STUDIES ON THE HYDRATION OF POLYELECTROLYTES

by

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PREFACE

For more than a century it has been realized that solvation, or more specifically hydration when the solvent is water, plays an important rôle in the chemistry of solutions. The interest has been centered mostly around simple ions but the problem of hydration is also of great importance in the physical chemistry of proteins, nucleic acids and other ionic hydrophilic colloids as well as in the electrolytic behaviour of synthetic polyelectrolytes. Despite its fundamental importance, very few quantitative studies of hydration of macromolecular ions have hitherto been carried out.

In the present work a quantitative approach to this problem has been made in three directions: a) theoretically, through calculations of the degree of dielectric saturation of water near polymeric and related simple ions, b) experimentally, through evaluation of solvent electrostriction from density measurements of polymeric and simple ion solutions and c) through salting-out data. Attempts have been made to correlate, whenever possible, the data obtained by these different approaches and on the whole satisfactory consistency between the various types of experimental and theoretical results has been obtained.

Estimation of relative extents of hydration of polyions in relation to analogous simple ions taken as the corresponding monomeric species is the aim of the work in principle. It must be stressed that attempts to make absolute estimates of these quantities have not been made, for such an approach is fraught with the commonly encountered difficulties of defining the extent of primary and secondary hydration. Therefore, relative estimates of the difference in primary hydration of simple and derived polymeric ions obtained theoretically in terms of dielectric saturation effects are compared with those obtained experimentally from salting-out and apparent molar volume measurements. Within this framework a largely self-consistent set of data is presented. In this comparative approach several models for the charged species have been examined: a linear polyion, a spherically coiled polyion, a planar colloidal ion and as reference a simple ion with spherical symmetry.

A small part of the present work, namely construction of a prototype gas solubility apparatus, its calibration and the measurements of a few preliminary solubilities, was presented in a thesis in the final year of the B.Sc. (Honours) course at this University.

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LIST OF IMPORTANT SYMBOLS

a	Radius of charged particle.
b	Booth's constant = 1.08×10^{-8} e.s.u.$^{-2}$.
c_2	Concentration of non-electrolyte in moles per cubic centimeter.
C_2^o	Concentration of non-electrolyte in pure solvent in moles per liter.
C_2	Concentration of non-electrolyte in salt solution in moles per liter.
$\overline{C}$	Concentration of polyion in macromoles per liter.
d	Density of solution.
d_o	Density of pure water.
D	Electric displacement.
e	Electronic charge (4.80×10^{-10} e.s.u.).
E	Electrical field intensity or applied field intensity.
f	Activity coefficient of an ion.
F	Actual field intensity.
G	Gibb's free energy.
I	Polarization: number of moments per unit volume.
k	Boltzmann constant (1.38×10^{-16} erg, degree^{-1} mole^{-1}).
k_s	Salting-out constant.
l	Length of polyion.
m	Concentration of simple electrolytes in moles per liter, concentration of polyelectrolytes in ions per liter or concentration of the counterions in moles per liter.
$\overline{m}$	Concentration of polyelectrolyte in terms of ionizable groups (monomoles per liter).

M	Molecular weight.
M	Abbreviation for molarity.
n	Refractive index n^2 for water = 1.78
n	Concentration in number of molecules per unit volume.
N	Avogadro's number (6.023×10^{23} molecules per mole).
p	Polarization per unit volume.
$\bar{p}$	Polarization per unit volume (Kirkwood's theory).
P	Molar polarization.
$\bar{P}$	Molar polarization (Kirkwood's theory).
r	Distance from centre of charged particle.
r_d	Distance from a charged particle where $\epsilon_d = 55$
r_h	Radius of primary hydration shell.
r_o	Radius of a spherically coiled polyelectrolyte.
R	Radius of the volume of solution available to a charged particle.
R	Gas constant.
S	Solubility of a non-electrolyte in a salt solution.
S_o	Solubility of a non-electrolyte in pure water.
T	Absolute temperature.
u	Reduced potential from the centre of a spherically coiled polyelectrolyte.
U	Interaction energy between an ion and a non-electrolyte.
v_a	Actual molar volume of an ion.
v_o	Molar volume of water (18 mls./mole).
v_o^h	Molar volume of water in the primary hydration shell (12.6 mls./mole).

