular weight of the solute, and d the density of the solution. Inserting equation II·14 into II·11 and substituting $n_1\bar{V}_1^o = \frac{1000}{d_o}$ the following expression is obtained:

$$\phi_K = \frac{1000}{md_o}(\beta-\beta_o) + \beta\phi_v \qquad \text{II·15}$$

It may similarly be shown that if n_2/V is expressed as the number of moles of solute in 1000 cc. of solution, then

$$\phi_K = \frac{1000}{c}(\beta-\beta_o) + \beta_o\phi_v \qquad \text{II·16}$$

From equations II·11 and II·9 it follows that, at infinite dilution, the partial molal compressibility becomes, as expected, identical with the apparent molal compressibility, ec.,

$$\bar{K}_2 = \phi_{K_2} + c\left(\frac{\partial \phi_K}{\partial c}\right) \qquad \text{II·17}$$

As in the case of ϕ_v, the concentration dependence of ϕ_K at dilute concentration follows closely the simple form

$$\phi_K = \phi_K^o + S_K c^{\frac{1}{2}} \qquad \text{II·18}$$

It has been pointed out in Chapter I, section (4-iii), that accurate coefficients of compressibility necessary for the determination of ϕ_K^o, i.e., as $c \rightarrow o$, cannot be obtained from normal isothermal P-V relationships and that the measurement of the velocity of sound through solutions is employed to determine compressibility coefficients accurately at high dilutions. The velocity u in $cm.sec.^{-1}$ through a medium of density d in $g.cm.^{-3}$, is given by

$$u^2 = \frac{10^6}{\beta_s d} = \frac{10^6 C_p/C_v}{\beta d} \qquad \text{II·19}$$

when the adiabatic and isothermal compressibilities, β_s and β, are expressed in bar $^{-1}$.

The adiabatic compressibilities, β_s, differ from the desired isothermal compressibilities, β, by the quantity (128)

$$\delta = \beta - \beta_s = \frac{0.0239\,\alpha^2 T}{C_p d} \qquad \text{II·20}$$

where α is the coefficient of thermal expansion of the solution, C_p the specific heat at constant pressure and d the density of the solution.

The apparent molal adiabatic compressibility may be defined as

$$\phi_{K(s)} \equiv \frac{1000}{c}(\beta_s - \beta_{o(s)}) + \beta_{o(s)}\phi_v \qquad \text{II·21}$$

and if equation II·21 is subtracted from equation II·15, the expression for the true apparent molal compressibility, the following expression is obtained

$$\phi_K = \phi_{K(s)} + \frac{1000}{c}(\delta - \delta_o) + \delta_o \phi_v \qquad \text{II·22}$$

The coefficient δ_o corresponds to equation II·20 applied to the pure solvent. It can be seen that the evaluation of apparent molal isothermal compressibilities may be carried out from sound velocity measurements, if the quantities δ, δ_o and ϕ_v are known. This is necessary if an evaluation of the standard partial molal quantity, $\bar{K}_2^o$, is desired.

Chapter III

A Theory of Electrostriction*

1. General

A number of properties associated with ions in solution, e.g., their salting-out behaviour (31), partial standard g. ionic entropies (8,111), and partial g. ionic volumes (106,111) are determined by the electrical influence of the ions on the solvent, in particular the electrostriction of the solvent caused by the ionic field. The interpretation of some of these properties therefore requires a detailed knowledge of the electrostriction behaviour.

It has been shown previously (p. 56, Chapter I) that electrostriction may be expressed as the difference between the intrinsic or actual volume occupied by the salt in solution and the partial molal volume of the salt i.e.,

$$V_e = V_i - \bar{V}_i^o \qquad \text{III}\cdot 1$$

if ionic volumes are considered. The intrinsic ion volume V_i, or the physical volume occupied by the ion regarded as an impenetrable unit, has been evaluated by some authors assuming the ion to be a hard sphere of radius r_i, such that

$$V_i = 4/3\pi r_i^3 \qquad \text{III}\cdot 2$$

The usual method of calculating the volume of electrostriction is based on use of the Born equation I·1 (or some modified form of this relation (8)) which gives the free energy

* This part of the thesis has been published as an original paper (129) by the candidate.

of charging of ions in aqueous solution; by differentiation with respect to pressure, the change in volume associated with the presence of the ion is given by the expression

$$V_e = \frac{(ze)^2}{2r_i\epsilon_o}\left(\frac{\partial \ln \epsilon_o}{\partial P}\right)_T \qquad \text{III-3}$$

where ϵ = the dielectric constant, P = the pressure, e = the electronic charge, and z = valence. Unfortunately, this method is based on a model in which it is assumed spherical symmetry obtains around the ion and the solvent is a continuum. The treatment can be improved, to some extent, if dielectric saturation of the solvent is taken into account (8); however, the void space in the solvation complex (31,93) and the finite dimensions of the solvent molecules, factors which are of fundamental importance in electrostriction, cannot be included fully in such an approach.

Padova (111) has carried out the most detailed treatment of electrostriction based on the Born equation. The method has also been followed in principle by several other authors (8,106,122) and involves at some stage an integration from the periphery of the ion to infinity. Values for the volume of electrostriction are obtained either (a) by taking an average value for the field-dependent variables such as the dielectric constant, compressibility and density (9,106) over all the solvent extending from the surface of the ion, or (b) by integration over certain successive shell elements about the ion (111) where the dielectric constant is either considered to be independent of field, i.e., $(\partial\epsilon/\partial P)_{T,E}$ is constant and

equal to $(\partial\epsilon_o/\partial P)_T$, or a function of the field strength. The extent of solvent electrostriction which the latter calculations predict is far too large for some ions (cf.111), e.g., -200ml. $(g.ion)^{-1}$ for an ion the size of Mg^{++}. The principal difficulty here is the use of a continuous integration to obtain the overall extent of electrostriction in the region where discreteness of solvent structure becomes significant.

Some workers (122, 151) have assumed that the reason for the apparently large volumes of electrostriction of solvent caused by ions is due to the change in size of the cavity associated with the presence of an ion in solution. However, there has been much evidence (106, 130) to show that the radii of ions effective in aqueous solution are the crystal radii. Thus, Benson and Copeland (106) have shown, by consideration of a simple free volume model in which the ions are assumed to be hard spheres of ionic radius r_i embedded in a cavity of radius $r_c > r_i$, that in the case of solutions the cavity radius is at the best only a few hundredths of an Angstrom greater than the hard-sphere radius. The same result is reached intuitively (see Chapter 1) by noting that the enthalpies of solution of most salts are very small if not zero. This then implies that the lattice energies and solvation energies must be nearly equal. Since both depend on the inverse first powers of the ionic radii, it may thus be concluded that the electrostatic compressions must be also nearly the same in the two phases. These effective radii in the solid crystal lattice and in the

solution "lattice" will be determined by the balance of attractive and repulsive forces in the equilibrium ion - ion or ion-solvent configuration.

Appreciable compressibility of the ions themselves would, at first sight, appear to be somewhat improbable; however, a subtle point arises with regard to the nature of the dissolution process considered. If the process were

$$\text{Ion (gas)} \longrightarrow \text{Ion (solution)} \qquad \text{III}\cdot 4$$

then the compressibility may be significant. Thus, the ion in the gas phase is not subject to any compressional interactions with other neighbours, but in solution two effects arise; (a) the electrostatic pressure (see below) caused by the polarising and attracting influence of the ion on surrounding solvent dipoles; and (b) the intrinsic cohesion or internal pressure in the liquid solvent. However, III·4 is not the process normally involved in considering the volume change accompanying dissolution of an ion from a crystal lattice to a solvated state in solution, nor is it the process involved in ionisation of a solute (e.g. in acid or base ionisation) in solution or in formation of a partially charged or dipolar transition state. Also, Stokes (150) has shown that the failure of the Born equation for the free energy of charging of ions in aqueous solution is due primarily to the fact that the crystal radius is not appropriate for the calculation of the electrostatic self energy of the ion <u>in vacuo</u> (<u>cf.</u> Laidler and Pegis (6)). An alternative choice, the van der Waals radius, leads to excellent agreement. The van der Waals radii of ions in the gaseous state

are some 20 - 40% larger than the crystallographic radii of these ions. This is understandable since the outer parts, i.e. with regard to the electron distribution, will expand considerably when an ion is isolated in the gas phase. Consequently, in a dissolution process such as III·4 , the dissolved charged species can be regarded as being initially placed in a spherical cavity in the dielectric medium, of the same size as the cavity it would occupy in the gas phase. In highly polar solvents such as water, compression of the cavity will be of a considerable magnitude and would arise because of the local hydrostatic pressure brought about by the electrostatic interactions between the charge in the cavity and the solvent dipoles. A compressive effect will also occur even if polarisation of the solvent is absent owing to the cohesive pressure of the solvent surrounding the solute particle. The relation between the effective hydrostatic pressure and the electrostatic field is given by the expression;

$$P = \frac{(\epsilon - 1)}{8\pi} E^2 \qquad \text{III·5}$$

where E = the electrostatic field and ϵ the dielectric constant of the medium. Whalley (122) has shown by consideration of a process such as III·4 , if electric saturation does not occur, that the compression of the ion appears to be a good deal greater than the electrostriction of the solvent in solvents of high dielectric constant such as water.

If, however, the dissolution process considered is

Ion (crystal) ⟶ Ion (solution) III·6

then the change of extent of compression of the ion itself is small and the electrostatic volume of solvation is hence determined primarily by electrostriction of the solvent. Process III·6 is relevant to the practical case of dissolution of a salt to a solvated state in solution. Development of a theory of electrostriction based on a dissolution process such as III·6 therefore appears to be more relevent to actual experimental results.

The electrostriction theory of Whalley is based on a structureless dielectric continuum model which can merely be applicable to water. It further assumes that dielectric saturation does not occur in the solvent medium. This is probably only true for very large ions. The treatment of Whalley would appear to be more satisfactory for large compressible ions such as those of the tetraalkylammonium salts, but for solutions of such ions, clathrate or "iceberg" effects (72) might then also be important in determining ΔV in expression III·1. Conway and Bockris (100), in modifying an earlier approach by Darmois (23), were the first to take into account the fact that the effective volume of the solvating water molecules around ions would depend on ionic radius and local field and, on this basis, derived primary solvation numbers from data on partial ionic volumes.

Before proceeding further, it is necessary to offer some comments which will serve to clarify the origin of electrostriction. Normal water is a tetrahedrally coordinated liquid

having a large structural free volume (55). Thus, cubically packed water molecules would have a volume of 12.5 ml. mole^{-1} compared with the observed value of 18.07 ml. mole^{-1} at 25°C and 1 atm. The main contribution to volume change associated with the presence of ions will be that arising from local collapse of the solvent structure, as pointed out by Bernal and Fowler (55). Thus, in an ion-solvent complex, the actual size of the water molecules themselves nearly changes but the spatial arrangement of solvent molecules around the ion is modified.

In the present work, it will therefore be justifiable to suppose that electrostriction of the solvent itself is, in most cases, the main effect which makes $\bar{V}$ different from $V_{int.}$ (taken as the crystal lattice volume), e.g., for the small monatomic and polyatomic inorganic ions. However, in order to obviate the difficulties associated with the use of a continuous solvent model treated by means of the Born equation (e.g. with regard to the problem of integration over a distance from the surface of the ion across a region where the discrete nature of the solvent must be considered) it is preferable to concentrate attention on the local behaviour of the solvent itself. For this purpose, it will be assumed that the only role of the ion is to provide the polarising electrostatic field which acts on the solvent.

It is clear that some compromise must be made with regard to the calculation and the model used in so far as one can only introduce dielectric saturation effects calculated on the basis of Booth's and Grahame's treatments (see later),

which involve a continuous model for the solvent. However, in the present calculations, no attempt will be made to estimate the overall electrostriction by an integration with respect to distance from the ion, except as an indicative example. A continuous dielectric theory is therefore chosen to calculate the local specific volume change which must then be related to overall electrostriction by means of some molecular model of the solvent configuration near an ion. In the present calculations, the pressure dependence of such derivatives as β, the coefficient of specific compressibility, and $d\epsilon/dP$, the pressure derivative of dielectric constant will also be taken into account.

2. Model

It will be assumed that an ion is a hard incompressible sphere and, for the purposes of the calculation, is surrounded (a) by a spherical primary coordination shell of solvent the thickness of which is equal to the diameter of a solvent molecule and (b) beyond this region, by a series of annular shell elements. Each shell is regarded as being submitted to a constant electrostatic field arising from the ion. This mean field in each shell* may be calculated from electrostatic principles and will decrease from

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* This discontinuous representation of the solvation and associated field will, in reality, be limited to the primary coordination region near the ion. Further out, thermal disordering effects will tend to smooth out the orientation and distribution of water molecules (cf. the radial distribution function (55)).

one shell to another until a region of zero field intensity is reached. For most univalent ions, it will be sufficient to consider the primary coordination shell as the region associated with the electrostriction, while for multivalent ions a larger spherical volume element will be involved.

For the purpose of the calculation, each shell or shell element is regarded as being separated from its neighbour by a semi-permeable membrane so that liquid could flow from one shell to another. Any net flow of the liquid is, however, prevented if the chemical potential μ of the system is kept constant during the process of charging the ion (132). The change in volume V of the liquid with the field E during this isothermal charging process has been derived by Frank (132) as

$$\frac{1}{V}\left(\frac{\partial V}{\partial E}\right)_{\mu,T} = \frac{-E}{4\pi}\left(\frac{\partial \epsilon}{\partial P}\right)_{E,T} \qquad \text{III·7}$$

where ϵ is the dielectric constant and P the pressure. The tendency for the fluid to be sucked in under the influence of the field, is counterbalanced by an internal pressure, simultaneously built up, which maintains the system in equilibrium. Therefore, provided that the dependence of ϵ on P and E, and that of P on E is known, it is possible to solve equation III·7 and obtain the change in volume of the liquid which represents the electrostriction associated with the presence of the ion.

The methods employed in treating the thermodynamics of systems in an electrostatic field (prior to the treatment of Frank (132)) did not enable the field strength E to be written as a variable of state of the fluid in as general a sense as that

in which the pressure P and the temperature T can be treated as variables of state. Frank described an "apparatus" in which, through a thought experiment, the whole of a sample of fluid may be subjected to a uniform electrostatic field under controlled conditions. The application of Gibbsian thermodynamics is then carried out in such a manner that E enters the formalism in a way which is essentially conjugate to the ways in which P and T enter and makes possible a clarification of the relation between electrostriction pressure and thermodynamic pressure.

3. Calculations

1) Electrostriction at Low Fields

The variation of volume with field intensity is given by equation III·7 , but the simplest way of solving this equation is to use the method suggested by Frank (132) in which that effective pressure P is calculated which, in the absence of the field, would produce the same volume change that E produces. The treatment proceeds by making use of the relation

$$\frac{dv}{v} = -\beta \, dP \qquad \text{III·8}$$

which defines the isothermal compressibility β. This practical effective pressure must not be confused, however, (see below) with the internal pressure mentioned above and is obtained from the combination of equation III·7 and III·8 ; thus

$$dP = \frac{E}{4\pi\beta} \left(\frac{\partial \epsilon}{\partial P} \right)_{E,T} dE \qquad \text{III·9}$$

There are no *à priori* simple theoretical expressions relating β and $\left(\frac{\partial \epsilon}{\partial P}\right)_{E,T}$ to pressure. However, several empirical relations have been proposed which reproduce the existing experimental data for compressibility of water fairly well. The experimental results of Adams (133) on the compressibility of water up to 10,000 bars are reproduced rather well by the Tait -Gibson equation (134):

$$-\frac{1}{v}\left(\frac{\partial V}{\partial P}\right)_{E,T} = \beta = \frac{D}{B+P} \qquad \text{III·10}$$

where D and B are known empirical constants characteristic of the liquid and have the values 0.1366 and 2.997×10^9 dynes cm.$^{-2}$ for water at 25°C (135). The constant B is chosen such that P represents the pressure in excess of one atmosphere. Owen and Brinkley (135, 136) have suggested, by analogy with the Tait - Gibson equation, that the variation of the dielectric constant with pressure should be of the form:

$$\frac{1}{\epsilon}\left(\frac{\partial \epsilon}{\partial P}\right)_{E,T} = \frac{A}{B+P} \qquad \text{III·11}$$

where the constant A is equal to 0.1754 and B is the same as in the Tait - Gibson equation. Hamann (131) has shown that this equation in fact fits Scaife's data (137) up to 6,000 atm. to within one per cent.

A question arises here about the nature of P in equations III·10 and III·11 in relation to that in equation III·7 ; thus, should the compressibility and the variation of

the dielectric constant with pressure be taken at the internal pressure or at the effective pressure? This problem does not arise in the treatments of other authors (106, 111, 122) since they all considered the variation of ϵ with pressure to be independent of pressure. The problem is basically what the relation is between electrostriction pressure, as discussed in electrostatics, and the thermodynamic pressures defined in terms of constraints imagined to be imposed on an experimental system. This relationship can be clarified by distinguishing between total or resultant pressure, as used in the thermodynamic sense, and the components of pressure which are given by mechanistic analysis. An example of such a distinction is found in the interpretation which can be offered for the thermodynamic equation of state

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T \qquad \text{III·12}$$

which represents the external or thermodynamic pressure P as the balance which must be applied to make up the difference between the "thermal" (distending) pressure $T\left(\frac{\partial P}{\partial T}\right)_V$, and the "internal" (cohesive) pressure, $\left(\frac{\partial U}{\partial V}\right)_T$.

Similarly, Frank (132) has shown that the total electrostriction pressure has "tractive" and "contractive" components. The "tractive" pressure, which is the internal pressure mentioned previously, prevents the flow of liquid from a region of high

density to one of low density but does not "cause" the change in density or electrostriction of the fluid. It is the "contractive" pressure, essentially as involved in equation III·9 , which "causes" the electrostriction. It is therefore correct to assume that the pressure quantities which appear on both sides of equation III·9 , and in all subsequent relations, are equivalent, since the physical properties

$$\beta, \left(\frac{\partial \epsilon}{\partial P}\right)_{E,T} \text{ and } \left(\frac{\partial n^2}{\partial P}\right)_{E,T} \qquad \text{(see equation III·24)}$$

should be taken at that pressure which effectively causes the electrostriction, rather than at the pressure which is incidentally associated with the electrostriction.

The correctness of this treatment is indicated by the fact that the same relation (equation III·16), which arises from the combination of equations III·10 and III·11 with III·7, III·8 and III·9 , can be deduced without reference to the "contractive" pressure or the practical experimental pressure involved in equations III·10 or III·11 , by working in terms of densities rather than pressures * (see below).

Equation III·11 can now be integrated using the boundary condition that $\epsilon = \epsilon_o = 78.54$ when P=o; combination with equations III·9 and III·10 then gives the variation of pressure with field as

$$dP = \frac{A \epsilon_o (1+r/b)^A \, E dE}{4 \pi D} \qquad \text{III·13}$$

With the boundary condition that P=o when E=o, the effective

* The equivalence of these two methods of approach was pointed out by Professor H.S. Frank in a private communication.

pressure is obtained as a function of field only, viz:

$$\log (1+P/B) = \frac{1}{1-A} \log \left(\frac{A(1-A)\epsilon_o E^2}{8\pi BD} + 1 \right) \qquad \text{III·14}$$

Equation III·10 may also be integrated using the boundary condition that, when P=o, V=V_o = 18.07 ml., the molar volume of water at 25°C, then

$$\log \frac{V_o}{V} = D \log (1+ P/B) \qquad \text{III·15}$$

which, when combined with equation III·14, gives the volume as a function of field intensity as

$$\log \frac{V_o}{V} = G \log (KE^2 + 1) \qquad \text{III·16}$$

If V is expressed in ml. and E in e.s.u., the two constants have the values

$$G = \frac{D}{(1-A)} = 0.1659$$

and $$K = \frac{A(1-A)\epsilon_o}{8\pi BD} = 1.1025 \times 10^{-9}$$

As mentioned previously, equation III·16 also follows in terms of densities. From equation III·10 written in terms of density, and from equation III·11 , the following relation may be deduced by integration

$$\left(\frac{\rho}{\rho_o} \right)^{1/D} = \left(\frac{\epsilon}{\epsilon_o} \right)^{1/A} \qquad \text{III·17}$$

where ρ_o and ϵ_o are the normal bulk density and static dielectric constant, respectively. In the paper of Drunk (1902) it has been

shown that equation III·7 may be written as

$$-\frac{1}{V}\left(\frac{\partial V}{\partial E^2}\right)_{u,T} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial E^2}\right)_{u,T} = \frac{\beta\rho}{8\pi}\left(\frac{\partial \epsilon}{\partial \rho}\right)_{E,T} \qquad \text{III·18}$$

Then with $(\partial\epsilon/\partial\rho)_{E,T}$ from equation III·17 , i.e.

$$\left(\frac{\partial \epsilon}{\partial \rho}\right)_{E,T} = \frac{\epsilon_o A}{D} \quad \frac{\rho^{\frac{(A-D)}{D}}}{\rho_o^{A/D}} \qquad \text{III·19}$$

and β from equation III·10 written in terms of densities, the following relation is obtained

$$\rho^{(1-A-D)}\, d\rho = \frac{\epsilon_o A}{8\pi B} \times \frac{1}{\rho_o^{(A-1)/D}} \times dE^2 \qquad \text{III·20}$$

Integration of equation III·20 with the boundary condition $\rho = \rho_o$, when $E=o$, gives for low field conditions,

$$\left(\frac{\rho}{\rho_o}\right)^{\frac{1-A}{D}} = \frac{(1-A)\, A\epsilon_o\, E^2}{8\pi BD} + 1 \qquad \text{III·21}$$

which, upon taking logarithms, leads to

$$\log\left(\frac{\rho}{\rho_o}\right) = \frac{D}{1-A} \log\left(\frac{A(1-A)\,\epsilon_o\, E^2}{8\pi BD} + 1\right) \qquad \text{III·22}$$

This is equivalent to equation III·18 , since $\frac{\rho}{\rho_o} = \frac{V_o}{V}$. Hence the pressures in equations III·8 , III·9 and those in III·10 and III·11 can be used equivalently.

ii) Electrostriction at High Fields

In the above treatment, it was assumed that the dielectric constant was independent of the field intensity which would be true only at relatively low fields. It is now generally accepted that near small univalent and all multivalent ions the

dielectric constant has a much lower value than its bulk value due to dielectric saturation. The dielectric constant also changes with E as a result of electrostriction (132) but this effect is small compared with that arising from electric saturation.

Since the fields near most ions will be sufficient to cause considerable depression of the dielectric constant, it will generally be necessary to take into account this effect. While the experimental dependence of ϵ on E is known only for low fields, it is possible to use various theoretical treatments (94, 138, 139) to obtain a reasonable estimate of these effects. Since these treatments give a rather sharply varying dependence of ϵ on D with increasing distance from the ion, they should be sufficient to represent the leading effects of dielectric saturation, e.g. as in theories of the double layer (139), and for partial molal entropies and free energies of ions in aqueous solutions(6).

The variation of the differential dielectric constant ϵ_d with field has been derived by Kirkwood (136) and extended by Booth (94), but Grahame (139) has shown that the results of the latter theory can be represented closely by the empirical relation

$$\epsilon_d = \frac{dD}{dE} = \frac{\epsilon_0 - n_0^2}{1 + bE^2} + n_0^2 \qquad \text{III-23}$$

where n_0^2 is the square of the refractive index of water taken as 1.78 at 25°C and one atmosphere, b is a constant which has the value 1.00×10^{-6} when E is expressed in e.s.u. and D is the die-

lectric displacement. Padova (111) has shown from considerations of the Nernst - Drude equation (105) that it is the differential and not the integral dielectric constant (cf.31) which should appear in equation III·7 .

In order to calculate $\left(\frac{\partial \epsilon}{\partial P}\right)_{E,T}$ when ϵ is taken as a function of field intensity, the value of $\left(\frac{\partial n^2}{\partial P}\right)_{E,T}$ will be required. Rosen (140) has measured the refractive index of water up to 1,500 atm. and an equation having the same form as that of equation III·11 , namely

$$\frac{1}{n_o^2}\left(\frac{\partial n_o^2}{\partial P}\right)_{E,T} = \frac{C}{B+P} \quad , \qquad \text{III·24}$$

represents the data satisfactorily. The constant C has the value 0.0665 for water at 25°C. It will be noted here that it would be desirable to have data for n_o^2 up to rather higher pressures than were investigated by Rosen.*

* Since the publication of these results, Professor S.D. Hamann in a private communication, has pointed out that Zel'dovich and co-workers (141) have found that the empirical formula

$$n(\rho, T) = 1.334 + 0.334\,(\rho - 1) - 1.90 \times 10^{-5}\rho\, T \qquad \text{III·25}$$

(where ρ = density in $g.cm^{-3}$; T = temperature in °C) holds remarkably well at shock wave pressures as high as 150,000 atmospheres. By combining this relation with a suitable equation of state, Rosen's relation might be improved upon.

The dielectric constant may be obtained as a function of E and P from equations III·11, III·23 and III·24 as

$$\epsilon = \frac{1}{1+bE^2}\left(\epsilon_o(1+P/B)^A - n_o^2\,(1+P/B)^C\right) + n_o^2\,(1+P/B)^C \qquad \text{III·26}$$

and the variation of ϵ with pressure is obtained by differentiating equation III·26 with respect to pressure under conditions of constant E. Thus

$$\left(\frac{\partial \epsilon}{\partial P}\right)_{E,T} = \frac{1}{(1+bE^2)B}\left(\frac{\epsilon_{oA}}{(1+P/B)^{1-A}} - \frac{n_o^2\,C}{(1+P/B)^{1-C}}\right)$$

$$+\frac{n_o^2\,C}{B(1+P/B)^{1-C}} - \frac{1}{(1+bE^2)^2}\left(\epsilon_o(1+P/B)^A - n_o^2\,(1+P/B)^C\right)\left(\frac{\partial b}{\partial P}\right)_{E,T} \qquad \text{III·27}$$

The term $\left(\frac{\partial b}{\partial P}\right)_{E,T}$, which has been previously evaluated (111), is found to be relatively small and it can be shown that the last term of equation III·27 may be neglected in comparison with the other terms.

An expression for dP can be obtained from equations III·9, III·10 and III·27 as

$$dP = \left(4\pi D(1+bE^2)\right)^{-1}\left(\epsilon_{oA}(1+P/B)^A - n_o^2 C\,(1+P/B)^C\right) E\,dE$$

$$+\frac{n_o^2 C}{4\pi D}\,(1+P/B)^C\,dE \qquad \text{III·28}$$

An exact analytical solution of this equation cannot be obtained but two limiting cases may be derived. At low field intensities, bE^2 may be neglected in comparison with unity, and equation III·28 may be integrated to recover equation III·14 as expected. At high fields, $E > 10^5$ e.s.u., the first term of equation III·28

is small compared with the second and may be neglected. Then the remaining relation may be integrated with the usual boundary condition to give P as a function of E,

$$\log (1+ P/B) = \frac{1}{1-C} \log \left(\frac{C(1-C) n_o^2 \quad E^2}{8\pi BD} + 1 \right) \qquad \text{III·29}$$

Then, by combination with equation III·15 , the ratio of normal and electrostricted volumes is obtained as

$$\log \frac{V_o}{V} = G_s \log (K_s E^2 + 1) \qquad \text{III·30}$$

where $$G_s = \frac{D}{1-C} = 0.1469$$

and $$K_s = \frac{C(1-C) n_o^2}{8\pi B D} = 1.1023 \times 10^{-11}$$

Equation III·30 may be evaluated explicitly to give $\Delta V (= V_o - V)$ as a function of field strength.

4. General Numerical Solution

While the specific exact solutions of equation III·28 under conditions corresponding to the high field and low field approximations are of practical and academic interest, nevertheless the field near many ions of intermediate size will be of such a value (5×10^3 - 5×10^5 e.s.u.) as to make the exact solutions inapplicable. A numerical solution of equation III·28 was therefore made in order to evaluate P as a function of E over a large range of values of E including that for the intermediate field region. Equation III·28 may be integrated by means of a digital computer using the Runge-Kutta method.

Since the integrand is very wide in terms of E (0 to $> 10^6$ e.s.u.), a variable size of integration step h has been used with increasing field E as indicated in Table 1. For a given interval of field values, h was taken as $< 0.1\%$ of the lowest E value in the interval. Smaller intervals of h were also taken but did not change the calculated values of F as f (E) by more than 1-2%. Some values of F as f(E) are given numerically in Table 1 and were selected from a much larger tabulation printed out of the computer. A graphical representation of F as f(E) is given in Fig. 1. The numerical data for the general solution correctly become identical (at the appropriate fields) with the results for the high and low field approximations which were evaluated separately as a test of the calculations and are shown as the dashed lines in Fig. 1.

The numerical function F(E) enables V(E) to be obtained numerically using equations III.10 or III.15 , and hence Δv, the electrostriction per mole of water, may be computed as a function of E; the results are shown in Fig. 2 and selected data are given in Table 2. Similarly, the effective local compressibility β may be obtained as shown in Fig. 3.

5. Discussion of the Theoretical Results

The above treatment of electrostriction enables the change in volume of water to be calculated as a function of field intensity. The principal difficulty with the above treatment of electrostriction is that the empirical equation giving the dependence of the index of refraction on pressure is

based on data only up to 1500 atmospheres while the effective pressures, significant for electrostriction, which are involved near ions will be at least ten times larger. The justification for the extension of the relation to higher pressures lies in the great similarity between the equations relating compressibilities, dielectric constant and index of refraction to pressure. Since this type of equation fits the compressibility and dielectric constant data to fairly high pressures, it is not unreasonable to suppose that equation III·24 should be valid with regard to prediction of at least an approximate value for the refractive index in a similar range of high pressures. The suggestion by Hamann (see footnote p. 98) is relevant here.

Table 1

Calculated Values of Contractive Pressure P_2 and local Compressibility β as a Function of Field (Intermediate Field Region)

Field E (e.s.u.)	Pressure P_2 dynes cm.$^{-2}$	Compressibility β $\times 10^{12}$ dyne^{-1}cm.^{2}	Integration interval h.
1.014 x 10^2	4.139 x 10^4	45.645	
1.413 "	5.839 "	45.644	< 0.1
2.014 "	1.635 x 10^5	45.643	
3.540 "	5.334 "	45.636	
1.510 x 10^3	9.043 x 10^6	45.508	
3.010 "	3.470 x 10^7	45.123	
4.010 "	5.957 "	44.756	
5.510 "	1.057 x 10^8	44.091	
7.010 "	1.590 "	43.346	10
9.510 "	2.556 "	42.059	
1.051 x 10^4	2.951 "	41.554	
1.301 "	3.925 "	40.360	
1.701 "	5.392 "	38.686	
1.901 "	6.073 "	37.955	
2.313 "	7.383 "	36.624	12.5
4.064 "	1.170 x 10^9 "	32.829	
5.010 "	1.358 "	31.412	
6.018 "	1.536 "	30.165	15.6
7.794 "	1.829 "	28.346	
9.792 "	2.139 "	26.656	
1.090 x 10^5	2.310 "	25.777	19.5
1.821 "	3.525 "	20.975	
2.702 "	5.374 "	16.342	24.4
3.718 "	7.357 "	13.212	
4.057 "	9.291 "	11.133	
5.060 "	1.315 x 10^{10}	8.483	
6.094 "	1.799 10^{10}	6.510	
7.126 "	2.376 "	5.109	30.5
8.162 "	3.053 "	4.030	
9.196 "	3.826 "	3.316	
1.000 x 10^6	4.513 "	2.840	E/100
3.001 "	4.221 x 10^{11}	0.322	

Note on Table: Four or five significant figures are used for expressing the data. This is only to record to a reasonable accuracy, the results of the calculations from the computer. The actual calculated values are probably only reliable to 10 - 50% owing to uncertainties in the applicability of some of the constants used at high pressures and to other assumptions involved in the calculations. However, we may expect the form of the dependencies of F, v and β on E to be reasonably satisfactory; thus, the significant functions in the treatment of hydration are log F, $\beta - \beta_o$ and $v - v_o$ and the error in these quantities should not exceed 10 - 20 %.

Figure 1. Numerical solutions to pressure-field relationships Eq.(III·28). Low-and high-field approximations Eqs. (III·14) and (III·29), respectively shown as dashed lines.

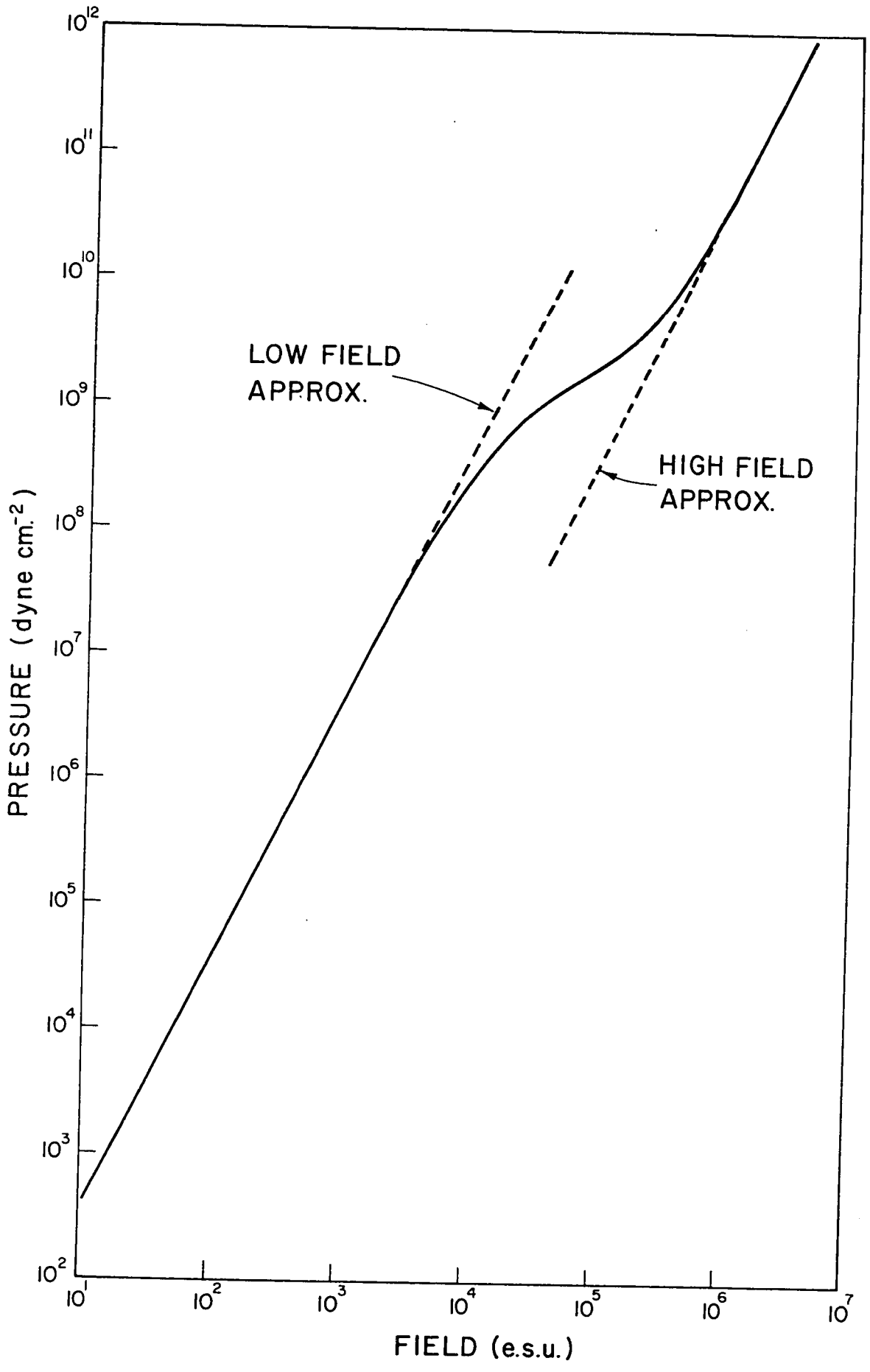

LOW FIELD
APPROX.
HIGH FIELD
APPROX.
PRESSURE (dyne cm.$^{-2}$)
FIELD (e.s.u.)
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}

Table 2

Calculated Electrostriction Δv ml. $mole^{-1}$ of water as a Function of Field (Intermediate Fields)

Δv (ml.)	E(e.s.u.)
0 ↓ 5.10^{-4}	0 ↓ 4.00×10^{2}
0.010	2.00×10^{3}
0.030	3.00×10^{3}
0.065	5.51×10^{3}
0.201	9.51×10^{3}
0.536	2.31×10^{4}
0.995	6.01×10^{4}
1.36	1.09×10^{5}
1.82	1.82×10^{5}
2.36	2.70×10^{5}
3.17	4.06×10^{5}
5.08	8.16×10^{5}
5.71	1.00×10^{6}

Note on table: Comments on table 1 apply also here.

Figure 2. Electrostriction Δv $cm.^3$ $mole^{-1}$ water as a function of field associated with the ion.

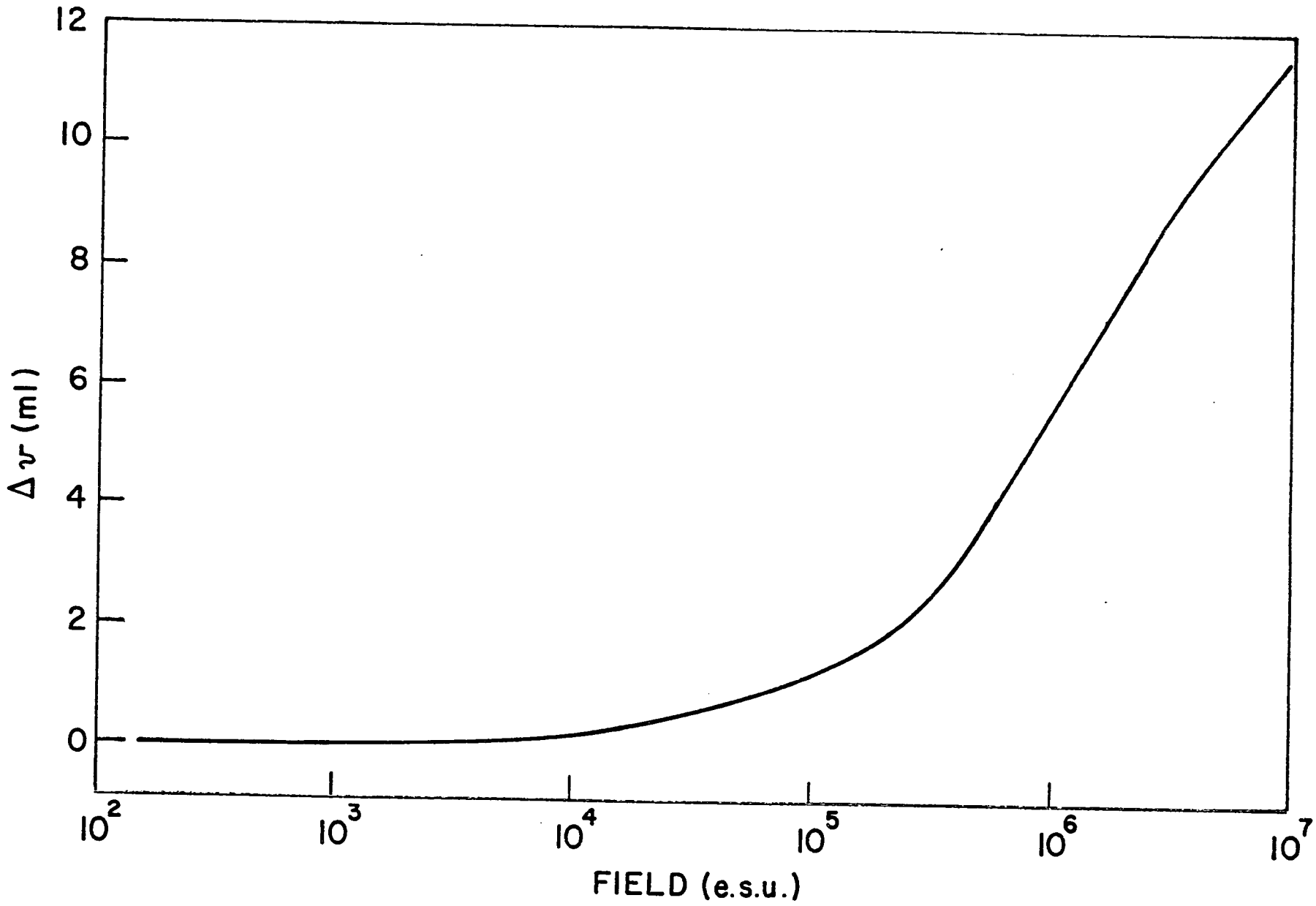
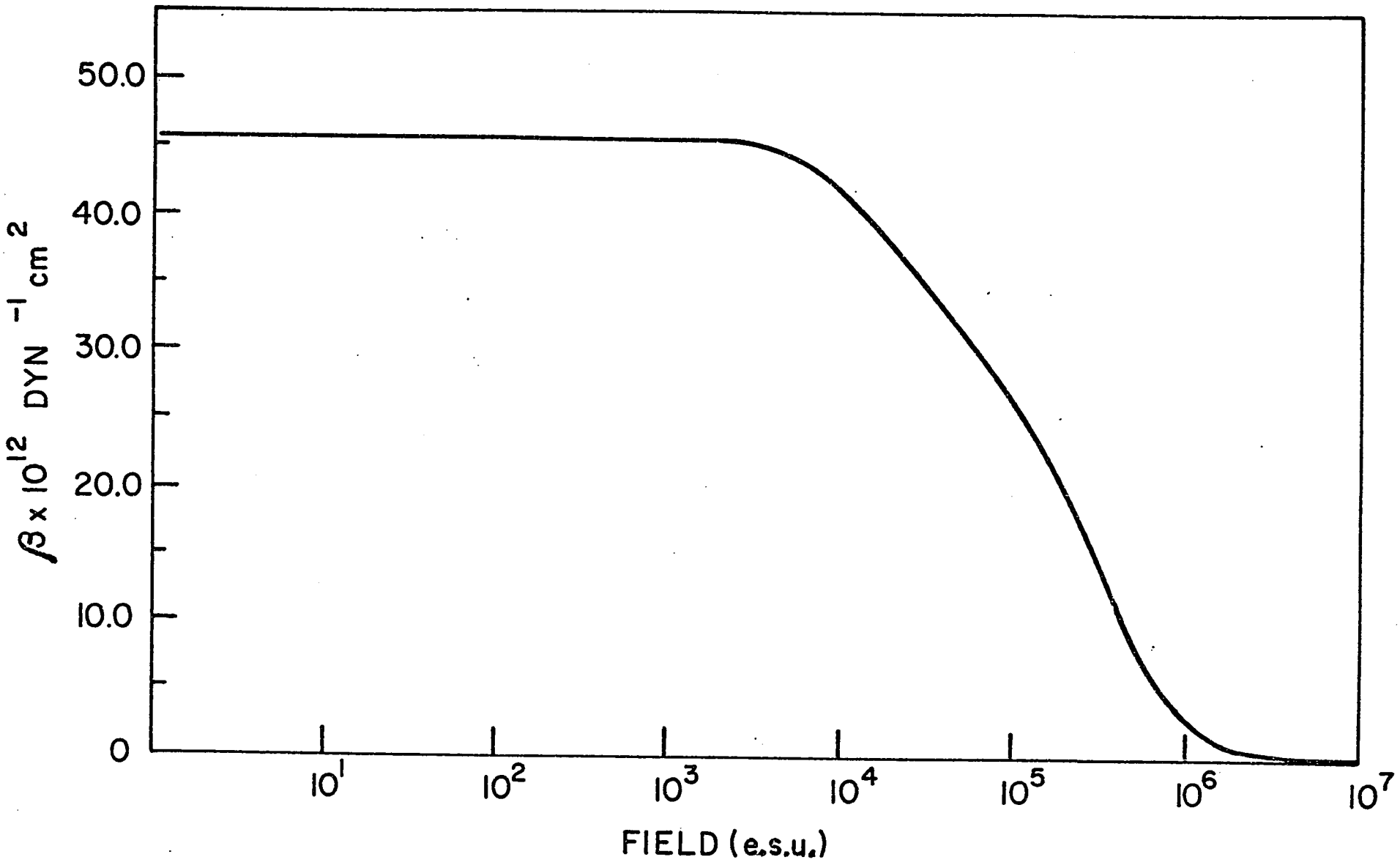

12
10
8
6
4
2
0
Δν (mI)
10^2
10^3
10^4
10^5
10^6
10^7
FIELD (e.s.u.)

Figure 3. Effective local compressibility β of water as a function of field associated with the ion.


50.0
40.0
30.0
20.0
10.0
0
$\beta \times 10^{12}$ DYN $^{-1}$ cm ^{2}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
FIELD (e.s.u.)