V	Total volume of a system.
$\overline{V}_2$	Partial molar volume of non-electrolyte.
V_s	Molar volume of the (liquid) salt.
$\overline{V}_s$	Partial molar volume of a salt (= $\phi_v{}^o$).
x	Reduced distance from centre of spherically coiled polyelectrolyte.
x_o	Reduced radius of a spherically coiled polyelectrolyte.
X	Reduced radius of the volume available to each spherically coiled polyelectrolyte.
z_i	Valency of ion $_i$.
α	Degree of dissociation or ionization.
α_t	Total polarizability.
α_o	Induced polarizability.
β	Dielectric increment.
β_o	Compressibility of water.
ε	Dielectric constant - usually integral dielectric constant.
ε_o	Dielectric constant at zero field strength = 78.5 at 25°C.
ε_d	Differential dielectric constant = dD/dE.
ε_i	Integral dielectric constant = D/E.
ψ	Potential.
ϕ_v	Apparent molar volume.
$\phi_v{}^o$	Apparent molar volume at infinite dilution.
μ	Dipole moment of individual molecules in solution.
μ_o	Dipole moment of a molecule in the gaseous state.
$\overline{\mu}$	Vector sum of the moment of the central molecule plus that of all the neighbours.

σ	Charge density.
λ	Charge separation on a linear polyion or planar colloidal ion.
$[\eta]$	Intrinsic viscosity.

ABSTRACT

Three approaches to the study of hydration of polymeric ions in relation to that of analogous simple ions have been made as follows:

In the first part of the thesis, information is sought regarding the hydration of polyions by evaluating the degree of dielectric saturation near the charged particles. Previously, this had been done only in the case of isolated simple ions assumed to be point charges. Since the ionic atmosphere can never be removed from the polyions, even in very dilute solutions, the simple electrostatic field cannot be used in the evaluation of the extent of dielectric saturation. The dielectric constant has therefore been obtained directly as a function of the distance from the polyion from a solution of the Poisson-Boltzmann equation and previously published relations between dielectric constant and field intensity. The solutions have been obtained by numerical methods using a digital electronic computer.

The Poisson-Boltzmann equation was solved by this method for the following models: simple ions, cylindrical polyions, spherical polyions and planar colloidal ions. The relative degrees of dielectric saturation were calculated and related to the relative extents of primary hydration for the different ionic models. The effect of dielectric saturation on the field and potential functions is also discussed

for the various ion models.

The second part of the thesis deals with solvent electrostriction and the determination of salting-out by polyelectrolytes. In order to interpret the experimental data obtained on the salting-out of non-electrolytes (argon, ethylene, d-l leucine and benzamide) by polyelectrolytes (sodium polyphosphates, potassium polymethacrylate and poly-4-vinyl-N-n-butylpyridinium bromide), it was first found necessary to modify the existing salting-out theories for simple ions and a proposed theory for polymeric ions, by taking into account the effect of dielectric saturation of the solvent near the ions. Such effects are shown to be important in determining salting-out constants and, in fact, lead to the recognition of the necessity for taking into account the specific structure (e.g. effective radius) of the primary hydration shell. Other modifications to the theory are also suggested.

In the modified salting-out theory referred to above, the radius of the primary hydration shell is required. The third part of the thesis therefore describes the evaluation of this parameter from experimentally measured apparent molar volumes for simple and polymeric ions. The significance of these apparent molar volumes in relation to the hydration of the polymeric and simple ions is also discussed.

I. INTRODUCTION

SOLVATION

The outstanding importance of water as a solvent for salts is due to its anomalously high dielectric constant, which in turn is due to the polar nature of its molecules and to their tendency to form a hydrogen bonded tetrahedrally coordinated structure. Most simple electrostatic theories of electrolyte solutions usually assume the solvent to be a continuous, uniform medium. However, water, being formed of discrete polar particles, will interact with the ions, and the neglect of specific structural aspects of these interactions will usually lead to serious errors in such electrostatic theories.