The calculations are based on a continuous dielectric model which is justifiable since the effects calculated are essentially independent of the size or symmetry of the ions. The change of specific solvent volume can be used to calculate the total electrostriction associated with the presence of ions in solution provided that a suitable model for solvent coordination about ions is adopted. If the results of the calculation are to be related directly to the experimental electrostriction volume ΔV, then some non-thermodynamic methods are necessary to separate ΔV into ionic components (56, 60, 118) since the change in volume of the salt, ΔV, may be measured experimentally for a pair of ions only. Once ΔV is known for individual ions, (see below) the model described in section 2 can then be used to relate ΔV to the calculated change in solvent volume Δv if the assumption is made that the number of solvent molecules in the first shell is equal to the coordination number x_1 for the primary shell of the ion, the number of solvent molecules in the second shell is equal to the second time-average coordination number x_2, etc., Then the total electrostriction for a given ion is represented by

$$\Delta V = x_1 \Delta v_1 + x_2 \Delta v_2 \qquad \text{III·31}$$

The average field in each shell is required to calculate the local volume changes Δv_1 and Δv_2 and would be estimated approximately by combining a suitable theory of dielectric saturation with the electrostatic field relation (8), $E = -\frac{ze}{\epsilon r^2}$, where r is the effective distance between the centre

of the ion and the water molecule, or with the Poisson - Boltzmann relation (31).

The explicit equations relating the change in volume of water and field intensity are obviously only valid under strictly limited conditions. The low field approximation will fail for fields above 10^3 e.s.u., so that any treatment of electrostriction which neglects dielectric saturation effects will give erroneous results except for the conditions existing near large ions. The high field approximation would seem, in most cases, to be much more satisfactory for the interpretation of volume changes associated with hydration. For example, it is reasonable to assume that virtually all the electrostriction occurs in the first coordination shell surrounding the ion in the case of most univalent ions.

Two particular cases may be considered to test the validity of the treatment, e.g. Na^+ , F^- and a tervalent ion. Blandamer and Symons (142) have recently suggested that the experimental ionic radii obtained by Gourary and Adrian (143) are more satisfactory than Pauling's for the discussion of properties of ions in solution. On this basis, the radii of Na^+ and F^- are approximately equal and have the value of 1.17Å. The average electrostatic field acting on the water molecules in the first coordination shell is given by $\frac{-z\,e}{\epsilon r^2}$ where ϵ is taken * as 1.78 in the primary hydration shell and r is the distance (2.55Å) from the centre of the ion to the centre of a neighbouring water molecule. Thus the change in the effective molar volume of

* Somewhat larger values, e.g. up to ca.6, (146) might, however, be applicable in this region since libration contributions to the dielectric polarisation may arise (56, 60)

water for the field corresponding to the middle of the first coordination shell is obtained from equation III·30 as 2.6 ml. If the coordination numbers of both Na^+ and F^- are assumed to be 4 (cf. 100,130) then the ΔV calculated from equation III·31 would be 20.8 ml., a figure which agrees quite well with the values which may be derived from interpretations of experimental data (111, 118, 144, 145) e.g., for $NaF_{aq.}$ as listed below:

ΔV ml. for Na^+F^- aq.	Reference
Between 17.9 and 20.8	Padova (111)
18.6	Deno and Spink (144)
21.1	Noyes (145)

Using the full numerical solution for P as f (E), Δv=3.1 for these ions, so that ΔV= 24.8 ml. if x_1=4 for Na^+ and F^- ions (55). Electrostriction effects beyond the first coordination shell would not exceed 5% of the primary shell contribution for univalent ions as may be seen from Table 2.

Equation III·30 may be checked further by calculating the molar volume of the water in the first coordination shell near a tervalent ion. Such ions probably have 6 water molecules primarily coordinated and in a hexagonal arrangement (cf. octahedral hydrate complexes) and 8 other more weakly coordinated water molecules further out (147). The minimum distance between the centre of the ion and that of a water molecule primarily coordinated is 2.0Å, and the molar volume at this distance calculated from equation III·30 is 10.3 ml. The volume which may be estimated on the basis of an hexagonal

model of 6 incompressible spheres of radii 1.38Å is 11.9 ml. which is in satisfactory agreement with the figure estimated above. Generally, x may be estimated if individual values of $\bar{V}_i$ are evaluated by some non-thermodynamic method of separating the ionic contributions in $\bar{V}$ for a salt and allowance for dead space in packing is made (31).

Finally the compressibility data will enable some better interpretation of compressibility measurements on aqueous solutions of ions (cf. 101, 126) to be made. The proposition that "hydration numbers" can be obtained by assuming that the effective compressibility of water in the primary hydration layer is zero (101) is evidently unacceptable except in the case of very small ions, e.g. Mg^{++}, Li^{+} which have very high surface charge densities. The field in the primary hydration layer of a great many ions is between 5×10^4 and 5×10^6 e.s.u. From Fig. 3 it may be seen that there is still significant local compressibility in the region of such ions and that the assumption that the local value of β is negligible will be incorrect.

It will be seen from the above theoretical analysis that individual partial g. ionic volumes of ions are required for proper evaluation of ΔV_i and comparison with the theoretical results. A new method for splitting the total partial molal volume of a salt into ionic components has accordingly been developed and is presented in sections of the thesis to follow. The new method has the advantage that it is less à priori and less empirical than previous methods (109, 117, 118) and is based on an experimental principle rather than an arbitrary theoretical one.

Chapter IV

Experimental

1. Partial Molal Volumes

i) Apparatus Used

Examination of the procedures for density measurements (148) indicates that the differential, magnetically balanced float method of Lamb and Lee (149, 150) has yielded excellent results, but it appears from the infrequency of its use to be a difficult technique. A single float magnetic balancing technique has been used also by MacInnes (151). Dilatometric methods, until very recently (121), involved procedures which did not appear to be well suited to work at high final dilutions (152, 153, 154). The method employed in the present work is the hydrostatic balance method of Kohlrausch (155), based on the Archimedian principle, which was shown by Wirth (156) to give a high degree of accuracy when used differentially. The differential methods allow a more direct comparison of sample and reference solution, and provide for partial cancellation of errors.

A photograph of the differential buoyancy balance used is shown in Fig. 4. A schematic diagram showing the principal parts of the apparatus appears in Fig. 5. The vessels, in which the solvent and solution were placed, were made of Pyrex tubing of 48 mm. i.d., fitted snugly in two holes cut in a horizontal sheet of plexiglass, which could be moved in and out below the balance when solutions were

Figure 4. Photograph of differential buoyancy apparatus.

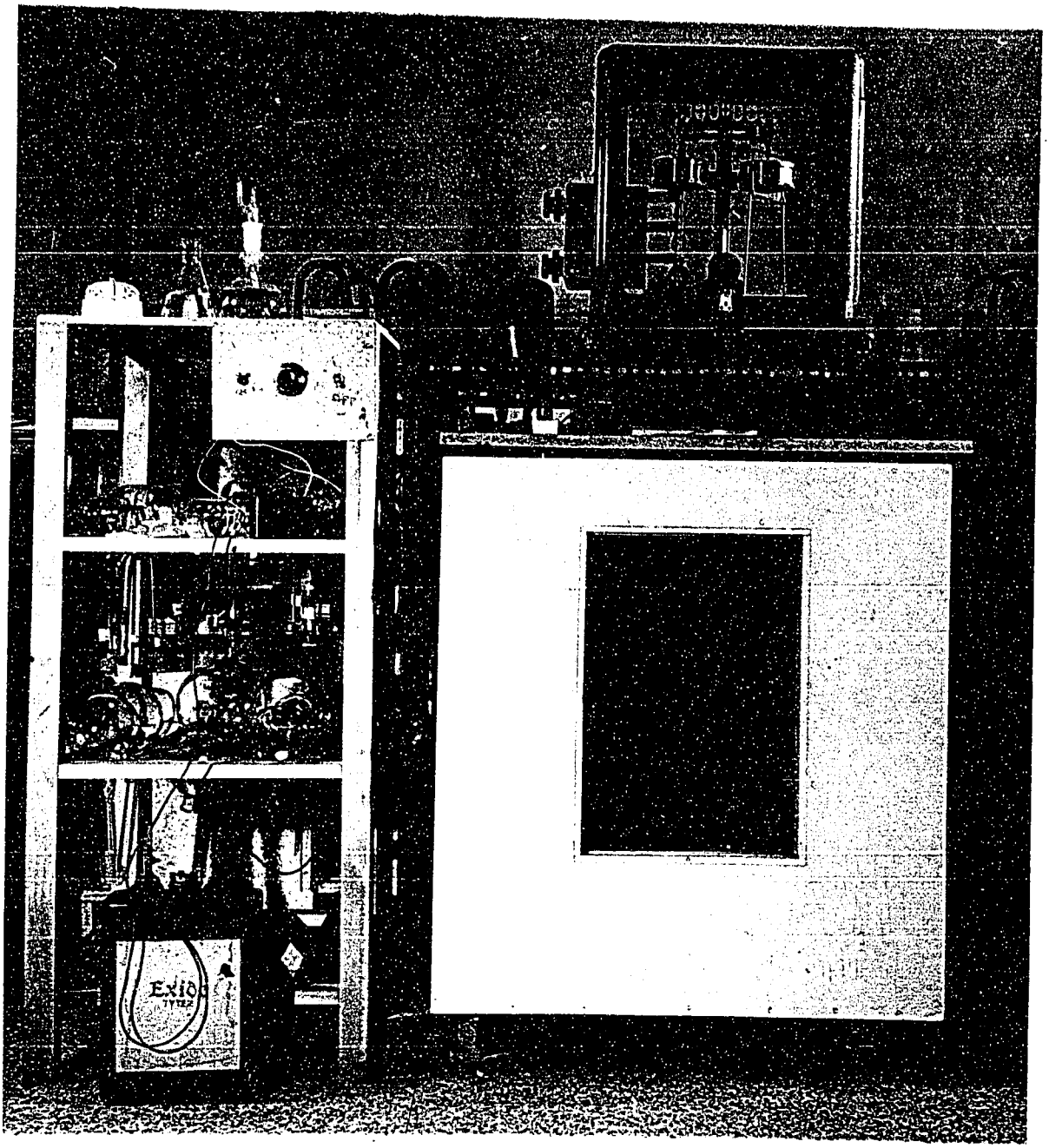
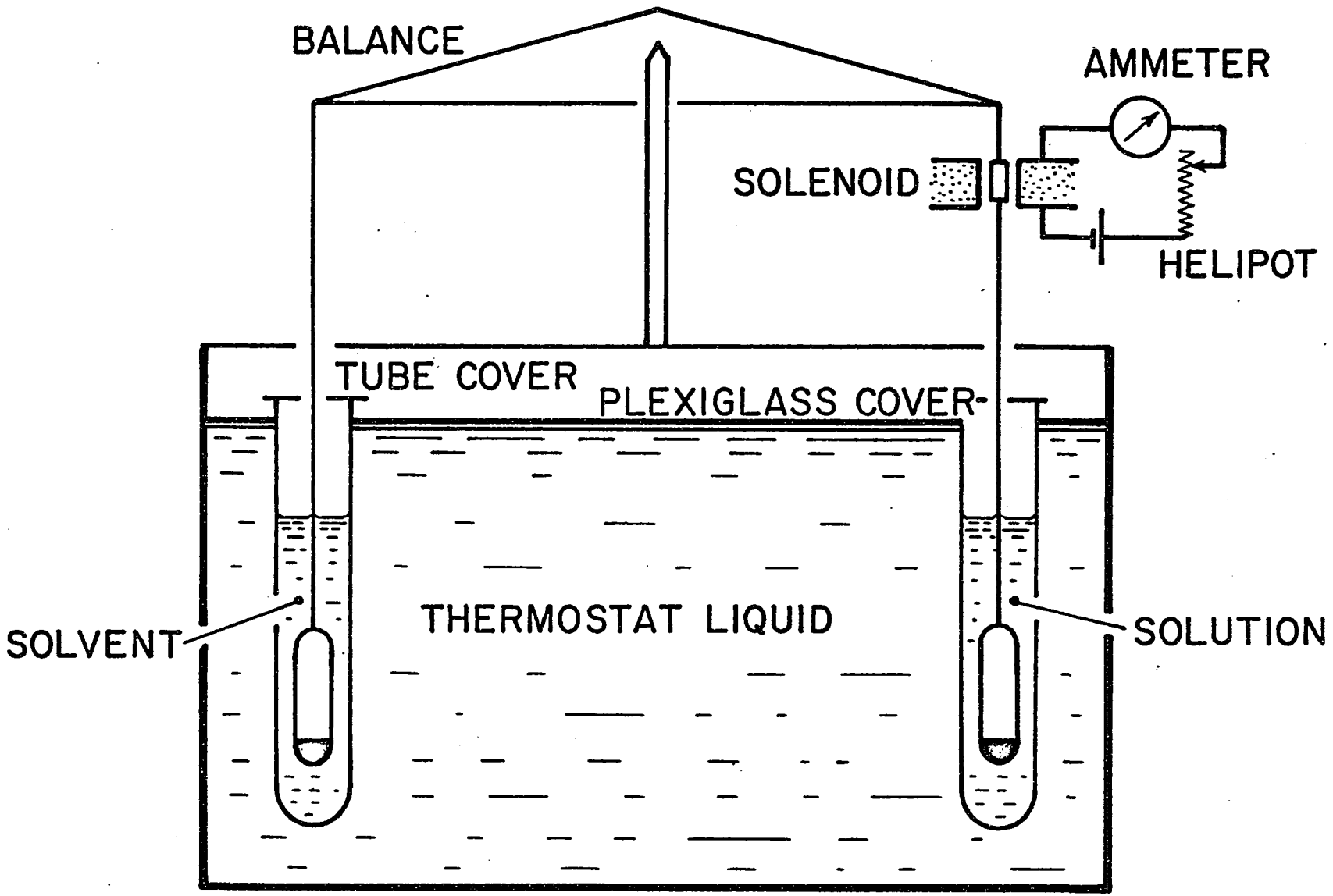

EXIDE

Figure 5. Differential buoyancy balance with variable electromagnetic bias.


BALANCE
AMMETER
SOLENOID
HELIPOT
TUBE COVER
PLEXIGLASS COVER
THERMOSTAT LIQUID
SOLVENT
SOLUTION

changed. To assure that the vessels were vertical, i.e., to prevent sticking between the floats and the vessel, metal hooks were employed to keep the plexiglass plate horizontal. Vertical mountings, of sufficiently large bore to just allow passage of the vessels, extended downwards 5" from the plexiglass sheet to assure satisfactory alignment of the two vessels.

The floats, blown of Pyrex tubing of 40 mm. o.d., were cylindrically shaped with a conical base and a spherical top. The floats had a volume of about 120 ml. and were loaded with mercury to have an average apparent density of about 1.12. The suspension wires were fastened to glass hooks glass-blown on the tops of the floats. The lower parts of the suspension wires were initially made of fine Pt wires black-platinised at the contact with the solution meniscus but fine tungsten wires of 0.0015" - 0.002" diameter were later found to be preferable. The upper parts of the suspending wire were fine gold plated chains connected to the pans of the balance.

All measurements were made in a large, well lagged water thermostat provided with an annular window and heated by means of a partially immersed electric bulb; temperature was controlled by a large mercury thermo-regulator; the bath was located in a room, the temperature of which was controlled to 1°C. A high speed stirrer situated deep into the bath provided good circulation.

The Archimedian weights of the immersed bulbs were determined differentially by means of a calibrated balance

(Bosch) to 0.1 mg. in ca. 15 g. apparent weight. Approach to an equilibrium condition of balance was always made with the solution float descending to the equilibrium position. This was achieved by applying an adjustable bias provided by a solenoid acting on a small iron cylinder in the suspension wire on the solution-side of the differential buoyancy balance, as shown schematically in Fig. 5.

ii) Accuracy of Apparatus, Errors, and Calibration

The overall accuracy of the apparatus was sufficient to allow densities to be evaluated to six decimal places. The volumes of the floats were determined precisely by weighing in pure water and in air at 25°C with buoyancy corrections in the latter measurements. The temperature of the bath was maintained constant to 0.01°C and measured on a previously calibrated thermometer having a 12 inch scale for a range of 6°C. Temperature differences across the thermostat from one vessel to the other were undetectable. This accuracy of temperature control was sufficient to enable density differences of 2 in the sixth decimal place to be significant. The floats were scrupulously examined in each measurement for adhering small air bubbles which were removed if present.

The presence of dissolved air was shown to have no effect on the results provided it was present in both the solvent and solution tubes. Any tendency for salting-out of the dissolved air in the solution vessels was insufficient to affect the results significantly at the dilutions of salts used.

No difficulty with regard to surface tension effects and wetting properties of the solutions with respect to the wire was encountered. The application of an adjustable bias provided by the solenoid acting on the small iron cylinder in the suspension wire (Fig.5) on the solution-side improved reproducibility in the sixth decimal place in the density measurements presumably by maintaining a uniform meniscus configuration, and eliminating variations in weight due to evaporation of the salt solution on the wetted wire. The length of suspension wire submerged during a run with any particular salt was always kept the same in both the solvent and solution vessels.

The density measurements were reproducible to 3 in the sixth decimal place and the absolute accuracy of the measurement was determined with test runs on KCl solutions; the values agreed to within 0.06 ml. mole^{-1} or ca. 0.1% of the published data (156).

iii) Purification of Salts

(A) Tetra-n-alkylammonium halide salts

The salts used were Eastman reagent grade materials. They were purified at least once by recrystallisation; in some cases, for example, with the higher members of the bromide and chloride series, second recrystallisations were carried out to assure highest purity. The purification of the salts is not well described in the literature and considerable difficulty was found in determining the best solvents for recrystallisation since the solubility behaviour of each salt is

somewhat specific and most of the salts are quite soluble both in aqueous and non-aqueous solvents. Accordingly, the solvents and conditions used for the recrystallisations are recorded in Table 3.

Each salt, after purification, was dried at 60-70°C *in vacuo* for at least three days prior to use. In the case of the iodide compounds, the salts were kept under subdued light to prevent decomposition when measurements were not being carried out.

TABLE 3

Solvents and conditions for recrystallisation of the tetra-n-alkylammonium halide salts

Salt	Solvent for recrystallisation
$(CH_3)_4NI$	Double distilled water
$(C_2H_5)_4NI$	EtOH
$(C_3H_7)_4NI$	"Spectroquality" Me_2CO
$(C_4H_9)_4NI$	"Spectroquality" Me_2CO/Et_2O (75/25 by volume)
$(CH_3)_4NBr$	MeOH/EtOH (50/50 by volume)
$(C_2H_5)_4NBr$	MeOH
$(C_3H_7)_4NBr$	"Spectroquality" Me_2CO
$(C_4H_9)_4NBr$	EtOAc/Et_2O (75/25 by volume)
$(C_5H_{11})_4NBr$	EtOAc
$(CH_3)_4NCl$	MeOH/Et_2O (80/20 by volume)
$(C_2H_5)_4NCl$	MeOH
$(C_3H_7)_4NCl$	First recrystallised from EtOAc by adding chilled Et_2O to the soln. and then cooling to -10^oC. Crystals washed well with Et_2O. Salt then recrystallised twice from (40% EtOH-20% Et_2O-40% EtOAc by volume).
$(C_4H_9)_4NCl$	Same as for $(C_3H_7)_4NCl$ except for use of (20% EtOH-40% Et_2O-40% EtOAc by volume).

(B) n-Alkylamine hydrogen chloride salts

a) Purification of $CH_3NH_2 \cdot HCl$, $(CH_3)_2NH \cdot HCl$, and $(CH_3)_3N \cdot HCl$

The salts used were Fisher highest purity reagent grade materials. They were recrystallised twice from methanol-diethyl ether mixtures of varying volume compositions. The volume percent of diethyl ether never exceeded 30. In some cases, removal of some of the solvent on a rotating vacuum flash evaporator had to be carried out to induce the salt to recrystallise. The use of a cooling mixture of crushed ice-salt slush near 0°C also helped the recrystallisation to occur. Each salt, after purification, was dried at 50°C *in vacuo* for 4-6 days prior to use.

b) Preparation and Purification of Triethylamine and Tri-n-propylamine hydrogen chloride.

α) Triethylamine hydrogen chloride

Triethylamine hydrogen chloride was prepared by bubbling dry HCl gas into triethylamine. The amine was Eastman reagent grade material that had been purified by distillation under a nitrogen atmosphere at 55 mm. Hg pressure. The HCl gas was dried by bubbling through concentrated H_2SO_4 before being passed into the amine. The impure salt was recrystallised twice from ethanol and dried *in vacuo* at 50°C for 3 days prior to use.

β) Tri-n-propylamine hydrogen chloride

Tri-n-propylamine hydrogen chloride was prepared by bubbling dry HCl gas at a moderate rate into a 1:1 (or less by volume) mixture of benzene and Eastman reagent grade tri-

n-propylamine under a nitrogen atmosphere. The HCl gas was again dried by passing through concentrated H_2SO_4 and the amine was previously purified by distillation under a nitrogen atmosphere at 15 mm.Hg. pressure. A crushed ice-sodium chloride cooling slush was used to cool the reaction vessel down to 0^o - 5^oC. This minimises elimination of alkyl halide which can occur as a side reaction at higher temperature. The resulting salt was washed well with petroleum ether and then recrystallised from chloroform with the aid of diethyl ether to diminish solubility. The recrystallised salt was washed on the filter with chilled diethyl ether and dried in a vacuum oven - without heat. It was removed from the vacuum oven, ground thoroughly, and then placed in the vacuum oven at 50^oC for 4-6 days.

(C) Alkylamine hydrogen iodide salts

The hydrogen iodide salts of n-propyl, di-n-propyl, and tri-n-propylamine were prepared in a similar manner. HI gas, dried by passing through a U-tube containing P_2O_5, was bubbled into a mixture of amine and nitromethane. The amine in every case was purified by distillation under reduced pressure. The reaction system was essentially closed except for a P_2O_5 drying tube over a positive pressure safety outlet. A very moderate rate of bubbling was required to prevent excessive localised heating. Such heating produced a precipitate containing an appreciable amount of iodine which was undesirable. The reaction flask was cooled by a dry ice-acetone mixture to - 15^oC.

The salts were recrystallised from ethanol-diethyl ether mixtures at least three times and dried at 60°C *in vacuo* for 4-6 days. As in the case of the tetra-*n*-alkylammonium iodide salts, these compounds were kept under subdued light to prevent decomposition when measurements were not being carried out.

iv) Examination of the Purity of the Compounds Used

(A) Tetra-n-alkylammonium halides

The careful recrystallisation procedure carried out on these reagent grade salts was considered sufficient to provide compounds of a reasonably high degree of purity. However, an attempt to provide an independent criterion for the extent of purity was thought advisable. Melting point determinations were carried out, but in some cases, due to the high melting point, decomposition temperatures had to be noted. In all cases there was good agreement with literature values.

One extensive gravimetric determination was carried out on a compound to provide some absolute knowledge of the purity. Three different samples of Eastman reagent grade $(n\text{-}C_3H_7)_4NBr$ were recrystallised separately as outlined in section (iii-A) of this chapter. Two gravimetric determinations of bromide were carried out on each sample according to the procedure outlined in Kolthoff and Sandell (157). A control determination of bromide ion in reagent grade KBr was simultaneously carried out with sample III.(Table 4) The KBr salt was not recrystallised but simply dried at 80°C *in vacuo*. The percentage bromide ion found, based on the theoretical amount of bromide ion expected in the sample, is shown in Table (4a)

The results indicate that the $(\underline{n}\text{-}C_3H_7)_4NBr$ is sufficiently pure and it is felt that similar purification techniques carried out on the other salts should be expected to provide a similar degree of purity. The value for KBr is rather low, but, considering that it was not recrystallised, the value is in fair agreement with the anticipated degree of purity in reagent grade KBr.

(B) Alkylamine hydrogen chloride salts

The melting points of the recrystallised alkylamine hydrochlorides were in good agreement with literature values (158), except in the case of the tri-n-propylamine salt. The reported melting point of 90°C was in considerable disagreement with the experimental melting point of 137°C. A gravimetric determination of chloride ion in tri-n-propylamine hydrogen chloride, according to the method outlined in Kolthoff and Sandell (157), showed that the compound contained 99.95% of the theoretical amount of chloride ion expected in the compound, assuming that the compound was $(\underline{n}\text{-}C_3H_7)_3N.HCl$ (Table 4b). It would appear that the literature melting point is incorrect.

(C) Alkylamine hydrogen iodide salts

The purity of all three compounds was determined by means of a volumetric determination of iodine (159). The results are shown in Table (4c).

Table 4

Results of Gravimetric Determination of Br^- in $(n\text{-}C_3H_7)_4NBr$

a)

Salt	%Br^- found	%Br^- found	%Br^- found
	Sample I	Sample II	Sample III
$(n\text{-}C_3H_7)_4NBr$	99.69 99.78	99.81 99.60	99.66 99.67
KBr	- - - -	- - - -	- - 98.42

Results of Gravimetric Determination of Cl^- in $(n\text{-}C_3H_7)_3N.HCl$

b)

Salt	%Cl^- found
$(n\text{-}C_3H_7)_3N.HCl$	99.82 99.98

Results of Volumetric Determination of I^- in $n\text{-}C_3H_7NH_2.HI$, $(n\text{-}C_3H_7)_2NH.HI$, and $(n\text{-}C_3H_7)_3N.HI$.

c)

Salt	%I^- found
$n\text{-}C_3H_7NH_2.HI$	99.60 99.50
$(n\text{-}C_3H_7)_2NH.HI$	99.90 99.60
$(n\text{-}C_3H_7)_3N.HI$	99.40 99.50

v) Procedure Used in Density Determinations

The solutions were made up volumetrically in calibrated volumetric flasks at 25°C. An exact weight of salt, weighed by difference, was placed in each flask. The salt was then dissolved in double distilled water and brought to approximately three milliliters below the calibration mark on the flask. The volumetric flasks were thermostated at 25±0.03°C, and shaken periodically for approximately thirty minutes. The solution was then brought to the mark with double distilled water kept at the same thermostated temperature. The solutions remained in this constant temperature bath until measurements were carried out.

The tungsten suspension wires were prepared the day prior to that for their use in the density measurements. The wire was thoroughly cleaned first by soaking in CCl_4, then in methanol and finally washed and allowed to soak in pure water for a day. When the wires were not used they were kept in the pure solvent water.

The mercury loaded floats and the vessels in which the pure solvent and solutions were placed, were scrupulously cleaned before each run. A run usually consisted of between 8-12 density measurements.

Each run was started with a "zero determination" (both floats in the pure solvent). The level of the solvents in the vessels was precisely marked so that the length of submerged suspension wire would never vary during a run.

The covered vessels, with the solvent and floats in them, were allowed to come to temperature equilibrium with the water bath (approximately 20 minutes). The caps were then removed from the vessels, the floats moved in a vertical direction several times to assure thermal homogenity of the solvent, and the suspending wires connected to the floats. The floats were scrupulously examined in each measurement for adhering small bubbles which were removed if present. Approach to an equilibrium condition of balance was then attempted. Once an approximate equilibrium balance position was obtained, this point was then repeatedly approached with the float rising or descending to the equilibrium point on the solution side. This was achieved by applying an adjustable positive or negative bias provided by the solenoid acting on the small iron cylinder in the suspension wire on the right-hand side of the differential buoyancy balance. The time taken to obtain a reproducible balance position in pure solvent varied between 15 - 30 minutes. This stringent procedure was followed on account of the importance of this reference reading. Any error in this "wt_o" reading introduces a constant error in the absolute density measurements which effectively shifts the extrapolated value for the apparent molal volume at infinite dilution.

The right-hand vessel was then emptied and dried. A solution of known concentration was placed in the vessel to the same precise level as that noted for the pure solvent. A change in the procedure outlined in the previous paragraph was employed for the determination of the balance position in this

case. An approach to the equilibrium balance position "wt" was always made with the solution float descending to the equilibrium position. This procedure improved reproducibility in the sixth decimal place in the density measurements presumably by maintaining a uniform meniscus configuration, as mentioned previously, and eliminating variation in weight due to possible evaporation of the salt solution on the wetted wire. The difference in density between the pure solvent and that of the solution can be obtained from the difference in weight, "$wt-wt_o$", and the known volume of the float on the solution side.

2. Compressibility

i) Apparatus Used

A photograph of the apparatus is shown in Fig. 6. The apparatus consists of two main parts:

a) the test vessel and the mechanical assembly holding the resonant frequency transducers, shown in Fig. 7, and

b) the associated electronic components shown diagramatically in Fig. 8.

The density measuring apparatus described in section 1, is also utilised in the determination of compressibility coefficients. The apparatus shown in Fig. 6 is designed to provide a technique for the direct measurement of the difference between the velocity of sound in two liquids. The principle of the method was originally suggested by Carstensen (127) and the design of his apparatus has generally formed the basis of the present apparatus. Mechanical refinements in the sliding assembly and more up to date electronic components have been incorporated to improve the precision.

(A) The Mechanical Assembly and Test Vessel

The first test vessel consisted of a plexiglass ($\frac{1}{2}$" thick sheet) rectangular container divided into two compartments by a dividing section in which there was a large circular hole. A polyethylene plastic film window was inserted over this circular hole. It was made leak-proof by means of a circular silicone O-ring placed between the dividing section and a pressure plate which could be pressed against the dividing wall of the vessel by means

Figure 6. Photograph of differential velocity measuring apparatus.

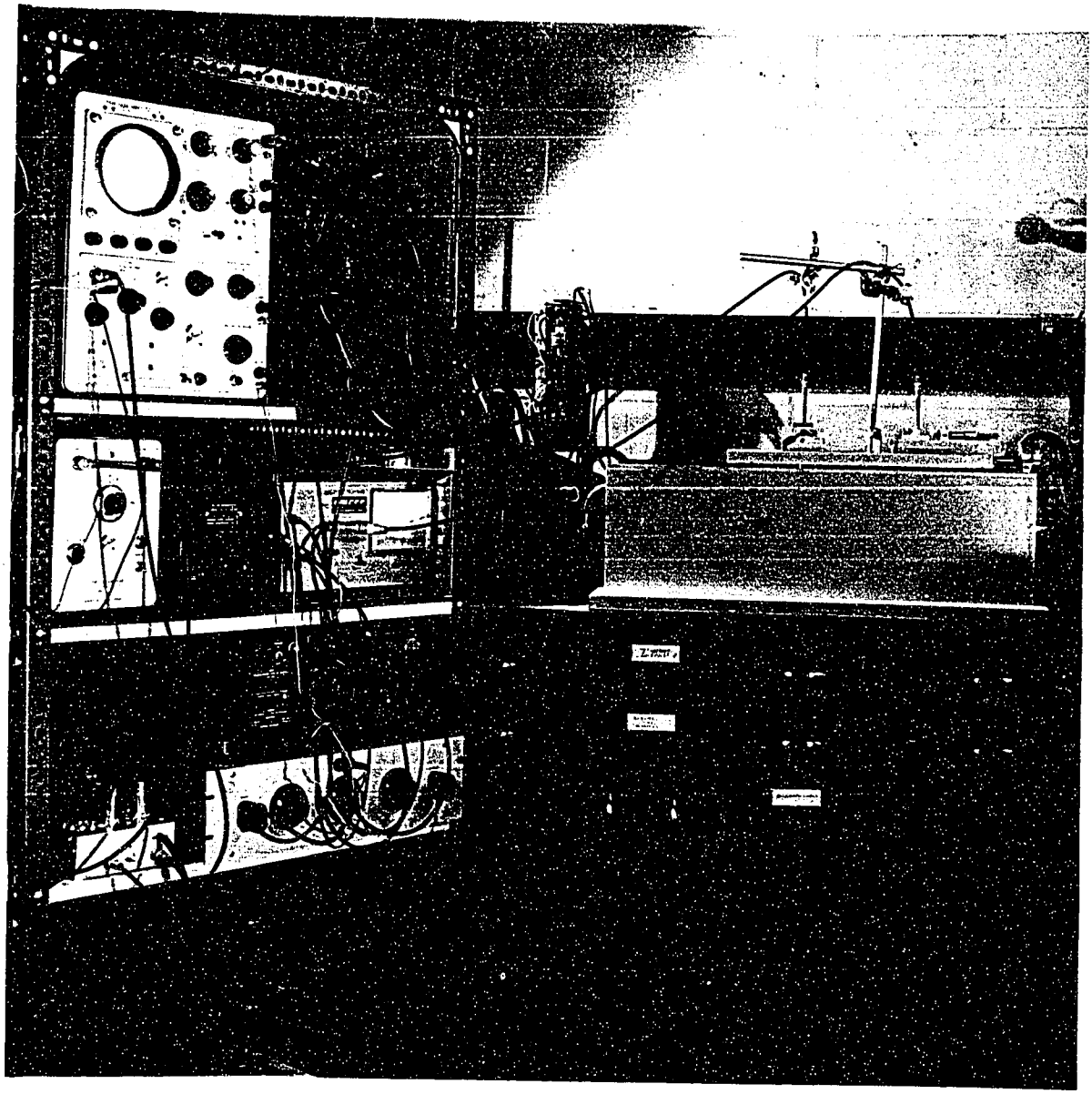


Figure 7. Mechanical assembly and physical arrangement of transducers for differential velocity measurement.

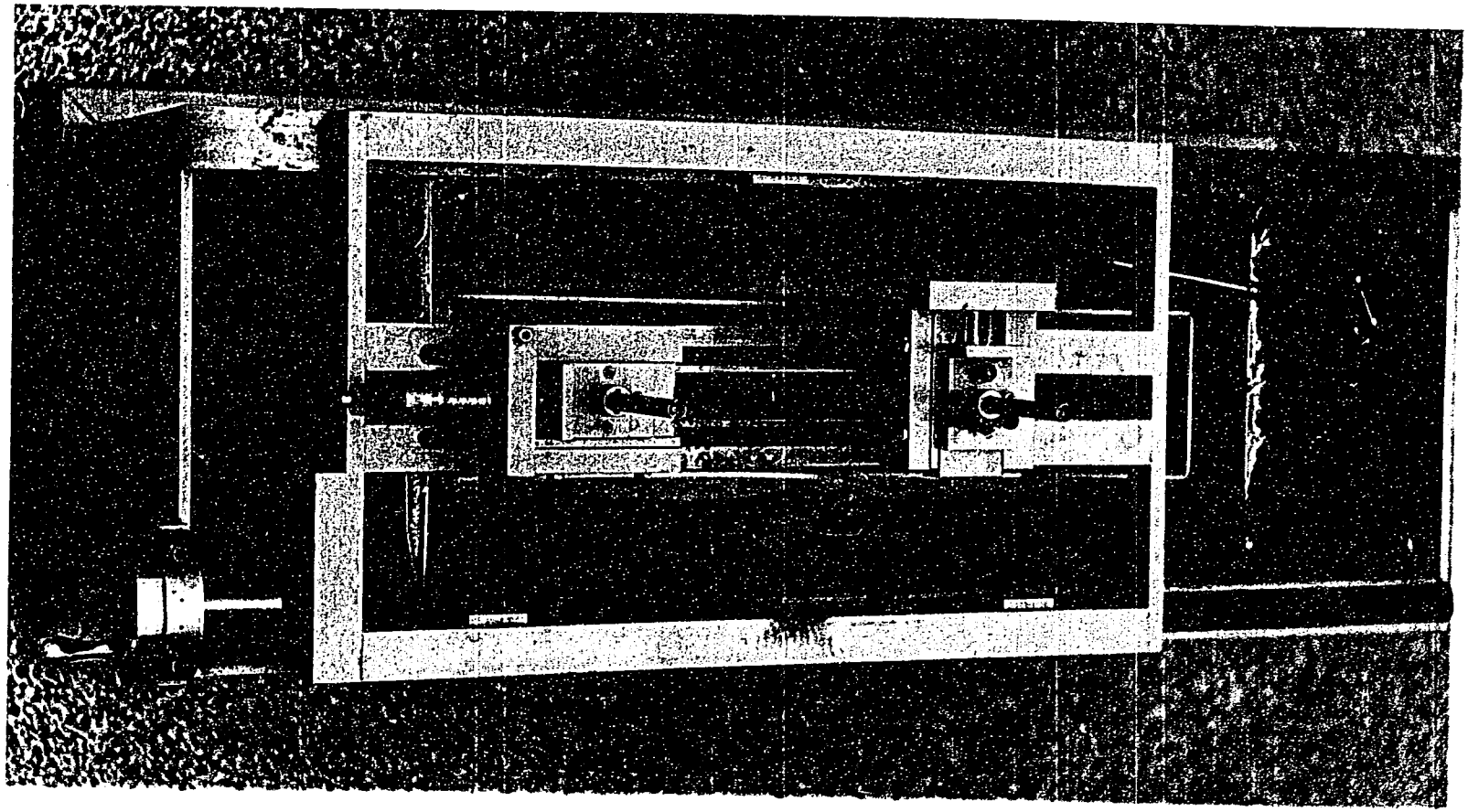
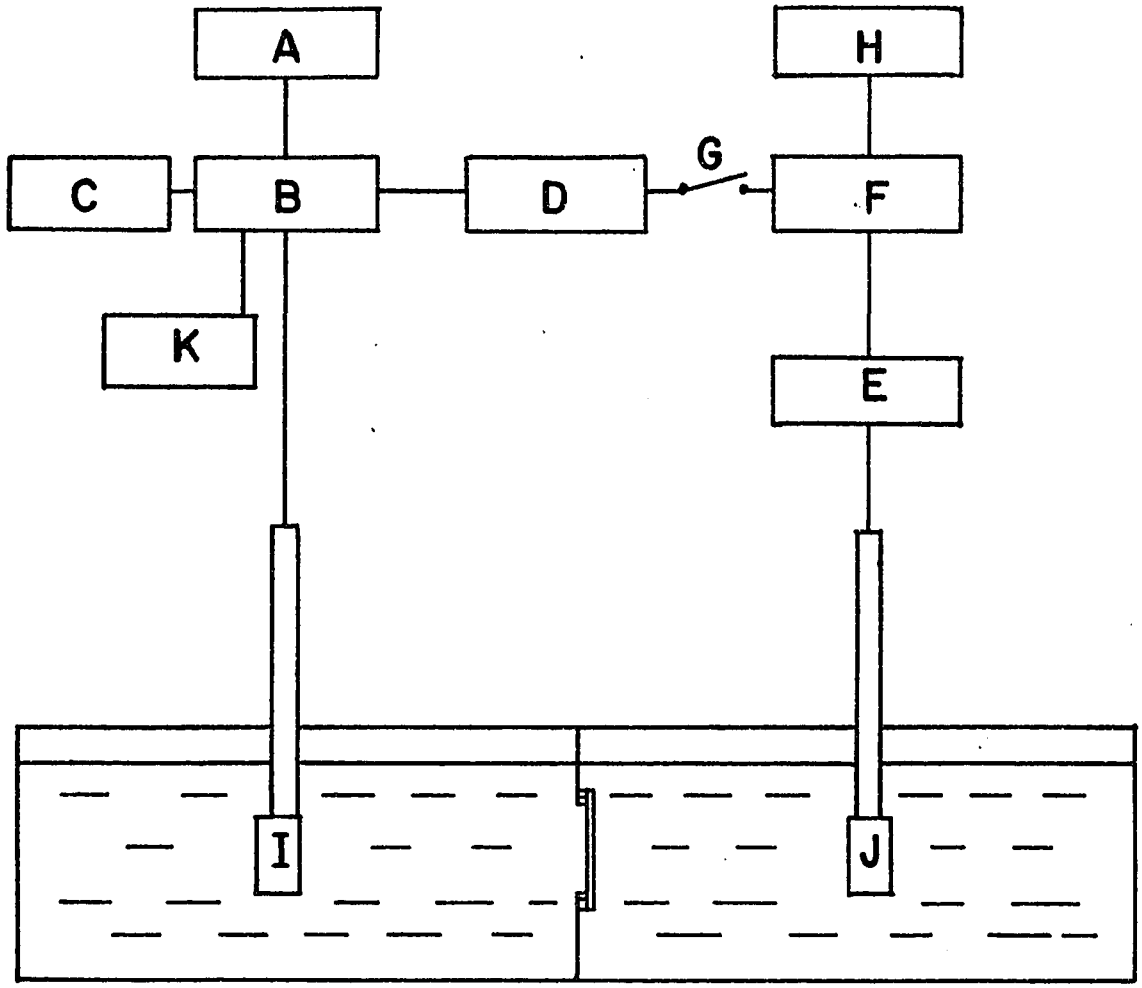


Figure 8. A block diagram of the electrical circuit used for differential velocity measurement.



KEY

A - R.F. Oscillator

B - Pulse Modulator

C - Pulse Generator

D - Decade Attenuator

E - Broad Band Amplifier

F - Tuned Amplifier and Mixing Circuit

G - Phase Comparison (On-off switch in Mixing Circuit)

H - Oscilloscope

I - Source Transducer

J - Receiver Transducer

K - Frequency Meter

of teflon screws. Therefore the vessel was able to hold one compartment filled with pure solvent, the other with the solution under investigation. No change of concentration was observed due to leakage.

The volume of the original test vessel was too large for some salt solutions used and a second vessel was designed. It was made of 3/32" thick stainless steel sheet electrically arc-welded together. The polyethylene plastic film window was employed again as a covering for the circular hole in the vessel divider. Threaded studs protruded from one side of the divider and allowed a pressure plate to be clamped against the film and the silicone O-ring. All components of the vessel were made of stainless steel material except for the plastic film and O-ring.

The test vessel was mounted on four supports in a stainless steel thermostat bath such that five sides of the test vessel were in constant contact with circulating thermostated water. This constant temperature water was thermostated in a well-lagged and covered bath situated next to the apparatus. The stainless steel bath was insulated with 2 layers of asbestos cloth.

Around the stainless steel bath was situated a $\frac{1}{4}$" rectangular aluminium frame rigidly held in place on a grooved wooden base. This aluminium frame was the support for the sliding assembly which was guided in its movement along the axis of the test vessel by means of two locating V-blocks

that rested on a triangular rail. The assembly was supported on the opposite side by a ball bearing which rolled on a flat machine surface. The entire assembly could be moved along the axis of the test vessel by a micrometer screw 24" long. The threaded screw was rigidly held in place at one extremity by a support block fitted on the aluminium frame with the threaded extremity extending through a threaded hole in the sliding assembly. The screw had a metric thread of 1 millimeter pitch and the screw shaft was fixed to a rotatable disc graduated into one hundred equal divisions. Manual movement of this disc propelled the sliding assembly along the main vessel axis.

The mechanical transducer supports cannot be completely rigid. The support for the receiving transducer was mounted in a guided traverse and could be moved by a micrometer screw in the direction of the axis of the test vessel. The source transducer support was a plate screwed to a guided traverse by means of three fine threaded screws. This three centred support allowed precise alignment of the source transducer with respect to the receiver transducer. The traverse in this instance could be moved in a direction perpendicular to the main axis of the test vessel and was controlled by another micrometer screw. These precise alignment features are necessary since the transducers have very directional behaviour at higher frequencies. The transducers were held in their supports by means of a screw. The transducer support traverses

and their guide blocks had machine-finished surfaces of contact, since any friction which might cause bending or twisting stresses must be eliminated for accurate work.

The transducers used were Glennite ceramic units purchased from Gulton Industries Inc. They were approximately 1 to 1½ inches in diameter and 0.01 to 0.1 inches thick, depending on their resonant frequencies.

The mechanical backbone of the transducer holder was a 3/8" diameter brass tube soldered to a machined brass disc having the same inside diameter as the ceramic disc. The electrical contact was made through a BNC chassis mount female connector with the flange turned down to fit the tube. After soldering a rod to the centre conductor terminal, the assembly was soldered into the brass tube. A small teflon washer supported the centre rod. The ceramic disc which fits in the brass disc was backed by ¼"thick low-density balsa wood. A pliobond cement was used to stick the disc to the backing, and this to the brass disc.

The ceramic transducers were silver coated on each surface and had 1/16" wide gold foil leads attached near the edge of each electrode, extending radially. To maintain shielding, the lead from the back electrode passed through an insulated hole in the brass disc and was soldered to the centre conductor. A short length of 3/8" i.d. tubing was slipped over the hole and fixed in place, one end being soldered to the brass disc, the other to the 3/8" brass tube backbone. The lead from the front electrode was soldered to this sleeve. The part

of the assembly that was to be under the liquid surface was covered with General Electric RTV rubber silicone cement and allowed to dry. To reduce electrical pickup between the transducers, a coat of epoxy silver conductive synthetic coating was used over the silicone rubber layer and extended up to the brass. Finally, another coating of silicone rubber was placed over the silver paint. Sufficient drying time, usually 24 hours, was allowed between each application of the coating to ensure complete insulation.

(B) The Associated Electronic Components

The radio frequency (R.F.) oscillator or signal source was a General Radio 1211-C unit powered by a General Radio 1201-B unit regulated power supply. This unit oscillator provided a frequency range of 0.5 to 50 Mc in two ranges and had a power output of at least 200 milliwatts into a 50-ohm load at any frequency.

The pulse modulator was a specially built unit with a useful radio frequency range of 0.5 to 11 Mc. The power output was a minimum of 1 watt over the R.F. range at load impedances of 50 to 100 ohms. The R.F. drive signal required was 0.1 volts. It had a useful pulse width range of 20 to 100 microseconds and a pulse height requirement of +5 to +12 volts peak to peak. Over the range of 20 to 100 microseconds pulse width, the unit will produce pulsed R.F. signals over the useful R.F. range with a turn-on and turn-off time of less than 5 cycles of R.F. at 1 Mc. frequency.

The pulse generator was a General Radio 1217-B unit powered by a 1201-B General Radio power supply. It had a pulse repetition frequency of 2.5 cps to 500 kc. The output pulse duration was from 10 nsec. to 1 sec. in seven decade ranges and the rise time of any transient when terminated into a 50- or 100-ohm cable was less than 20 nanoseconds (nsec.).

The frequency of the signal was measured by means of a U.S. Army Signal Corps frequency meter type BC-221-AH, capable of measuring frequencies in the range of 125 to 20,000 kc and powered by dry cell batteries. The meter consisted of four principle operating parts:

a) a variable frequency oscillator, which is a source of R.F. signal of adjustable frequency;

b) a crystal oscillator circuit, which enables the frequencies emitted by the variable frequency oscillator circuit to be checked;

c) a detector or mixer circuit, which detects the difference of the frequencies of the preceding two oscillator circuits after combining the two frequencies electronically;

d) an audio-amplifying circuit which amplifies the difference or beat frequencies produced in the detector or mixer circuit when impulses from the crystal oscillator, or from an outside source, are mixed with impulses from the variable frequency oscillator.

The pulse modulated signal output from the pulse modulator is sent through the source transducer and picked up by the

receiver transducer after passage of the ultrasonic signal through the liquid. The signal is then amplified by a Tektronix 1121 broad band amplifier which is a self-contained two-stage amplifier. Over-all gain of the unit is 100. Thus, with maximum input of ± 10 mV, the output is ± 1V. A turret-type step attenuator permitted attenuation of the input signal from 1X to 500X in nine calibrated steps. This allowed a signal of up to ± 5 volts at the input connector without overloading the amplifier. Connection between the Type 1121 and the equipment it is to drive was via a matched 93-ohm coaxial cable. The band pass is from 5 cps to 12.0 Mc at highest attenuation.

The receiver transducer signal, after amplification by the broad band amplifier, is sent into a preamplifier, PA-620, made by the Arenberg Ultrasonic Laboratory. The amplifier is a general purpose device that makes available a tuning coil which will resonate at any frequency from 6-60Mc with a capacitive source from 5 to 100 pfd due to the ultrasonic transducers and cables. It narrows the pass band by means of introducing variable resistors and tuning coils into the circuits. The coils are slugtuned and may be easily varied to peak the signal at any frequency in the range. Insertion of a second signal at fixed impedance level for comparison purposes is allowed, and with proper phase adjustments, this stage can act as a cancelling device. The signal to noise ratio is improved and sufficient gain, with a low noise figure, is also obtained. The important features from the

viewpoint of its use in this apparatus are that it acts as an adjustable filter and provides a mixing circuit which enables a phase comparison to be made.

The most critical part of the electrical system is the decade attenuator, which must be adjusted during measurement to achieve a good null in the phase comparison measurement. The attenuator network used was a Daven, 3 decade type, direct reading unit, that provided accurate performance in the radio frequency range from 0 to 10 Mc. The 3 decades were 10 step, 10db per step, 1db per step, and 0.1db per step, respectively. The decade attenuator had a frequency characteristic of $\pm$ 0.2db at 0 to 10 Mc, in each of the 0.1db and 1db per step decades, and $\pm$ 0.5db in the 10db per step decade.

The resulting waveform was viewed on a Tektronix 543A oscilloscope with a Tektronix type L plug-in preamplifier in the vertical-deflection system. The risetime of this unit was between 12-15 nsec.

All electronic components were connected by means of Amphenol RG-58 A/U coaxial cables terminated in BNC standard connectors. The components were mounted in a rack and were well grounded to a utility water-pipe. The BNC connectors and the wire ends were dipped in methanol after they were soldered together to prevent any stray capacitive effects that may arise from grease etc. These stray capacitive effects distort the signal at the high frequencies employed.

ii) Accuracy of Apparatus and Technique

The technique to be described here has proven capable

of precise velocity difference measurements equivalent to a sensitivity of the order of 2-3 parts in 10^5 in a measurement of the velocity itself. It was mentioned in the previous section that the source and receiving transducers are mounted on a sliding assembly, the source being in the pure reference solvent, and the receiver in the test solution. The physical separation of the transducers is held constant, and the entire transducer assembly is moved along the axis of the test vessel by the micrometer screw.

In order to measure the relative phase of the received signal, the output of the receiver transducer was added to the reference signal which came directly from the R.F. oscillator. A sharp minimum in the sum is observed on the oscilloscope when the signals are exactly out of phase and of equal amplitude (adjusted by means of the attenuator). The phase of the received signal depends, among other things, upon the number of acoustic wavelengths "n" which separate the source and receiver. If the physical separation of the transducers is "a", and the path length in the reference solvent is "y", then

$$n = \frac{y}{\lambda_w} + \frac{a-y}{\lambda_x} \qquad \text{IV.1}$$

where λ_w and λ_x are wavelengths in the reference solvent and test solution, respectively. If the transducer assembly is moved along the axis of the test vessel a distance Δy until the received signal undergoes a 360° phase change, then the acoustic path length is increased to

$$n+1 = \frac{y + \Delta y}{\lambda_w} + \frac{a - y - \Delta y}{\lambda_x} \quad \text{if} (\lambda_x > \lambda_w) \qquad \text{IV.2}$$

Subtracting these equations, and introducing velocities instead of wavelengths, the following expression is obtained,

$$* \; u_x - u_w = u_w^2 \frac{1}{f\Delta y - u_w} \qquad \text{IV•3}$$

where f is the frequency, and u_x and u_x are velocities in the reference solvent and test solution respectively.

Equation IV•3 shows that the accuracy of the measurement of the difference of velocity is determined by the precision with which the frequency f and the quantity Δy may be measured. The quantity $f\Delta y$ is much larger than u_w, hence, errors related to the measurement of Δy determine the limit of accuracy of the velocity difference technique.

Many factors, including the electrical and mechanical characteristics of the measuring system as well as the stability of the solution under investigation determine the accuracy which, in practice, can be achieved in the determination of Δy.

No part of the electrical system is particularly critical except the attenuator, which must be adjusted during measurements to achieve a good null. Any phase shift in this unit which accompanies a gain change would appear as a change in velocity. Filtering to eliminate harmonics in the signal presented to the oscilloscope is essential. In this particular apparatus this was achieved by means of the slug-tuned coils in the Arenburg preamplifier which narrow the band-pass frequencies.

The use of pulsed sound in velocity measurements raises the question of the effect on the precision of the phase determination in the distribution of frequencies

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* The sign of Δu, i.e., $u_x - u_w$, was determined for a given solute by employing the transducers interferometrically at a high solute concentration.

associated with the pulse. Pulse lengths used are between the orders of 10^{-3} and 10^{-4} second. Calculation shows that the half-width of the effective frequency band of such a pulse is of the order of 500 to 5000 cycles, i.e., less than 0.05 percent of the carrier at the operating frequency range (8.2-8.6 Mc). The pulse generator and pulse modulator units employed in the apparatus have sharp cut-off properties and the signal viewed on the oscilloscope enables one to make adjustments such that a good null is obtained. The amplitude distribution of the frequencies composing the pulse must remain effectively constant as the transducer assembly is moved from one null to another. The effect of absorption in the liquid, or asymmetry in the compensating attenuator, is completely negligible. Hence, the distribution of frequencies remain as constant as is permitted by the stability of the pulse generator, which was very good with the particular unit employed.

Another important factor with regard to error is that the mechanical assembly must be of such a design that there is no production of slight changes in transducer separation when the carrier assembly is moved. The particular design and materials employed in the present apparatus achieved this goal. At low frequencies the transducers become less directional and reflections are limiting factors in the determination of Δy. (see also below). The frequency range covered in this work was high enough to minimize this problem.

The velocity difference technique has the effect of minimising the electrical and mechanical limitations of the measuring system. The real limiting factor in the eventual accuracy obtainable by this precision measuring system lies in the stability of the test solution both in temperature and concentration. The temperature coefficient of the velocity difference $(u_x - u_w)$ can be quite significant for most substances. Thus, to keep temperature effects in the velocity difference below one part in 10^4 requires control of the temperature of the solutions to $\pm$ 0.01°C. The temperature coefficient of the difference in velocity between, for example, water and an aqueous solution will, in general be somewhat smaller than the temperature coefficients of the velocities themselves. For such measurements, the velocity difference technique is less sensitive to temperature fluctuations than conventional direct methods of velocity measurement by means of interferometers.

The temperature of the test solution and reference solvent in these measurements was maintained constant to 25 $\pm$ 0.03°C and measured on the previously calibrated thermometer having a 12 inch scale for a range of 6°C used in the density measurements. The temperature was controlled by a mercury thermo-regulator with the temperature sensing device situated directly in the water bath around the test vessel; the thermostating liquid water was pumped from an adjacent supply bath that was well lagged and heated by means of a partially immersed electric bulb. The apparatus, including the bath, was situated in a room, the temperature of which was maintained between 24-25°C. Temperature differences between the

compartments were not greater than 0.01°C and were generally not detectable.

Change in concentration of the test solution through evaporation was minimised by covering both the test vessel and the outer temperature bath. Only a slot was provided in the test vessel cover to permit motion of the transducer assembly. Considering that the room temperature was very close to the bath temperature, errors from change of concentration due to evaporation were considered negligible.

The main sources of error in the frequency measurement were due to small variations in the value of the battery supply voltage, calibration, as well as deviations in crystal frequency. The maximum possible error in the frequency measurement, over the frequency range employed, was 0.03 percent.

The velocity difference measurements were obtained with an absolute precision of ± 0.04 $m.sec.^{-1}$ or less, and the absolute accuracy of the measurement was determined with test runs on KCl solutions. The values of the measured velocities agreed to within 0.1 $m.sec.^{-1}$ of the published data by Owen and Kronick (125), in the concentration range 0.05-0.25 molar.

iii) Systems Studied and Purification of Salts

The adiabatic compressibility coefficients of the systems mentioned below were calculated from the velocities of sound and corresponding density measurements using

equation II·19. The systems studied in double distilled water as the solvent, were: (a) the series of tetra-n-alkyl-ammonium iodides and bromides R_4NX with R=Me to R=n-Butyl, (b) the series of n-alkylamine hydrochlorides from $CH_3NH_2 \cdot HCl$ to $(CH_3)_4NCl$, and (c) the neutral amines CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$.

The purification procedure for the three homologous series of salts has been described in section (1.-iii) of this chapter. Eastman reagent grade anhydrous dimethylamine and trimethylamine were obtained in sealed ampoules and used without any further purification. The methylamine employed was an Eastman reagent grade 30 percent aqueous solution and was used without further purification.

iv) Actual Experimental Procedure

The solutions were made up volumetrically in 1 litre ground-glass stoppered volumetric flasks calibrated at 25°C. The purified salts were weighed by difference and placed in the flasks, whereas the amine liquids were added to give approximate concentrations and the exact concentration was then determined by titration with a standardised HCl solution. The neutral amine solutions were made up in 0.025 N KOH to suppress ionisation. Since the differential method was employed, the reference solvent in these cases was also 0.025 N aqueous KOH. The flasks containing the solutions were placed in a thermostat at 25± 0.05°C and filled to a point a few milliliters below the calibration mark. They were periodically shaken and after

thermal equilibration, the solutions were made up to the calibrated mark.

Prior to the commencement of a run, the electronic components were allowed to warm-up for one hour. The test solutions were pre-thermostated in a water bath at approximately 25.2°C prior to use. This was done in order to counterbalance the extra heat loss of the solutions when they were placed in the stainless steel bath and in effect kept the bath temperature from dropping excessively. Thermal equilibrium was consequently established in a much shorter time interval.

The stainless steel test vessel with reference solvent in one compartment and test soltuion in the other was placed in the stainless steel water bath. Before each run, the polyethylene plastic film was carefully checked for leakage by filling a compartment with water and observing if there was passage of water from one compartment to the other. The transducer holder assembly was then put in place with the source transducer in the reference solvent and the receiver transducer in the test solution.

Two 3/4 inch thick polystyrene filler blocks coated with silicone rubber cement were placed lengthwise along the inside walls of each compartment of the test vessel. They had stainless steel slugs in them to counterbalance the buoyancy effect and were used to decrease the compartment volume as well as provide a low density material for minimising reflections. The slotted plexiglass test vessel covers were then put

in place and the transducers connected to the electronic assembly. Because of the rapid heat conduction of the stainless steel test vessel, no problem was encountered in thermostating the liquids in the test vessel to a constant temperature within twenty to thirty minutes. Periodic manual stirring was carried out in each compartment.

Final adjustments of the electronic components were made until a sharp null point was observed on the oscilloscope screen. These adjustments were carried out while the test vessel and contents reached thermal equilibrium. Numerous measurements were made in order to obtain a precisely reproducible value of the displacement "Δy". Finally, after this measurement was carried out, part of the test solution was placed in a stoppered flask for a density determination according to the procedure outlined previously in section (1.-v) of this chapter. The test vessel and its components were removed from the bath, thoroughly washed with pure solvent, dried and made ready for the next determination of velocity difference.

Chapter V

RESULTS

1. Partial Molal Volumes

i) Graphs and Tabulations

(A) General

It was previously shown in Chapter II how the apparent and partial molal volumes of salts in solution may be calculated from the densities of these solutions. In this chapter, the results obtained for the particular systems that were studied will be shown in graphical and tabular form. Only a selection from the total number of experimental graphs obtained have been chosen to illustrate typical extrapolation procedures and experimental results. Complete experimental results for the volume studies are tabulated in Appendix I.

(B) Extrapolation Procedure

The Debye-Hückel theory of electrolytes furnishes the following limiting law in molarity c for partial molal volumes of a solute at high dilutions

$$\bar{V}_2 = \bar{V}^o_2 + k\alpha^{3/2} c^{1/2} \qquad V\cdot1$$

as shown by Redlich and Rosenfeld (160) who indicated the factors determining the limiting slope $k\alpha^{3/2}$, where α is a valence factor equal to unity for 1:1 electrolytes and k is a constant that contains the pressure dependent terms ϵ and c, the dielectric constant and concentration, respectively. An exact theoretical determination of the limiting slope for partial molal volumes of strong electrolytes as a function of $c^{1/2}$ has until recently been prevented by the lack of precise measurements

of the dielectric constant ϵ of water as a function of pressure. Recently, Redlich and Meyer (161) have given a value for the constant k as 2.792 (25°C) (or 1.868 for apparent molal volumes) based on precise measurements of the dielectric constant ϵ of water as a function of pressure by Owen and co-workers (162).

A more complete equation for the partial molal volume of an electrolyte is (163)

$$\bar{V}_2 - \bar{V}_2^o = \frac{S_{(v)} c^{\frac{1}{2}}}{1 + Ac^{\frac{1}{2}}} + \frac{W_{(v)} c}{(1 + Ac^{\frac{1}{2}})^2} + K_{(v)} c \qquad V \cdot 2$$

where the parameters $S_{(v)}$ ($\equiv k \propto^{3/2}$), $W_{(v)}$, $K_{(v)}$ and A are defined by the following equations:

$$S_{(v)} = 2.303 \nu RT \, S_{(a)} \, \frac{1}{2}\left(\frac{3\partial \ln \epsilon}{\partial P} - \beta\right) \qquad V \cdot 3$$

$$W_{(v)} = -2.303 \nu RT \, S_{(a)} A \, \frac{1}{2}\left(\frac{\partial \ln \epsilon}{\partial P} - \frac{2\partial \ln \overset{o}{a}}{\partial P} - \beta\right) \qquad V \cdot 4$$

$$K_{(v)} = 2.303 \nu RT \, B\left(\frac{\partial \ln B}{\partial P} + \beta\right) \qquad V \cdot 5$$

$$S_{(a)} = \frac{1}{\nu} \sum_1^P \nu_j z_j^2 \, (\epsilon T)^{-3/2} \, 1.290 \times 10^6 \qquad V \cdot 6$$

$$A = \overset{o}{a} \, (\epsilon T)^{-1/2} \, 35.56 \qquad V \cdot 7$$

$$B = f(c, \epsilon, k, T \text{ and } \overset{o}{a})$$

where R = gas constant per mole;

T = absolute temperature;

ν = sum of the number of cations and anions produced by dissociation of one molecule of electrolyte;

ϵ = dielectric constant of solvent;

β = coefficient of compression of solvent;

$\overset{o}{a}$ = mean distance of approach of ions in $\overset{o}{\text{A}}$ngstrom units;

k = Boltzmann constant;

z = valence;

P = pressure.

The following expression is obtained for $\bar{V}_2 - \bar{V}_2^o$ upon further expansion of equation V·2:

$$\bar{V}_2 - \bar{V}_2^o = S_{(v)} c^{\frac{1}{2}} + (K_{(v)} + W_{(v)} - S_{(v)} A)\, c + (S_{(v)} A^2 - 2\, A\, W_{(v)})\, c^{3/2} + \ldots \quad V \cdot 8$$

Assuming for the purpose of deriving an extrapolation function for $\bar{V}_2$ that the limiting law is obeyed, the value of $S_{(v)}$ may be replaced by 2.792 and the following equation* written (cf.161):

$$\bar{V}_2 - \bar{V}_2^o = 2.792\, c^{\frac{1}{2}} + hc \qquad V \cdot 9$$

A plot of $\bar{V}_2 - 2.792 c^{\frac{1}{2}}$ against concentration thus gives (cf.161) an intercept of $\bar{V}_2^o$, the value of $\bar{V}_2$ at infinite dilution and a slope h, which expresses any concentration dependence (taken to the linear term) not allowed for in the limiting law term in $c^{\frac{1}{2}}$.

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* It is to be noted that the limiting law may not, in fact, exactly apply (164) (see Discussion, Chapter VI) to the very salts that are considered in this work. However, the limiting slope 2.792 in $c^{\frac{1}{2}}$ is only used to derive an extrapolation function (cf.161) more suitable for obtaining the $\bar{V}_2^o$ values precisely.

(C) Tetraalkylammonium Halides

a) Relationship between the Volumes of the Homologous Ions

The values of the parameter h are listed in Table 5. In all cases, it is seen that the slope h is negative or slightly positive. The latter condition arises only in the case of $(CH_3)_4NI$.

Typical extrapolations of ϕ_2, the apparent molal volume, with respect to $c^{1/2}$, down to zero $c^{1/2}$ and $\bar{V}_2 - 2.792c^{1/2}$ with respect to c, down to zero c, are shown in Fig. 9, and Figs. 10a and 10b respectively. Numerical data for $\bar{V}_2^o$ are also given in Table 5. The dependence of h on the molecular weight of the cation is shown in Fig. 11 and it may be seen that the values of the parameter h indicate a non-linear dependence (in the case of the iodide and bromide series) on the molecular weight of the cation. The value of the slope for $(C_2H_5)_4NBr$ appears to differ considerably from the curve that passes smoothly through the remaining points for that halide series. This slope was verified by carrying out another series of partial molal volume determinations but no significant change in the value of h for this salt was observed.

The partial molal volumes $\bar{V}_2^o$ for the members of each series of tetraalkylammonium halide salts are plotted as a function of molecular weight of the organic cation in Fig. 12 and a virtually straight line relationship is obtained for each series. The data for the corresponding ammonium salts have also been included for comparison but the linear relations

TABLE 5

Values of $\bar{V}_2^o$ and h in Equation V.9 (25°C)

Salt	$\bar{V}_2^o$ (±0.2) ml.g.mole^{-1}	h(±5%) ml.l.mole^{-2}	Maximum conc. for linearity in V_2-2.792$c^{\frac{1}{2}}$ relation
Me_4NCl	107.3	-4.60	0.07
Et_4NCl	166.9	-21.0	0.06
n-Pr_4NCl	232.9	-38.1	0.05
n-Bu_4NCl	294.1	-50.3	0.035
Me_4NBr	114.3 (114.8)# (114.25)+	-0.72	0.20
Et_4NBr	174.3 (175.3)#	-19.4	0.09
n-Pr_4NBr	239.4 (240.8)#	-22.0	0.06
n-Bu_4NBr	300.9 (302.9)#	-40.0	0.04
n-Am_4NBr	363.9 (365.6)#	-64.3	0.04
Me_4NI	125.8 (125.75)+	+0.13	0.13
Et_4NI	185.5	-6.0	0.08
n-Pr_4NI	250.7	-14.4	0.05
n-Bu_4NI	312.4	-26.5	0.04

Values of Wen and Saito (120)

+ Values of Levien (188)

Figure 9. A plot of apparent molal volume ϕ_2 with respect to the square root of concentration $c^{\frac{1}{2}}$ for $(CH_3)_4NBr$, $(\underline{n}\text{-}C_3H_7)_4NBr$ and $(\underline{n}\text{-}C_4H_9)_4NBr$.

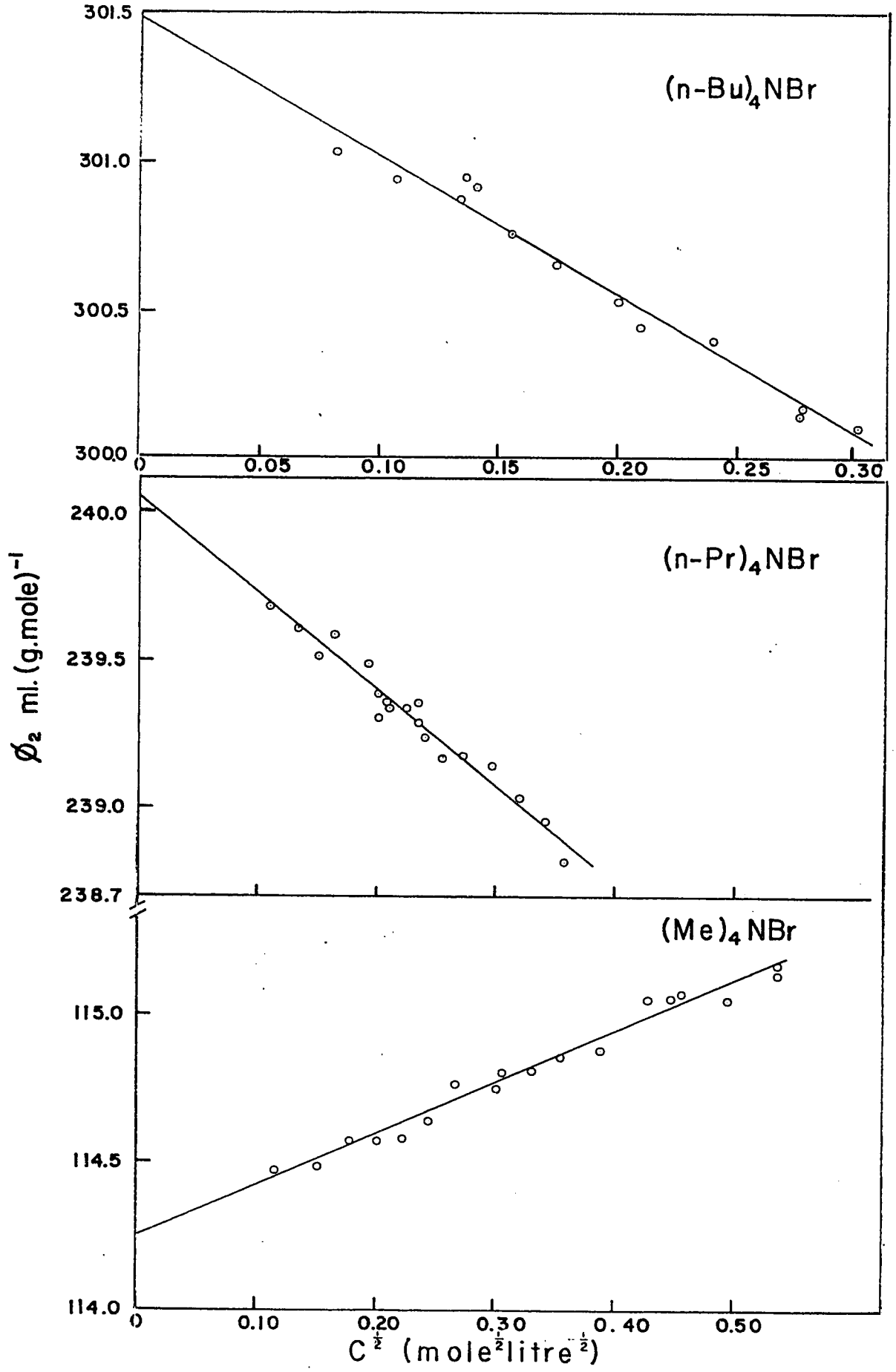

301.5
301.0
300.5
300.0
0
0.05
0.10
0.15
0.20
0.25
0.30
(n-Bu)4NBr
240.0
239.5
239.0
238.7
(n-Pr)4NBr
115.0
114.5
114.0
0.10
0.20
0.30
0.40
0.50
(Me)4NBr
Ø2 ml.(g.mole)-1
C½ (mole½litre-½)

Figure 10a. A plot of $\bar{V}_2 - 2.792c^{\frac{1}{2}}$ with respect to concentration c for $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$.

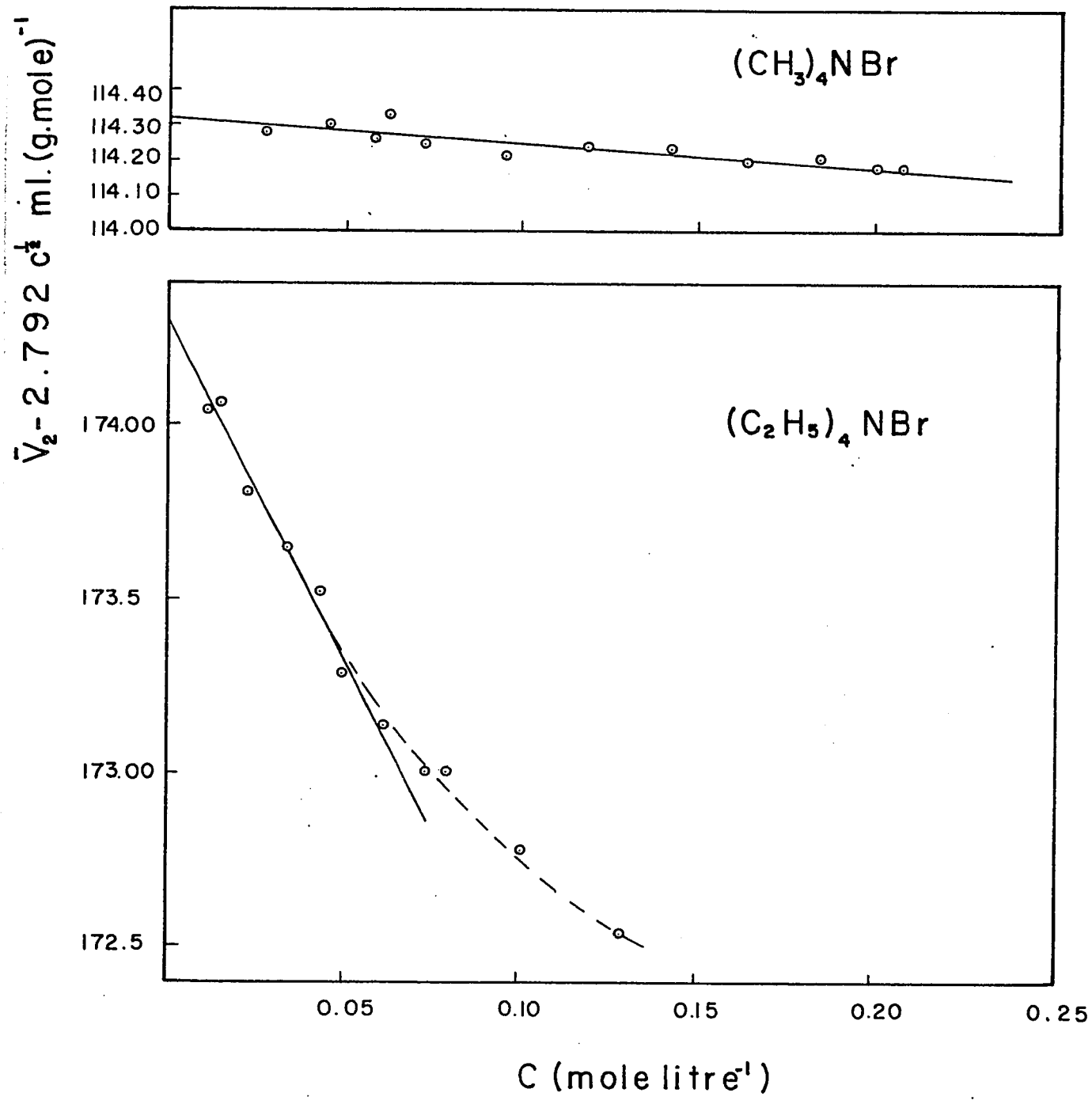

$(CH_3)_4NBr$
114.40
114.30
114.20
114.10
114.00
$(C_2H_5)_4NBr$
174.00
173.5
173.00
172.5
$\tilde{V}_2 - 2.792\, c^{\frac{1}{2}}$ ml.(g.mole)$^{-1}$
0.05
0.10
0.15
0.20
0.25
C (mole litre^{-1})

Figure 10b. A plot of $\bar{V}_2-2.792c^{\frac{1}{2}}$ with respect to concentration c for ($\underline{n}$-$C_3H_7)_4NBr$ and ($\underline{n}$-$C_4H_9)_4NBr$.

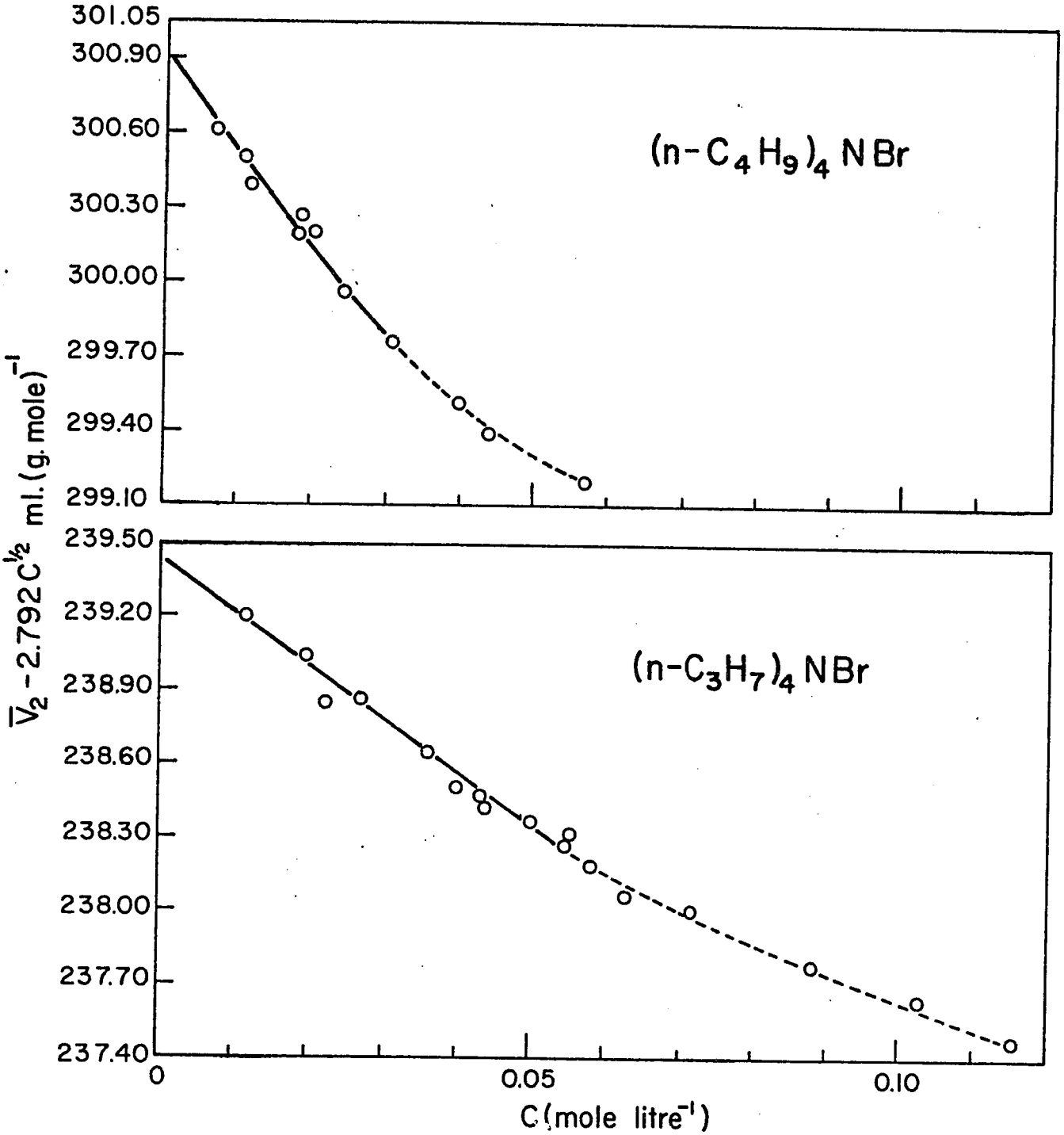

301.05
300.90
300.60
300.30
300.00
299.70
299.40
299.10
$(n-C_4H_9)_4NBr$
239.50
239.20
238.90
238.60
238.30
238.00
237.70
237.40
$(n-C_3H_7)_4NBr$
$\bar{V}_2 - 2.792C^{1/2}$ ml.(g.mole)$^{-1}$
0
0.05
0.10
C(mole litre^{-1})

Figure 11. Values of h for the various R_4NX salts as a function of the molecular weight of the cation.

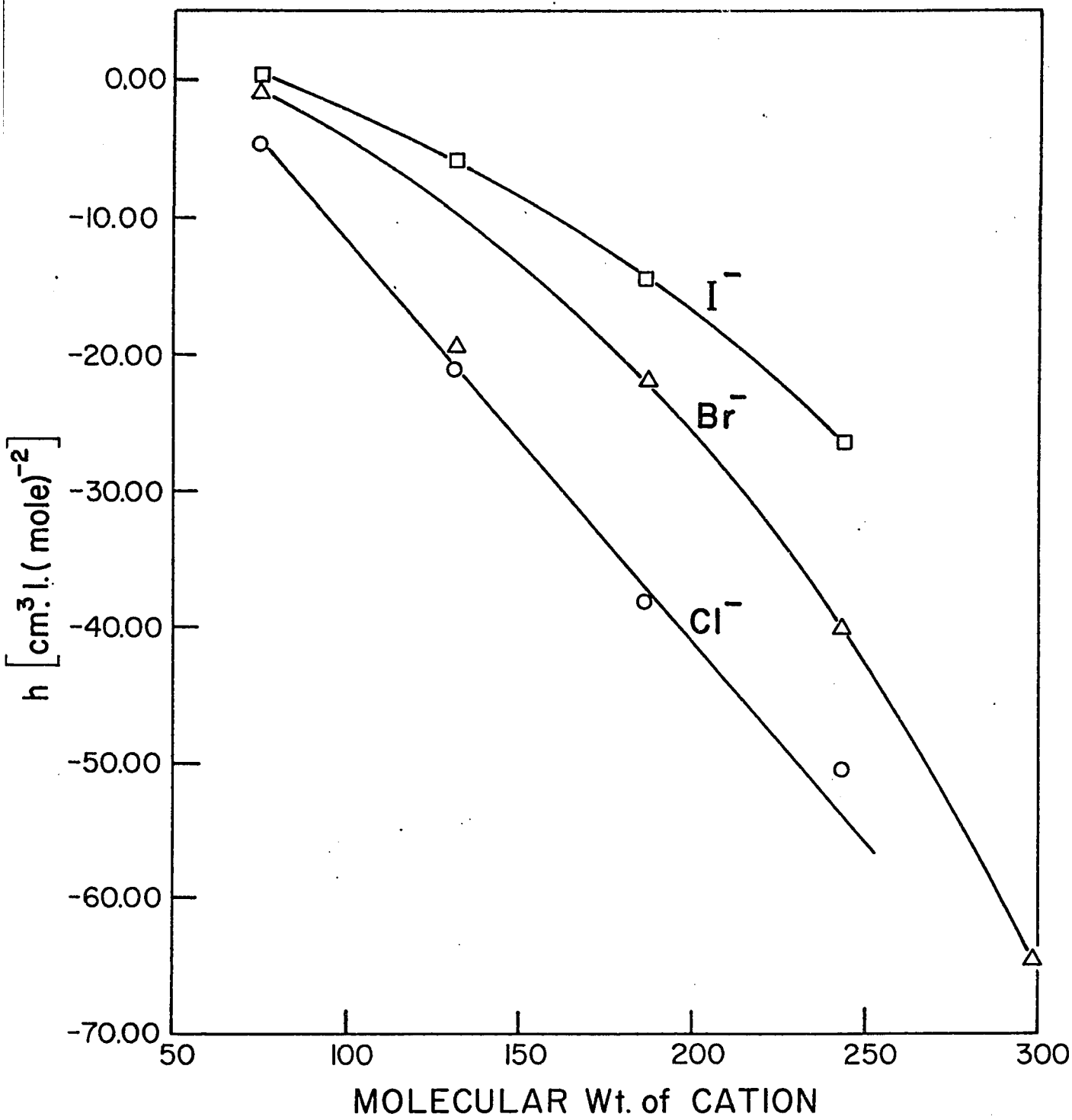
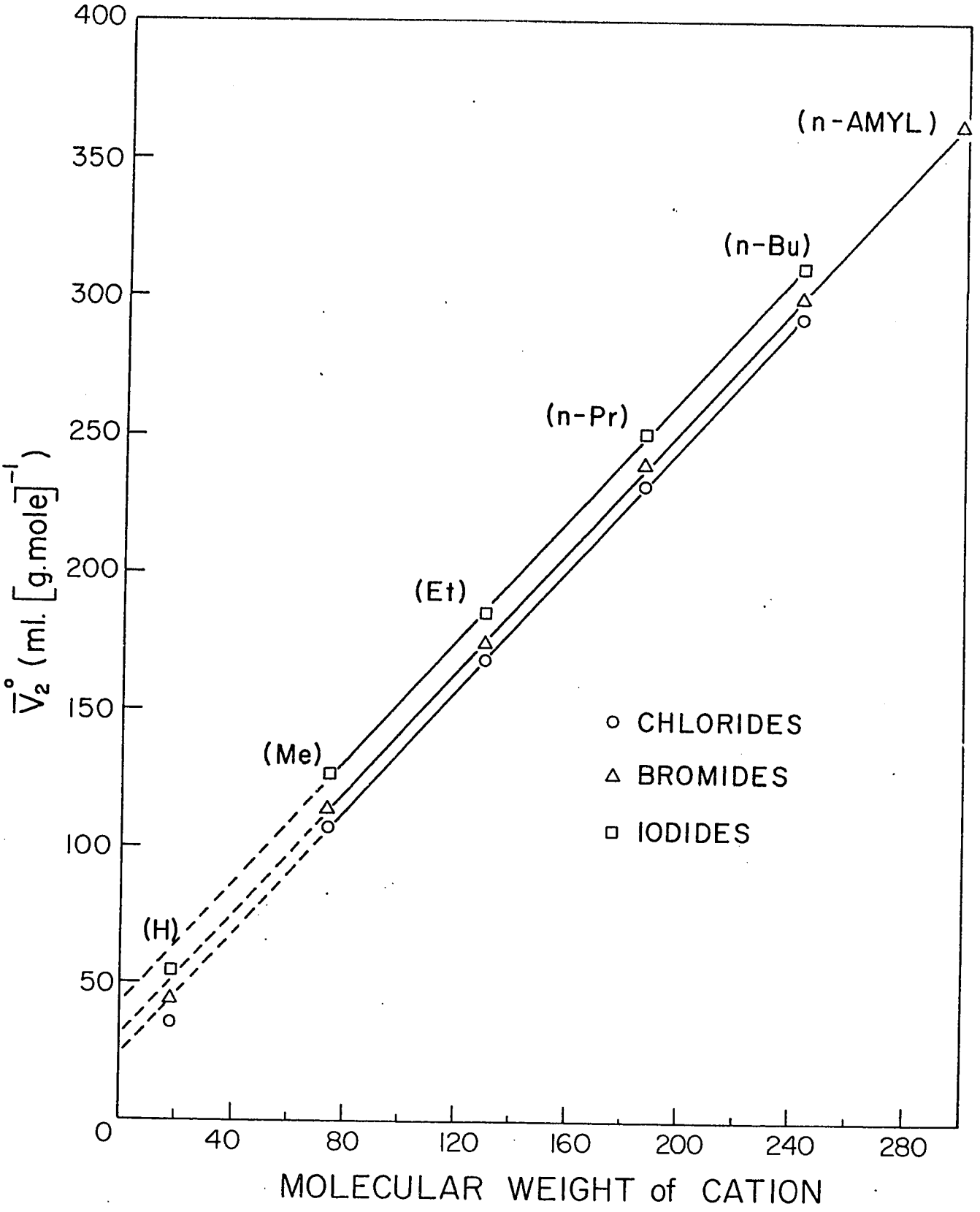

0.00
-10.00
-20.00
-30.00
-40.00
-50.00
-60.00
-70.00
h [cm³ l. (mole)⁻²]
50
100
150
200
250
300
MOLECULAR Wt. of CATION
I⁻
Br⁻
Cl⁻

Figure 12. Values of $\bar{V}_2^o$ for three series of R_4NX salts as a function of the molecular weight of the cation.


400
350
300
250
200
150
100
50
0
40
80
120
160
200
240
280
(n-AMYL)
(n-Bu)
(n-Pr)
(Et)
(Me)
(H)
CHLORIDES
BROMIDES
IODIDES
$\bar{V}_2^\circ$ (ml. [g.mole]$^{-1}$)
MOLECULAR WEIGHT of CATION

for the tetraalkylammonium salts will, of course, not necessarily be expected to pass through the points for the ammonium salts since the latter will be significantly hydrated (see Discussion, Chapter VI).

The relationship between the partial molal volumes of consecutive members of an homologous series of tetraalkylammonium salts having a common anion may be represented by the equations:

$$\bar{V}^{o}_{R_4N^+X^-} = \bar{V}^{o}_{R'_4N^+X^-} - b(\Delta m.w.) = \bar{V}^{o}_{R'_4N} + \bar{V}^{o}_{X^-} - b(\Delta m.w.) \qquad V\cdot10$$

and

$$\bar{V}^{o}_{R'_4N^+X^-} = \bar{V}^{o}_{R''_4N^+X^-} - b(\Delta m.w.) = \bar{V}^{o}_{R''_4N^+} + \bar{V}^{o}_{X^-} - b(\Delta m.w.) \qquad V\cdot11$$

where R", R' and R are homologous alkyl groups and (Δm.w.) is the change of molecular weight of the salt in going up the homologous series from R to R' or from R' to R", i.e., by four methylene groups and b is the specific volume of the methylene groups in ml.g.$^{-1}$ CH_2 groups. The values of the coefficient b are shown in Table 6.

For the purposes of comparison, the corresponding b values for homologous neutral tri-n-alkylamines in water, methanol and n-hexane were also measured and are shown in Table 7.

In water, the b value is quite similar to that for the corresponding pair of quaternary salts. In general, the difference between first and second members of the series would not necessarily be expected to be the same as the values of the differences for higher members owing to the change of

TABLE 6

Values of the coefficient b in Equations V·10 and V·11.

Salt Series	Me_4N^+ b	Et_4N^+ b	$\underline{n}$-Pr_4N^+ b	$\underline{n}$-Bu_4N^+ b	$\underline{n}$-Am_4N^+
Chlorides	1.062	1.167	1.108	-	
Bromides	1.069	1.164	1.094	1.122	
Iodides	1.064	1.164	1.094	-	

TABLE 7

Values of the Coefficient b for Homologous Neutral Tri-$\underline{n}$-alkylamines in Water, Methanol, and $\underline{n}$-Hexane.

$(CH_3)_3N$	b= 0.984 (in 0.01 N aq. KOH to suppress ionisation)				
$(C_2H_5)_3N$					
$(CH_3)_3N$	b= 1.089		$(C_2H_5)_3N$	b= 1.161	
$(C_2H_5)_3N$	b= 1.311		$(\underline{n}\text{-}C_3H_7)_3N$		
$(\underline{n}\text{-}C_3H_7)_3N$	b= 1.222	(in MeOH)		b= 1.148	(in $\underline{n}$-hexane)
$(\underline{n}\text{-}C_4H_9)_3N$	b= 1.210		$(n\text{-}C_5H_{11})_3N$		
$(\underline{n}\text{-}C_5H_{11})_3N$					

environment of methyl groups. The biggest volume increment for the salt series is from C_2H_5 to $\underline{n}$-C_3H_7 and this is also the case for the tri-$\underline{n}$-alkylamines in MeOH.

The significant linearity which the plots in Fig. 12 nevertheless exhibit, suggests that the data might be extrapolated to zero cation molecular weight to give the individual partial g. ionic volume of the co-anions, Cl^-, Br^- or I^-. This extrapolation is shown in Fig. 12 and the individual anion partial volumes are listed in Table 8. The differences of extrapolated values of individual partial g. ionic volumes and the thermodynamic difference from data for alkali halides having a common cation are also shown in Table 8. (Further discussion is given in Chapter VI).

TABLE 8

Differences of Extrapolated values of Individual Partial g. Ionic Volumes and the Thermodynamic Difference from Data for Alkali Halides having a Common Cation.