Ion-solvent interactions can be divided into three types, corresponding to three regions in the neighborhood of the ion. The strongest interactions give rise to what is known as primary hydration (1). The water molecules in this innermost region are immobilized (2) by the electric field of the ion, but only temporarily since, except for a few trivalent ions (3, 4), they remain in "activated" exchange equilibrium with the remainder of the solvent (5, 6 page 54). It has been suggested (7) that the energy of interaction between a representative water molecule and the ion be used as a criterion for defining primary hydration; if this energy of interaction is larger than the mean kinetic energy kT of water molecules in the bulk, the representative water molecule is assumed to be involved in primary hydration of the ion. However, a more precise definition of primary hydration should probably take into account the exchange of water molecules in the immediate vicinity of the ion; the degree of hydration can, in fact, be regarded as a measure of the frequency of this exchange relative to the normal exchange of solvent water with a reference water molecule in the bulk.

The interactions beyond the first hydration shell lead to a region in which the water structure is broken down* locally (8, 9, 10). The water molecules in this intermediate region are less organized in a quasi-crystalline arrangement than they are in the bulk, or in other words, the exchange of water molecules is more rapid here than in pure water. The "structure breaking" effect presumably arises from an approximate balance between two competing orienting influences which act on a given water molecule: the normal structural orienting influence of neighbouring water molecules through hydrogen bonding with a given water molecule and the orienting influence of the ionic field. These secondary interactions are relatively more important with large ions where the primary hydration is negligible and can account in some measure

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* The converse of this, i.e. structure promotion, has been discussed by Frank and Evans (10) in term of so-called "iceberg" formation but such effects are involved mainly in aqueous solution of non-electrolytes or with very large ions (see also page 192).

for the anomalous behaviour of some of these ions (11, 12).

The third hydration region refers to the remainder of the solvent beyond the structure-breaking region which can still be affected slightly by the ionic field, but essentially has the same structure as the pure solvent. In most cases, this hydration can be neglected.

The degree of hydration can be expressed in terms of the volume or radius of the hydration shell, or in terms of the number of water molecules contained in this shell. Most of the methods that have been used to measure hydration express the degree of hydration in terms of the concept of the so-called hydration number (1). This, however, has many disadvantages. The assignment of a volume to the water molecule in the first hydration shell which determines the hydration number in this shell is often difficult (13). This concept may also lead to a false interpretation of solvation; the statement that a salt, say CsBr, has a hydration number of one may be interpreted as referring to a salt having a water molecule bound to it in a way similar to the water of crystallization in a solid hydrate. Actually, the two are quite different. In a crystal, the water molecules are bound in a fashion where they have lost all translational motion and there is usually a definite stoichimetric quantity of water (not necessarily chemically bound) associated with the salt. However, in solutions, there is a rapid exchange between the hydration water and the free water molecules of the bulk, and it is only on a time-average basis that we may speak of a "hydrate" water molecule. This classification of hydration also makes the comparison of primary hydration and secondary hydration somewhat ambiguous. For these reasons, it is often preferable simply to express the hydration in terms of a volume or radius of a region of associated water near to the ion, specifying, for example, the minimum limit of the energy of this association, e.g. kT as chosen by Azzam (7).

Any electrolytic property which is influenced by the ion-solvent interactions could theoretically be used to evaluate the extent of hydration near ions. In practice, the problem is much more difficult since most methods will effectively measure different proportions of the first, second and even third hydration regions. The main methods that have been used to determine hydration numbers have been critically reviewed by Bockris (1) and Conway and Bockris (14) and it is, in fact, found that most of these methods give discrepant values. The hydration numbers found, however, fall into two groups; the first, giving lower values, corresponds approximately to primary hydration, while the second, giving much larger values, has been assumed by Bockris (1) to refer to secondary hydration but, in fact, does not correspond to any simple picture of the degree of hydration and is probably due to other effects or interactions neglected in the evaluation of the hydration number. Nevertheless, all these methods still show the correct relative magnitudes of extent of hydration of different ions.