Ions X^-	$\bar{V}^o_{X^-}$ (from extrapolation) ml.(g.ion)$^{-1}$	Ions $X_1^- - X_2^-$	Difference $\Delta\bar{V}^o_{X_1^- - X_2^-}$ ml.(g.ion)$^{-1}$ From $\bar{V}^o_{X^-}$	From $\bar{V}^o_{salt}$ data *
Cl^-	23.6±0.2 ≠	$I^- - Cl^-$	18.6(7)	18.61
Br^-	30.9±0.2	$I^- - Br^-$	11.3(1)	11.56
I^-	42.2±0.2	$Br^- - Cl^-$	7.3(6)	7.01

* From ref. (134) p. 361

≠ Least squares uncertainty in the intercepts based on a linear plot. Based on the variation of b values across the series, the uncertainty in $\bar{V}^o_{X^-}$ would not exceed 0.5 ml.

b) Concentration Dependence of $\bar{V}$

The observed concentration dependencies of $\bar{V}_2$ values for the tetraalkylammonium salts have anomalously large linear contributions determined by h in comparison with those for inorganic 1:1 electrolytes (161).

The concentration dependence of $\bar{V}$ is given by equation V.8 to the 3/2 power in c. In the representation of the results by equation V.9 the term $K_{(v)} + W_{(v)} - S_{(v)}A$, which represents h for moderately low concentrations, will be of primary importance. For these large ions, the direct effect of hydration in the terms $K_{(v)}$ would be relatively small and the other terms $W_{(v)}$, A and $S_{(v)}$ are given by equations V.4, V.7 and V.3 respectively. However, other factors can be involved in $K_{(v)}$ for these large ions and will be treated in Chapter VI. Expressing $d\ln\epsilon/dP$ in $dyne^{-1}cm.^2$, equation V.4 then becomes;

$$W_{(v)} = -0.9551x10^{10}\ \mathring{a}(d\ln\epsilon/dP - 2d\ln\mathring{a}/dP - \beta) \qquad V.12$$

where $d\ln\epsilon/dP$ may be taken as $47.10x10^{-12}$ $dyne^{-1}$ $cm.^2$ (161) and $\beta = 45.24x10^{-12}$ $dyne^{-1}cm.^2$ Theoretical interpretation of the observed slopes must be made in terms of $\mathring{a}$ and $d\ln\mathring{a}/dP$ which are unknown for these salts. However, three estimates of the latter term may be made as follows for exploratory purposes.

i) Using Whalley's mean value (122) for the compressibility of ions in a dielectric medium, $d\ln\mathring{a}/dP$ may be obtained as $5.85x10^{-12}$ $dyne^{-1}$ $cm.^2$ which gives $W_{(v)}$ from equation V.12 as $-0.130\mathring{a}$.

(ii) Taking a value ten times larger, viz - 58×10^{-12} dyne^{-1} cm.^{2}, which may apply at low pressure, gives $W_{(v)}$ as -1.126Å.

(iii) Also d ln Å/dP may be estimated from the previous electrostriction calculations, (129) and Chapter III, as - 2.8×10^{-12} dyne^{-1} cm.^{2} if it is assumed that the pressure dependence of Å will be determined by the compressibility of hydration water at the fields of 10^4-10^5 e.s.u. which arise near ions (129); this procedure gives a value $W_{(v)} \doteq$ - 0.0724Å. Neglecting $K_{(v)}$ for low concentrations, would give h as

h=1.047Å (case (i)); h=-2.044Å (case (ii)); h=0.989Å (case (iii)). Then, from equation V·8 , with the values of $S_{(v)}$ and A obtained from equations V·3 and V·7 respectively, the values of Å may be estimated from the experimental values of h (Table 5) for the data towards infinite dilution (i.e. down to 0.01 molar) and are shown in Table 9. The purpose of this calculation is to see to what extent the derived values of Å are reasonable and how they depend on the cation-anion pair.

The values of Å increase as expected with increasing cation size and show regular changes for a given cation with variation of the anion, an effect that could be associated with hydration of the anions. However, the estimates of Å for the two limiting cases (ii) and (iii) give in both cases improbably large values. Since negative values of Å are already predicted for the Me_4NI salts and an increase of d ln Å/dP produces smaller values of Å, the very large values of Å for the larger cation salts cannot be diminished to reasonable magnitudes

TABLE 9

Calculated Values of $\mathring{a}$ in Å for the Tetraalkylammonium Salts

Salt	$\frac{d\ln\mathring{a}}{dP} = -2.8\times10^{-12}$ dyne^{-1}cm.^{2}	$\frac{d\ln\mathring{a}}{dP} = -5.85\times10^{-12}$ dyne^{-1}cm.^{2}	$\frac{d\ln\mathring{a}}{dP} = -58.0\times10^{-12}$ dyne^{-1}cm.^{2}
	$W_{(v)} = -0.0724\mathring{a}$	$W_{(v)} = -0.1295\mathring{a}$	$W_{(v)} = -1.26\mathring{a}$
Me_4NCl	4.6	4.4	2.25
Et_4NCl	21.3	20.0	10.3
$\underline{n}$-Pr_4NCl	38.5	36.4	18.6
$\underline{n}$-Bu_4NCl	50.9	48.1	24.6
Me_4NBr	0.72	0.68	0.35
Et_4NBr	19.6	18.5	9.5
$\underline{n}$-Pr_4NBr	22.3	21.0	10.8
$\underline{n}$-Bu_4NBr	40.4	38.2	19.5
$\underline{n}$-Am_4NBr	65.0	61.4	31.5
Me_4NI	- 0.13	- 0.12	- 0.06
Et_4NI	6.1	5.7	2.9
$\underline{n}$-Pr_4NI	14.6	13.8	7.0
$\underline{n}$-Bu_4NI	26.8	25.3	12.9

(ca. 5-8 Å) by choice of a higher value of d ln $\mathring{a}$/dP without obtaining impossible values for the smaller cation salts. The choice of values of d ln $\mathring{a}$/dP is further guided by the fact that for KI and RbI, the observed values of h and $\mathring{a}$ (15) lead to estimates of d ln $\mathring{a}$/dP of -9.34×10^{-6} and -46.5×10^{-6} bar^{-1}, respectively. It must be noted that d ln $\mathring{a}$/dP will also probably be characteristic of the particular pair of ions concerned so that no more than the trend of the resulting $\mathring{a}$ values for the several homologous series considered may be discussed. These exploratory calculations nevertheless lead to the conclusion that the anomalously large linear concentration-dependent terms, which are found for these salts, cannot be explained within the framework of the Debye-Hückel theory with any reasonable values of the two parameters involved.

The results of these calculations enable the coefficient of the $c^{3/2}$ term in equation V.8 to be estimated. The values are sufficiently large for appreciable contributions from the $c^{3/2}$ term to appear in the concentration range fitted by a linear hc term. Such effects are most significant for the salts of the larger ions. Therefore, it may be supposed that the large $\mathring{a}$ values arise, in fact, from use of a linear equation in a concentration range where higher terms in c are still significant and the h terms for these salts should be considered in a different manner, as follows.

If it is supposed that the empirical extrapolation to obtain $\bar{V}^o$ values is satisfactory (for example, it gives $\bar{V}^o$ for Me_4NBr within 0.15ml. $mole^{-1}$ of the single value

given by Stokes and Hepler (121) obtained by another method; agreement is exact if extrapolation of apparent molal volumes is used), then from equation V·2, neglecting $K_{(v)}$ at low concentrations,

$$(\bar{V}_2-\bar{V}_2^o)\ (1+Ac^{\frac{1}{2}})^2 = S_{(v)}c^{\frac{1}{2}} + (S_{(v)}\ A + W_{(v)})\ c \qquad V\cdot 13$$

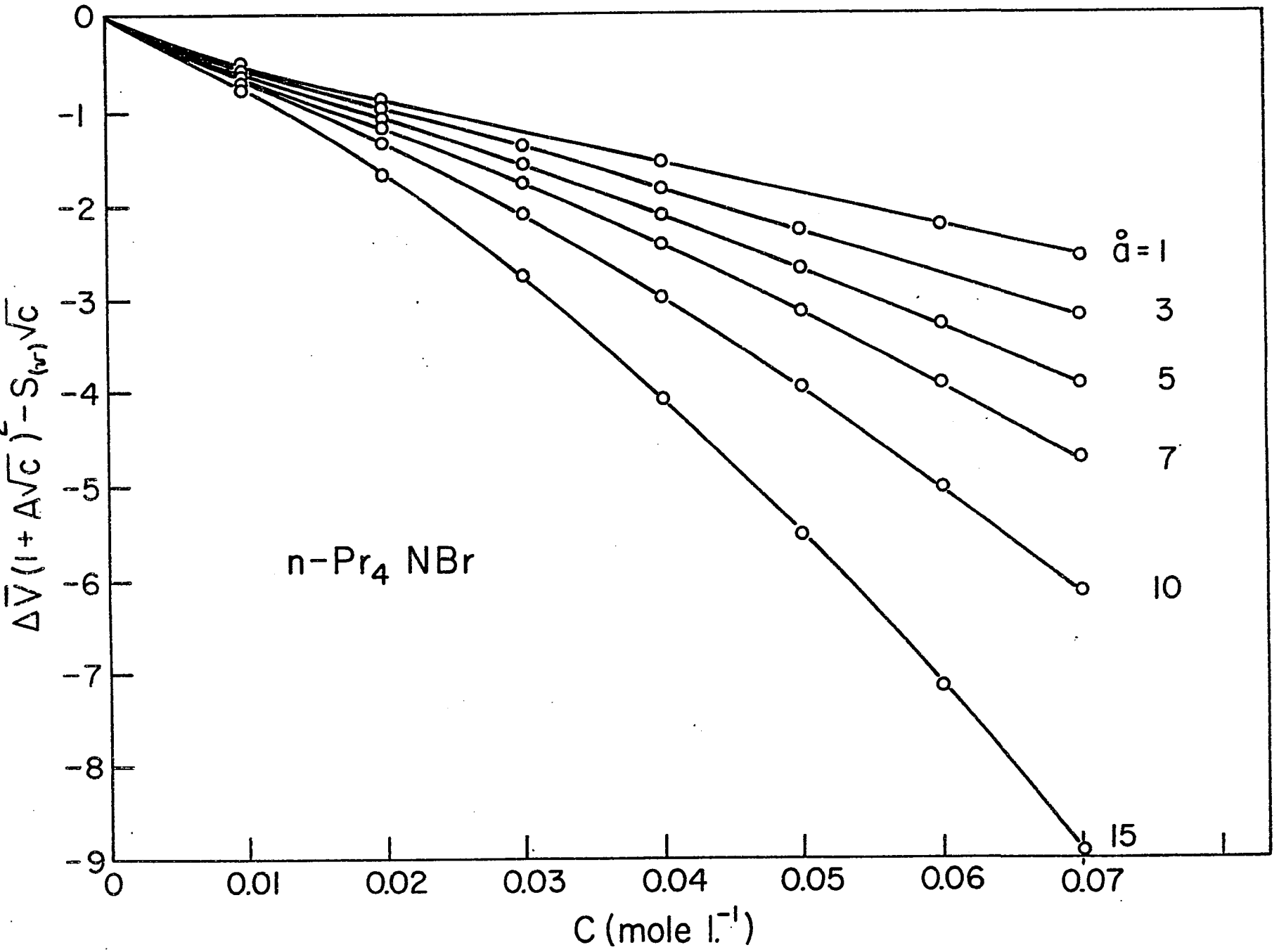
so that $(\bar{V}_2-\bar{V}^o{}_2)(1+Ac^{\frac{1}{2}})^2 - S_{(v)}c^{\frac{1}{2}}$ should be linear in c. This relation involves no neglect of higher powers of c and the relation should ideally be applicable with a single value of $\overset{o}{a}$ in A for each salt. A test of this method is shown in Fig. 13. The experimental data are fitted best with $\overset{o}{a}=7\pm 1\overset{o}{A}$ but there are still significant deviations from linearity above 0.035 molar. This value of $\overset{o}{a}$ is to be compared with the lowest value given in Table 9, viz. 10.8$\overset{o}{A}$. The corresponding value of $W_{(v)}$ is found to be limitingly -49×10^{-5} dyne^{-1}cm.^{2} which is some 8 times larger than the upper limiting value required to express results for $HClO_4$ solutions discussed by Wirth and Collier (165). The procedure using equation V·13 seems preferable to that assuming only a linear term hc.

Finally, $\overset{o}{a}$ values may be obtained more directly from estimates of the ionic radii of the tetraalkylammonium salts. It has been shown (31, 166) that the "true" non-hydrated volumes of ions V_i can be related to the true ionic radius by the empirical relation

$$V_i = 2.51r^3 + 3.15r^2 \text{ ml. (g.ion)}^{-1} \qquad V\cdot 14$$

which was deduced by allowing for the dead-space around the ions

Figure 13. A plot of $(\bar{V}_2 - \bar{V}_2^o)(1+Ac^{\frac{1}{2}})^2 - S_{(v)}\ c^{\frac{1}{2}}$ against concentration c for $\underline{n}$-Pr_4NBr.


0
-1
-2
-3
-4
-5
-6
-7
-8
-9
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
C (mole l.⁻¹)
$\Delta\bar{V}(1+A\sqrt{C})^2 - S_{(r)}\sqrt{C}$
n-Pr$_4$ NBr
å = 1
3
5
7
10
15

in water treated as a non-continuous medium composed of molecules of finite size, comparable with the size of the ion. By subtracting the values of $\bar{V}^{o}_{X^-}$ for the halide anions as deduced above, the average $\bar{V}^{o}$ values for the large cations are obtained. Assuming no significant electrostriction of the solvent, the formal radii r can then be calculated from equation V·14. The data obtained, which are referred to as formal radii (since the ions will not be ideally spherical) are shown in Table 10 (col. g) in comparison with the results (cols. a-f) of other estimates made in previous publications by different methods. The radii in col. a were calculated from bond lengths and are probably somewhat too large because of non-sphericity of the ions. The values in cols. b-e are based on conductance data uncorrected for any structure-promoting effects the ions may have in the water solvent.

If it is assumed that the $\mathring{a}$ values of the particular tetraalkylammonium salts considered are equal to the sum of the ionic radii deduced above, then from the experimental values of the parameter h and neglecting the hydration term $K_{(v)}$ at low concentrations, an estimate of d ln $\mathring{a}$/dP may be obtained. The values of $\mathring{a}$ (deduced from formal ionic radii) and d ln $\mathring{a}$/dP (from $h \equiv W_{(v)} - S_{(v)}A$ equation V·8) for the three halide series of tetraalkylammonium salts studied are shown in Table 11. It is to be noted that both $\mathring{a}$ and d ln $\mathring{a}$/dP are characteristic of the particular pair of ions concerned and the magnitudes of $\mathring{a}$ shown in Table 11 are somewhat more reasonable than those in Table 9. The very large values of d ln $\mathring{a}$/dP for the salts

Table 10

Formal Radii of Tetraalkylammonium and Halogen Ions at 25°C in Å

Ion	a	b	c	d	e	f	g
Me_4N^+	3.47	2.47				2.7	2.85
Et_4N^+	4.00	3.05	2.76			3.2	3.48
$n\text{-}Pr_4N^+$	4.52	3.57				3.7	3.96
$n\text{-}Bu_4N^+$	4.94			3.50	3.63	4.1	4.37
$n\text{-}Am_4N^+$							4.71
Cl^-							1.76
Br^-							1.96
I^-							2.21
Ref.	(167)	(168)	(169)	(170)*	(170)**	(144)***	Present Results.

Notes: (1) * From association constants; ** from the limiting ionic mobility; *** from the Parachor.

(2) Radii are quoted to three significant figures only to illustrate trends and for comparative purposes. Absolute significance by a given method is probably not better than 1 in the first decimal place.

Table 11

Values of $\mathring{a}$ in Å and d ln $\mathring{a}$/dP in $dyne^{-1}$ $cm.^2$ for the Tetraalkylammonium Salts Based on Formal Radii of the Ions Obtained from Equation V·14

Salt	$\mathring{a}$ (Å units)	$d\ln\mathring{a}/dP$ $\times 10^{12}$ ($dyne^{-1}$ $cm.^2$)
Me_4NCl	4.6[1]	-3.28
Et_4NCl	5.2[4]	-160.8
n-Pr_4NCl	5.7[4]	-298.5
n-Bu_4NCl	6.1[3]	-380.5
Me_4NBr	4.8[1]	+ 41.1
Et_4NBr	5.4[4]	-137.7
n-Pr_4NBr	5.9[4]	-144.9
n-Bu_4NBr	6.3[3]	-281.8
n-Am_4NBr	6.6[8]	-454.9
Me_4NI	5.0[6]	+ 50.3
Et_4NI	5.6[9]	- 6.25
n-Pr_4NI	6.1[9]	- 72.8
n-Bu_4NI	6.5[8]	-161.8

containing larger cation groups may be associated with structure promotion around the ion, an effect which depends on the size of the cation (120).

(D) Alkylamine Hydrogen Halide Salts

Plots of ϕ_2, the apparent molal volume, with respect to $c^{\frac{1}{2}}$, for the* alkylamine hydrogen chlorides are shown in Fig. 14 and 15. A similar plot for the alkylamine hydrogen iodides is shown in Fig. 16. Extrapolations of $\bar{V}_2 - 2.792c^{\frac{1}{2}}$ with respect to c, down to zero c, are shown in Figs. 17, 18 and 19 for the respective alkylamine hydrogen chlorides and iodides. Numerical data for $\bar{V}_2^{\,o}$ and h for the alkylamine hydrogen halide salts are also given in Table 12.

The relationship between the partial molal volumes of consecutive members of an homologous series of alkylamine hydrogen halide salts having a common anion may be represented by equations of an equivalent form to those for the homologous series of tetraalkylammonium salts. Values of the coefficient b, i.e. the specific volume of the methylene groups in ml. g^{-1} CH_2 group for the alkylamine hydrogen halide salts are shown in Table 13. The dependence of $\bar{V}_2^o$, the value of $\bar{V}_2$ at infinite dilution, on the number of carbon atoms in the salt is shown comparatively in Fig. 20 for the symmetrical tetraalkylammonium halide and alkylamine hydrogen halide salts.

ii) Accuracy of Results

The experimental conditions employed in the determination of the apparent molal volumes enabled the density measurements

* The extent of hydrolysis of the methyl ammonium ions was calculated and found to be insignificant, even at the lowest concentrations employed.

Figure 14. A plot of ϕ_2, the apparent molal volume, with respect to $c^{\frac{1}{2}}$ for $CH_3NH_3^+Cl^-$, $(CH_3)_2NH_2^+Cl^-$ and $(CH_3)_3NH^+Cl^-$.

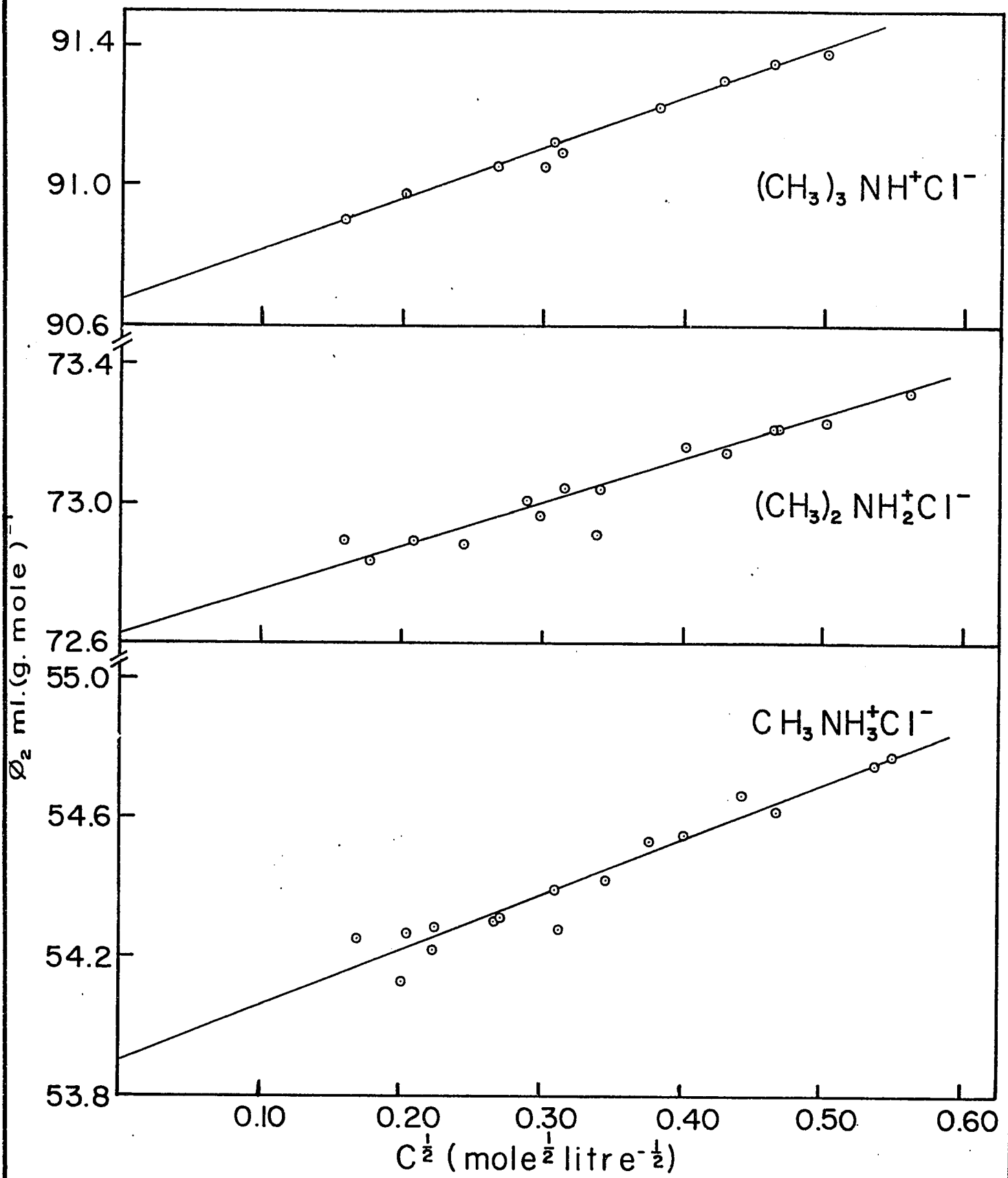

91.4
91.0
90.6
$(CH_3)_3 NH^+Cl^-$
73.4
73.0
72.6
$(CH_3)_2 NH_2^+Cl^-$
55.0
54.6
54.2
53.8
$CH_3 NH_3^+Cl^-$
ϕ_2 ml.(g. mole)$^{-1}$
0.10
0.20
0.30
0.40
0.50
0.60
$C^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ litre$^{-\frac{1}{2}}$)

Figure 15. A plot of ϕ_2, the apparent molal volume, with respect to $c^{\frac{1}{2}}$ for $(C_2H_5)_3NH^+Cl^-$ and $(\underline{n}\text{-}C_3H_7)_3NH^+Cl^-$.

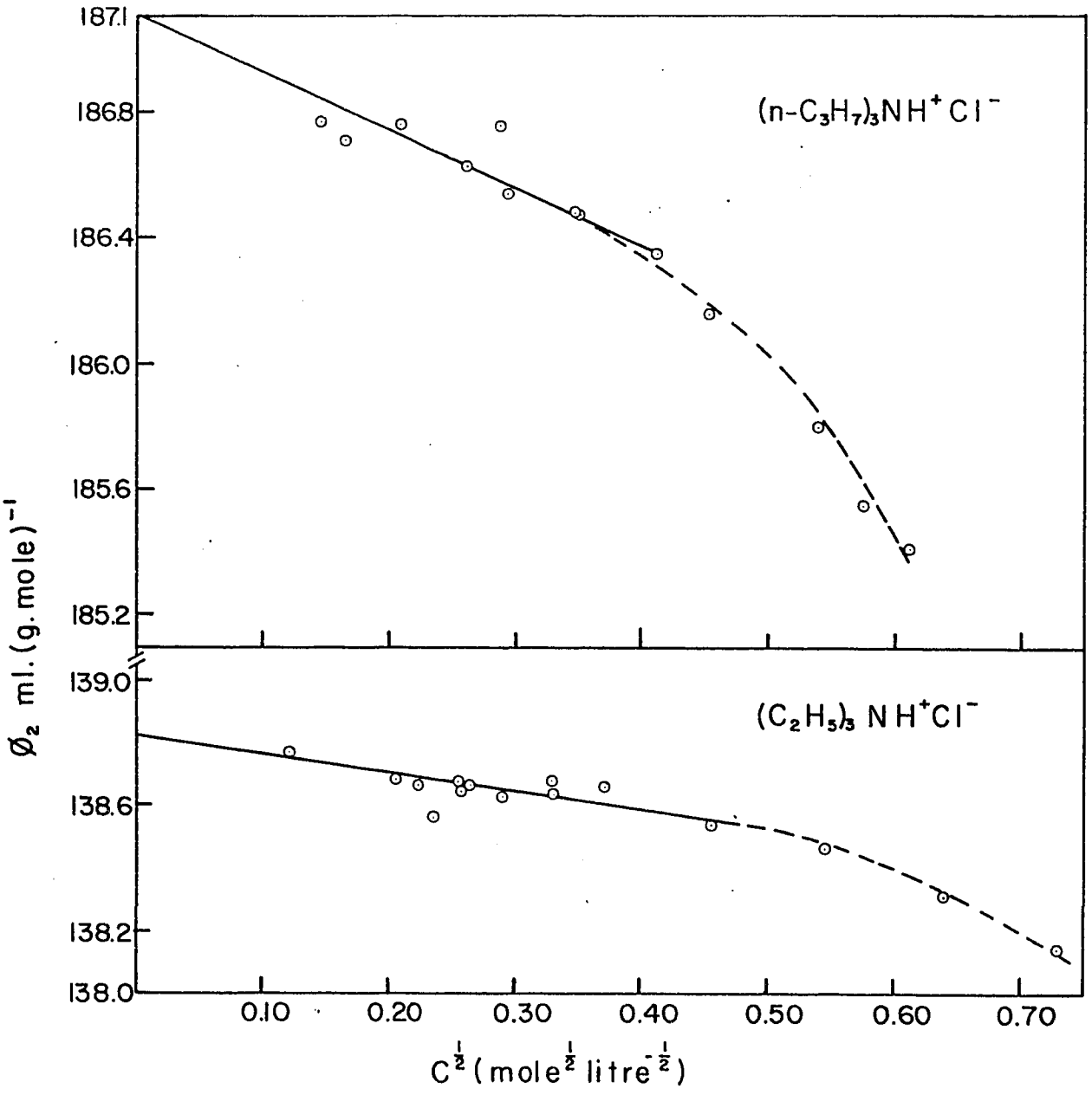
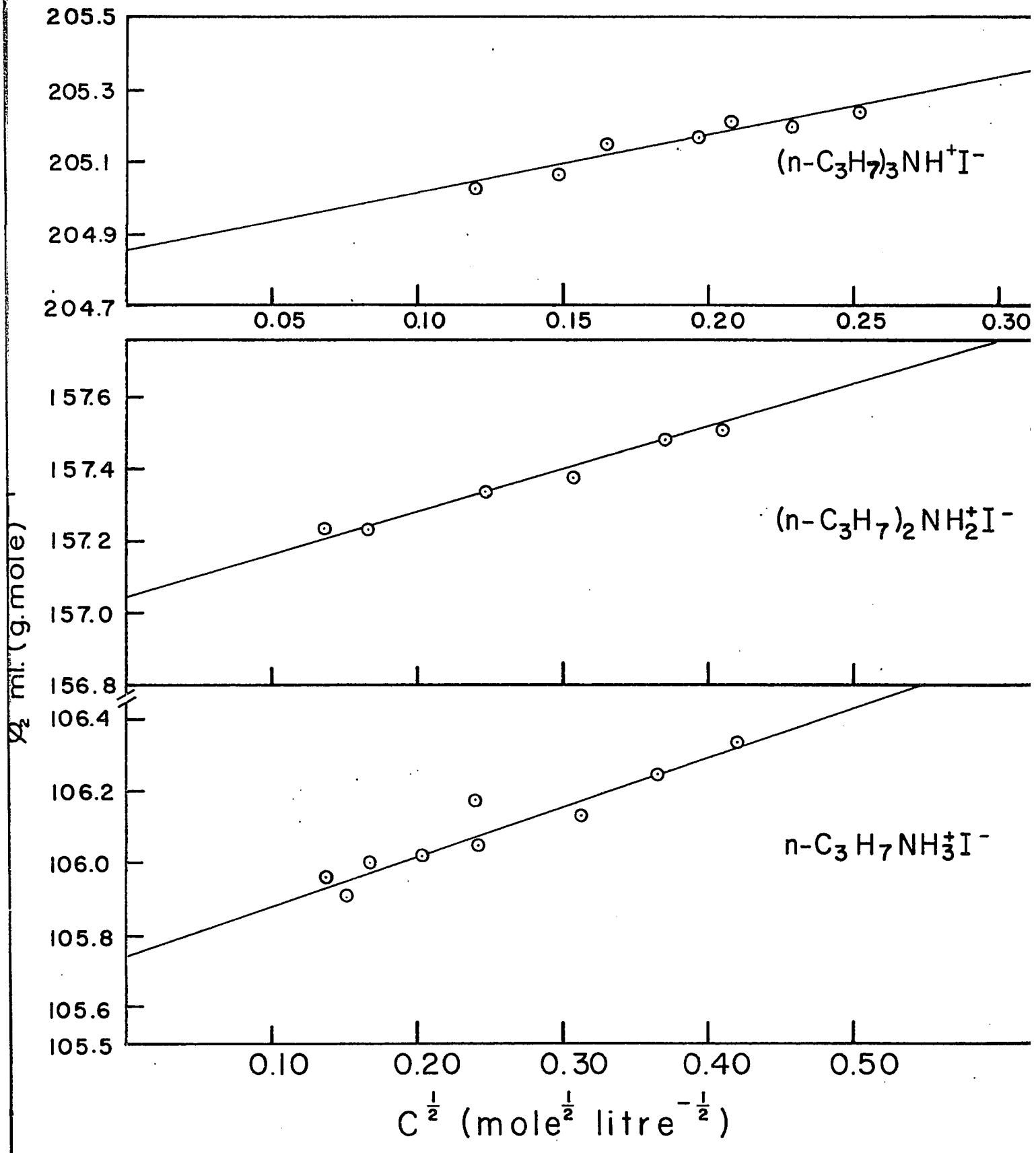

187.1
186.8
186.4
186.0
185.6
185.2
139.0
138.6
138.2
138.0
$(n\text{-}C_3H_7)_3NH^+Cl^-$
$(C_2H_5)_3NH^+Cl^-$
ϕ_2 ml. (g. mole)$^{-1}$
0.10
0.20
0.30
0.40
0.50
0.60
0.70
$C^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ litre$^{-\frac{1}{2}}$)

Figure 16. A plot of ϕ_2, the apparent molal volume, with respect to $c^{\frac{1}{2}}$ for $\underline{n}\text{-}C_3H_7NH_3^+I^-$, $(\underline{n}\text{-}C_3H_7)_2NH_2^+I^-$ and $(\underline{n}\text{-}C_3H_7)_3NH^+I^-$.


205.5
205.3
205.1
204.9
204.7
0.05
0.10
0.15
0.20
0.25
0.30
$(n\text{-}C_3H_7)_3NH^+I^-$
157.6
157.4
157.2
157.0
156.8
$(n\text{-}C_3H_7)_2NH_2^+I^-$
106.4
106.2
106.0
105.8
105.6
105.5
0.10
0.20
0.30
0.40
0.50
$n\text{-}C_3H_7NH_3^+I^-$
Φ_2 ml. (g.mole)
$C^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ litre$^{-\frac{1}{2}}$)

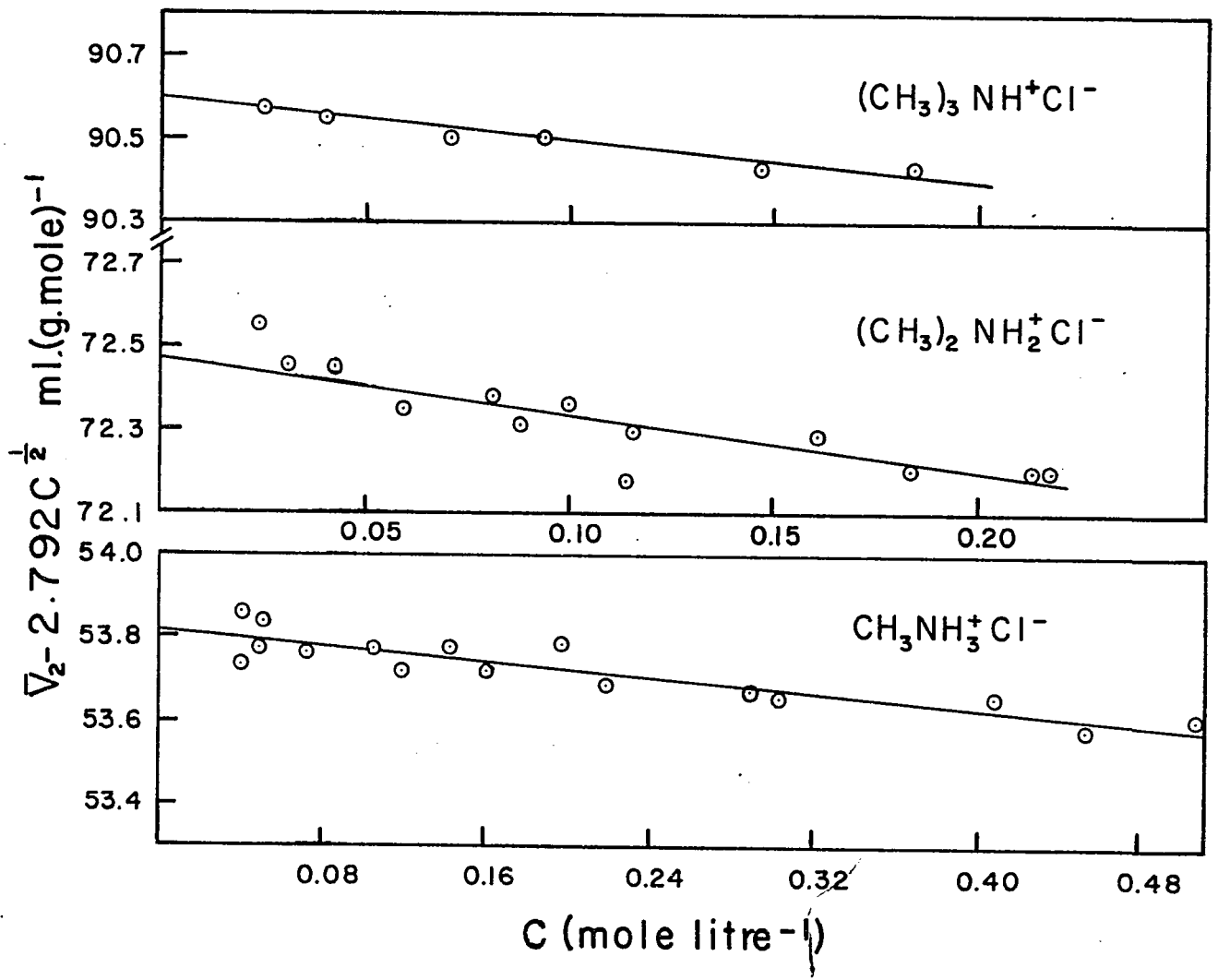

90.7
90.5
90.3
72.7
72.5
72.3
72.1
54.0
53.8
53.6
53.4
$(CH_3)_3 NH^+Cl^-$
$(CH_3)_2 NH_2^+Cl^-$
$CH_3NH_3^+Cl^-$
0.05
0.10
0.15
0.20
0.08
0.16
0.24
0.32
0.40
0.48
$V_2 - 2.792C^{\frac{1}{2}}$ ml.(g.mole)$^{-1}$
C (mole litre^{-1})

Figure 17. A plot of $\bar{V}_2 - 2.792c^{\frac{1}{2}}$ with respect to concentration c for $CH_3NH_3^+Cl^-$, $(CH_3)_2NH_2^+Cl^-$ and $(CH_3)_3NH^+Cl^-$.

Figure 18. A plot of $\bar{V}_2$-2.792$c^{\frac{1}{2}}$ with respect to concentration c for $(C_2H_5)_3NH^+Cl^-$ and $(\underline{n}\text{-}C_3H_7)_3NH^+Cl^-$.

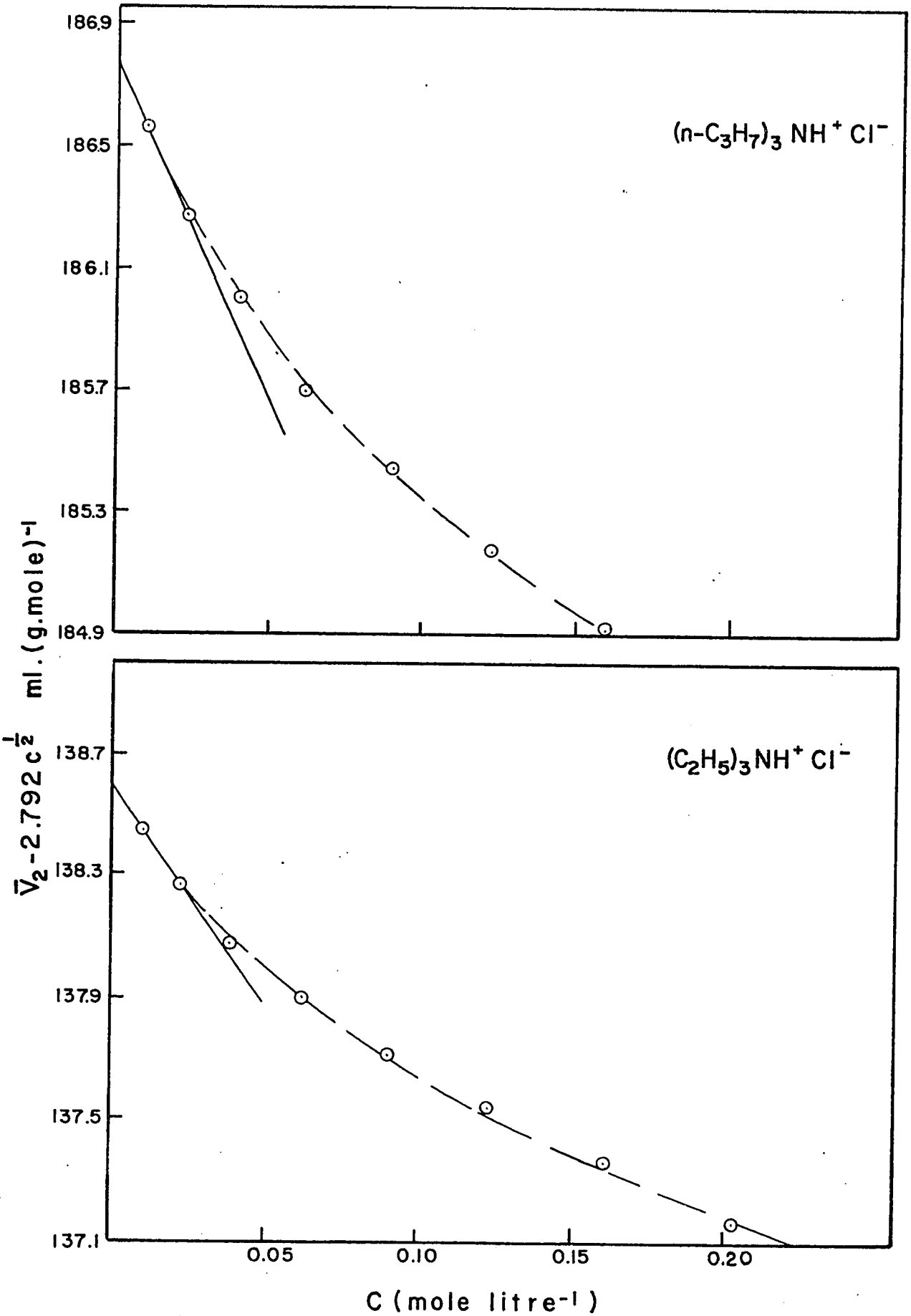

186.9
186.5
186.1
185.7
185.3
184.9
$(n\text{-}C_3H_7)_3\,NH^+\,Cl^-$
138.7
138.3
137.9
137.5
137.1
$(C_2H_5)_3NH^+\,Cl^-$
$\bar{V}_2 - 2.792\,c^{\frac{1}{2}}$ ml.(g.mole)$^{-1}$
0.05
0.10
0.15
0.20
C (mole litre^{-1})

Figure 19. A plot of $\bar{V}_2 - 2.792c^{\frac{1}{2}}$ with respect to concentration c for $\underline{n}\text{-}C_3H_7NH_3^+I^-$, $(\underline{n}\text{-}C_3H_7)_2NH_2^+I^-$ and $(\underline{n}\text{-}C_3H_7)_3NH^+I^-$.