It is possible to obtain quantitative information about the hydration of ions only if independent knowledge of the structure of the three hydration shells is obtained separately. This is difficult since there is a continuous transition between them. However, it is possible to obtain some information about the thickness of each shell, particularly the primary layer, if semi-empirical methods are used. Most of the properties of electrolytes which depend on ion-solvent interactions are determined by interactions in the first and second hydration shells only. In such cases, the third hydration region may be assumed negligible. The extent of the first hydration region of an ion is determined by the electrical field at the ion which is usually strong enough to immobilize the water molecules rotationally and translationally in that region (although librative motions are still important (15)). As the size of the ion increases, the field intensity just outside the ion decreases and the extent of primary hydration tends to decrease. Beyond a certain radius, the field intensity will be sufficiently small for it to be assumed that the primary hydration is negligible. The hydration of large ions is therefore only associated with structure-breaking effects and possibly other more specific interactions such as van der Waals short range interactions. By studying the electrolytic properties of large ions (e.g. by conductance, partial molar volume, salting-out measurements etc.) information can, in some cases, be obtained about the secondary hydration. Then, by correcting for this secondary hydration, information about the primary hydration of simple ions can be obtained.

This kind of procedure has been followed by Robinson and Stokes (6, chapter 6) and by Nightingale (11) to evaluate the radius of the first hydration shell from mobility data. Assuming that Stokes' law for viscous flow holds for ions, the radius r_s of migrating or diffusing species may be evaluated from the limiting ionic equivalent conductance λ^o and the viscosity of the solvent η^o, or from the limiting ionic diffusion coefficient D^o (11) from the relation

$$r_s = 0.820z/\lambda^o\eta^o = 0.732 \times 10^{-9}T/D^o\eta^o \qquad [I-I]$$

where z is the absolute charge of the ion and T the absolute temperature. The Stokes radius r_s obtained gives the correct dependence of the extent of primary hydration on the nature of the ion but is smaller than the crystal radius "a" for intermediate and large ions (it is, of course, larger than "a" for small ions, e.g. Li^+, Na^+, F^- etc.). This is a result of structure breaking effects and of the inapplicability of Stokes' law to molecular species. Nightingale proceeds by assuming that the hydration radius r_h is equal to the crystal radius "a" for large ions ("a" > 4 Å). From a calibration curve of r_h versus r_s, the radius of the primary hydration shell may be obtained for all simple ions. Nightingale, by this method, has evaluated the hydration radii of many simple ions and some more complex ones, and his results have been reproduced in Table 1*. The main conclusions to be drawn from this table is that all the hydrated ions have a radius of at least 3.3 Å and that all ions with crystal radii less than 4 Å will at least have a small amount of primary hydration. However, it must be remembered that for ions with radii between 2 and 4 Å the secondary hydration (associated with structure-breaking) could be just as important as, if not more so than, the primary hydration. Therefore, the total hydration of these ions may appear negligible or even negative (16). Nightingale's assumption that the volume of the ion in solution is equal to the crystal volume may be questioned since there is a fair amount of evidence indicating that the molar volumes of free ions differ slightly from the corresponding crystal volumes (17, 18, 19) which are smaller owing to internal compression effects. Therefore, some small error may have been introduced here.

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* The values for r_h are recorded to 2 decimal places as in the original paper but it is doubtful if the data are significant to this implied degree of accuracy.

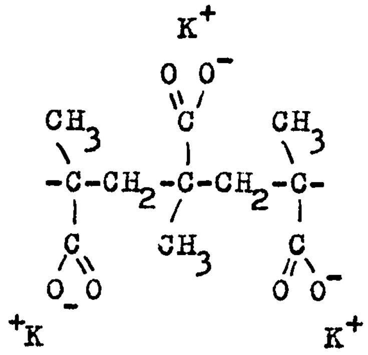
Table 1

COMPARISON OF CRYSTAL AND HYDRATION RADII (IN Å UNITS) AT 25°C.