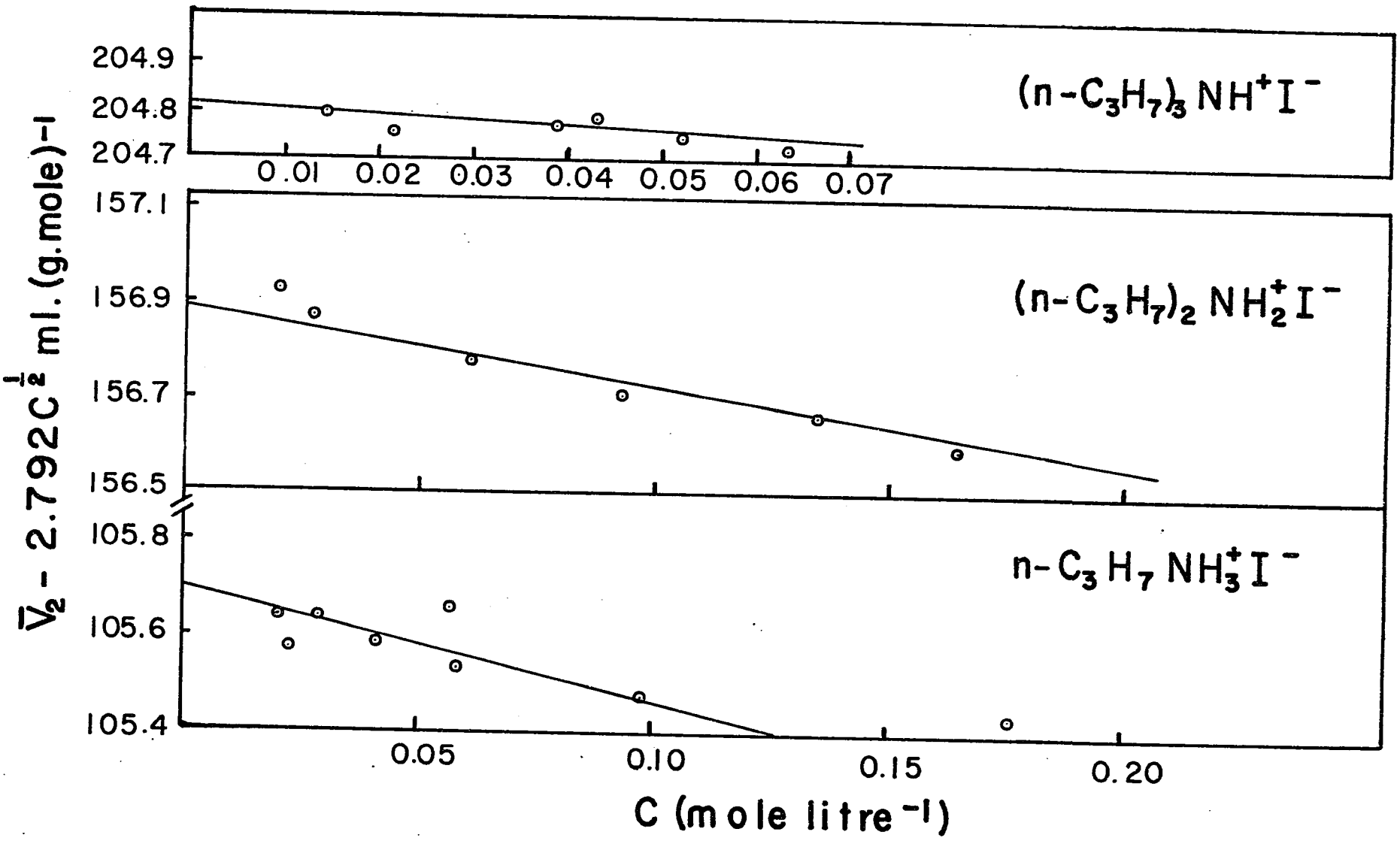

$\bar{V}_2 - 2.792C^{\frac{1}{2}}$ ml.(g.mole)$^{-1}$
204.9
204.8
204.7
0.01
0.02
0.03
0.04
0.05
0.06
0.07
$(n\text{-}C_3H_7)_3NH^+I^-$
157.1
156.9
156.7
156.5
$(n\text{-}C_3H_7)_2NH_2^+I^-$
105.8
105.6
105.4
0.05
0.10
0.15
0.20
$n\text{-}C_3H_7NH_3^+I^-$
C (mole litre^{-1})

Table 12

Values of $\bar{V}_2^o$ and h for Alkylamine Hydrogen Halide Salts (25°C)

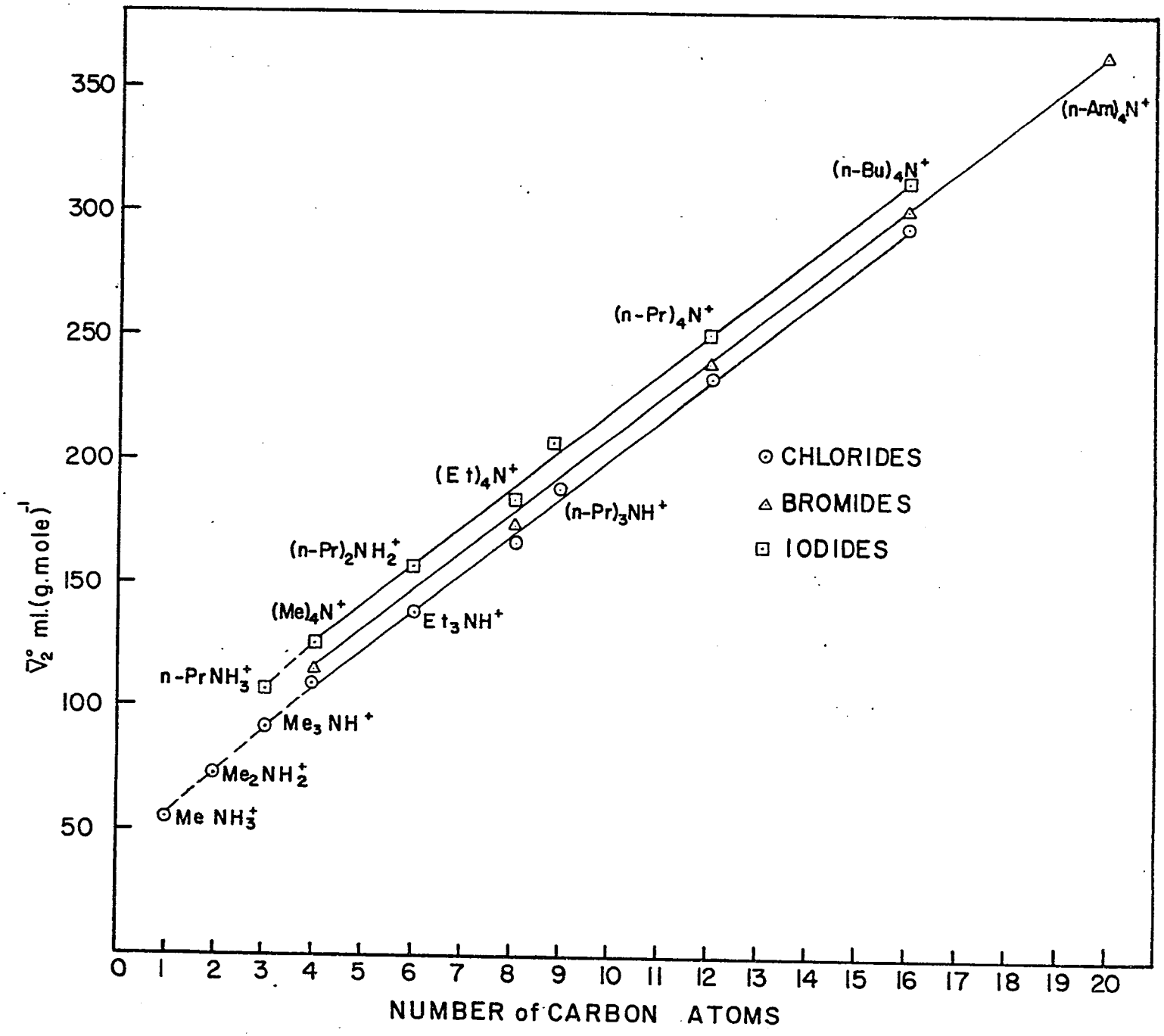
Salt	$\bar{V}_2^o(\pm 0.2)$ ml.g.mole^{-1}	h(±5%) ml.l.mole^{-2}
$CH_3NH_3^+Cl^-$	53.81	-0.439
$(CH_3)_2NH_2^+Cl^-$	72.4[7]	-1.33
$(CH_3)_3NH^+Cl^-$	90.5[9]	-1.00
$(CH_3)_4NCl$ (for comparison)	107.3	-4.60
$(C_2H_5)_3NH^+Cl^-$	138.6	-14.4
$(n\text{-}C_3H_7)_3NH^+Cl^-$	186.8	-22.4
$n\text{-}C_3H_7NH_3^+I^-$	105.7	-2.20
$(n\text{-}C_3H_7)_2NH_2^+I^-$	156.9	-1.60
$(n\text{-}C_3H_7)_3NH^+I^-$	204.8	-1.03
$(n\text{-}C_3H_7)_4NI$ (for comparison)	250.7	-14.4

Table 13

Values of the Coefficient b for Homologous Series of Alkylamine Hydrogen Halide Salts

Salt	b
$CH_3NH_3^+ Cl^-$	
	1.330
$(CH_3)_2NH_2^+ Cl^-$	
	1.292
$(CH_3)_3NH^+Cl^-$	
	1.141
$(C_2H_5)_3NH^+Cl^-$	
	1.145
$(\underline{n}\text{-}C_3H_7)_3NH^+Cl^-$	
$\underline{n}\text{-}C_3H_7NH_3^+ I^-$	
	1.217
$(\underline{n}\text{-}C_3H_7)_2NH_2^+ I^-$	
	1.139
$(\underline{n}\text{-}C_3H_7)_3NH^+I^-$	

Figure 20. A plot of $\bar{V}_2^o$ as a function of the number of carbon atoms in the salt for the symmetrical tetraalkylammonium halide and alkylamine hydrogen halide salts.


350
300
250
200
150
100
50
∇_2° ml.(g.mole)$^{-1}$
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
NUMBER of CARBON ATOMS
$(n\text{-}Am)_4N^+$
$(n\text{-}Bu)_4N^+$
$(n\text{-}Pr)_4N^+$
$(Et)_4N^+$
$(n\text{-}Pr)_2NH_2^+$
$(Me)_4N^+$
$n\text{-}PrNH_3^+$
$(n\text{-}Pr)_3NH^+$
Et_3NH^+
Me_3NH^+
$Me_2NH_2^+$
$MeNH_3^+$
CHLORIDES
BROMIDES
IODIDES

to be obtained with a reproducibility of three in the sixth decimal place. A check on the absolute accuracy of the measurements was determined as described on p. 109 by means of test runs on KCl solutions; satisfactory agreement with the published data (156) was obtained (cf. p. 109).

The error in ϕ_2, equation II·4, the apparent molal volume at a finite concentration, may be expressed by the relation

$$\delta\phi_2 = \frac{-1000 - mM_2}{md^2}\delta d - \frac{1000(d_o-d)}{dd_o m^2}\delta m \qquad V\cdot 15$$

A discussion of the deviations in ϕ_2 is complicated by the fact that according to equation V·15 there are two groups of sources of error which affect the measurements in entirely different ways. At high concentrations $\delta\phi_2$ is determined principally by the second term in equation V·15. At low concentrations the first term far outweighs the second term. Therefore consideration has to be made as to the deviations δd at low concentrations, and δm at high concentrations.

In the case of most of the salts studied in this work, all deviations were attributed to the density determination and a mean error $\delta d = \pm 3\times10^{-6}$ is obtained for concentrations < 0.2 m. Actually the precision of the density determinations is better because the δm term is not negligible at the higher concentrations. The sensitivity of the Archimedian balance (0.1 mg unit of the scale) corresponds to $\delta d = 1\times10^{-6}$.

Taking into account the mean value of $\delta\phi_2$ at the higher concentrations and the possible analytical error, the uncertainty

of ϕ_2 is estimated to be 0.06 ml.mole^{-1}.

iii) Accuracy of Derived Results

The partial molal volume $\bar{V}_2$ at a finite concentration is obtained according to equation II·7 . The precision for the partial molal volume is ± 0.1ml.mole^{-1} based on the error in ϕ_2, b and the least squares uncertainty in the slope of ϕ_2 as a linear function of $c^{\frac{1}{2}}$. Least squares uncertainty in the intercepts $\bar{V}_2^o$, the partial molal volume at infinite dilution, based on a linear plot of $\bar{V}_2 - 2.792c^{\frac{1}{2}}$ against c is ±0.2 ml.mole^{-1} and the uncertainty in the slopes is 5%.

The satisfactory agreement between the data in the last two columns of Table 8 and the reasonable linearity of the three plots in Fig. 12, indicate that the individual partial g. ionic volumes can be obtained for the three halide ions with a least squares uncertainty of 0.2 ml. (g.ion)$^{-1}$ for a linear plot and, at the worst, with an intrinsic uncertainty of about 0.5ml.(g.ion)$^{-1}$, bearing in mind the point mentioned previously that small but specific variations of b occur up the homologous series of ions.

2. Apparent Molal Adiabatic Compressibilities

i) Graphs and Tabulations

In Chapter II it was shown that the apparent molal adiabatic compressibility of a solution may be obtained by measuring the density and velocity of sound in the solution. Values of the apparent molal adiabatic compressibilities for the first four members of the homologous symmetrical tetraalkylammonium bromide series in aqueous solution at 25°C are shown in Table 14. Included in this table are the values of the density, velocity of sound and coefficient of adiabatic compressibility at different concentrations. Typical extrapolations of the apparent molal adiabatic compressibility with respect to $c^{\frac{1}{2}}$ down to zero $c^{\frac{1}{2}}$ are shown in Fig. 21 and Fig. 22 for $(CH_3)_4NBr$, $(C_2H_5)_4NBr$, $(\underline{n}\text{-}C_3H_7)_4NBr$ and $(\underline{n}\text{-}C_4H_9)NBr$. Tables 15, 16 and 17 contain values of the apparent adiabatic compressibility, density, velocity of sound and coefficient of adiabatic compressibility for the aqueous solutions of the series CH_3NH_3Cl to $(CH_3)_4NCl$, $(CH_3)_4NI$ to $(\underline{n}\text{-}C_4H_9)_4$ NI and CH_3NH_2 to $(CH_3)_3N$, respectively.

TABLE 14

Values of the Apparent Molal Adiabatic Compressibility $\phi_{K(s)}$ for Four Tetraalkylammonium Bromide Aqueous Solutions at 25°C.

Salt	conc. moles litre^{-1}	density g.cc.$^{-1}$	Δu metre sec.$^{-1}$	u metre sec.$^{-1}$	$\beta(s) \times 10^6$ bar^{-1}	ϕ_2 cc.(g. mole)$^{-1}$	$\phi_{K(s)} \times 10^4$ cc.(g.mole bar)$^{-1}$
$(CH_3)_4NBr$	0.04158	0.998706	2.61	1499.68	44.521	114.52	-4.07
	0.04998	0.999038	3.11	1500.18	44.477	114.58	-3.55
	0.06187	0.999511	3.83	1500.90	44.413	114.59	-3.35
	0.07156	0.999877	4.32	1501.39	44.368	114.76	-2.17
	0.08926	1.000588	5.42	1502.49	44.271	114.74	-2.43
	0.10805	1.001326	6.53	1503.60	44.173	114.81	-2.12
	0.12715	1.002076	7.71	1504.78	44.071	114.86	-2.08
	0.15029	1.002988	9.01	1506.08	43.955	114.88	-1.55
	0.19960	1.004903	11.93	1509.00	43.703	115.05	-1.02
	0.28738	1.008333	16.98	1514.05	43.263	115.13	-0.26
$(C_2H_5)_4NBr$	0.02214	0.997852	2.51	1499.58	44.565	174.36	-5.98
	0.03052	0.998164	3.44	1500.51	44.496	174.11	-5.63
	0.04779	0.998817	5.33	1502.40	44.355	173.65	-5.15
	0.06187	0.999333	6.87	1503.94	44.241	173.74	-4.68
	0.07501	0.999811	8.31	1505.38	44.136	173.84	-4.20
	0.09981	1.000711	11.02	1508.09	43.938	173.97	-3.60
	0.14984	1.002575	16.46	1513.53	43.541	173.79	-2.98
	0.20123	1.004499	21.96	1519.03	43.143	173.64	-2.20
	0.30377	1.008342	32.98	1530.05	42.363	173.49	-0.97
$(n\text{-}C_3H_7)_4NBr$	0.01567	0.997480	2.75	1499.82	44.567	239.42	-10.28
	0.02209	0.997663	3.86	1500.93	44.493	239.15	-9.76
	0.03075	0.997899	5.37	1502.44	44.393	239.31	-9.33
	0.03106	0.997906	5.42	1502.49	44.390	239.36	-9.12
	0.03332	0.997971	5.85	1502.92	44.362	239.28	-9.67
	0.03981	0.998147	7.01	1504.08	44.287	239.38	-9.42
	0.04106	0.998185	7.17	1504.24	44.275	239.30	-8.83

TABLE 14 - cont'd

	0.04346	0.998248	7.61	1504.68	44.246	239.37	-9.08
	0.05855	0.998673	10.21	1507.28	44.075	239.23	-8.40
	0.06270	0.998793	10.95	1508.02	44.026	239.16	-8.61
$(n\text{-}C_4H_9)_4NBr$	0.01616	0.997417	3.90	1500.97	44.502	300.44	-19.64
	0.01758	0.997447	4.25	1501.32	44.480	300.58	-19.64
	0.01759	0.997447	4.25	1501.32	44.480	300.59	-19.51
	0.01806	0.997451	4.38	1501.45	44.472	300.95	-19.83
	0.02537	0.997624	6.13	1503.20	44.361	300.57	-19.19
	0.03068	0.997742	7.40	1504.47	44.281	300.65	-18.64
	0.03371	0.997816	8.08	1505.15	44.237	300.48	-19.03
	0.03500	0.997851	8.40	1505.47	44.217	300.32	-18.19
	0.04383	0.998048	10.48	1507.55	44.086	300.45	-17.27
	0.05659	0.998342	13.46	1510.53	43.900	300.40	-15.96
	0.07731	0.998833	18.50	1515.57	43.587	300.18	-16.22

TABLE 15

Values of the Apparent Molal Adiabatic Compressibility $\phi_{K(s)}$ for Aqueous Solutions of CH_3NH_3Cl, $(CH_3)_2NH_2Cl$, $(CH_3)_3NHCl$ and $(CH_3)_4NCl$ at 25°C.

Salt	conc. moles litre^{-1}	density g. cc.$^{-1}$	Δu metre sec.$^{-1}$	u metre sec.$^{-1}$	$\beta_{(s)} \times 10^6$ bar^{-1}	ϕ_2 cc.(g. mole)$^{-1}$	$\phi_{K(s)} \times 10^4$ cc.(g.mole bar)$^{-1}$
CH_3NH_3Cl	0.04113	0.997600	2.64	1499.71	44.569	54.26	-19.99
	0.05037	0.997723	3.16	1500.23	44.532	54.28	-19.09
	0.06199	0.997879	3.92	1500.99	44.480	54.28	-19.35
	0.07026	0.997988	4.45	1501.52	44.444	54.30	-19.37
	0.14192	0.998915	8.28	1505.90	44.145	54.53	-18.25
	0.19630	0.999602	11.79	1509.41	43.910	54.67	-18.38
	0.30395	1.000973	17.67	1515.29	43.510	54.77	-16.32
	0.40769	1.002248	23.76	1521.38	43.107	54.93	-15.73
	0.45211	1.002814	26.33	1523.95	42.938	54.93	-15.52
	0.50749	1.003469	29.15	1526.77	42.751	55.03	-14.77
	0.59012	1.004480	33.40	1531.02	42.471	55.09	-13.97
$(CH_3)_2NH_2Cl$	0.02492	0.997276	1.90	1498.97	44.627	72.62	-17.27
	0.04425	0.997451	3.31	1500.38	44.535	72.66	-16.30
	0.06201	0.997602	4.58	1501.65	44.453	72.83	-15.47
	0.08180	0.997765	6.01	1503.08	44.362	73.00	-14.89
	0.09987	0.997919	7.35	1504.42	44.277	73.04	-14.78
	0.16114	0.998435	11.74	1508.81	43.996	73.16	-14.11
	0.21518	0.998889	15.61	1512.68	43.751	73.21	-13.71
	0.25043	0.999185	17.81	1514.88	43.611	73.23	-12.75
	0.31453	0.999704	22.40	1519.47	43.326	73.32	-12.50

TABLE 15 cont'd

$(CH_3)_3NHCl$	0.02545	0.997174	2.26	1499.33	44.610	90.90	-14.72
	0.03024	0.997192	2.67	1499.74	44.585	91.09	-14.13
	0.04066	0.997250	3.53	1500.60	44.531	90.88	-13.44
	0.04098	0.997248	3.61	1500.68	44.527	90.97	-13.95
	0.06158	0.997350	5.25	1502.32	44.425	90.94	-12.25
	0.07071	0.997387	6.10	1503.17	44.373	91.05	-12.72
	0.07813	0.997420	6.63	1503.70	44.340	91.09	-11.84
	0.09018	0.997481	7.57	1504.64	44.282	91.05	-11.26
	0.09369	0.997491	7.92	1504.99	44.261	91.12	-11.53
$(CH_3)_4NCl$	0.02187	0.997099	2.22	1499.29	44.616	107.59	-13.59
	0.02564	0.997106	2.57	1499.64	44.595	107.66	-12.67
	0.03384	0.997133	3.34	1500.41	44.548	107.41	-11.91
	0.04559	0.997151	4.51	1501.58	44.478	107.66	-11.71
	0.05203	0.997168	5.10	1502.17	44.442	107.61	-11.23
	0.05882	0.997180	5.77	1502.84	44.402	107.68	-11.14

TABLE 16

Values of the Apparent Molal Adiabatic Compressibility $\phi_{K(s)}$ for Aqueous Solutions of $(CH_3)_4NI$, $(C_2H_5)_4NI$, $(n\text{-}C_3H_7)_4NI$ and $(n\text{-}C_4H_9)_4NI$ at 25°C.

Salt	conc. moles litre^{-1}	density g. cc.$^{-1}$	Δu metre.sec.$^{-1}$	u metre sec.$^{-1}$	$\beta(s) \times 10^6$ bar^{-1}	ϕ_2 cc.(g. mole)$^{-1}$	$\phi_{K(s)} \times 10^4$ cc.(g. mole.bar)$^{-1}$
$(CH_3)_4NI$	0.08993	1.003809	2.20	1499.27	44.319	126.24	+8.46
	0.09460	1.004155	2.29	1499.36	44.298	126.30	+8.64
	0.09997	1.004551	2.41	1499.48	44.274	126.37	+8.84
	0.10353	1.004828	2.51	1499.58	44.256	126.28	+8.70
	0.10967	1.005282	2.64	1499.71	44.228	126.34	+8.85
	0.11117	1.005368	2.67	1499.74	44.222	126.58	+9.05
	0.11888	1.005954	2.79	1499.86	44.189	126.51	+9.34
$(C_2H_5)_4NI$	0.03171	0.999333	2.37	1499.44	44.507	185.65	+6.14
	0.03286	0.999413	2.46	1499.53	44.498	185.74	+6.14
	0.04212	1.000082	3.12	1500.19	44.430	185.67	+6.89
	0.04851	1.000542	3.57	1500.64	44.383	185.68	+7.20
	0.04906	1.000572	3.62	1500.69	44.378	185.87	+7.15
	0.07458	1.002434	5.26	1502.33	44.199	185.48	+8.99
	0.09857	1.004145	6.97	1504.04	44.024	185.70	+9.33
$(n\text{-}C_3H_7)_4NI$	0.02643	0.998715	3.63	1500.70	44.460	250.94	+2.17
	0.04093	0.999635	5.57	1502.64	44.305	250.80	+3.25
	0.05071	1.000236	6.87	1503.94	44.201	251.14	+3.87
	0.06713	1.001289	9.00	1506.07	44.030	250.84	+4.80
	0.11407	1.004263	15.04	1512.11	43.550	250.76	+6.93
	0.14264	1.006084	18.63	1515.70	43.265	250.66	+8.02
$(n\text{-}C_4H_9)_4NI$	0.01564	0.997956	3.19	1500.26	44.520	312.25	-7.98
	0.01979	0.998198	4.04	1501.11	44.459	312.19	-7.85
	0.02035	0.998227	4.16	1501.23	44.450	312.30	-8.15
	0.03048	0.998816	6.19	1503.26	44.304	312.30	-6.89
	0.04959	0.999931	10.00	1507.07	44.031	312.16	-5.50

TABLE 17

Values of the Apparent Molal Adiabatic Compressibility $\phi_{K(s)}$ for Aqueous Solutions of CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ at 25°C (in 0.025 N. aq. KOH to suppress ionisation; same solution used in reference compartment)

Solute	conc. moles litre^{-1}	density g.cc.$^{-1}$	Δu metre sec.$^{-1}$	u metre sec.$^{-1}$	$\beta(s) \times 10^6$ bar^{-1}	ϕ_2 cc.(g. mole)$^{-1}$	$\phi_{K(s)} \times 10^4$ cc.(g.mole bar)$^{-1}$
CH_3NH_2	0.07120	0.996368	1.83	1498.90	44.672	40.73	+7.13
	0.07433	0.996337	1.91	1498.98	44.669	40.75	+7.20
	0.08092	0.996271	2.04	1499.11	44.664	40.78	+7.50
	0.09031	0.996175	2.28	1499.35	44.654	40.85	+7.55
	0.10053	0.996055	2.53	1499.60	44.644	41.06	+7.73
	0.10811	0.995969	2.74	1499.81	44.636	41.16	+7.78
	0.11882	0.995865	3.05	1500.12	44.622	41.14	+7.55
	0.14239	0.995632	3.70	1500.77	44.594	41.12	+7.38
$(CH_3)_2NH$	0.06468	0.996174	2.54	1499.61	44.638	58.78	+8.81
	0.07680	0.995991	3.06	1500.13	44.616	59.02	+8.83
	0.08372	0.995902	3.27	1500.34	44.607	58.32	+8.90
	0.09592	0.995776	3.72	1500.79	44.586	58.51	+8.98
	0.10630	0.995580	4.21	1501.28	44.566	59.06	+9.03
	0.12130	0.995385	4.79	1501.86	44.540	58.96	+8.99
	0.16497	0.994778	6.64	1503.71	44.457	59.01	+8.59
	0.19875	0.994260	8.16	1505.23	44.391	59.28	+8.42
$(CH_3)_3N$	0.03082	0.996519	1.97	1499.04	44.657	76.50	+3.73
	0.04499	0.996202	2.92	1499.99	44.614	78.15	+4.52
	0.04582	0.996188	2.99	1500.06	44.611	78.11	+4.40
	0.04615	0.996177	3.00	1500.07	44.611	78.22	+4.67
	0.04994	0.996102	3.25	1500.32	44.599	78.21	+4.56
	0.06312	0.995858	4.05	1501.12	44.563	78.19	+5.21
	0.09905	0.995166	6.29	1503.36	44.461	78.34	+5.78
	0.15623	0.994032	10.35	1507.42	44.272	78.65	+4.54

Figure 21. A plot of apparent molal adiabatic compressibility $\phi_{K(s)}$ as a function of the square root of the concentration $c^{\frac{1}{2}}$ for $(CH_3)_4NBr$ and $(C_2H_5)_4NBr$ at 25°C.

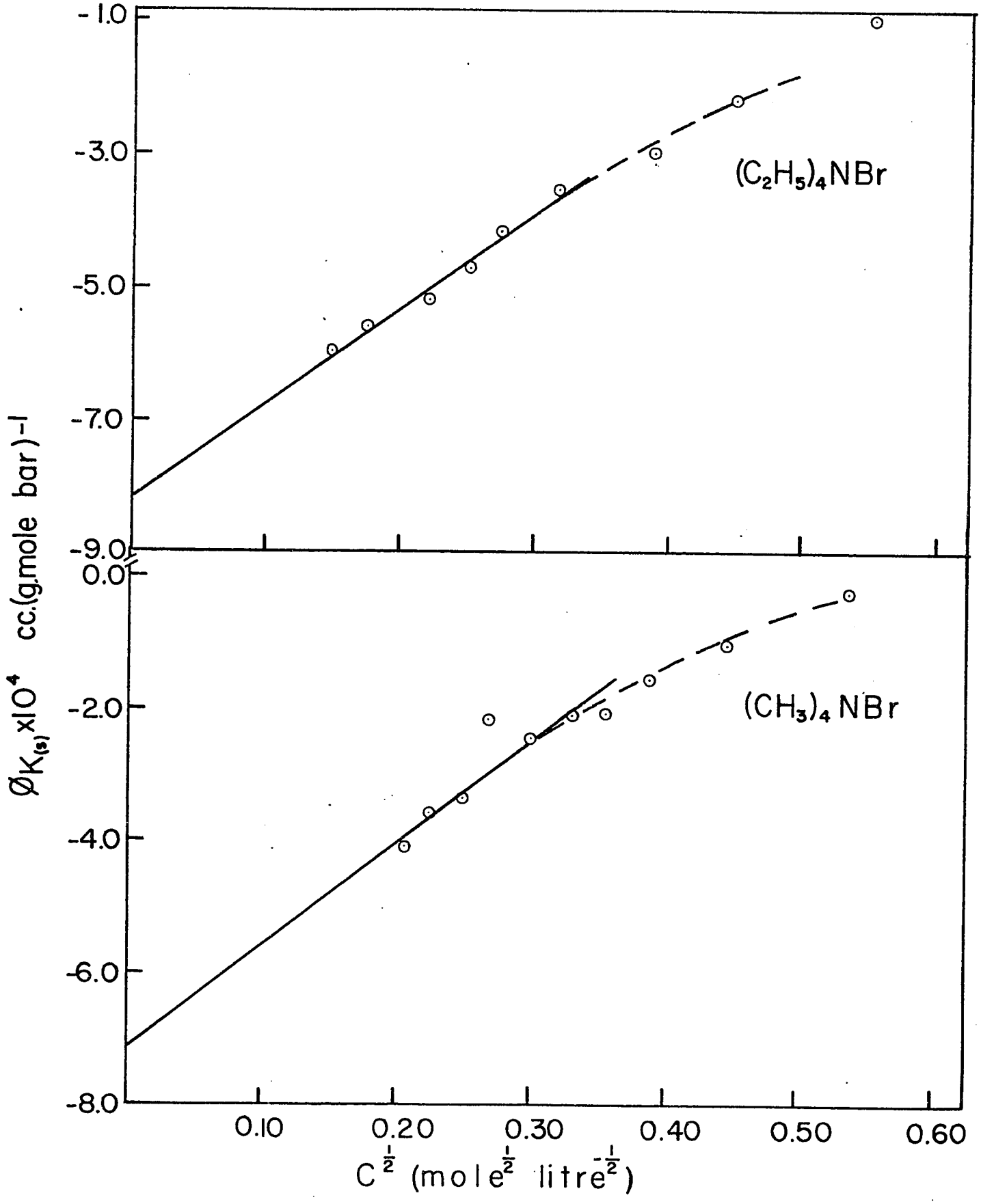
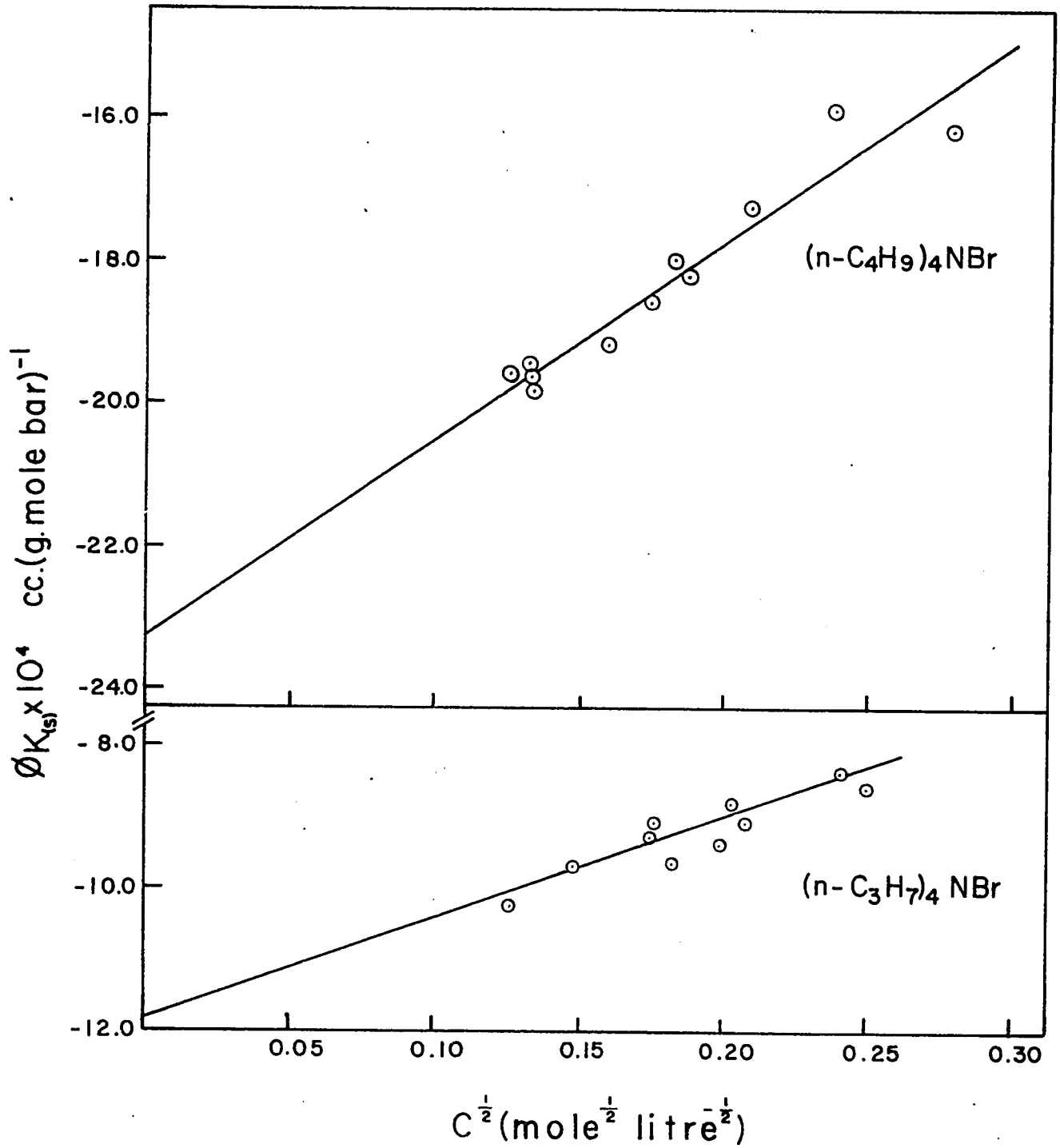

-1.0
-3.0
-5.0
-7.0
-9.0
0.0
-2.0
-4.0
-6.0
-8.0
$(C_2H_5)_4NBr$
$(CH_3)_4NBr$
$\phi_{K(s)} \times 10^4$ cc.(g.mole bar)-1
0.10
0.20
0.30
0.40
0.50
0.60
$C^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ litre$^{-\frac{1}{2}}$)

Figure 22. A plot of apparent molal adiabatic compressibility $\phi_{K(s)}$ as a function of the square root of the concentration $c^{\frac{1}{2}}$ for $(\underline{n}\text{-}C_3H_7)_4NBr$ and $(\underline{n}\text{-}C_4H_9)NBr$ at 25°C.


-16.0
-18.0
-20.0
-22.0
-24.0
- 8.0
-10.0
-12.0
$\phi K_{(s)} \times 10^4$ cc.(g.mole bar)$^{-1}$
$(n\text{-}C_4H_9)_4NBr$
$(n\text{-}C_3H_7)_4NBr$
0.05
0.10
0.15
0.20
0.25
0.30
$C^{\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ litre$^{-\frac{1}{2}}$)

ii) Extrapolation Procedure

It was assumed that the concentration dependence of the apparent molal adiabatic compressibility $\phi_{K(s)}$ follows closely the simple form

$$\phi_{K(s)} = \phi^{o}_{K(s)} + S_{K(s)} c^{\frac{1}{2}} \qquad V\cdot16$$

which is expected in the case of the apparent molal compressibility ϕ_K in dilute solutions. This relationship is derived by differentiation with respect to pressure of the limiting law concentration relation for the apparent molal volume as a function of concentration, viz.

$$\frac{\partial}{\partial P}\left[\phi_v = \phi^{o}_{v} + S_{(v)} c^{\frac{1}{2}}\right] \qquad V\cdot17$$

which leads to

$$\phi_K = \phi^{o}_{K} - \left[\left(\frac{\partial S_{(v)}}{\partial P}\right)_T + \frac{\beta S_{(v)}}{2}\right] c^{\frac{1}{2}} \qquad V\cdot18$$

or in terms of the apparent molal adiabatic compressibility,

$$\phi_{K(s)} = \phi^{o}_{K(s)} - \left[\left(\frac{\partial S_{(v)}}{\partial P}\right)_H + \frac{\beta_{(s)} S_{(v)}}{2}\right] c^{\frac{1}{2}} \qquad V\cdot19$$

where

$$S_{K(s)} = -\left[\left(\frac{\partial S_{(v)}}{\partial P}\right)_H + \frac{\beta_{(s)} S_{(v)}}{2}\right] \qquad V\cdot20$$

The values of the apparent molal adiabatic compressibilities at infinite dilution $\phi_{K(s)}$ and the slopes $S_{K(s)}$ for the three

series of salts studied are shown in Table 18. These slopes and intercepts are based on the limiting values taken at the lowest concentrations employed in the experiments. It was difficult to achieve the desired low concentration values of $\phi_{K(s)}$ for some of the salts on account of the restriction imposed by the length of the test-vessel employed in the frequency range 8.3-8.45 megacycles. At higher concentrations, the slopes of plots of apparent molal adiabatic compressibility as a function of $c^{\frac{1}{2}}$ decrease for most of the salts. This occurs usually at a concentration > 0.15 molar. In the case of $(CH_3)_4NI$, a very narrow concentration range had to be studied owing to the limitation of the length of test-vessel at low concentration and the relative insolubility of $(CH_3)_4NI$ at higher ones (ca. 0.12 molar).

The apparent molal adiabatic compressibility of the aqueous mono-, di- and trimethylamine solutions are shown graphically in Fig. 23 as a function of the concentration c (mole litre^{-1}). In each case, the apparent molal adiabatic compressibility passes through a maximum which occurs in the concentration range 0.09 - 0.11 molar for each of the three amines. It is rather difficult to obtain the extrapolated values $\phi^{o}_{K(s)}$ for these three compounds owing to the non-linear variation of $\phi_{K(s)}$ with concentration.

The values of the apparent molal adiabatic compressibility at infinite dilution for the three series of salts studied are shown in Fig. 24 as a function of the number of

TABLE 18

Values of $\phi^{\circ}_{K(s)}$ and $S_{K(s)}$ in Equation V·16 (25°C)

Salt	$\phi^{\circ}_{K(s)}(\pm 0.25)\times 10^{4}$ cc.(g.mole bar)$^{-1}$	$S_{K(s)}(\pm 8\%)\times 10^{4}$ cc.l$^{\frac{1}{2}}$.(g.mole)$^{-3/2}$bar^{-1}
$(CH_3)_4NBr$	-7.1	+15.4
$(C_2H_5)_4NBr$	-8.2	+14.2
$(\underline{n}\text{-}C_3H_7)_4NBr$	-11.8	+13.7
$(\underline{n}\text{-}C_4H_9)_4NBr$	-23.3	+27.5
$(CH_3)_4NI$	+3.3	+17.2
$(C_2H_5)_4NI$	+1.6	+25.3
$(\underline{n}\text{-}C_3H_7)_4NI$	-2.25	+27.2
$(\underline{n}\text{-}C_4H_9)_4NI$	-11.9	+28.6
CH_3NH_3Cl	-22.0	+10.0
$(CH_3)_2NH_2Cl$	-20.2	+18.2
$(CH_3)_3NHCl$	-18.1	+21.5
$(CH_3)_4NCl$	-16.6	+23.4

Figure 23. A plot of apparent molal adiabatic compressibility $\phi_{K(s)}$ as a function of the concentration c for CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ at 25°C.

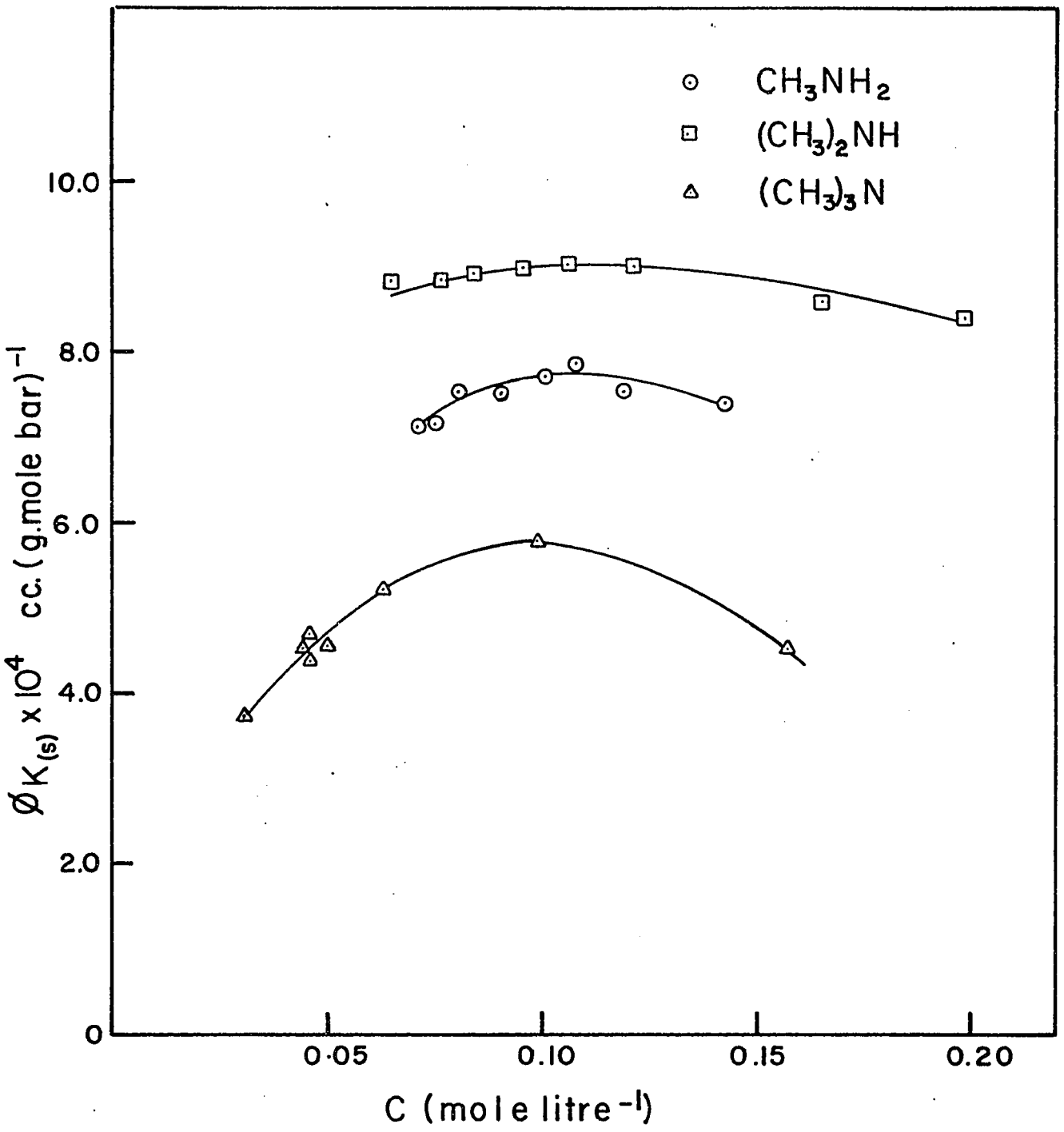
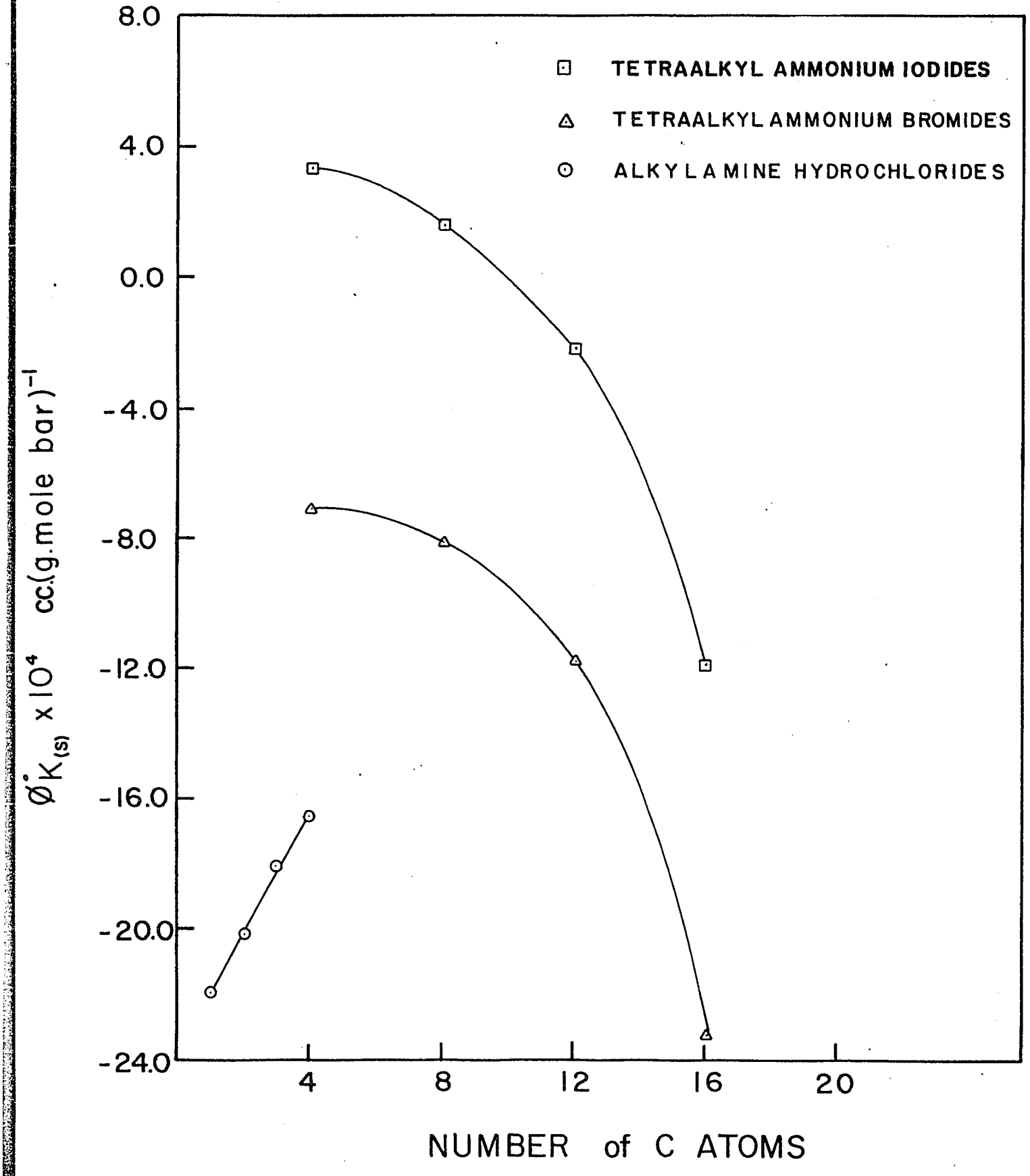
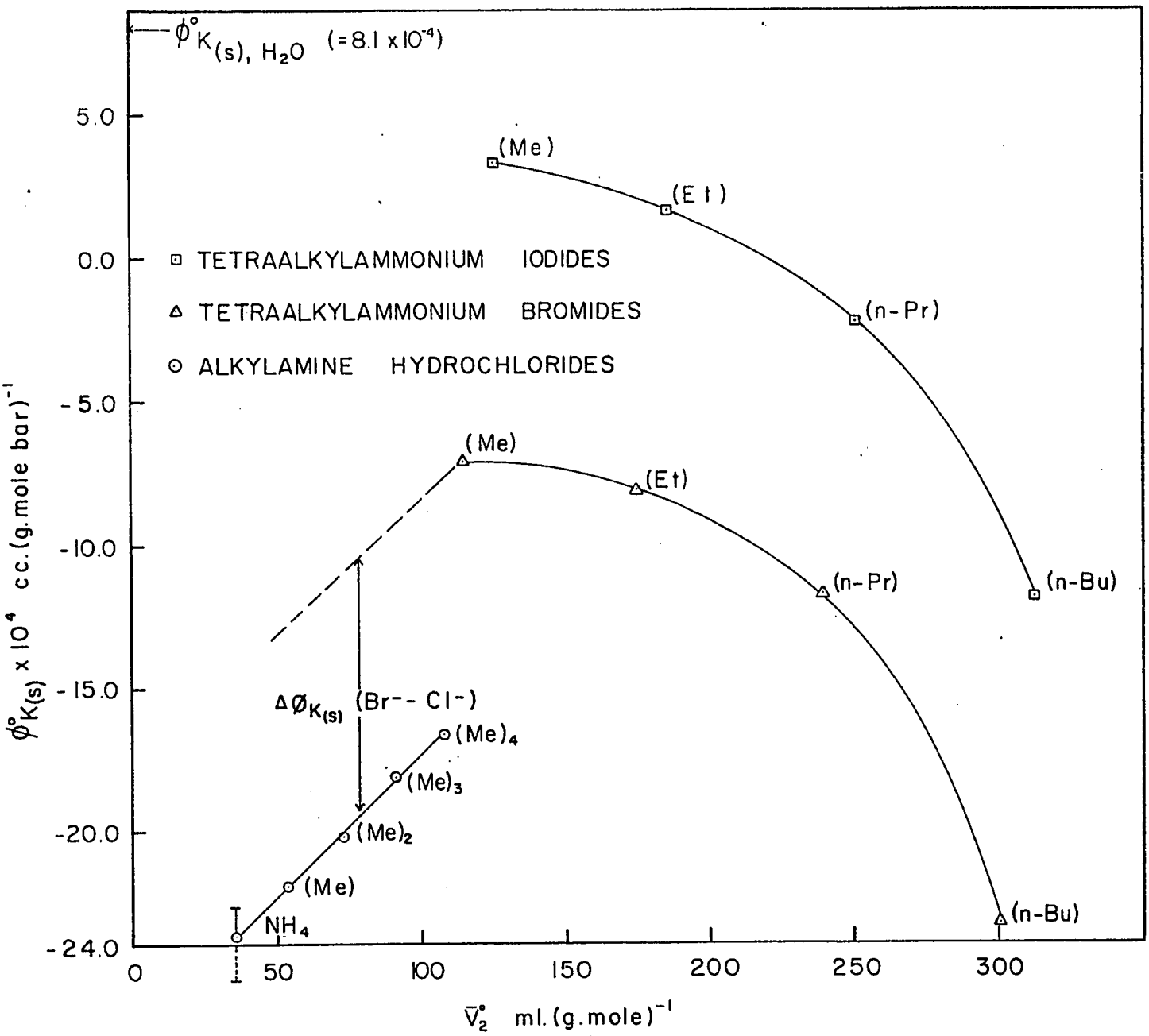

CH_3NH_2
$(CH_3)_2NH$
$(CH_3)_3N$
10.0
8.0
6.0
4.0
2.0
0
0·05
0.10
0.15
0.20
$\phi K_{(s)} \times 10^4$ cc. (g.mole bar)$^{-1}$
C (mole litre^{-1})

Figure 24. A plot of apparent molal adiabatic compressibility at infinite dilution $\phi_{K(s)}^{o}$ as a function of the number of carbon atoms in the salt for the series of salts $(CH_3)_4NBr \rightarrow (\underline{n}\text{-}C_4H_9)NBr$, $(CH_3)_4NI \rightarrow (\underline{n}\text{-}C_4H_9)_4NI$ and $CH_3NH_3Cl \rightarrow (CH_3)_4NCl$.