Ion	"a"	r_h	Ion	"a"	r_h
Li^+	0.60	3.82	Pb^{+2}	1.32	4.01
Na^+	0.95	3.58	Al^{+3}	0.50	4.75
K^+	1.33	3.31	Cr^{+3}	0.64	4.61
Rb^+	1.48	3.29	Fe^{+3}	0.60	4.57
CS^+	1.69	3.29	La^{+3}	1.15	4.52
Ag^+	1.26	3.41	Ce^{+3}	1.1	4.52
Tl^+	1.44	3.30	Tm^{+3}	0.9	4.65
NH_4^+	1.48	3.31	$Co(NH_3)_6^{+3}$	2.55	3.96
$(Me)_4N^+$	3.47	3.67	F^-	1.36	3.52
$(Et)_4N^+$	4.00	4.00	Cl^-	1.81	3.32
$(n\text{-}Pr)_4N^+$	4.52	4.52	Br^-	1.95	3.30
$(n\text{-}Bu)_4N^+$	4.94	4.94	I^-	2.16	3.31
$(n\text{-}Pe)_4N^+$	5.29	5.29	NO_3^-	2.64	3.35
Be^{+2}	0.31	4.59	ClO_3^-	2.88	3.41
Mg^{+2}	0.65	4.28	BrO_3^-	3.08	3.51
Ca^{+2}	0.99	4.12	IO_3^-	3.30	3.74
Sr^{+2}	1.13	4.12	ClO_4^-	2.92	3.38
Ba^{+2}	1.35	4.04	IO_4^-	3.19	3.52
Ra^{+2}	1.52	3.98	MnO_4^-	3.09	3.45
Mn^{+2}	0.80	4.38	ReO_4^-	3.30	3.52
Fe^{+2}	0.75	4.28	CO_3^{-2}	2.66	3.94
Co^{+2}	0.72	4.23	SO_4^{-2}	2.90	3.79
Ni^{+2}	0.70	4.04	SeO_4^{-2}	3.05	3.84
Cu^{+2}	0.72	4.19	MoO_4^{-2}	3.23	3.85
Zn^{+2}	0.74	4.30	CrO_4^{-2}	3.00	3.75
Cd^{+2}	0.97	4.26	WO_4^{-2}	3.35	3.93

It should be noted at this point that, although main hydration effects arise from electrostatic ion-dipole interactions, some specific interactions, e.g. hydrogen bonding, and van der Waals' short range forces may enhance the hydration of some particular ions, e.g. of H^+, OH^- and oxy-anions. These special effects will be assumed negligible in this thesis and will only be considered as a basis for explanation of some anomalous results.

The behaviour of polyelectrolytes in solution is much more complicated than that of analogous simple ions since they have a more complex structure. Polyelectrolytes may occur in forms approximating to large spheres, coils, rods or plates in solution. In addition, their shape may change depending on charge density of the polymer and the ionic strength of the solution; a linear polyacid or polybase will exist as a random statistical coil at low degrees of neutralization, but this coil will open up as the degree of neutralization increases, and will tend to coil up again if an excess of simple electrolyte is added (20). Another characteristic of these molecules that complicates their study is their tendency to undergo association with their counter-ions. Wall (21, 22, 23, 24) has studied this problem extensively using radioactive tracer methods and he finds that some polyelectrolytes, e.g. some polyphosphates, may be as much as 75% associated. In spite of these difficulties, a large amount of theoretical and experimental work has been carried out in the last fifteen years on account of the interest and importance of this field. However, the reviews of Eisenberg and Fuoss (20), Rice (25) and Conway and Dobry (26) show that knowledge of the electrochemical properties of polyelectrolytes is still in its infancy compared with the state of knowledge of simple electrolytes. From the point of view of the degree of hydration, the problem is more that of representing the local structure of the polyion and associated solvent rather than the overall shape of the macromolecule. For example, we may consider a typical linear polyelectrolyte like potassium polymethacrylate:



it is obvious that, while the assumption that a charged sphere is a fairly good model for a simple ion, the assumption that polyions may be represented by uniformly charged rods (51, 52) is only an approximation, valid only under rather limiting conditions. However, such models do explain, at least qualitatively, some of the properties of these molecules.

The extent of knowledge of hydration of polyions is virtually negligible. The little work that has been done on the experimental determination of their extent of hydration gives discrepant results. Thus, it has been argued that D.N.A. (27) increases the internal structure of water very significantly, but hyaluronic acid (28) has been stated to have very little effect on the solvent. This is virtually the only work that has been done hitherto on hydration of polymeric ions. Most of this experimental evidence appears to be, however, highly doubtful and qualitative in nature as will be shown in Chapter II. Although the hydration problem is not a simple one in this case, it is, however, a very important one, both on account of its interest in the chemistry of electrolyte solutions and in the field of biophysics.

In addition to the local charge on a polyion, the first, second and further neighbours on the chain will all contribute to the local field intensity and the extent of hydration can be much larger, as it will be shown later, than for a corresponding simple electrolyte at the same ionic concentration.

The aims of the work described in this thesis will be to evaluate the relative degrees of hydration of polyions by calculation of the extent of dielectric saturation of the solvent and then to correlate these results with experimentally determined salting-out constants and apparent molar volume measurements for the polyions at various degrees of ionization.

Theoretical studies of hydration are possible if we consider an isolated ion; for example, it is possible to calculate the number of water molecules necessary to give maximum stability to ion in solution (29, 30, 31). Unfortunately, in the case of polyions no matter how dilute the solution is considered, the ion will still retain some ionic atmosphere of gegen-ions. Also, the shape, charge density, concentration and size of the polyions will determine to some extent the hydration of these molecules. Therefore, such absolute calculations of hydration by the methods which have been used, e.g. by Bernal and Fowler (27) and Eley (30), for simple ions cannot be carried out for polyions with the same degree of rigour and certitude as for simple ions.

However, for the study of hydration of polyions, it will be sufficient for the purposes of obtaining initial <u>quantitative</u> data to make comparisons of the relative degrees of hydration of the polyions compared with that of corresponding simple ions. In this approach, it will be considered satisfactory to compare the degrees of <u>primary</u> hydration since the largest differences between poly and simple ions should occur in this primary shell. Since the primary hydration depends to a large extent on the field intensity in the immediate vicinity of the ion, relations which depend on this field may be used to compare hydration of different molecules. As will be shown later, dielectric saturation relations are ideal for such comparisons. Also, since the effects to be considered are largely short range ones (within 10 Å from the polyion axis), the calculations will not depend to any important extent on details of the overall macromolecular configuration except in the case of closely coiled polyions (where special calculations will be made) at low degrees of ionization.

DIELECTRIC CONSTANT AT HIGH FIELD INTENSITY

It is well known that the dielectric constant of water in the primary hydration shell is much lower than in the pure solvent (2). The electrical field near a small ion is large enough to immobilize the water molecules and to remove or reduce their rotational or librational freedom. The dielectric constant in this region should be the same as, or approach, the one measured at very high frequencies; when the dielectric constant is measured at frequencies so high that the permanent dipoles are unable to contribute to the polarization, then the dielectric constant becomes equal to the square of the optical refractive index n^2 and is often called the optical dielectric constant (32, page 88). At low field strength, the dielectric constant is effectively constant and may be taken as the ordinary static dielectric constant. The problem of importance in the theory of ionic hydration is to evaluate the dielectric constant at intermediate distances from the ion.

At relatively high fields, the differential and integral dielectric constants must be distinguished. If a small external field were superimposed on the field of the ion for the purpose of measuring the local dielectric constant, then the dielectric constant would depend on the direction in which it was measured (i.e. on the vector of the applied test field). The differential dielectric constant refers to the one measured in a radial direction to the ion (33 page 117) and is defined as

$$\mathcal{E}_d = \frac{dD}{dE} \qquad [I-2]$$

where D is the dielectric displacement and E is the electrical field strength. This dielectric constant has the advantage of being independent of the small applied measuring field (34, page 424). The integral dielectric constant refers to the dielectric constant measured when a small external field is applied perpendicularly to the radial line, and is defined as

$$\mathcal{E}_i = \frac{D}{E} \qquad [I-3]$$

This is the dielectric constant usually used in electrostatics. These two dielectric constants are identical at very low and very high field intensities but are different at intermediate fields. They can however be related by

$$\mathcal{E}_d = \mathcal{E}_i + E \frac{d\mathcal{E}_i}{dE} \qquad [I-4]$$

The dielectric displacement is also related to the applied electrical field by the general relation

$$D = E + 4\pi I \qquad [I-5]$$

where I, the polarization, is defined as the electric moment per unit volume.

From equations [I-3] and [I-5] the integral dielectric constant can be related to the polarization.

$$\mathcal{E}_i - 1 = \frac{4\pi I}{E} \qquad [I-6]$$

Also from its definition, the polarization can be related to the actual field intensity F by

$$I = nm = n\alpha_t F \qquad [I-7]$$

where n is the number of molecules per c.c., m is the electric moment of the molecule and α_t is the total polarizability of the molecule. Therefore, depending on the relation existing between E and F, the dielectric constant may be predicted from the field intensity and the properties of the molecule.