8.0
4.0
0.0
-4.0
-8.0
-12.0
-16.0
-20.0
-24.0
4
8
12
16
20
NUMBER of C ATOMS
$\phi^{\circ}_{K(s)} \times 10^{4}$ cc.(g.mole bar)$^{-1}$
TETRAALKYL AMMONIUM IODIDES
TETRAALKYL AMMONIUM BROMIDES
ALKYLAMINE HYDROCHLORIDES

carbon atoms in the salt. The apparent molal adiabatic compressibility $\phi^{o}_{K(s)}$ increases in a linear manner with the number of carbon atoms in the alkylamine hydrochloride series. However, in the tetraalkylammonium bromide and iodide series, $\phi^{o}_{K(s)}$ decreases non-linearly with increasing number of carbon atoms. The dependence of $\phi^{o}_{K(s)}$ on the partial molal volume of the salt at infinite dilution $\bar{V}^{o}_{2}$ is shown in Fig. 25. Again, as in the case of $\phi^{o}_{K(s)}$ as a function of the number of carbon atoms (see Fig. 24), there appears to be a linear relation between $\bar{V}^{o}_{2}$ and $\phi^{o}_{K(s)}$ in the case of the alkylamine hydrochloride salts only. Assuming this linear relationship and taking the value of $\bar{V}^{o}_{2}$ for NH_4Cl (171) as 35.98, the $\phi^{o}_{K(s)}$ value for NH_4Cl may be predicted to be -23.7×10^{-4}. There appears to be little work carried out on the apparent molal adiabatic compressibility of NH_4Cl. However, Corey (172) has measured one value of $\phi_{K(s)}$ at 25°C and c=1.0827 mole litre^{-1}. Assuming the slope of $\phi_{K(s)}$ as a function of $c^{\frac{1}{2}}$ to be less than that obtained for CH_3NH_3Cl (Table 18) - and in fact using the one value of Corey and taking $S_{K(s)}$ to be equal to 8×10^{-4} or 10×10^{-4}, $\phi^{o}_{K(s)}$ for NH_4Cl is obtained as -24.7×10^{-4} and -22.6×10^{-4}, respectively. These limits are shown by a vertical line in Fig. 25 where the datum for NH_4Cl is shown for comparison.

Figure 25. A plot of apparent molal adiabatic compressibility at infinite dilution $\phi^{o}_{K(s)}$ as a function of the partial molal volume at infinite dilution $\bar{V}^{o}_{2}$ for the different salts.


$\phi^\circ_{K(s),\,H_2O}$ (=8.1 x 10^{-4})
5.0
0.0
-5.0
-10.0
-15.0
-20.0
-24.0
0
50
100
150
200
250
300
$\phi^\circ_{K(s)}$ x 10^4 cc.(g.mole bar)$^{-1}$
$\bar{V}_2^\circ$ ml.(g.mole)$^{-1}$
TETRAALKYLAMMONIUM IODIDES
TETRAALKYLAMMONIUM BROMIDES
ALKYLAMINE HYDROCHLORIDES
(Me)
(Et)
(n-Pr)
(n-Bu)
(Me)
(Et)
(n-Pr)
(n-Bu)
$\Delta\phi_{K(s)}$ (Br$^-$ - Cl$^-$)
(Me)$_4$
(Me)$_3$
(Me)$_2$
(Me)
NH$_4$

iii) Accuracy of Results

The absolute accuracy of the measurements was determined in test runs on KCl solutions. Employing the experimental data obtained in this work for $\phi_{K(s)}$ of KCl along with thermodynamic quantities given in reference (124) to evaluate δ, (equation II·20), it was possible to convert $\phi_{K(s)}$, the apparent molal adiabatic compressibility, into ϕ_K the apparent molal compressibility. The partial molal compressibility at infinite dilution $\bar{K}_2^o$ was determined by extrapolating the apparent molal compressibility ϕ_K with respect to $c^{\frac{1}{2}}$ down to zero $c^{\frac{1}{2}}$. The values of $\bar{K}_2^o$ agreed to within 0.40×10^{-4} cc. $(\text{g.mole bar})^{-1}$ of the published data (125), i.e., to within 0.9%.

The error in $\beta_{(s)}$ (equation II·19), the coefficient of adiabatic compressibility, may be expressed by the relation:

$$\delta\beta_{(s)} = -\frac{2\times10^6 \delta u}{u^3 d} - \frac{10^6 \delta d}{u^2 d^2} \qquad \text{V·21}$$

where δu is the error in the velocity of sound in the solution and δd is the error in the density of the solution. From equation IV·3, it may be shown that δu is given by:

$$\delta\Delta u = - \frac{u_w^2(\delta f \Delta y + f \delta \Delta y)}{(f\Delta y - u_w)^2} \qquad \text{V·22}$$

where δf is the error in the frequency and $\delta \Delta y$ the error in the measured phase change of the signal. The error in the frequency δf is quite small and the errors related to the measurement of Δy determine the limit of accuracy of the velocity difference technique.

The absolute error in δu was within the range 0.02 - 0.04 metre sec^{-1} and the mean error in the density determinations was 3×10^{-6} $g.cc.^{-1}$. Based on the above errors, the uncertainty of $\beta_{(s)}$ is estimated to be 0.003×10^{-6} bar^{-1}.

iv) Accuracy of Derived Results

The apparent molal adiabatic compressibility $\phi_{K(s)}$ is obtained according to equation II·21 and the error in $\phi_{K(s)}$ may be expressed by the relation:

$$\delta\phi_{K(s)} = \frac{-1000(\beta_{(s)}-\beta_{o(s)})\delta c + 1000\, c\,\delta\beta_{(s)}}{c^2} + \beta_{o(s)}\delta\phi_2 \qquad V\cdot 23$$

The precision for the apparent molal adiabatic compressibility based on the errors $\delta\beta_{(s)}$, $\delta\phi_2$ and δc is ± 0.25 cc.(g.mole.bar)$^{-1}$. Least squares uncertainty in the intercepts $\phi^{o}_{K(s)}$ (the apparent molal adiabatic compressibilities at infinite dilution) based on linear plots of $\phi_{K(s)}$ against $c^{\frac{1}{2}}$ is ± 0.5 cc.(g.mole bar)$^{-1}$ and the uncertainty in the slopes is 8%.

Chapter VI

DISCUSSION

1. Experimental and Derived Results for Partial Molal Volumes of the Tetraalkylammonium Halides

i) General

A considerable part of the partial molal studies in this work is concerned with the tetraalkylammonium halide salts. Previous work has shown that tetraalkylammonium salts exhibit some of the more important and interesting quantitative deviations from the limiting laws for conductance (173) and activity coefficients (174, 175). A number of other peculiarities in their behaviour, e.g. the anomalous salting-in of simple non-electrolytes (31, 176, 177) and the enzyme inhibiting properties of these salts has led to the necessity of examining their behaviour in aqueous solutions in more detail (120, 164). These peculiarities (72, 120, 164) are thought to be due to the large size and hydrophobic character of the cations of the salts and the associated local modification of the water structure (or more exactly, of the fluctuating association-dissociation equilibrium amongst hydrogen bonded water molecules in the liquid (72, 12)) which these cations can bring about.

ii) Concentration Dependence of $\bar{V}_2$

Perhaps the most significant result obtained from partial molal volume studies in this work for both the tetraalkylammonium and alkylamine hydrogen halide salts is the indication of the large negative (and very slightly positive) slopes obtained for plots of ϕ_2 as a function of $c^{\frac{1}{2}}$ (also obtained by Wen and Saito (120) for the tetraalkylammonium

bromide series at higher concentrations). This result is also manifested in the plots of $\bar{V}_2 - 2.792c^{\frac{1}{2}}$ as a function of c. The negative and widely differing values of the slope of a plot of ϕ_2 vs. $c^{\frac{1}{2}}$ is in contradiction to the Debye-Hückel limiting law. The discrepancy can be traced to the fact that the Debye-Hückel theory does not take into account the solute-water interactions which appear to be important in determining the apparent molal volume (and correspondingly the activity coefficient) of tetraalkylammonium salts even in dilute solutions. From Table 5, it may seem that there is a general decrease in h as the size of the cations increases but there is a reverse effect, for a given cation, with increasing radius of the co-anion. These results, therefore offer evidence that the hydrophobic character of the tetraalkylammonium salts is responsible, in part, for the observed large negative concentration dependence of $\bar{V}_2$.

A possible explanation for these values of h is simply that they arise from the second term of equation V·8 which takes into account the distance of closest approach. The term $W_{(v)}$ in equation V·4 depends on the distance of closest approach $\overset{o}{a}$ and on $d\ln\overset{o}{a}/dP$. The factor $K_{(v)}$ (equation V·5) takes into account all other effects such as hydration and self-salting-out and was not considered in the estimates of $\overset{o}{a}$ and $d \ln \overset{o}{a}/dP$ carried out in Chapter V.

The exploratory calculations carried out in Chapter V indicated that the h values could not be accounted for satisfactorily by any choice of distance of closest approach

$\mathring{a}$ and d ln $\mathring{a}$/dP which determine $W_{(v)}$. The most reasonable method employed, using $\mathring{a}$ values based on the radii of the ions obtained from equation V·14 , causes d ln $\mathring{a}$/dP to vary from $+ 40\times10^{-12}$ dyne^{-1} cm.^{2} for R = methyl to $- 450\times10^{-12}$ dyne^{-1} cm.^{2} for R=amyl. The term d ln $\mathring{a}$/dP is not known exactly for any salts (although estimates have been given by Wirth and Collier (165) for $HClO_4$ solutions) but it may be surmised that the larger the ion the more compressible, or deformable, it should be, so that d ln $\mathring{a}$/dP would tend to be more negative with increasing size of the ion. However, it is questionable if the extent of variation of the magnitude of d ln $\mathring{a}$/dP indicated above is correct. Furthermore a positive value for Me_4NBr seems improbable. Therefore, it appears that taking into account only the distance of closest approach is an insufficient basis for the explanation of the observed h values.

The concentration dependence of $\bar{V}_2$ can be obtained from the pressure derivative of the partial molal free energy of electrolytes. The factors which are important in the prediction of activity coefficients should therefore also be responsible for the concentration dependence of $\bar{V}_2$. The main contributions to the non-ideal free energy of simple ions in moderately concentrated solutions are (cf.18) those associated with long-range coulomoic forces, hydration of ions and mutual salting-out. The hydration term (26), which effectively takes into account the number of water molecules effectively removed in a thermodynamic sense from their role as bulk solvent because of the hydration of ions, is probably unimportant (see p.211) in the

present case because of the large size of the cations studied in the present work, and the chloride and bromide ions are only slightly or negligibly hydrated (17o). A mutual (ion-cavity) salting-out effect occurs (18) in addition to the hydration effect and arises since an ion of finite size forms a cavity in the solution which is less polarisable than the solvent water. Neglect of this term in the interpretation of activity coefficients of simple electrolytes results (18) in an apparent increase in hydration numbers for the anions in the order $Cl^- < Br^- < I^-$ (16) which is contrary to other evidence (100, 179).

The influence of mutual salting-out on the concentration dependence of $\bar{V}_i$ can be obtained from the relation derived previously (18) for the contribution of mutual salting-out to the non-ideal free energy in the case of a 1:1 salt, viz:

$$\ln f_{so} = \frac{e^2 c}{2000 \epsilon kT} \left(\frac{1}{3} \frac{\bar{V}_A^{\theta}}{r_{h(M)}} + \frac{\bar{V}^o_M}{r_{h(M)}} + \frac{1}{3} \frac{\bar{V}^o_M}{r_{h(A)}} + \frac{\bar{V}^o_A}{r_{h(A)}} \right) \qquad \text{VI·1}$$

and

$$\Delta V = \nu RT \, d \ln f_{so}/dP \qquad \text{VI·2}$$

where ν, the number of ions forming the electrolyte MA, is equal to 2 and $\bar{V}^o_M$, $\bar{V}^o_A$, $r_{h(M)}$ and $r_{h(A)}$ are the respective partial g. ionic volumes and radii of the hydrated ions. By differentiating equation VI·1 with respect to pressure, the following expression is obtained:

$$\Delta V = \frac{e^2 N c}{1000 \epsilon} \left\{ \left[\bar{V}_A^o \ (\beta - d \ln \epsilon / dP) - \bar{K}_A^o \right] \left[1/3 r_{h(M)} + 1/r_{h(A)} \right] \right.$$

$$- (\bar{V}_A^o + \bar{V}_M^o/3) \ d \ln r_{h(A)}/dP$$

$$+ \left[\bar{V}_M^o \ (\beta - d \ln \epsilon / dP) - \bar{K}_M^o \right] \left[1/3 r_{h(A)} + 1/r_{h(M)} \right]$$

$$\left. - (\bar{V}_M^o + \bar{V}_A^o/3) \ d \ln r_{h(M)}/dP \right\} \qquad \text{VI·3}$$

where β is the coefficient of compressibility of water, and $\bar{K}_M^o$ and $\bar{K}_A^o$ are the partial molal g. ionic compressibilities ($\bar{K}_i^o = - d\bar{V}_i^o/dP$). This equation cannot be solved exactly since the terms $d \ln r_h/dP$ are not known; however, since they are probably negative, the concentration dependence of $\Delta V/c$ can be shown to be positive. Since reasonable values for $\bar{V}_i^o$ and $\bar{K}_i^o$ (145) are known for the halide ions, it can also be shown that the slope $\Delta V/c$ increases as the size of the anion increases. Hence, the increase in the parameter h with increasing size of the halide ion could be caused by the mutual salting-out effect.

The contribution of long-range coulombic interactions to the activity coefficient is given exactly by the Debye-Hückel theory only for very dilute solutions (11, 180). In moderately concentrated solutions, Frank and Thompson (11) have shown that the use of a disordered lattice model (cf. 18), which predicts a cube-root dependence on concentration for the logarithm of the rational mean activity coefficient is preferable to the Debye-Hückel ionic atmosphere treatment. Frank has also shown that

such a model would be even more applicable with salts of large ions like those studied in this work. Furthermore it may be expected that in moderately concentrated solutions, the contribution of the coulombic forces to the concentration dependence of $\bar{V}_2$ will be linear in $c^{1/3}$ rather than in $c^{\frac{1}{2}}$ and therefore equations V·2 and V·8 can be expected to hold only for very dilute solutions.

In addition to long-range coulombic forces and mutual salting-out, the hydrophobic character of the R_4NX salts will cause a certain amount of mutual salting-in between the large cations (arising from sharing of structure - promoted regions of solvent about the ions; 180, 164), and this will affect both the activity coefficients and the partial molal volumes and can result limitingly in some association (164). This mutual salting -in acts in an opposite sense to the mutual salting-out effect for the activity coefficients and the same should also be true for the partial molal volumes. This could explain the results of Wen and Saito (181) on tetraethanolammonium salts; these salts would suffer a large mutual salting-out because of their size but no "structure -promotion" mutual salting-in since they are not hydrophobic; hence a positive concentration dependence of $\bar{V}_2$ would arise, as is observed (181).

There is much uncertainty in the quantitative prediction of activity coefficients of ordinary electrolytes in moderately concentrated solutions (18) and this uncertainty becomes even larger for tetraalkylammonium salts. Therefore, any attempt to obtain theoretically the pressure derivative

of the non-ideal free energy cannot be expected to be very successful. However, it does seem that (a) an increase in the distance of closest approach will cause a decrease in the slope h; (b) an increase in hydrophobic character will decrease h; (c) an increase in size of the anion (salting-out effect) will decrease $|h|$, and (d) an increase in the size of the anion will increase $|h|$ (cavity effect).

Amongst other factors that may influence the concentration dependence of $\bar{V}_2$, is the fact that equation V·8 is a slowly converging series, especially for large ions, and a considerable amount of overlap of terms may occur. This could mean that $\bar{V}_2 - 2.792c^{\frac{1}{2}}$ is a linear function of c only in extremely dilute solutions and that experimentally the measurements are not sensitive enough to indicate the deviations from linearity at higher concentrations; alternatively the contributions from mutual salting-out and salting-in, being linear in c, may overshadow the contribution of the term associated with the distance of closest approach and $d \ln \mathring{a}/dP$.

iii) Radii of the Tetraalkylammonium Ions.

If the "true" radii of the R_4N^+ ions in solution were known, their intrinsic volume $V_{int.}$ could be calculated and the "negative electrostriction"* caused by these salts evaluated from $\bar{V}_i^o$. These radii cannot unfortunately be obtained with precision but have been estimated from bond lengths (167) and conductance data (170) as was shown in Table 10.

* Strictly, the term electrostriction must be reserved for the usually negative volume changes caused by the effect of a field on a polarisable medium. The term "negative" electrostriction is used here simply to refer to the positive volume change that will accompany structure promotion in water.

Deno and Spink (144) have estimated $V_{int.}$ from the Parachor. The latter method may be questioned since the Parachor is based on volumes in the pure liquid state while $V_{int.}$ refers to molecules in solution. Nevertheless, the values of $V_{int.}$ obtained seem to account for the observed salting-in of benzene by tetraalkylammonium salts. The radii corresponding to $V_{int.}$ were deduced from equation V·14. Data from these different methods for obtaining r were previously compared in Table 10 and were called formal radii (see Chapter V). The effective radii estimated from $\bar{V}_i^o$ (equation V·14) are also given for comparison, although these radii may include a contribution from "negative electrostriction" so that the "true" radii of these ions would be smaller than the effective radii estimated from $\bar{V}_i^o$ (since $\bar{V}_i > V_{int.}$). At present it is difficult to assign reliable values to the "true" radii of the R_4N^+ ions, but Hepler and co-workers (121) have set the limits of 2.41 to 2.65 Å for the radius of Me_4N^+. Hence, (see Table 10) some "negative electrostriction" may, in fact, be involved.

iv) Non-Electrostatic Effects

It was previously pointed out that recent and earlier work on the thermodynamics of solutions of tetraalkylammonium salts (164,174,175*) has revealed unexpected deviations from the Debye-Hückel theory for activity and osmotic coefficients in the limiting-law concentration range. Some of these deviations (174) are negative ones which could not hitherto be explained in terms

* The work in ref. 175 has, however, been criticised by Stokes (182) and is also inconsistent with the data of Bower and Robinson (ref.(174)). It has been further refuted by Prue and Prini (183) on the basis that the e.m.f. measurements used to obtain the activity coefficients are erroneous owing to the formation of a complex $2AgI \cdot NR_4I$ between the Ag-AgI electrode and the R_4NI salt.

of the classical framework of the electrostatic theory of long-range coulombic interactions. The negative deviations could be explained by conventional ion-pairing but such effects are unlikely to arise with these salts at the dilutions involved. For example, they are not supported by the conductance behaviour of some of these salts (184; cf.188). A possible reason for the observed deviations is the special kind of ion-association postulated by Diamond (164) in terms of structure-promotion effects(following a similar suggestion of Frank (180)). Also the role of nearest neighbour interaction effects giving a $c^{1/3}$ rather than a $c^{\frac{1}{2}}$ law in log $\gamma_{\pm}$ has been discussed previously (11, 18, 26) and the possibility of this applying to the results for quaternary ammonium salts has been pointed out by Frank (180). These suggestions put forward to explain the non-ideal behaviour are certainly cogent for the types of electrolytes considered here and until recently there has been little reason to explore other effects outside the classical electrostatic framework of the conventional theories. However, another factor which will be of quite general significance and has seemingly been neglected in previous theories of electrolyte solutions is the relative size of the solute and solvent molecules.

It was commonly believed until 1937 that all athermal solutions would always be regular, i.e. the relative size of "solute" and "solvent" would not influence the ideality of the entropy of mixing. Fowler and Rushbrooke (185) pointed out that this would not be the case and provided a theory of

the deviation from ideality which would result in non-electrolyte solutions of a "dimer" in its corresponding "monomeric" solvent. More detailed treatments for molecules of different shapes and sizes have been given by Guggenheim (186). Such effects have not been considered for electrolyte solutions presumably because the well-known electrostatic theories of long-range interactions and those of short-range ion-solvation effects (15, 17, 18, 26) have hitherto provided a satisfactory basis for discussion of the thermodynamics of inorganic electrolytes, the small ions of which are usually of comparable size to that of the solvent molecules in the case of aqueous solutions. However, with tetra-alkylammonium salts, the cations will be approximately some 5 (in the case of $(CH_3)_4 N^+$) to 19 (in the case of $(\underline{n}\text{-}C_5H_{11})_4N^+$) times larger than the solvent water molecules.

For an ion composed of r groups (which will be called the r-mer) each occupying a solvent lattice position, the relative partial molar free energy $\Delta\mu_r$ can be written in the usual way as:

$$\Delta\mu_r = \mu_r - \mu_r^o = RT \ln \left(a_r/a_r^o\right) \qquad \text{VI·4}$$

where a_r^o is the activity or fugacity of pure r-mer, a_r is that for the r-mer in the mixture of r with a solvent 1 and μ_r^o is the chemical potential of r-mer in the standard state. $\Delta\mu_r$ is given from the statistical-mechanical lattice theory (186) as

$$\Delta\mu_r = RT \ln \frac{N_r}{N_r+N_1/r} \left(\frac{N_r+N_1/r}{N_r+N_1/q}\right)^{\frac{zq}{2}} \qquad \text{VI·5}$$

for a mixture of N_r moles of r-mer in N_1 moles of solvent. The parameters z, q and r are related by

$$q = r - \frac{2r}{z} + \frac{2}{z} \qquad \text{VI·6}$$

from which it may be noted that q is always less than r (because r is a positive integer >1), except when it is equal to r which arises when r=1 (ordinary regular solution case for solute and solvent having the same size) or when $z=\infty$ (Flory's approximation (187)); in equation VI·6, z is the coordination number for the lattice and q is a parameter defining the number zq of pairs of neighbouring sites of which one is a member of the r-fold group constituting the r-mer and the other is not; in the athermal solution all configurations are, of course, assumed to have the same energy. When $z = \infty$,* volume fraction lattice statistics will apply and the relation corresponding to equation VI·5, which must be derived by differentiating the appropriate expression (186) for the free energy of mixing is

$$\Delta\mu_r = RT \ln \frac{N_r}{N_r+N_1/r} - RT\,(r-1)\,\frac{N_1/r}{N_r+N_1/r} \qquad \text{VI·7}$$

The ideal solution law corresponding to equation VI·5 is

$$\Delta\mu_r = RT \ln \frac{N_r}{N_r+N_1} \qquad \text{VI·8}$$

so that comparison of the terms in equation VI·5 and those in

---

* When $z = \infty$, the term in round brackets in equation VI·5 is unity since q = r, so that volume fraction statistics then apply as investigated by Glueckauf (17) for hydrated small ions.

VI·7 gives the rational activity coefficient for the r-mer, and this quantity is denoted by f_{ne} to stress its non-electrostatic origin. In these terms, it will be seen from equations VI·5 or VI·7 that negative deviations from Raoult's law for the r-mer will always result. However, the activity coefficient (to be denoted by γ) relative to the infinite dilution reference state is required in order to relate it to the Debye-Hückel activity coefficient; hence it is required to relate the thermodynamic behaviour to the limiting Henry's law case (189) rather than to the Raoult's law behaviour of the solute. Hence, if the limiting value of f_{ne} (to be denoted as f^{o}_{ne}) as $N_r \rightarrow o$ in finite N_1 can be obtained, γ can be evaluated as f_{ne}/f^{o}_{ne}. An explicit result for γ_{ne} in these terms cannot easily be obtained from equations VI·5 and VI·8. However, one can proceed by evaluating a quantity a/a_o (cf. equation VI·4) from equation VI·5, where a/a_o is a ratio of hypothetical vapour pressure of r-mer in the solution to that in the pure state. The ratio a/a_o can be calculated from equations VI·8 (Raoult's law case) and VI·5 and then plotted against molar concentration. For the non-ideal solution, equation VI·5, $(a/a_o)/c$ can also be plotted against c and extrapolated to c=o to give a limiting slope k_H of the plot of a/a_o vs. c. The actual values of a/a_o calculated from equation VI·5 at finite c can then be compared with the values that would arise if $a/a_o = k_H c$ applied at all finite concentrations (Henry's law case). The ratio of these two values of a/a_o at any concentration then gives γ_{ne} at that concentration.

It follows by geometrical calculations (cf.(189), particularly Fig. 18-1) that this ratio of a/a_o values is equal to the ratio f_{ne}/f^o_{ne}, which is the activity coefficient contribution γ_{ne} required for relation to the electrostatic Debye-Hückel mean activity coefficient γ where $\gamma = \gamma_e \gamma_{ne}$.

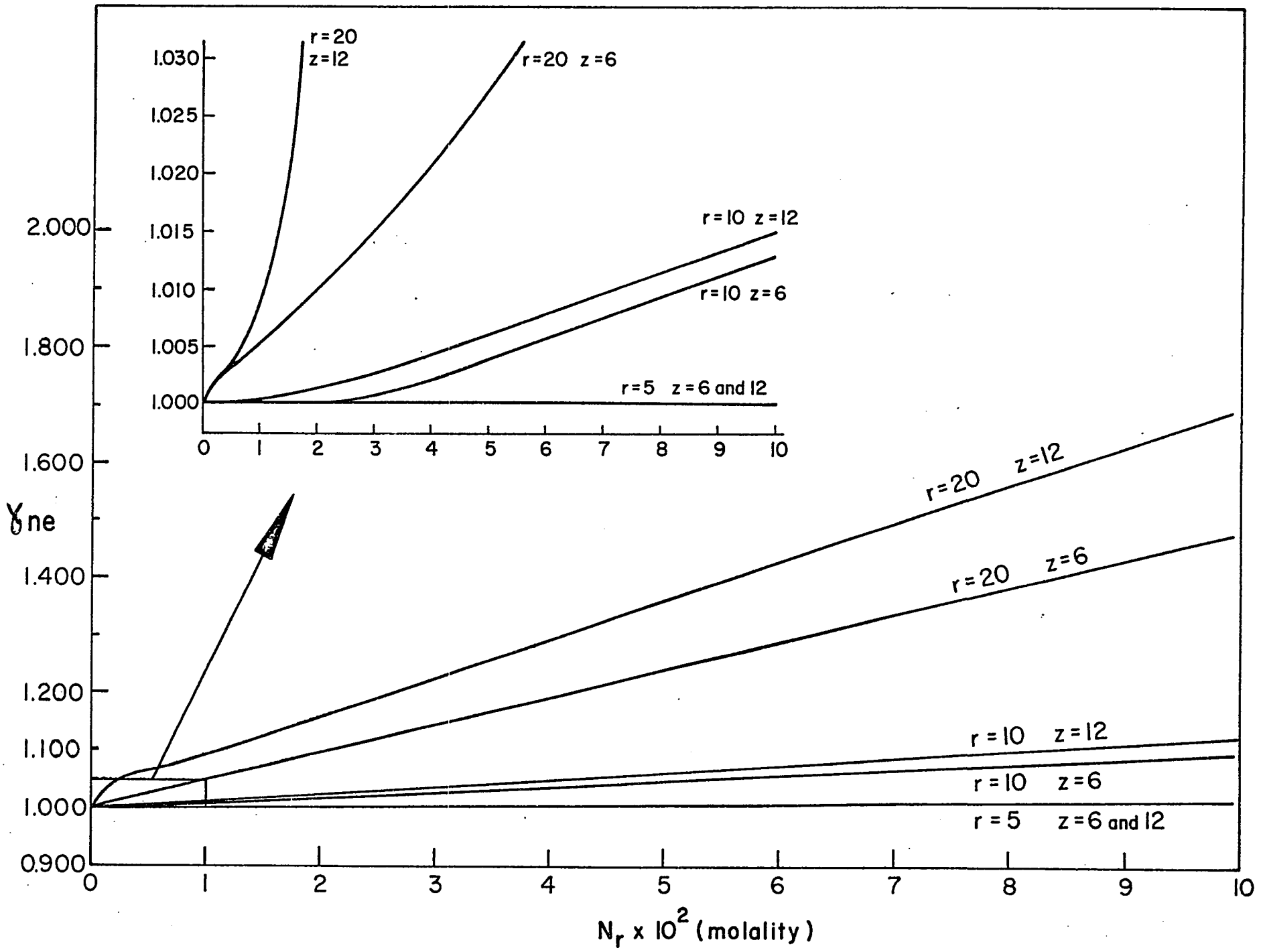
In the limiting case of $z = \infty$, an approximate analytical result can be obtained for γ_{ne} from equations VI·7 and VI·8

$$\ln \gamma_{ne} \doteq (r-1)^2 \frac{N_r}{rN_r + N_1} \qquad \text{VI·9}$$

Results of the numerical explorations of the properties of equation VI·5 in relation to VI·8 are shown in Fig. 26. It may be seen that substantial deviations ($\gamma_{ne} > 1$) from the Debye-Hückel result arise at moderate concentrations (0.1M) and for larger values of r they persist to quite low concentrations (0.01M)

It has been shown in Chapter V that the tetraalkylammonium salts exhibit anomalously large negative linear dependencies on molar concentration c (slope term h) after the usual limiting law $c^{\frac{1}{2}}$ term has been eliminated. Substantial deviations from the limiting-law slope for $\bar{V}$ will persist quite significantly into the limiting-law concentration region (0.0001-0.002 M) based on the values of h obtained. Since the ion size factor can give rise to an appreciable concentration dependent term in the non-ideal partial molal free energy of the solute r-mer, the derivative of this contribution with respect to

Figure 26. A plot of values of the non-ideal activity coefficient γ_{ne} as a function of the molality of r-mer.


r=20
z=12
r=20 z=6
r=10 z=12
r=10 z=6
r=5 z=6 and 12
1.030
1.025
1.020
1.015
1.010
1.005
1.000
0 1 2 3 4 5 6 7 8 9 10
2.000
1.800
1.600
1.400
1.200
1.100
1.000
0.900
γne
r=20 z=12
r=20 z=6
r=10 z=12
r=10 z=6
r=5 z=6 and 12
0 1 2 3 4 5 6 7 8 9 10
$N_r \times 10^2$ (molality)

pressure may give a corresponding contribution to the difference $\bar{V}-\bar{V}^{o}$ for various concentrations. For the tetraalkylammonium salts, h is experimentally found to become more negative with increasing r, i.e. in the series Me to Bu; γ_{ne} for a given z becomes larger with increasing r or for a given r increases with increasing z. Very qualitatively, the observed effects could hence arise, in part, if r or z effectively became smaller with increasing pressure.

The contribution of the ion-solvent size ratio effect seems of the right order of magnitude to explain part of the observed deviations from Debye-Hückel behaviour at low concentrations. These deviations are in the same direction as the conventional salting-out effects (26, 31) and the cavity salting-out effect (18). However, it should be noted that relative size effects in binary mixtures of non-electrolytes (19, 190) give rise to smaller deviations from ideality than would be predicted in terms of the statistical lattice theories, and indeed in the case of completely spherical molecules in a continuum, the lattice theory would not be meaningful. However, in reference (19), a rather different experimental situation is involved from that considered here. In the present case, although Me_4N^+ is almost spherical, the higher members e.g. $\underline{n}$-Bu_4N^+ are not and must present to the solution a group of four chains in a variety of conformations but in an overall tetrahedral configuration. Also, the treatment might be criticised on the basis that the equations used are for particles in a linear

arrangement rather than for four n-alkyl groups linked tetrahedrally. This limitation may not, however, be so serious as it may seem, since Guggenheim (186) has calculated the activities of solvent in solutions of linear tetramers and tetrahedral tetramers and finds surprisingly little difference between the calculated thermodynamic behaviour of such species.

2. Results for Partial Molal Volumes of the n-Alkylamine Hydrogen Halide Salts

The trend in the magnitude of the experimental h parameter (Table 12) for the n-alkylamine hydrogen halide salts indicates that there is a general decrease in h as the size of the cation increases but there is a reverse effect, for a given cation, with increasing radius of the co-anion. This behaviour is similar to that exhibited by the results obtained with the R_4NX salts and offers evidence that the hydrophobic character of the cation is responsible, in part, for the negative concentration dependence of $\bar{V}_2$. Successive substitutions of a methyl group for a hydrogen atom in the series $MeNH_3Cl$ to Me_3NHCl does not appear to change the magnitude of h significantly (although the magnitude of h for all three salts is greater than that for Me_4NCl, as would be expected - see Table 12). An insignificant change in h also arises in the case of the iodide series n-Pr NH_3I to n-Pr_3NHI, although the values of h are larger than that obtained for n-Pr_4NI. However, as the size of the alkyl group is increased in the tri-n-alkylammonium chloride salts, there is a considerable decrease in h (h becomes more negative).

These results generally indicate that the observed negative concentration dependence of $\bar{V}_2$ is larger when (a) the nitrogen atom in a salt of the type NH_4X, is completely surrounded by four alkyl substituents and (b) for a given number of alkyl substituents in the cation, the size of the substituent alkyl group is increased, bearing in mind of course that the anion size shows a reverse effect with regard to the magnitude of the experimental h value for a given cation.

These results, indicate furthermore, that the charge-bearing nitrogen atom can still exert a reasonable charge effect when the large cation is not symmetrical. The charge effect tends to give a positive concentration dependence of $\bar{V}_2$. Recent work (177) on the salting-in of benzene by substituted quaternary ammonium bromide solutions $R_{4-n}H_nN^+Br^-$, where R is an alkyl group and n varies between 0 and 3, indicates that with the symmetrical quaternary ammonium salts, the salting-in appears to be a linear function of the number of carbon atoms in the cations, while with the salts containing less than four alkyl groups, the salting-in is less and depends on the symmetry of the cation. The difference between these two types of behaviour was explained by the possibility of a certain amount of salting-out occurring near the charge-bearing nitrogen atom when the cations are not symmetrical. The present results on the volume studies appear to confirm the explanation for the observed salting-in results(177).

Previous studies on the partial molal volumes of CH_3NH_3Cl, $(CH_3)_2NH_2Cl$ and $(CH_3)_3NHCl$ were carried out by Hamann and Lim (191). They employed a pycnometer method to obtain density values in order to calculate $\bar{V}_2^o$ for these salts. Their extrapolated $\bar{V}_2^o$ values are not in good agreement with the present results for $\bar{V}_2^o$ of these salts, the difference being 3% for the first member to 1% for the last.

The thermodynamic partial g.ionic volume difference for $\Delta V_{I^-Cl^-}$ may be verified in the case of the salts $(\underline{n}\text{-}C_3H_7)_3$ NHI

and $(\underline{n}\text{-}C_3H_7)_3$ NHCl (Table 12). The value of 18.0 ml.(g.ion)$^{-1}$ is in reasonable agreement with the partial g.ionic volume difference obtained from the symmetrical tetraalkylammonium halide series (Table 8). No attempt has been made to obtain formal radii for these asymmetrical cations because of the non-spherical nature of the cation.

Another factor that is apparent from the data in Table 13 and Fig. 20, concerns the hydration of successive members in a series such as R_3NH^+, $R_2NH_2^+$, RNH_3^+ (and NH_4^+). Thus, for diminishing substitution of the N^+ centre, and hence for a bigger local charge effect, the b value is greater than that for the R_4N^+ series and this effect must be attributed to an increasing degree of hydration as the N^+ becomes more exposed in the direction of the above series. A similar trend of entropies of ionisation is also observed (207). Further discussion is given in section 7 of this Chapter.

3. The Problem of Individual Ionic Volumes

i) General

It was pointed out in the Introduction that various methods (90, 101, 110, 118, 145, 178) have been suggested for separating partial molal volumes of electrolytes at infinite dilution into their ionic components, $\bar{V}_i^o$, but the most reliable are based on attempts to relate the ionic volume to some function of the crystal radii of ions (100, 109, 118, 179). In this respect, the tetraalkylammonium halides are ideal for determining partial g.ionic volumes since the cation size may be varied to a much larger extent than in the series of alkali metal ions. The principle proposed in this work for obtaining partial g. ionic volumes is based on the evidence (Fig. 12) that the values of $\bar{V}_i^o$ for the tetraalkylammonium ions are linear functions of their molecular weights.

ii) Assignment of Individual Ionic Contributions

It seems reasonable to suppose that the plots in Fig. 12 would not be linear if specific hydration effects were associated with the cations and indeed for the smallest ion NH_4^+, where significant hydration effects might be expected (100), the data for the $NH_4^+X^-$ salts fall below the line of best fit. Thus, it may be supposed that the tetraalkylammonium ions are not hydrated in the normal sense (55, 111, 115, 129) involving significant electrostriction. Recent calculations (129) indicate that water electrostriction about an ion the size of $(CH_3)_4N^+$ would be <1ml. while for higher homologues the effect would be

negligible; conversely for NH_4^+, the electrostriction would be ca. 2-3 ml. g. ion^{-1}. The positive slopes of ϕ_2 and $\bar{V}_2$ as a function of $c^{\frac{1}{2}}$ for the $(CH_3)_4NX$ salts also seem to corroborate the view that in the close vicinity of $(CH_3)_4N^+$, the water structure is under some influence of the charge (cf. Wen and Saito (120)). However, since these salts are known to increase the degree of ice-like structure in water, the net shift in equilibrium of the water molecules towards a higher degree of association will cause a total decrease in the density of water, so that an apparent "negative electrostriction" may occur near the large cations. There are however good reasons (177) for expecting that this "negative electrostriction" would be proportional to the size of the organic ion, and an extrapolation such as that in Fig. 12 would eliminate this extra change in volume, if it were significant.

In Chapter V, it was shown that in terms of the actual numerical data (Table 5), the specific volume of the methylene groups, b, show some small but significant variations from a constant value (Table 6). It is felt that the differences between b values in Table 6 are quite significant since the same trend is found in independent experiments with the three different halide salts and with some neutral amines.

The significant differences of b from one salt series to the next are substantially smaller than the uncertainties in critical volume data for homologous hydrocarbons (192) from which a quantity similar to b can be obtained (192); the

partial molal volumes evidently provide a sensitive method for examining additivity of volumes of alkyl functions (recent work by Scheraga and Friedman (193) indicates a similar conclusion for alcohols). The conditions under which the $\bar{V}_i^o$ values are obtained also ensure automatically that the volumes are compared in "corresponding states" since excess solvent is present at a given constant temperature and electrostatic self-compression through electrostriction will be negligible for these large ions (129, 178).

It is evident that the volume changes per CH_2 group are sensibly constant between a given pair of cations with a series of co-anions, as thermodynamically expected for infinite dilution conditions. For a given co-anion, however, the volume difference factor b across the series of homologous salts is not quite constant, being significantly larger between Et_4N^+ and $n\text{-}Pr_4N^+$ than between the other three pairs of homologous ions. Measurements (192) of $\bar{V}_2^o$ for linear protonated amine salts of the type RNH_3Br also indicate that the $\bar{V}_2^o$ are not quite additive for each methylene group. This small lack of constancy of the volume increment may arise from: (a) slightly different space requirements per CH_2 of the alkyl groups as more conformations are available with increasing chain length and non-bonding interactions are involved; (b) different extents of hydrophobic interaction with the surrounding water, as with increasing chain length the inner CH_2 groups become less accessible to the water (e.g. in the case of the $n\text{-}Bu_4N^+$ ion) and give relatively less structure-promotion; (c) bending back of terminal groups on the

longer chains towards the body of the ion. Similar variations were also shown in Table 7 for neutral tri-n- alkylamines in MeOH and n-hexane.

The significant linearity which the plots in Fig. 12 nevertheless exhibit, suggests that the data can be extrapolated to zero cation molecular weight to give the individual partial g. ionic volumes of the co-anions, Cl^-, Br^- or I^-. It must be emphasised that the extrapolations below $(CH_3)_4N^+$ are only for mathematical purposes to obtain the $\bar{V}_i^o$ for the anions and do not imply that the $\bar{V}_i^o$ data for any hypothetical or real (e.g. NH_4^+) ions which might exist, and have molecular weights less than that of $(CH_3)_4N^+$, should actually fall on this line (for example, if hydration became significant, they would not, e.g. the case of NH_4^+ mentioned above). The problem of extrapolation can, of course, be avoided by obtaining the $\bar{V}_X^o$- quantities in equations V·10 and V·11 by direct computation from the measured $\bar{V}_2^o$ values for homologous salts and the observed mean slopes b.

The validity of the individual $\bar{V}_X^o$- values is indicated by comparison of the differences $\Delta\bar{V}_2^o$ between these extrapolated values for a pair of ions and those obtained from the average differences of actual partial molal volumes of alkali halide salts having a common cation (ref. 134, p. 361). The $\Delta\bar{V}_2^o$ values are compared in Table 8 and their derivation involves, of course, no non-thermodynamic assumptions.

The satisfactory agreement between the data in the last two columns of Table 8, and the reasonable linearity of

the three plots in Fig. 12, indicates that the individual partial g. ionic volumes can be obtained for the three halide ions with a least squares uncertainty of 0.2 ml $(g.ion)^{-1}$ for a linear plot and, at the worst, with an intrinsic uncertainty of about 0.5 ml. $(g.ion)^{-1}$, bearing in mind the variation of b (cf. p.150).

On the basis of the scale proposed for the partial g. ionic volumes at infinite dilution, the value for H^+ should be -5.7 ± 0.5 ml. $(g.ion)^{-1}$. This agrees moderately well with the absolute assignments of Couture and Laidler (109), $\bar{V}^o_{H+} = -6.0$ ml. $(g.ion)^{-1}$ and of Mukerjee (118), $\bar{V}^o_{H+} = -4.5$ ml. $(g.ion)^{-1}$.

Both these scales were based on choice of that value for $\bar{V}^o_{H+}$ which would allow the resulting $\bar{V}^o_i$ values for cations and anions of the same charge to fall on a common line with respect to the cube of the ionic crystal radius. Some objections may be raised to the principle involved in these methods because alkali metal and halide ions of the same size would not necessarily be hydrated to the same extent, since the water molecules in their hydration shells are oriented differently (112). In the method suggested here it is assumed that the volumes and "negative electrostriction" (if any) of the large ions are linear functions of their molecular weight, or constant; no assumptions need be made about what happens near the smaller co-anion. Because of the similarities in structure and known behaviour in water of these large cations, these assumptions seem justifiable.

Further evidence that the individual partial g.ionic volumes on the present scale are close to the absolute values is

obtained from deduction of the electrostriction of the halide ions. It was previously shown in equation V·14 that the intrinsic or "true" non-hydrated volumes of ions, $V_{int.}$, can be related to the "true" ionic radii r. From this equation, $V_{int.}$ of Cl^-, Br^- and I^- are found to be respectively 25.3, 31.4 and 40.1 ml. $(g.ion)^{-1}$. Comparison with the data in Table 8 indicates that the extents of electrostriction, defined by $V_{int.} - \bar{V}_i^o$, are 1.7, 0.5 and -2.1 ml. $(g.ion)^{-1}$, respectively. The "negative electrostriction" deduced for I^- adds support to the suggestion of Diamond (164) that the iodide ion increases, to a small extent, the structure of water in a way similar to that caused by the tetraalkylammonium ions. On this basis, he proposed a certain amount of "water structure-enforced" ion-pairing (cf. 168) between I^- and R_4N^+ causing a negative deviation from the Debye-Hückel law for activity coefficients as discussed above.

The present assignment of $\bar{V}_i^o$ values indicates that earlier scales (194) based on $\bar{V}_{H^+}^o$ equal to, or greater than zero must definitely be excluded. It seems now that for the proton (and correspondingly for other ions) the individual partial g. ionic volume can be specified to within about 0.5 ml., the individual hydration energy (113) to 2-3 kcal. $(g.ion)^{-1}$ and the individual partial g.ionic entropy to 1.5 e.u. (100).

4. Relation between Entropies of Ions in Solution and the Electrostriction

The calculations carried out in Chapter III concerning the local contractive pressure near ions and the corresponding local effective volumes allows Latimer and Kasper's method (107) for calculating the entropy change associated with compression of the solvent to be examined in a more sophisticated manner and the significance of this approach to be assessed more precisely.

In these previous calculations (107), the entropy change accompanying hydration was regarded as composed of two terms; (a) the entropy of "Born charging" $\Delta S_1 = \frac{(ze)^2}{2\, r_e \epsilon^2} \left(\frac{\partial \epsilon}{\partial T}\right)_P$ where ϵ is the dielectric constant and r_e an effective radius (7); and (b) the entropy associated with the compressional or electrostriction effects, given by

$$\Delta S_2 = -\int_r^{\infty} \int_1^P \frac{1}{V_o} \left(\frac{\partial V}{\partial T}\right)_P dP \times 4\pi r^2 \, dr \qquad \text{VI·10}$$

Latimer and Kasper assumed $\Delta S_1 << \Delta S_2$ and obtained satisfactory agreement with experiment using empirically modified ionic radii. The term ΔS_1 was assumed negligible on the basis that dielectric saturation effects would make it much less than ΔS_2. These assumptions are, however, incorrect for three reasons: (a) the entropy of Born charging includes any internal pressure effects associated with the dielectric polarisation and leaves nothing over to be attributed to pressure effects as such; (b) corrections for dielectric saturation do not diminish

the Born charging entropy to a small contribution; in fact, satisfactory agreement with experiment for cations is obtained when dielectric saturation effects are included, as shown by Laidler and Pegis (8); (c) if the entropy change is to be calculated by considering the compressional effect, allowance must be made for (i) the dependence of the expansibility $\frac{1}{V_o}\left(\frac{\partial V}{\partial T}\right)_P$ on pressure and (ii) the influence of dielectric saturation effects on the electrostatic effective pressure.

Latimer and Kasper used Zwicky's (195) equation for the effective pressure which did not take into account dielectric saturation or the variation of dielectric polarisation with pressure. If it is assumed that Latimer and Kasper's compression effect originates from the contractive pressure P of Frank (132), the previously developed equation for P as a function of ionic field, equation III·29 may be used and P is the effective pressure in Frank's sense (132) which will cause the same change of volume of the system as does the field. Then combination of the following expression of Frank (132)

$$dP = \frac{1}{8\pi\beta}\left(\frac{\partial \epsilon}{\partial P}\right)_{E,T} dE^2 \qquad \text{VI·11}$$

with the Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_{E,T} = -\left(\frac{\partial V}{\partial T}\right)_{P,E} \qquad \text{VI·12}$$

will give the entropy associated with ion - solvent interaction. The quantity dP in equation VI·11 may be expressed by equation III·29, according to the previous calculations. The data

obtained in Chapter III for the contractive pressure as a function of field E (plotted on the right-hand ordinate) is shown graphically in Fig. 27. Also the specific expansibility $\frac{1}{V_o}\left(\frac{\partial V}{\partial T}\right)_P$ is obtainable from Bridgman's data (196) up to 10,000 atm. as plotted in Fig. 28. The integral under this curve $\int_1^P \frac{1}{V_o}\left(\frac{\partial V}{\partial T}\right)_P .dP$ is then plotted again in Fig. 27 (left-hand ordinate) against the pressure, and values of this integral $I_{E,P}$ can then be interpolated in terms of the field from the same graph, and hence as a function of r for ions of a given radius, taking into account the dependence of local dielectric constant on r as calculated in a previous paper (31). Values of $I_{E,P}$ as a function of field with the corresponding relation to r are shown in Fig. 29. The dependence of $I_{E,P}$, multiplied by r^2, on r is shown explicitly in Fig. 30. Multiplication by 4π and further integration with respect to r then gives ΔS_2 (equation VI·10), as shown in Fig. 31. The dependence of ΔS_2 on r from the original calculation by Latimer and Kasper is shown for comparison in this Figure.

The experimental data for the electrostatic contribution to entropy of hydration, as tabulated by Laidler and Pegis (8), have also been plotted in Fig. 31, both as a function of the crystallographic ionic radius r_i and the effective radius r_a (taken from equation V·14 - see below). Anions and cations cannot be accommodated by a common curve, as also follows from the work of Laidler and Pegis (8) on the corrected Born equation.

Figure 27. Contractive pressure P as a function of ionic field E.

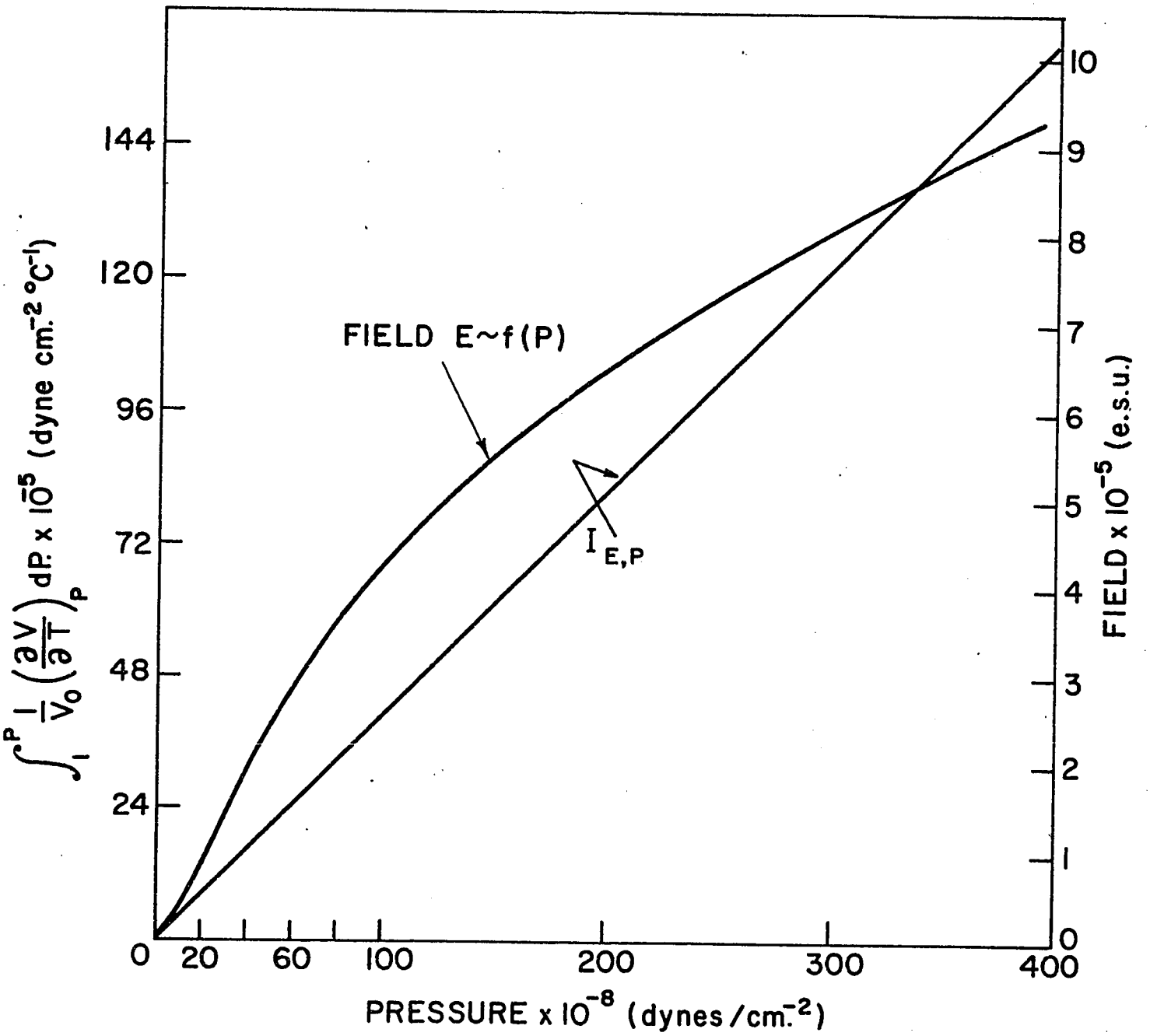

144
120
96
72
48
24
0
20
60
100
200
300
400
10
9
8
7
6
5
4
3
2
1
0
FIELD E~f(P)
$I_{E,P}$
$\int_1^P \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P dP \times 10^{-5}$ (dyne cm.$^{-2}$ °C^{-1})
FIELD $\times 10^{-5}$ (e.s.u.)
PRESSURE $\times 10^{-8}$ (dynes/cm.$^{-2}$)

Figure 28. Specific expansibility as a function of pressure (from data of Bridgman).

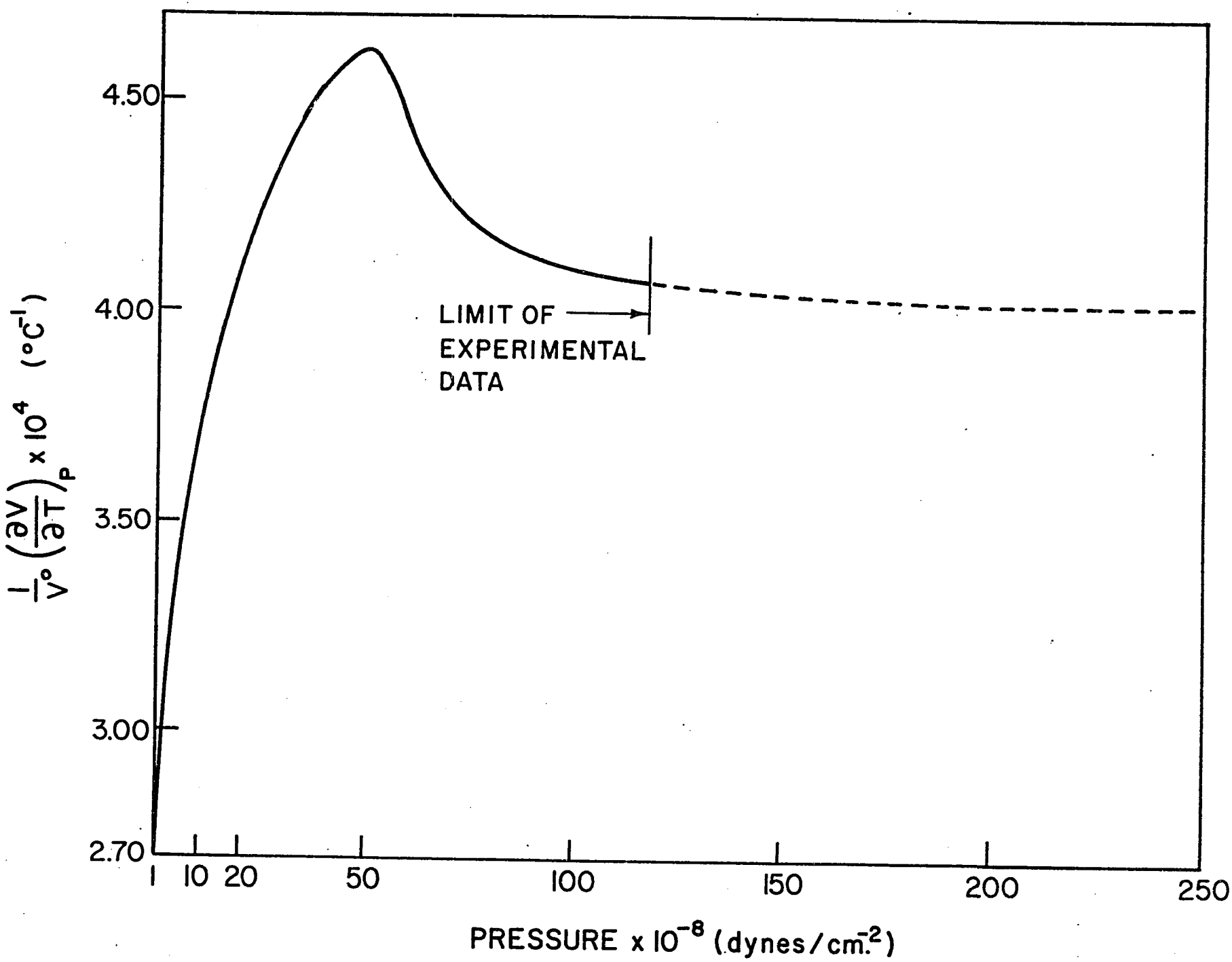

4.50
4.00
3.50
3.00
2.70
$\frac{1}{V^\circ}\left(\frac{\partial V}{\partial T}\right)_P \times 10^4$ (°C^{-1})
LIMIT OF
EXPERIMENTAL
DATA
1
10
20
50
100
150
200
250
PRESSURE x 10^{-8} (dynes/cm.$^{-2}$)

Figure 29. Values of the integral $I_{E,P}$ (from Figs. 27 and 28) as a function of field and ionic radius.

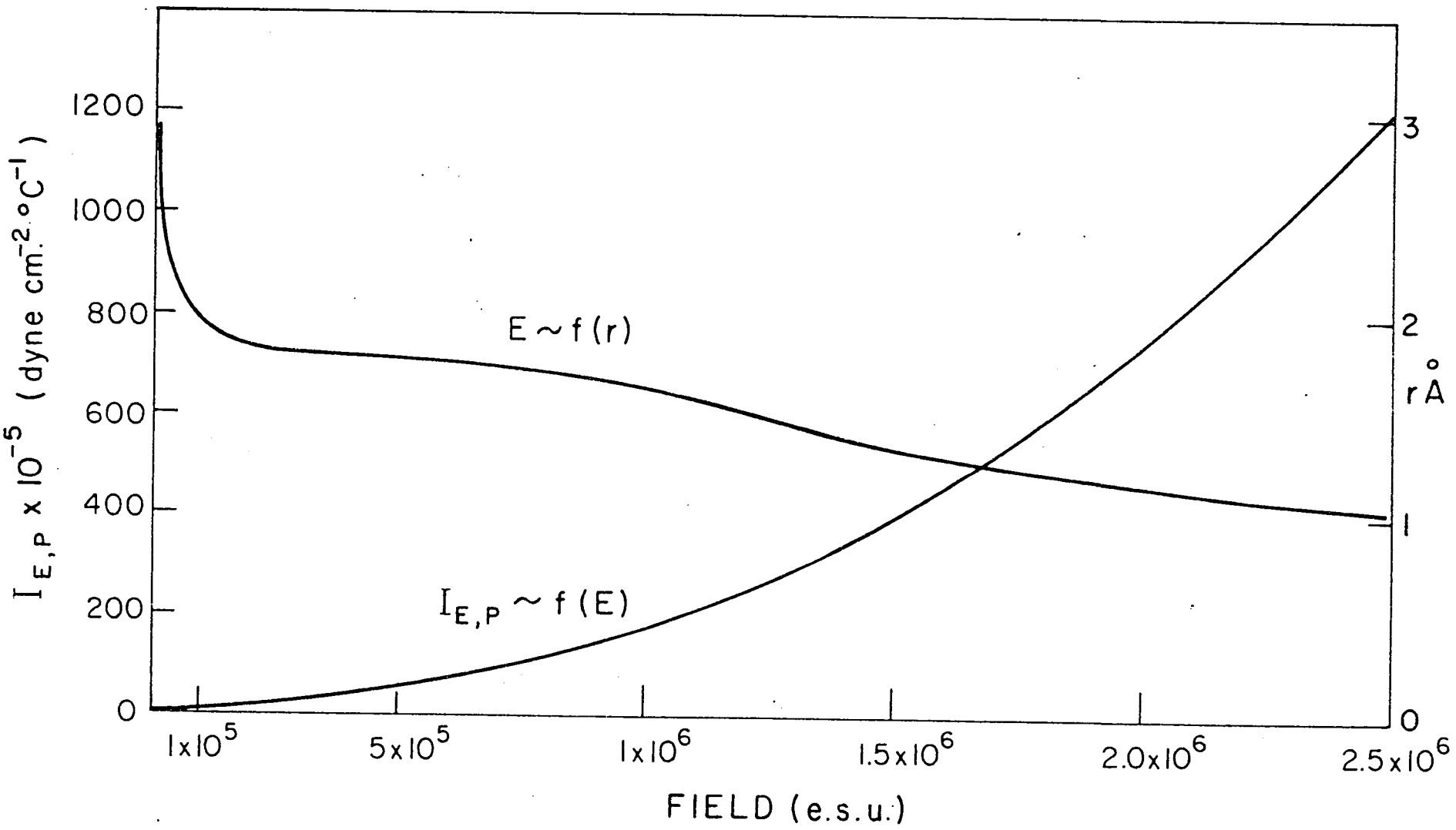

1200
1000
800
600
400
200
0
$I_{E,P} \times 10^{-5}$ (dyne $cm^{-2} \cdot °C^{-1}$)
E ~ f (r)
$I_{E,P}$ ~ f (E)
3
2
1
0
r Å
1x10^5
5x10^5
1x10^6
1.5x10^6
2.0x10^6
2.5x10^6
FIELD (e.s.u.)

Figure 30. Values of $I_{E,P}\, r^2$ as a function of r (from Fig. 29).

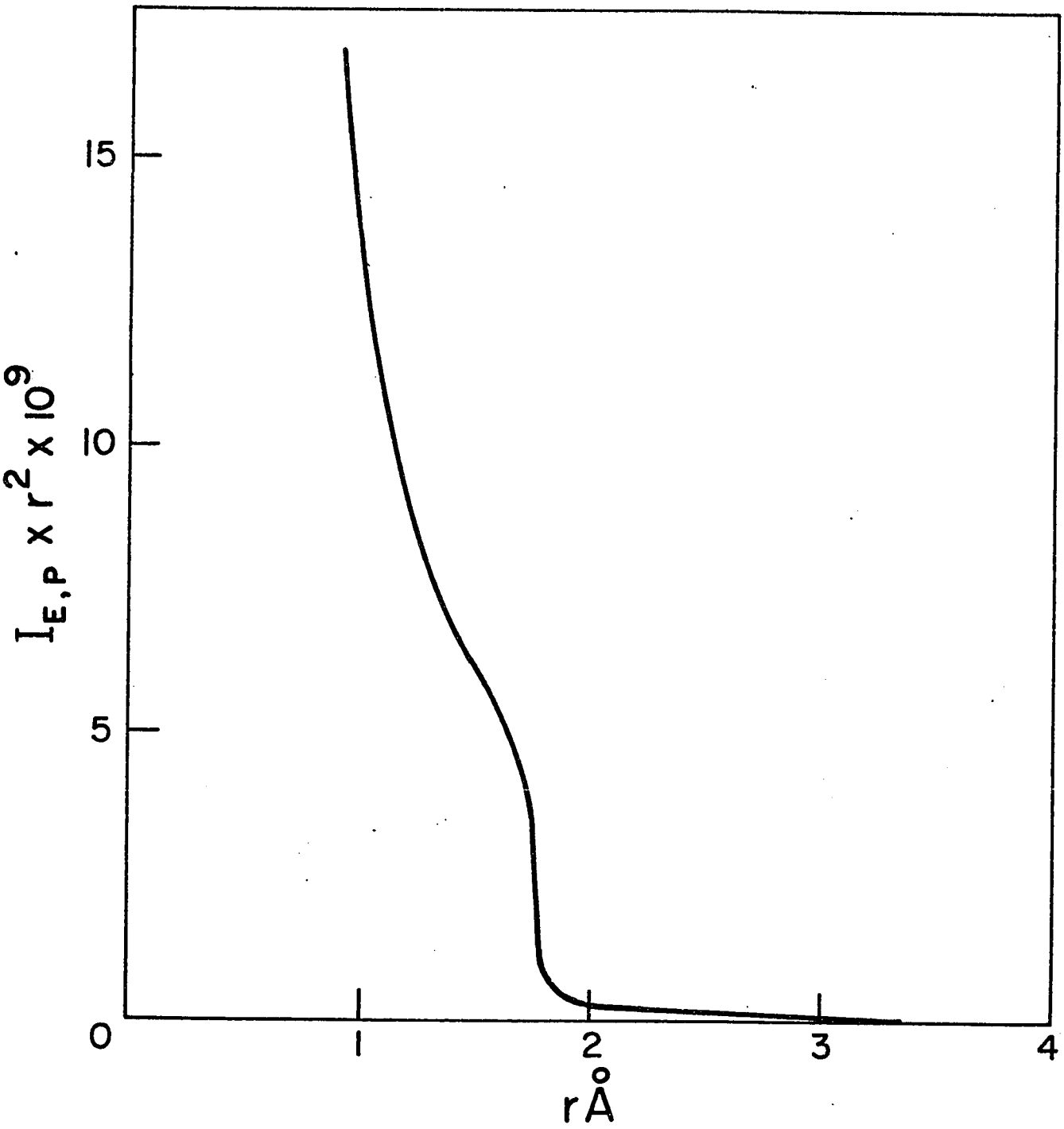
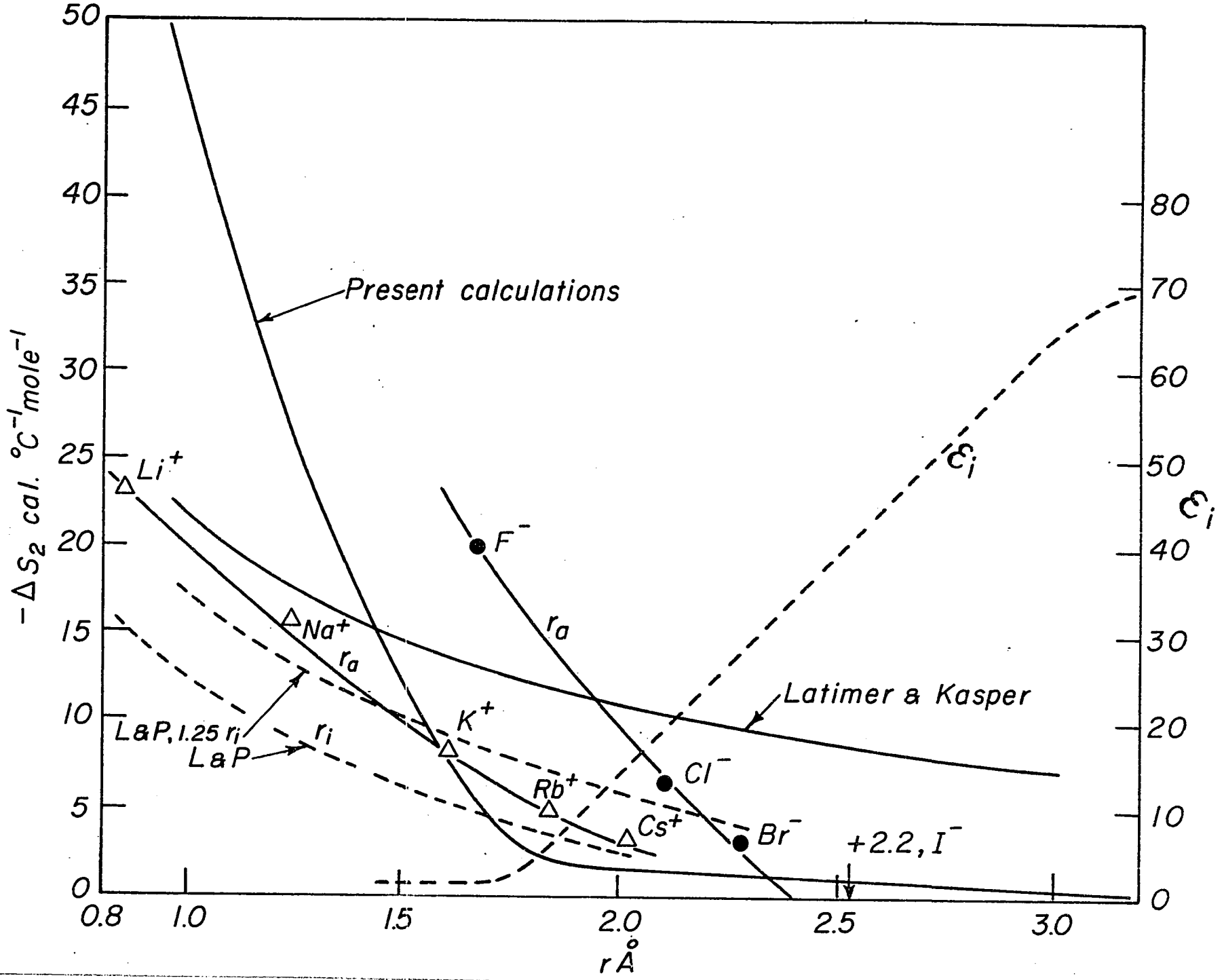

15
10
5
0
1
2
3
4
$I_{E,P} \times r^2 \times 10^9$
r Å

Figure 31. - ΔS_2, the compressional entropy of hydration as a function of ionic radius, with the integral local dielectric constant profile shown. Experimental values of ΔS_e are shown plotted in terms of r_i, $1.25r_i$ (8) or r_a (equation V·14).


50
45
40
35
30
25
20
15
10
5
0
80
70
60
50
40
30
20
10
0
$-\Delta S_2$ cal. $°C^{-1} mole^{-1}$
ε_i
ε_i
Present calculations
Latimer & Kasper
Li^+
Na^+
K^+
Rb^+
Cs^+
F^-
Cl^-
Br^-
+2.2, I^-
r_a
r_a
r_i
L&P, 1.25 r_i
L&P
0.8
1.0
1.5
2.0
2.5
3.0
r Å

The agreement of Latimer and Kasper's ΔS_2 values with experiment seems to be largely fortuitous for the theoretical reasons mentioned above and because the calculations involved the use of unrealistic effective radii (8). In the statistical mechanical theory of entropy of hydration given by Eley and Evans (56), the compressional effect is really included by consideration of the free volume for the bulk solvent and the "free area" for restricted two-dimensional translation of water molecules "adsorbed" at the ion. As in the corresponding calculation of electrostriction (111, 129), the Latimer and Kasper type of calculation involves integration up to the periphery of the ion. This is probably an important source of error since in the region near to the ion, the finite size and discreteness of solvent molecules becomes a factor of principal significance. The values of ΔS_2 are substantially more realistic if the integration of equation VI·10 is carried out with a lower limit of r equal to r_a, where r_a is obtained from equation V·14 by $r_a = \left(\frac{3}{4\pi} \times V_i\right)^{1/3}$, rather than with the limit of r as the crystallographic ionic radius. The difference of r_a from r_i becomes, of course, relatively more important the smaller is the ion and the correction to the crystallographic radius then depends on that radius. This seems intuitively preferable to using a constant correction factor. For ions larger than K^+ (r_a = ca 1.7Å), the entropy calculated by the above method will be relatively small and much less than Latimer and Kasper's values, but for the small ions the $-\Delta S_2$ is still surprisingly

large and greater than the experimental values.

It is to be noted that the present and the previous related calculations (107) do not include any non-electrostatic contributions to the entropy of hydration associated with solvent structure-promotion or breakdown (57), or with the limited free volume (at a given overall stoichiometric volume concentration of the ions) in the liquid phase (56, 197). The latter effect was, however, taken account of in the calculations of Eley and Evans (56). It is likely that the non-electrostatic effects are largely responsible for the specific deviations of the experimental hydration entropy values from the smooth relations which follow from theoretical calculations. In this connection, it must be remarked that monovalent anions, as a family, seem to behave in a specifically different manner from the corresponding isoelectronic cations as may be seen from Fig. 31 and (8). Similar effects are indicated in n.m.r. behaviour (71).

5. Electrostatic Entropies and Volumes of Electrostriction

It is of interest to examine the relation between the electrostatic contribution ΔS_e to the entropy of hydration and the volume of electrostriction defined by $\Delta V = V_{int.} - V_i^o$ where $V_{int.}$ is the intrinsic or physical volume occupied by the ion considered as an impenetrable solid and $\bar{V}_i^o$ is the partial molal volume at infinite dilution of the ion. The quantities ΔS_e and $\bar{V}_i^o$ have been separately related to effective ionic radii in previous publications of Laidler and Couture (109). On the basis of the calculations in the preceding section, and from previous

work (109) a relation between $\bar{V}_i^o$ and ΔS_e will be expected. This is shown in Fig. 32 for $\bar{V}_i^o$ values taken from the compilation of Mukerjee (118), $\bar{V}_{H^+}^o = -4.5$ ml., and ΔS_e values from Laidler and Pegis (8) using the absolute entropy of H^+ as -5.5 e.u. and ΔS_e defined (8) by

$$\Delta S_e = \bar{S}_i - \frac{3}{2} R \ln (\text{atomic wt.}) \qquad \text{VI·13}$$

where $\bar{S}_i$ is the absolute entropy of the ion. A general increase of $-\Delta S_e$ with ΔV is seen but the relations for monatomic monovalent cations and anions fall on lines with different slopes. The points for H^+ and Li^+ are distinctly anomalous probably owing to the specific interaction of H^+ with the water, and the resulting H bonding in $H_9O_4^+$, and the similar "acidic" polarisation effect produced in water by Li^+ ions. For the entropy change produced by these ions, the ΔV is too small, thus supporting a locally more structured region as arises in the $H_9O_4^+$ complex. Similarly, NH_4^+ produces much less electrostriction than the K^+ ion which has almost the same radius.

The relation between ΔS_e and ΔV may be considered less empirically, as follows, if the relation of Frank (132)

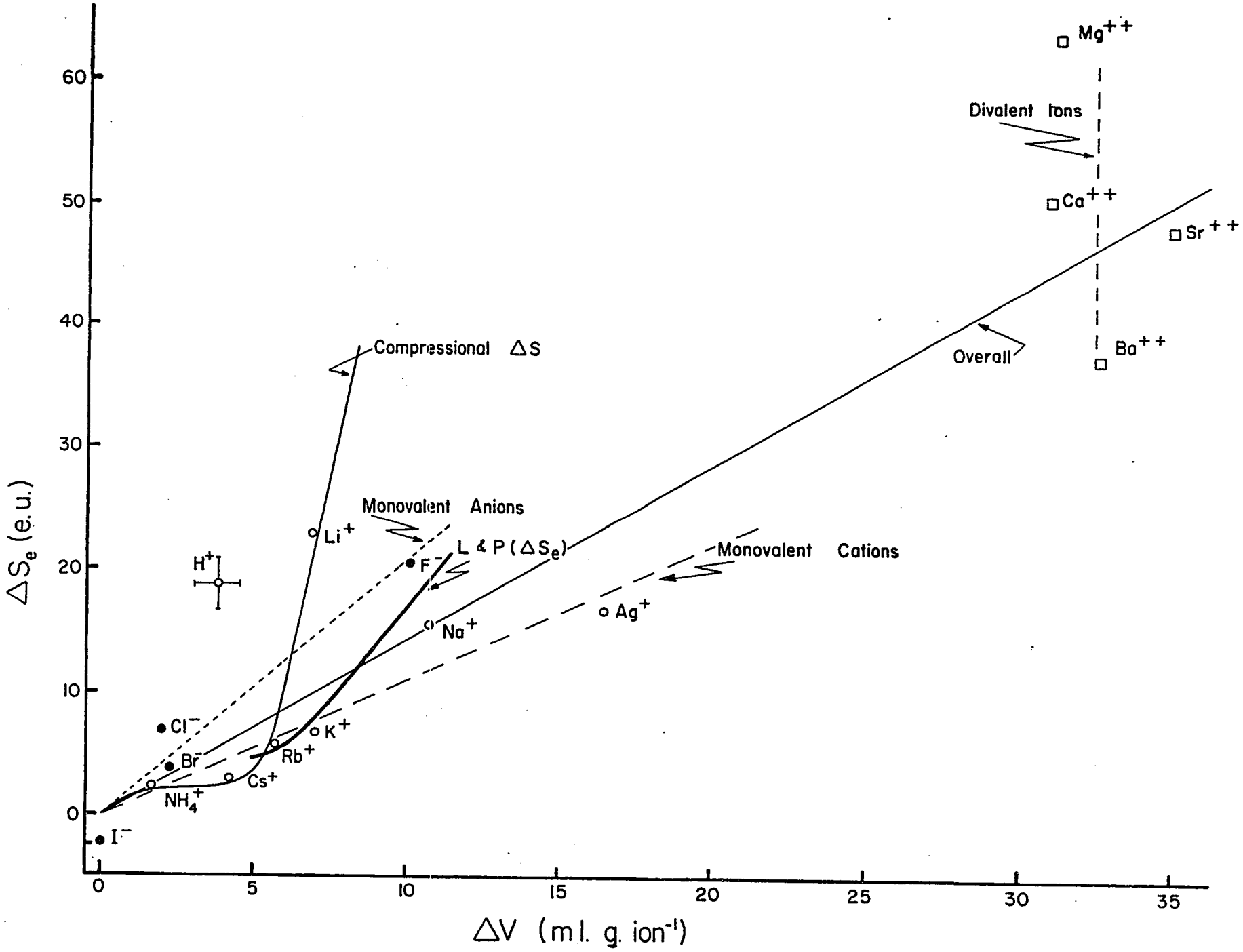
$$\left(\frac{\partial S}{\partial E^2}\right)_{u,T} = \frac{V}{8\pi} \left(\frac{\partial \epsilon}{\partial T}\right)_{P,E} \qquad \text{VI·14}$$

is combined with

$$\frac{1}{V}\left(\frac{\partial V}{\partial E^2}\right)_{u,T} = -\frac{1}{8}\left(\frac{\partial \epsilon}{\partial P}\right)_{E,T} \qquad \text{VI·15}$$

to obtain

Figure 32. Electrostatic contribution to the entropy of hydration of ions plotted against the volume of electrostriction calculated from ionic and partial molal volume.


Mg++
Divalent Ions
Ca++
Sr++
Ba++
Overall
Compressional ΔS
Monovalent Anions
Monovalent Cations
L & P (ΔSe)
Li+
F−
Na+
Ag+
K+
Rb+
Cs+
NH4+
Cl−
Br−
I−
H+
ΔSe (e.u.)
ΔV (ml. g. ion−1)
0
10
20
30
40
50
60
5
15
25
35

$$\left(\frac{\partial S}{\partial V}\right)_{u,T} = -\left(\frac{\partial \epsilon}{\partial T}\right)_{P,E} \Big/ \left(\frac{\partial \epsilon}{\partial P}\right)_{E,T} \qquad \text{V1·16}$$

Now dS and dV refer limitingly to changes of entropy and volume of the water in a region near the ions. By introducing hydration numbers n_s and n_v, then

$$\Delta S_h = n_s \, \Delta s \qquad \text{V1·17}$$

and

$$\Delta V = n_v \, \Delta v \qquad \text{V1·18}$$

where ΔS_h and ΔV are the total hydration entropy and electrostriction contributions per ion, and Δs and Δv are the local values per water molecule (102, 129). Limitingly then, from equation V1·16,

$$\Delta S_h / \Delta V \doteq \left(\frac{\partial \epsilon}{\partial T}\right)_{P,E} \Big/ \left(\frac{\partial \epsilon}{\partial P}\right)_{T,E} \qquad \text{V1·19}$$

which should approximately be a constant quantity for a given solvent and temperature and related to the slope of the line (s) in Fig. 32, provided "hydration" is defined as seen through ΔS_h and ΔV in some suitable way, e.g. in terms of the values of these quantities at some distance from ions at which a given E value is attained. Evaluation of equation V1·19 explicitly will, however, be difficult since the values of the partial derivatives at high E near the ions are not precisely known.

Some estimate of the relation of Δs and Δv may, however, be obtained by computing the local entropy change per unit volume of solvent around an ion as follows. From the

present calculations and those of Laidler and Pegis (8) it is possible to write

$$\Delta S_e = \int_a^\infty (\Delta s)_r \, 4\pi r^2 \, dr \qquad \text{VI·20}$$

where (Δs_r) is an entropy distribution function giving the local entropy change per unit volume at a distance r from the ion of effective radius a. Then

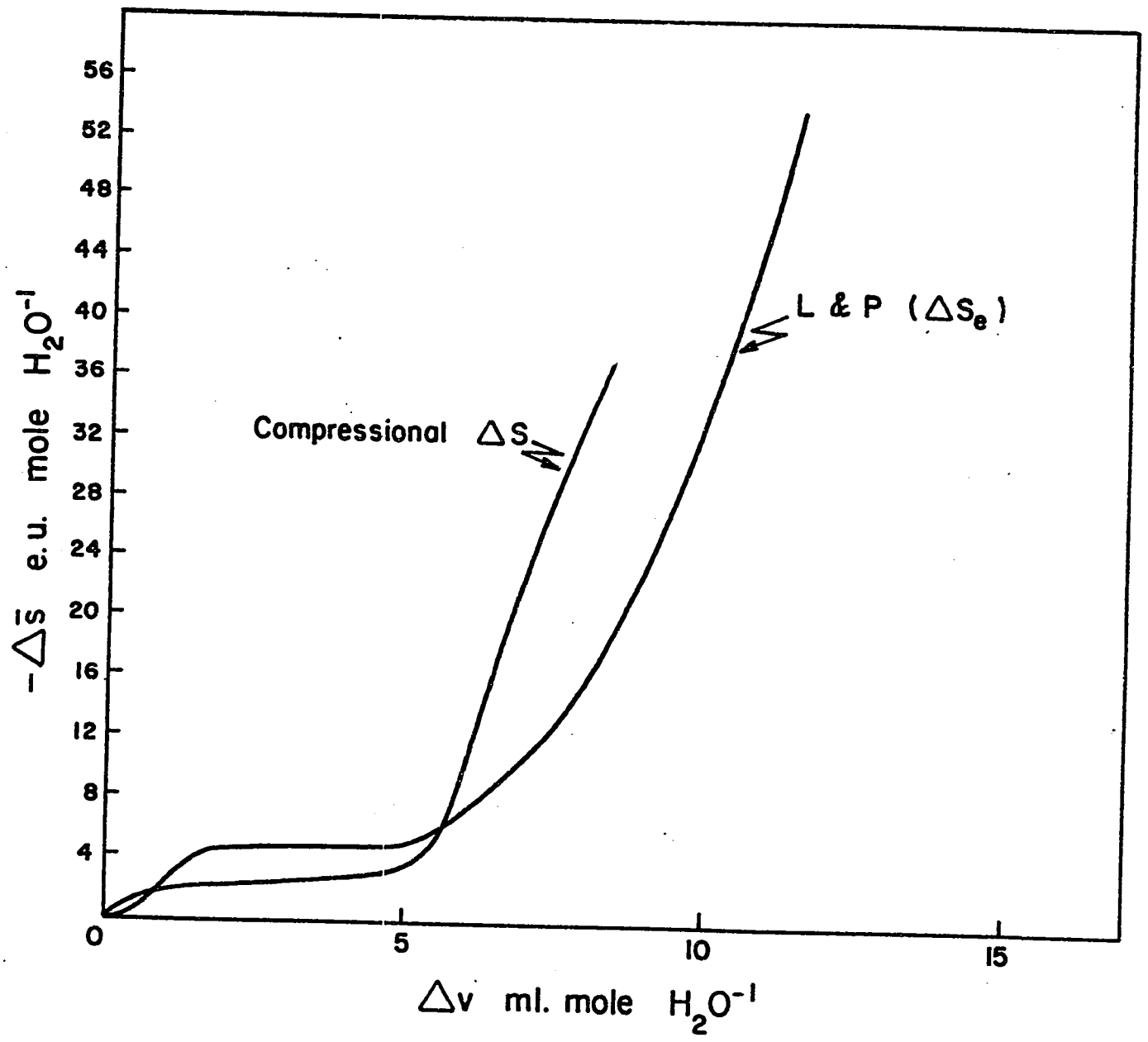
$$d\Delta S_e/dr = (\Delta s_r)\, 4\pi r^2 \qquad \text{VI·21}$$

or

$$(\Delta s_r) = \left(\frac{d\Delta S_e}{dr}\right)_r / 4\pi r^2 \qquad \text{VI·22}$$

Multiplying $(\Delta s)_r$ by v_h, the local molar volume of water (129), gives a quantity $(\Delta \bar{s})_r$ the entropy change per mole of water near an ion at a distance r. Δv is the corresponding local volume change of water per mole at r as previously calculated (129), so that both $(\Delta \bar{s})_r$ and Δv are now quantities referring locally to hydrate water per mole. The relation of $(\Delta \bar{s})_r$ to Δv is shown in Fig. 33 for $(\Delta \bar{s})_r$ values derived (a) from the calculations of Laidler and Pegis, and (b) from the present calculations of compressional entropy. Both functions tend to overestimate the negative entropy change associated with large Δv (or, vice-versa, Δv values are too low for the higher negative $(\Delta \bar{s})_r$ values). However, if Li^+ and the divalent ions are included (see Figs. 31 and 32), a more sensitive dependence of $-\Delta S_2$ on ΔV is indicated experimentally which may correspond to the right-hand regions of the curves in Fig. 33. The inflected nature of the curves

Figure 33. Local entropy ($\Delta\bar{S})_r$ and volume (ΔV) changes per mole of water near ions related for corresponding distances at which the respective changes occur.


56
52
48
44
40
36
32
28
24
20
16
12
8
4
0
5
10
15
$-\Delta\bar{s}$ e.u. mole H_2O^{-1}
Δv ml. mole H_2O^{-1}
Compressional ΔS
L & P (ΔS_e)

may also be associated with the rather critical region near the ion in which onset of dielectric saturation is rather sudden; because a continuous model is used in expressing dielectric constant as a function of field, and hence distance from the ion, the detailed validity of the relationship near to the ion may be the most serious source of error in this type of calculation. Also in both calculations for $(\Delta\bar{S})_r$, a continuous integration up to an effective ionic radius has been involved and this tends to overestimate the local entropy changes in the same way that it leads to an overestimation of the overall volume change (111, 129, 178).

Since these calculations were carried out, Hepler (207) has empirically shown that the volume change associated with a number of ionisation reactions is linearly related to the corresponding standard entropy change which is principally associated with changes of hydration in the reaction. The points are somewhat scattered but nevertheless a linear relation is indicated with a slope ca. 1 ml. $(e.u.)^{-1}$, which agrees with the mean value from the above calculation for monovalent ions. It is of interest that the data for ionisation of CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ are exceptions to this rule (see Fig. 35) in so far as the volume changes are too small. The entropy changes are, however, in the expected direction and of about the correct magnitude for successively decreasing extents of water binding in the series $CH_3NH_3^+ \rightarrow (CH_3)_3NH^+$.

6. Apparent Molal Adiabatic Compressibilities

The systematic study of the ultrasonic velocity behaviour of the electrolytic solutions mentioned in Chapter V has shown some regularities which may be interpreted in terms of two effects: (a) a structural one, due to the influence of the ions on the water structure, and (b) an electrostatic one.

The higher total compressibility of the tetraalkylammonium halide solutions in comparison with that of inorganic salt solutions, e.g. KCl, KBr indicates that the cation must cause this effect; for example $\phi^{o}_{K(s)}$ (KCl) = - 40×10^{-4} whereas $\phi^{o}_{K(s)}(Me_4NCl) = - 16.6 \times 10^{-4}$. It should be noted that this higher compressibility is not limited to the alkyl substituted NH_4^+ ion but that the NH_4^+ itself has a higher (i.e., less negative) apparent compressibility (172) than the inorganic ions, e.g.K^+. It appears that the ability of NH_4^+ to form H-bonds results in less influence on water structure. The same applies to H_3O^+.

Previous studies (72, 103, 174, 180, 198, 199, 200) on tetraalkylammonium salts seem to indicate a strong structural influence of the large tetraalkylammonium cation upon water. The structural influence has been described by terms such as "iceberg effect" (57), increase of ice-likeness (72,200), increase of extent of ice-patches (201), stabilisation of clusters (202), and "tightening" of hydrogen bonds between water molecules (164).

Interpretations of the present results may be made in terms of changes of the local compressibility of the solvent near the ions. It should be noted that the nature and bulkiness

of the large hydrophobic cations suggests that their intrinsic molecular compressibilities might possibly account for some of the apparent increase of compressibility in relation to that associated with small inorganic ions. However, in general, the intrinsic compressibility of ions themselves is expected to be much less than that of the solvent water, since in the latter case, it is the free volume that is principally diminished with increasing pressure. The compressibility of the ion itself will presumably be similar to that for water at very high pressures or to that for a close-packed metal. Previously, in Chapter III, it was pointed out that in the case of inorganic ions, when the process of taking the ions from the crystal lattice into the solution is considered, the compression of the solute appears negligible in comparison with that of the solvent. The intrinsic compressibility of the tetraalkylammonium ions may, nevertheless, be somewhat greater than that of small monatomic ions since the former are, in effect, microscopic droplets of a different phase in the water with some free space between the methylene groups on the alkyl residues R, particularly when R is large.

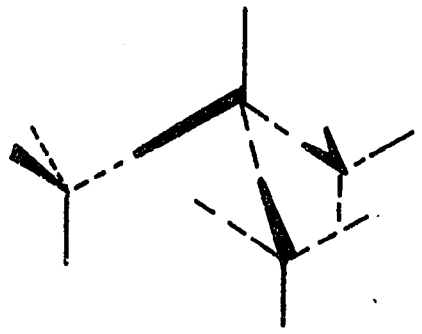
However, in the present case, if the intrinsic molecular compressibility of the cation made a significant contribution to the observed compression, the effect would be expected to be greatest for the largest cation, since it is reasonable to assume that the dead-space within the intrinsic volume of $\underline{n}\text{-}Bu_4N^+$ is greater than that in Me_4N^+. If this is the case,

then the plots of $\phi^{o}_{K(s)}$ as a function of $\bar{V}^{o}_{2}$ in Fig. 25 for the R_4NX salts should show a trend in the opposite direction to that observed, i.e. $\phi^{o}_{K(s)}$ should become less negative with increasing cation size for a given halide anion.

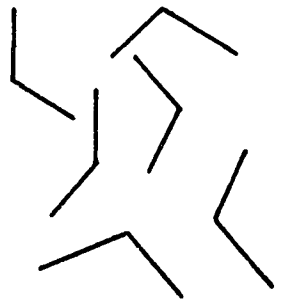
Qualitatively, three types of local solvent water may be distinguished near the ions considered in the present discussion. These are schematically shown in Fig. 34; (1) is the ice-like configuration postulated by Bernal and Fowler (55) and represents essentially the basic structure described by the terms mentioned previously (see above); (2) is free uncoordinated water (Némethy and Scheraga's "unbonded" lattice liquid state); and (3) water molecules that are under the immediate influence of a high electrostatic field near the ions and have suffered electrostriction.

The ice-like structure in Fig. 34(1) is regarded as being less compressible than bulk solvent water due to the stronger intermolecular framework of H-bonds. This is supported by the fact that the different forms of ice are substantially less compressible than liquid water. Numerical values of β for common ice (IceI) indicate that the coefficient of compressibility varies between 12×10^{-6} and 33×10^{-6} atm^{-1} (208,209) in the temperature range $-15^{o}C$ to $0^{o}C$. Solids in general have a much lower value of β as compared to water, e.g. Ag has a value of $\beta = 1 \times 10^{-6}$ atm^{-1}. Similarly in Chapter III it was shown that compressed H_2O has a lower value of β compared to water that is not subjected to higher pressures. Thus, the unbonded water molecules shown in Fig. 34(2) will tend to possess the highest compressibility because they may be pushed closer toge-

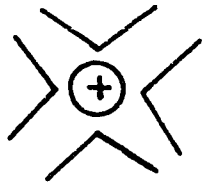
Figure 34. Schematic diagram showing different types of water species.



(1) ICE - LIKE CASE



(2) "UNBONDED" CASE



(3) ELECTROSTRICTED CASE

ther without H-bond rupture and the main effect will be to decrease the void space between the molecules. Finally the electrostricted water molecules in Fig. 34(3) will have actually undergone molecular compression caused by the electrostatic field about the ions, and these solvent molecules will be effectively far less compressible than the types 1 and 2. Therefore it seems reasonable to suppose that the relative order of increasing compressibility of the solvent species in Fig. 34 is $3 < 1 < 2$.

The study of the apparent molal adiabatic compressibility of the three series of salts in this work indicates that $\phi^{o}_{K(s)}$ increases (becomes less negative) for a given cation with increase of the anion size in the order $I^- > Br^- > Cl^-$. This trend in the behaviour indicates an electrostrictive effect due to the anion-solvent interactions (hydration effect). The higher field near the chloride ion will cause more electrostriction of the solvent water than in the case of the other anions, due to collapse of the local solvent water structure brought about by the field-dependent hydrostatic pressure. As a consequence, there would be a diminution in the amount of more compressible water of type 2 and an increase in the less compressible type 3. However, as the size of the halide ion increases, the local field becomes smaller and this decreases the electrostriction, thereby providing a larger amount of water of type 2(having a greater compressibility than that of type 3) and an apparent increase in the compressibility.

Although a complete series of alkyl substituted ammonium cations ranging from $MeNH_3X$ to $\underline{n}$-Bu_4NX and having a common anion have not been studied, it may be assumed (using the thermodynamic differences for $\Delta\phi^{o}_{K(s)}$ $(Br^{-}-Cl^{-})$ from Table 19) that the $\phi^{o}_{K(s)}$ values for such a series, viz. the bromide series, tend to go through a maximum. (see Fig. 25 - dashed line represents data for the $MeNH_3Br$, etc, series derived from the experimental data for the Cl^{-} series with the correction $\Delta\phi_{K(s)}$ $(Br^{-}-Cl^{-})$. The maximum occurs at Me_4NBr and it would appear that in the series of asymmetric cations extending from $MeNH_3$ to Me_4N there is a linear decrease in the amount of electrostricted water of type 3 and an increase in type 2. This would cause an apparent increase in $\phi^{o}_{K(s)}$. However, Et_4N^{+} ion appears to promote structure slightly, i.e. it increases the amount of type 1 water at the expense of type 3, thus decreasing the compressibility. This structure promotion is greatly increased in $\underline{n}$-Pr_4N^{+} and $\underline{n}$-Bu_4N^{+} with a consequent decrease in compressibility. Similar explanations have been used (210) to explain the non-linear decrease from Me_4N^{+} to $\underline{n}$-Bu_4N^{+} of the ratio of the Walden product for D_2O to that for H_2O as a function of ion size.

The non-linearity of the plots of $\phi^{o}_{K(s)}$ as a function of cation size precludes the possibility of using such a graph for estimating the $\phi^{o}_{i\ K(s)}$ for individual anions as was possible in the case of the partial molal volumes

(Fig. 12). However, some estimate of the differences of individual apparent g.ionic adiabatic compressibilities at infinite dilution, deduced from the data for tetraalkylammonium salts with a common cation or anion, are shown in Table 19. The difference in the magnitude of $\Delta\phi^{o}_{K(s)}$ and $\Delta\bar{K}^{o}_{2}$ for Cl^{-}-Br^{-} in Table 19 is, in part, due to the fact that the adiabatic and isothermal compressibilities differ according to equation II·20 . No work has been carried out on the determination of the coefficient of thermal expansion α or the specific heat at constant pressure C_p for $(CH_3)_4NX$ salts. Thus, $\bar{K}^{o}_{2}$ values for these salts are unobtainable from the ultrasonic velocity measurements. However, Owen and Simons (124) have shown that neglect of the correction of adiabatic to isothermal compressibilities causes an error of only 7.5% in $\bar{K}^{o}_{2}$ for sodium chloride and potassium chloride at 25°C. Neglect of this correction makes $\phi^{o}_{K(s)}$ somewhat more negative than $\bar{K}^{o}_{2}$.

TABLE 19

Differences of Apparent g. Ionic Adiabatic Compressibilities $\Delta\phi^{o}_{K(s)}$ at Infinite Dilution for Tetraalkylammonium Halides having a Common Cation or Anion.

Ions	$\Delta\phi^{o}_{K(s)}$ x10^4 cc.(g.mole.bar)$^{-1}$	$\Delta\bar{K}^{o}_{2}$ * x10^4 cc.(g.mole bar)$^{-1}$
Cl^--Br^-	-9.5	-8.6
Cl^--I^-	-19.9	
Br^--I^-	-10.4	
Me_4N^+-Et_4N^+	$+2.4^{+}(\pm 0.3)^{\pm}$	
Et_4N^+ - n-Pr_4N^+	$+3.7^{+}(\pm 0.1)^{*}$	
n-Pr_4N^+-n-Bu_4N^+	$+10.6^{+}(\pm 0.9)^{*}$	

* From ref. (125) for sodium and potassium salts.

\+ Average values from the bromide and iodide series.

* Mean average deviation.

No interpretation of the slopes $S_{K(s)}$ was attempted on account of the complexity of the factors that determine the quantity $S_{K(s)}$.

The apparent molal adiabatic compressibilities of the neutral (i.e. uncharged) alkylamines CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ were also studied and show a non-linear dependence on the concentration as shown in Fig. 23. The data for all three solutions tend to pass through a compressibility maximum at about 0.09-0.11 molar. Also, all three aqueous solutions exhibit a higher total compressibility in comparison with the corresponding three salts of the protonated amines that were studied. The order of the compressibilities is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$. The peculiar order of the overall compressibility of aqueous solutions of these basic compounds is not readily explicable. However, it may be assumed that for CH_3NH_2 and $(CH_3)_2NH$, increased alkyl substitution diminishes the local extent of normal bulk water structure and may produce more water of type 2 (Fig. 34) (i.e., free unbonded species of higher compressibility), due to the incompatibility of the structure promoted local solvent region caused by Me groups and the little disturbed local solvent region into which the H atoms of the cation seem to fit more readily. However, once the last H atom in the neutral amine has been substituted, the molecule has become more hydrophobic (but still retains of course the lone pair at the N) andthen may enhance the structure, increasing the water of type 1 (Fig. 34); hence the compressibility tends to decrease again. The higher overall compressibility of aqueous solutions of "acids", (particularly $HClO_4$ (204),

NH_4Cl(172)), than that of their corresponding salts, and the data for the partial molal entropy of H_2O (61) in electrolytic solutions, indicate that when solute molecules contain protons or atoms capable of forming H-bonds, they then have less influence on the structure of water than do isoelectronic ions of similar size.

7. Solvation Effects in the Ionisation Process

Solvation is a principal factor in the stabilisation of a cation in aqueous solution, both on account of the energy gained when optimum orientation of water molecules occurs around the base centre and through hydrogen-bonding of the type $\geqslant$N-H... OH_2, between water molecules and hydrogen atoms attached to the base centre. Similar factors in ionisation of acids have been considered in detail by Ives and Marsden (213), who also took into account other structural effects (see below). The stabilisation effects mentioned above will vary with the available space around the base centre; e.g. it should be less for a molecule like pyridine than for aniline. Also, it has been stated (205) that diminution of the number of hydrogen atoms available for bonding should decrease the base strength. The weakness of tertiary amines such as $(CH_3)_3N$ relative to corresponding secondary amines $(CH_3)_2NH$ has been attributed to this type of effect (205).

The data obtained in the present work allow the volumes associated with acid ionisation processes of the type

$$(R)_{4-n}NH_n^+ \rightleftharpoons (R)_{4-n}NH_{n-1} + H^+ \qquad \text{VI·23}$$

to be estimated for the four protonated amines $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$ and $(C_2H_5)_3NH^+$. The volume change associated with ionisation may be expressed as

$$\Delta\bar{V}^o_{ionis.} = \bar{V}^o_B + \bar{V}^o_{H^+} - \bar{V}^o_{BH^+} \qquad \text{VI·24}$$

In equation VI·24, $\bar{V}^{o}_{B}$ is the partial molal volume of the free alkylamine at infinite dilution obtainable from the density data required in the compressibility studies of the alkylamines. $\bar{V}^{o}_{BH^+}$ is the partial molal volume of the protonated alkylamines and may be calculated from the $\bar{V}^{o}_{2}$ data for the alkylamine hydrochloride salts (Table 12) and the value of the individual partial g. ionic volume for the chloride ion at infinite dilution deduced in the present work (Table 8). Subtraction of $\bar{V}^{o}_{Cl^-}$ from $\bar{V}^{o}_{BH^+Cl^-}$ gives $\bar{V}^{o}_{BH^+}$. The individual partial g. ionic volumes obtained for the halide ions(see the treatment given in Chapter V) lead to a value of -5.7 ml.$(g.ion)^{-1}$ for $\bar{V}^{o}_{H^+}$ (see Section 3, this Chapter). The volumes for the respective species shown on the right-hand side of equation VI·24 and $\Delta\bar{V}^{o}_{ionis.}$ are shown in Table 20. The values of $\Delta\bar{V}^{o}_{ionis.}$ do not vary greatly with the different protonated bases. The small positive increase in volume for the acid ionisation processes of the methyammonium ion series is to be expected since there is no net gain or loss of charge in the ionisation process. A similar slightly varying $\Delta\bar{V}^{o}_{ionis.}$ has been reported by Hamann and Lim (191) for the ionisation of a series of bases from NH_4OH to $(CH)_3NHOH$. Of course, the values $\Delta\bar{V}^{o}_{ionis.}$ in this case are large and negative ($\approx$-28 ml.$(g.mole)^{-1}$) as would be expected from the net gain of charge which results when the above bases become ionised.

The well-known anomalies in the effect of successively added alkyl groups on the base strengths of aliphatic amines

TABLE 20

Volumes of Ionisation $\Delta\bar{V}^{o}_{ionis.}$ for Processes of the Type $(R)_{4-n}NH^{+}_{n} \rightleftharpoons (R)_{4-n}NH_{n-1}+H^{+}$, where n Varies between 1 and 3 and R = methyl or ethyl.

Base	$\bar{V}^{o}_{B}$ ± ml.(g.mole)$^{-1}$	$\bar{V}^{o}_{BH^{+}Cl^{-}}$ * ml.(g.mole)$^{-1}$	$\bar{V}^{o}_{BH^{+}}$ ml.(g.ion)$^{-1}$	$\Delta\bar{V}^{o}_{ionis.}$ ml.(g.mole)$^{-1}$
CH_3NH_2	40.0	53.8	30.2	+4.1 ± 0.4
$(CH_3)_2NH$	58.6	72.5	48.9	+4.0 ± 0.4
$(CH_3)_3N$	77.9	90.6	67.0	+5.2 ± 0.4
$(C_2H_5)_3N$	119.7 +	138.6	115.0	-1.0 ± 0.4

± From compressibility data, Table 17.

* From Table 12.

\+ From experimental results required for Table 7.

in water have been explained by the interaction of the cations with water, in a series such as $CH_3NH_3^+$, $(CH_3)_2NH_2^+$ and $(CH_3)_3NH^+$. This can be expressed either by saying that the degree of hydrogen bonding with the solvent depends upon the number of hydrogen atoms bonded to the N centre in the cation (48, 205) or that the alkyl groups act by excluding water molecules from close interaction with the positive charge (49). This effect, working in opposition to the inductive effect, can produce the observed order of base strengths, i.e. the decrease in pK_A of $(CH_3)_3NH^+$ below that of $(CH_3)_2NH_2^+$ and $CH_3NH_3^+$, instead of a steady rise in base strength that would be expected on the basis of a progressively increasing inductive effect in the series $(CH_3)NH_2$, $(CH_3)_2NH$ and $(CH_3)_3N$. This view is supported by the observed entropy changes ΔS^o in reactions of the type

$$\geqslant NH^+ + H_2O \rightleftharpoons \geqslant N + H_3O^+ \qquad \text{VI·25}$$

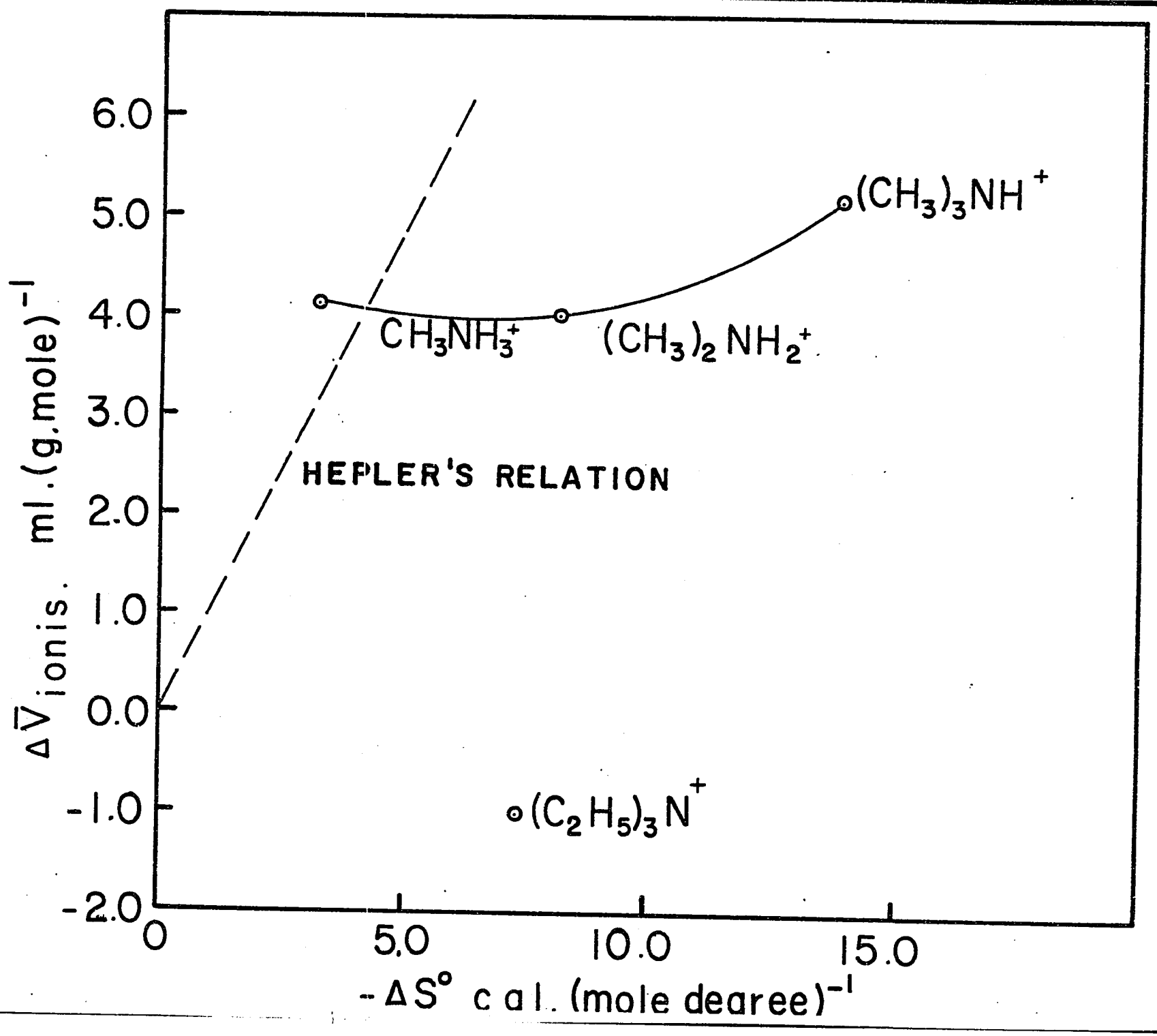
for which the ΔS^o values become more negative with increasing alkyl substitution, corresponding to decreasing total extent of orientation of water molecules around the cation presumably on account of the lack of space around the substituted N^+ ions in comparison with that available around H_3O^+. It is difficult to draw any final conclusion from the variation of the $\Delta\bar{V}^o_{ionis.}$ results for the methylammonium ions. However, the $\Delta\bar{V}^o_{ionis.}$ value for the trimethylammonium ion shows a greater increase relative to that for $(CH_3)_2NH_2^+$ and $CH_3NH_3^+$. This increase is greater than the possible experimental error in $\Delta\bar{V}^o_{ionis.}$ and indicates a more efficient packing of solvent water about this

ion relative to that around $CH_3NH_3^+$ and $(CH_3)_2NH_2^+$, or a less dense structural arrangement about the $(CH_3)_3N$ molecule relative to that around $(CH_3)_2NH$ and CH_3NH_2. The value of $\Delta\bar{V}^o_{ionis.}$ for the triethylammonium ion implies that there is very little overall change in the solvent arrangement (in terms of apparent volume change) between $(C_2H_5)_3NH^+$ and $(C_2H_5)_3N$, which is somewhat surprising.

The volumes of acid ionisation $\Delta\bar{V}^o_{ionis}$, for the salts studied in this work are shown in Fig. 35 as a function of ΔS^o (taken from ref.206)for the ionisation reactions of the type given in Equation VI·23. It can be seen that whereas the $\Delta\bar{V}^o_{ionis.}$increases by approximately 1 ml. $(g.mole)^{-1}$ through the homologous series of methylammonium ions, ΔS^o decreases by -10.6 e.u. The slight change in $\Delta\bar{V}^o_{ionis.}$ as opposed to the significant change in ΔS^o for these ionisation reactions strongly suggests that the entropy changes are perhaps more indicative of the interaction of the hydrophobic tails of the charged and uncharged molecules with the highly polar and associated aqueous medium, than are the normally predominant electrostrictive effects arising from ion-dipole interaction.

The above view on the importance of such interactions is further corroborated by examination of the values of ΔC_p which reflect similar effects. The ΔC_p values are large and positive (46), decreasing in the order $(CH_3)_3NH^+ > (CH_3)_2NH_2^+ > CH_3NH_3^+$. It is obvious that the normal electrostatic picture is inadequate to account for the ion-solvent interaction in these particular cases, especially in view of the tendency for ΔS^o

Figure 35. Volume change for ionisation reactions as a function of the entropy change in the reaction.


6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
0
5.0
10.0
15.0
$\Delta\bar{V}_{ionis.}$ ml.(g.mole)$^{-1}$
$-\Delta S^{\circ}$ cal. (mole degree)$^{-1}$
$(CH_3)_3NH^+$
$CH_3NH_3^+$
$(CH_3)_2NH_2^+$
HEPLER'S RELATION
$(C_2H_5)_3N^+$

and ΔC_p to vary in opposite directions. The evidence that many non-polar molecules have anomalously large negative entropies of solution in water, i.e. they increase the local order in the solvent (57,73,108), seems to indicate that this may be a predominant factor in determining the ΔS^o and ΔC_p values obtained for the ionisation reactions considered here. The above consideration has been applied mainly to ions and molecules which are spherical, or nearly so, and it is obvious that the problem will be much more difficult for the unsymmetrical species under discussion.

If specific solvent-solute interactions are considered, the solvent molecules may see the asymmetric solute cation as an apparently bifunctional molecule; thus, on the one hand, the hydrophobic tails (Me groups) of the ionic centre may tend to increase solvent order through "freezing" of the normal water structure; on the other hand, the N^+— H part of the molecule ion will tend to decrease the order or at best fit into the water structure without too much solvent structural disorganisation. As a consequence of increased alkyl substitution, an incompatibility would tend to arise between the existence of two rather differing solvent-ordered regions in the solvent volume immediately adjacent to the cation.

In the acid ionisation of protonated primary, secondary and tertiary amines, a number of apparently conflicting effects arise; the entropy and heat capacity behaviour are related in

an anomalous way and the volume changes on ionisation are unexpectedly independent of alkyl substitution at the N centre. The compressibilities, however, vary in the expected way (Fig. 23) with alkyl substitution and are rationally related to the entropy change.

It is therefore difficult to state specifically what may be occurring in the local solvent region around the neutral amines and their conjugate ions. However, the following effects should perhaps be considered in the case of the reactant acid ions; (a) decreased electrostriction or decreased H_2O orientation about the N^+— H end of the molecule will tend to contribute to increasing negative entropy for the acidic ionisation process in the reactant series $CH_3NH_3^+$ to $(CH_3)_3NH^+$ and correspondingly to an increase in the hydration entropy of the aminium ions themselves; (b) increased alkyl substitution at the N will tend to promote ice-like structure about the hydrophobic end of the ion and this will tend to cause a decrease of hydration entropy in the series of reactant ions $CH_3NH_3^+$ to $(CH_3)_3NH^+$. Considering the neutral amines which are the reaction products in the acid ionisation processes, the following effects may occur: (a) the orientation of solvent due to the N^+— H end of the ion will have now disappeared and it is doubtful if the neutral N atom itself could cause any appreciable degree of orientation that would make the entropy for the neutral amine series vary considerably on account of a change in alkyl substitution on the N; (b) the absence of

the $N-H^+$ moiety in the neutral amine implies that the neutral molecule is perhaps less "bifunctional" to the surrounding water so that the structure promotion caused by the alkyl groups would tend to be associated with a greater decrease in the hydration entropy in the neutral amine series CH_3NH_2 to $(CH_3)_3N$ than in the corresponding reactant ion series $CH_3NH_3^+$ to $(CH_3)_3NH^+$, where the electrostriction at the N^+ may interfere with the structure promotion at the Me groups.

The above discussion indicates that the more negative entropy change in the ionisation process (Equation VI·23) which occurs with increasing alkyl substitution may be due to either (a) decreasing orientation of water molecules around the cation and a corresponding increase in structure formation about the neutral conjugate amine or (b) a greater increase in structure promotion about the neutral amine than in the charged ion. The contrary variation of ΔS^o and ΔC_p for the ionisation process was earlier mentioned as strong evidence that the ionisation process cannot be interpreted on a simple electrostatic basis for this predicts that ΔC_p and ΔS should vary in the same sense with change of size or shape of the cation. Everett and co-workers (211) have discussed the inverse trend of ΔS and ΔC_p in the ionisation of some fatty acids and diammonium ions in terms of decreased flexibility in the hydrocarbon chain of the ion relative to that in the un-ionised molecule. They argued that in the case of the fatty acid anions, because

of the repulsion between regions of low dielectric constant by an ionic charge, the rotation about each -C-C- bond will be hindered, and the resulting entropy decrease will depend on the number of -C-C- bonds within range of the ionic charge in the product anion. Evans and Hamann (49) have pointed out, however, that the stiffening of the hydrocarbon chain is probably to be pictured, on a molecular basis, in terms of solvent molecules becoming oriented around the ion. Everett and co-workers (211) were further able to show that for at least two types of molecular motion (viz. simple harmonic motion and hindered rotation in a cosine field) restriction of the freedom, to an extent which results in considerable fall of entropy, may be accompanied by a very much smaller fall in heat capacity; in certain circumstances they showed that it may even lead to an increase in heat capacity (particularly in the case of hindered rotation).

The molecules and ions under consideration here are certainly not chain-like in nature and the restricted rotation, if any, would have to be about the $-C-N^+$ bond. However, this argument may still be significant in the present case. Whereas Everett and co-workers (211) and Hamann and Evans (49) rationalised the results for ΔS^o and ΔC_p for fatty acid ionisation processes in terms of the effects associated with orientation of the solvent about the ions, it is felt (and the above workers also noted this point) that attention should be focussed rather on the interaction with the solvent of

uncharged molecules and similarly the hydrophobic parts of the ions. It seems that the enhancement of water structure with increasing alkyl substitution on the ion or neutral amine may tend to cause a decrease of the entropy both through increased water orientation and possibly restricted rotation about the $-C-N^+$ bond(s) because of the apparent increase in rigidity of the ion- or molecule-solvent shell. This effect would tend to be greater for the neutral amines because of the disappearance of the $N-H^+$ part of the reactant ion and the associated electrostriction. Consequently part of the increase in negative entropy of the ionisation process with increasing alkyl substitution at the N, would be due to the more negative "structure-promotion" entropy of hydration of the neutral amine products relative to that for the ionic reactants. A corresponding rise in heat capacity for the ionisation process is still required, however, since the increasing build up of water structure and restricted rotation in the ionic reactants with increasing alkyl substitution will require a greater specific heat to "break down" this structure [cf. the C_p value of +50 cal.(deg. mole)$^{-1}$ for aqueous n-Bu_4NCl (72)]. The increasing positive values of ΔC_p with increasing alkyl substitution for the ionisation process are indicative of appreciable solvent rearrangement and the excessively large positive values may in part be attributed to the hindered rotation mentioned by Everett and co-workers (211). Further evidence for the structure enhancement of water about the

neutral amines and their conjugate ions is provided by n.m.r. studies of protolysis reactions of the ammonium ion and of the three methylammonium ions in aqueous solutions (212). Thus, it has been suggested (212) that the increased rate of protolysis for $MeNH_3^+$ over that for NH_4^+ has its origin in the cluster-promoting effect of methyl groups, which provide improved pathways for proton exchange through the ion-coordinated water and the intermediate structure-broken regions. Thus, the more methyl groups that are present, the greater is the number of hydrogen-bond pathways, whereas in the absence of a methyl group the speed of exchange is reduced and depends largely upon direct interactions between the exchanging species.

Finally, it may be noted that the conclusions from the compressibility measurements discussed in Section 6 in relation to the partial molar compressibilities of the neutral amines and their conjugate ion salts, are consistent with the arguments presented above in terms, for example, of the ΔS^o behaviour.

APPENDIX

Experimental results for the apparent molal volumes ϕ_2 and partial molal volumes $\bar{V}_2$ for the different alkylammonium salts are presented in tabular form in this Appendix, together with the respective solution densities for various concentrations.

Apparent Molal Volumes, Partial Molal Volumes and Densities of Four Tetraalkylammonium Chlorides at 25°C.

Salt	conc. mole litre^{-1}	$\phi_2 \pm 0.06$ ml.g.mole^{-1}	$\bar{V}_2 \pm 0.1$ ml.g.mole^{-1}	density $\pm$ 3x10^{-6} g.ml^{-1}
$(CH_3)_4NCl$	0.02030	107.60	107.63	0.997095
	0.02187	107.59	107.62	0.997099
	0.02564	107.66	107.70	0.997106
	0.03054	107.63	107.67	0.997118
	0.03883	107.65	107.69	0.997136
	0.04269	107.58	107.63	0.997148
	0.04559	107.66	107.71	0.997151
	0.05203	107.61	107.66	0.997168
	0.05244	107.67	107.72	0.997166
	0.05882	107.68	107.73	0.997180
	0.05949	107.65	107.70	0.997183
	0.06689	107.66	107.72	0.997199
$(C_2H_5)_4NCl$	0.01501	167.00	166.92	0.997036
	0.02331	166.93	166.83	0.997031
	0.03354	166.89	166.77	0.997025
	0.05408	166.81	166.65	0.997015
	0.07204	166.77	166.59	0.997007
	0.10303	166.71	166.50	0.996995
	0.16684	166.60	166.33	0.996981
$(n\text{-}C_3H_7)_4NCl$	0.01773	232.83	232.49	0.996865
	0.02439	232.66	232.20	0.996801
	0.03627	232.48	231.92	0.996691
	0.05875	232.12	231.51	0.996483
	0.07369	232.02	231.35	0.996347
	0.09646	231.94	231.17	0.996138
	0.12837	231.66	230.78	0.995873
$(n\text{-}C_4H_9)_4NCl$	0.01114	294.30	293.93	0.996875
	0.01296	294.14	293.75	0.996849
	0.02257	293.90	293.38	0.996707
	0.02920	293.72	293.13	0.996612
	0.03959	293.62	292.94	0.996461
	0.05079	293.40	292.63	0.996306
	0.07510	293.01	292.08	0.995980
	0.10295	292.77	291.69	0.995608

Apparent Molal Volumes, Partial Molal Volumes and Densities of Five Tetraalkylammonium Bromides at 25°C.

Salt	conc. mole.litre^{-1}	$\phi_2 \pm 0.06$ ml.g.mole^{-1}	$\bar{V}_2 \pm 0.1$ ml.g.mole^{-1}	density $\pm 3 \times 10^{-6}$ g.ml^{-1}
$(CH_3)_4NBr$	0.02682	114.62	114.74	0.998115
	0.04158	114.62	114.79	0.998702
	0.04998	114.65	114.85	0.999033
	0.06119	114.75	115.03	0.999474
	0.07156	114.76	114.99	0.999877
	0.08926	114.74	115.00	1.000588
	0.09451	114.80	115.06	1.000791
	0.10805	114.81	115.09	1.001326
	0.12715	114.86	115.09	1.002076
	0.15029	114.88	115.21	1.002988
	0.18355	115.05	115.41	1.004271
	0.19960	115.05	115.43	1.004903
	0.20787	115.07	115.45	1.005223
	0.28738	115.13	115.58	1.008333
	0.28974	115.17	115.62	1.008416
$(C_2H_5)_4NBr$	0.01086	174.41	174.33	0.997442
	0.01422	174.42	174.39	0.997564
	0.02214	174.36	174.22	0.997852
	0.04297	174.30	174.10	0.998611
	0.04906	174.41	173.90	0.998842
	0.07358	174.03	173.77	0.999744
	0.07879	174.05	173.78	0.999934
	0.09981	173.97	173.66	1.000711
	0.12836	173.88	173.54	1.001772
	0.14984	173.79	173.42	1.002575
	0.20123	173.64	173.22	1.004499
	0.20249	173.85	173.43	1.004506
	0.20408	173.72	173.30	1.004592
	0.24659	173.69	173.23	1.006170
	0.30377	173.49	172.98	1.008342
$(n\text{-}C_3H_7)_4NBr$	0.01171	239.68	239.50	0.997368
	0.02220	239.51	239.27	0.997658
	0.02683	239.59	239.33	0.997783
	0.03600	239.48	239.17	0.998038
	0.03981	239.38	239.06	0.998147
	0.04106	239.30	238.97	0.998185
	0.04346	239.37	239.04	0.998248
	0.04360	239.35	239.01	0.998253
	0.05002	239.34	238.98	0.998431
	0.05465	239.28	238.91	0.998562
	0.05515	239.35	238.97	0.998572
	0.05855	239.23	238.84	0.998673
	0.06270	239.16	238.76	0.998793
	0.07198	239.17	239.74	0.999050
	0.08619	239.14	238.67	0.999448
	0.10237	239.04	238.53	0.999909

	0.11528	238.96	238.42	1.000279
	0.12814	238.82	238.26	1.000657
$(\underline{n}\text{-}C_4H_9)_4NBr$	0.00658	301.03	300.84	0.997194
	0.01139	300.94	300.69	0.997302
	0.01763	300.87	300.56	0.997443
	0.01806	300.95	300.64	0.997451
	0.01959	300.91	300.59	0.997486
	0.02388	300.75	300.39	0.997585
	0.03960	300.53	300.07	0.997948
	0.03068	300.65	300.25	0.997742
	0.04383	300.45	299.97	0.998048
	0.05659	300.40	299.86	0.998342
	0.07631	300.15	299.52	0.998812
	0.09005	300.11	299.43	0.999132
$(\underline{n}\text{-}C_5H_{11})_4NBr$	0.00912	363.88	363.55	0.997191
	0.01216	363.77	363.37	0.997240
	0.01595	363.51	362.25	0.997304
	0.01867	363.66	363.10	0.997345
	0.02116	363.50	363.04	0.997388
	0.02514	363.45	362.89	0.997453
	0.02952	363.37	362.80	0.997526

Apparent Molal Volumes, Partial Molal Volumes and Densities of Four Tetraalkylammonium Iodides at 25°C.

Salt	conc. mole litre^{-1}	$\phi_2 \pm 0.06$ ml.g.mole^{-1}	$\bar{V}_2 \pm 0.1$ ml.g.mole^{-1}	density $\pm 3\times10^{-6}$ g.ml.$^{-1}$
$(CH_3)_4NI$	0.01230	125.99	126.09	0.997976
	0.01993	126.03	126.15	0.998551
	0.02025	126.07	126.20	0.998574
	0.03407	126.11	126.28	0.999614
	0.04151	126.16	126.35	1.000172
	0.05770	126.22	126.44	1.001388
	0.06094	126.21	126.44	1.001632
	0.07800	126.27	126.53	1.002910
	0.08629	126.34	126.61	1.003527
	0.13472	126.46	126.80	1.007149
	0.13878	126.49	126.83	1.007448
$(C_2H_5)_4NI$	0.00895	185.69	185.73	0.9971125
	0.03205	185.71	185.78	0.997279
	0.05491	185.74	185.84	1.001000
	0.09774	185.81	185.94	1.004076
	0.14530	185.86	186.01	1.007489
	0.19656	185.89	186.07	1.011167
$(n\text{-}C_3H_7)_4NI$	0.00981	251.04	250.98	0.997110
	0.02643	250.87	250.78	0.997215
	0.02643	250.94	250.85	0.998715
	0.04093	250.80	250.69	0.999635
	0.04516	250.92	250.80	0.999897
	0.06713	250.84	250.69	1.001289
	0.11407	250.76	250.57	1.004263
	0.14264	250.66	250.45	1.006084
$(n\text{-}C_4H_9)_4NI$	0.01078	312.43	312.38	0.997672
	0.01605	312.38	312.32	0.997978
	0.02016	312.32	312.25	0.998217
	0.02035	312.30	312.23	0.998227
	0.02128	312.28	312.21	0.998283
	0.02474	312.34	312.28	0.998482
	0.03650	312.28	312.19	0.999166
	0.04003	312.34	312.26	0.999368

Apparent Molal Volumes, Partial Molal Volumes and Densities of Five Alkylammonium Chlorides at 25°C

Salt	conc. mole litre^{-1}	$\phi_2 \pm 0.06$ ml.g.mole^{-1}	$\bar{V}_2 \pm 0.1$ ml.g.mole^{-1}	density $\pm 3\times10^{-6}$ g.ml^{-1}
CH_3NH_3Cl	0.02871	54.25	54.38	0.997433
	0.03985	54.13	54.29	0.997588
	0.04113	54.26	54.42	0.997600
	0.04961	54.22	54.40	0.997716
	0.05037	54.28	54.46	0.997723
	0.06199	54.28	54.52	0.997879
	0.07026	54.30	54.51	0.997988
	0.07271	54.31	54.52	0.998020
	0.09633	54.39	54.64	0.998328
	0.11969	54.42	54.69	0.998635
	0.14192	54.53	54.83	0.998915
	0.16167	54.54	54.85	0.999172
	0.19630	54.67	55.02	0.999602
	0.21805	54.62	54.99	0.999896
	0.28909	54.75	55.17	1.000785
	0.30395	54.77	55.20	1.000973
$(CH_3)_2NH_2Cl$	0.02489	72.89	72.99	0.997269
	0.03125	72.83	72.94	0.997327
	0.04323	72.89	73.02	0.997432
	0.05982	72.88	73.03	0.997580
	0.08180	73.00	73.17	0.997765
	0.08822	72.96	73.14	0.997825
	0.09987	73.04	73.23	0.997919
	0.11376	72.91	73.12	0.998056
	0.11575	73.04	73.25	0.998058
	0.16114	73.16	73.41	0.998435
	0.18412	73.15	73.41	0.998635
	0.21267	73.21	73.49	0.998890
	0.21518	73.21	73.49	0.998889
	0.25043	73.23	73.54	0.999185
	0.25143	73.23	73.53	0.999194
	0.31453	73.32	73.67	0.999704

$(CH_3)_3NHCl$	0.02545	90.90	91.02	0.997174
	0.04098	90.97	91.12	0.997248
	0.06158	90.94	91.13	0.997350
	0.07071	91.05	91.25	0.997387
	0.07813	91.09	91.32	0.997420
	0.09018	91.05	91.27	0.997481
	0.09369	91.12	91.35	0.997491
	0.14614	91.22	91.50	0.997724
	0.18379	91.30	91.62	0.997885
$(C_2H_5)_3NHCl$	0.01462	138.76	138.72	0.997038
	0.04288	138.69	138.63	0.997021
	0.05014	138.67	138.60	0.997018
	0.05579	138.57	138.49	0.997020
	0.06497	138.67	138.59	0.997009
	0.06603	138.64	138.56	0.997010
	0.06852	138.66	138.58	0.997007
	0.08426	138.63	138.54	0.997001
	0.10835	138.63	138.52	0.996986
	0.10904	138.67	138.57	0.996982
	0.13832	138.66	138.54	0.996965
	0.20805	138.54	138.43	0.996947
	0.29772	138.46	-	0.996929
	0.40967	138.31	-	0.996947
	0.53019	138.14	-	0.997003
$(\underline{n}\text{-}C_3H_7)_3NHCl$	0.02083	186.77	186.65	0.996913
	0.02668	186.71	186.58	0.996877
	0.04702	186.76	186.57	0.996744
	0.06729	186.63	186.40	0.996621
	0.08194	186.75	186.49	0.996519
	0.08541	186.54	186.28	0.996514
	0.11845	186.48	186.16	0.996314
	0.12142	186.47	186.15	0.996298
	0.16959	186.35	186.00	0.996020
	0.20529	186.16	-	0.995843
	0.29128	185.80	-	0.995441
	0.33058	185.55	-	0.995309
	0.37189	185.41	-	0.995143

Apparent Molal Volumes, Partial Molal Volumes and Densities of Three Alkylammonium Iodides at 25°C.

Salt	conc. mole litre^{-1}	$\phi_2 \pm 0.06$ ml.g.mole^{-1}	$\bar{V}_2 \pm 0.1$ ml.g.mole^{-1}	density $\pm 3 \times 10^{-6}$ g.ml^{-1}
$\underline{n}$-$C_3H_7NH_3I$	0.01923	105.95	106.04	0.998613
	0.02280	105.90	106.00	0.998905
	0.02812	106.00	106.11	0.999335
	0.04214	106.02	106.16	1.000475
	0.05692	106.17	106.23	1.001668
	0.05778	106.05	106.21	1.001745
	0.09755	106.13	106.34	1.004970
	0.17628	106.33	106.61	1.0111328
$(\underline{n}$-$C_3H_7)_2NH_2I$	0.01868	157.23	157.31	0.998399
	0.02693	157.23	157.33	0.998996
	0.06048	157.33	157.47	1.001417
	0.09259	157.38	157.56	1.003733
	0.13474	157.48	157.69	1.006761
	0.16432	157.51	157.74	1.008890
$(\underline{n}$-$C_3H_7)_3NHI$	0.01434	205.03	205.13	0.998005
	0.02209	205.06	205.18	0.998522
	0.03877	205.16	205.32	0.999631
	0.04330	205.20	205.37	0.999931
	0.05217	205.20	205.39	1.000522
	0.06343	205.23	205.43	1.001270

CLAIMS TO ORIGINAL RESEARCH

1) A theory of electrostriction of solvent water near ions has been developed. The change in solvent volume near ions has been related, using an appropriate molecular model, to the apparent change in the volume of the salt upon dissolution. This treatment has avoided the difficulties of previous calculations where use of the Born equation involved an integration over a distance from the ion where the continuum model on which the theory is based is least applicable.

2) A complete numerical solution for the effective pressure-field relation and the field-volume relation has been given for values of field in the range $0-10^7$ e.s.u.

3) Theoretical determinations of the local compressibilities of solvent water about ions, obtained from the effective pressure-volume relation that arises from the relations in (2), indicate that previous interpretations of compressibility data assuming an incompressible solvent hydration sphere are oversimplified except in cases where values of the local field exceed 10^7e.s.u.

4) The entropy change, associated with compression of the solvent, caused by the local contractive pressure near ions, has been calculated in a more sophisticated manner. It appears that the agreement between the results of the original calculations by Latimer and Kasper and the experimental ones was largely fortuitous.

5) The partial molal volumes $\bar{V}$ of a series of homologous tetraalkylammonium chlorides, bromides and iodides have been precisely measured at low concentrations using a differential buoyancy technique.

6) A principle has been proposed for obtaining individual $\bar{V}_i^o$ values and is based on a satisfactory experimental procedure with minimal à priori theoretical assumptions.

7) The anomalously large negative concentration dependence of $\bar{V}$ for the R_4NX salts has been characterised and discussed in terms of pressure derivatives of all quantities which determine the activity coefficient.

8) Qualitative estimates of the distance of closest approach $\overset{o}{a}$ and $d\ln\overset{o}{a}/dP$ have been obtained from the volume studies. These qualitative estimates of $d\ln\overset{o}{a}/dP$ indicate the importance of solvent structure promotion effects in the behaviour of solutions of R_4N^+ cations.

9) Formal effective ionic radii of the R_4N^+ and X^- ions have also been estimated, taking into consideration dead-space effects in the solvent and the local packing of solvent-solute species.

10) Non-electrostatic effects arising from the large difference in size between the R_4N^+ cations and the solvent molecules have been suggested as one of the reasons for the anomalies in the partial molal volume and activity behaviour exhibited by these salts.

11) The partial molal volumes of a series of alkylamine hydrogen chlorides and hydrogen iodides have been precisely measured at low concentrations.

12) The volumes of ionisation of methylammonium ions have been estimated and they are found to be relatively invariant with increased alkyl group substitution. Hydration and structural effects have been discussed.

13) A differential ultrasonic velocity measuring apparatus has been used to measure the adiabatic compressibilitites of salt solutions down to reasonably low concentrations with an accuracy much better than that of previous methods employing ultrasonic interferometry.

14) The partial molal adiabatic compressibilities of a series of homologous tetraalkylammonium bromides and iodides, a series of homologous methylammonium chlorides, and a series of homologous methylamines have been measured for the first time using the above differential ultrasonic velocity technique. Interpretations have been made in terms of local compressibility changes for solvent near the ions. Three types of solution water are distinguished qualitatively.

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