When the interactions between molecules can be neglected, as in the case of gases and non-polar liquids, the actual field may be replaced by the Lorentz field $E + 4\pi I/3$ (33, page 11). Therefore from equations [I-6] and [I-7]

$$\varepsilon_1 - 1 = \frac{4\pi\alpha_t n}{E} F = \frac{4\pi\alpha_t n}{E} \left(E + \frac{4\pi I}{3}\right) \qquad [I-8]$$

Replacing I by its value obtained from equation [I-6], equation [I-8] reduces to the Clausius-Mosotti equation (33, page 12)

$$\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} = \frac{4\pi\alpha_t n}{3} \qquad [I-9]$$

Debye (33, chapter 2) has extended this relation to polar molecules by showing that the total polarizability α_t is actually composed of two parts: the induced polarizability α_o and the permanent (orientation) polarizability $1/3\ \mu_o^2/kT$: i.e.,

$$\alpha_t = \alpha_o + \frac{1}{3}\frac{\mu_o^2}{kT} \qquad [I-10]$$

where μ_o is the dipole moment of the molecule in the gas phase. He has also extended this theory to obtain by a graphical method the dielectric constant as a function of the intensity of the applied field E and as a function of the distance from an ion. Unfortunately, his estimation of the saturation effect near an ion is much too large, e.g. in comparison to the effects observed experimentally at relatively low fields by Malsch (35). The main reason for the failure of this theory results from the assumption that the dipole-dipole interactions between molecules can be regarded as insignificant (32, page 28). In polar liquids and especially in the case of water, these interactions cannot be neglected. Therefore, the Debye theory should only hold for polar molecules in the gas phase or in very dilute solutions in non-polar solvents.

Many attempts have been made to improve the theory of dielectrics for polar molecules (32, Chapter 1) (36) and, amongst the most successful ones, the theory of Onsager (37) has received much attention. He obtained a better dependence of the actual field on the applied field in equation [I-8] by taking into account the dipole-dipole interactions between polar molecules. He has also shown that, at low field intensity, his equation gives practically the same results as Wyman's empirical relation for polar liquids (38)

$$\varepsilon_1 + 1 = h\,p \qquad [I-11]$$

where p is the polarization per unit volume* of the liquid

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* p should not be confused with I, the electric moment per unit volume, even though these two quantities are both unfortunately called polarizations and in many text books even have the same symbol (32). p is defined from equation [I-9] as

$$p = \frac{4\pi}{3}\,\alpha_t n.$$

I is also related to α_t by equation [I-7]

$$I = \alpha_t nF$$

Therefore, in a unit field, p and I differ by a factor $\frac{4\pi}{3}$

and is related to the molar polarization P by $p = P/\overline{V}$ where $\overline{V}$ is the partial molar volume. The empirical constant h was found to have the average value 8.5 for most polar liquids. Onsager's theory accounts very well for the dielectric constant of most polar liquids but fails in the case of associated liquids like water and alcohols.

Kirkwood (39) has improved Onsager's theory by considering in more detail the hindered rotation of dipoles in polar liquids and was able to predict the dielectric constant of water and other associated liquids from their dipole moments and other molecular properties.

Kirkwood's relation is a complex one but reduces to a very simple relation at low field intensity if the static integral dielectric constant is large compared with the optical one. His limiting equation is then (40 page 365)

$$\varepsilon_1 = \frac{9}{2}\,\overline{p} \qquad [I\text{-}12]$$

where $\overline{p}$ is related to the moments μ and $\overline{\mu}$ by the relation

$$\overline{p} = \frac{4}{3}\,\pi n \left\{ \alpha_o + \frac{\mu\overline{\mu}}{3kT} \right\} \; ; \qquad [I\text{-}13]$$

in this equation, μ is the moment of the individual molecule in solution and $\overline{\mu}$ is the vector sum of the moment of the central molecule plus that of all the neighbours which may affect its rotation and orientation. For non-associated polar molecules, $\mu\overline{\mu}$ may be related to μ_o (40, page 363), the moment of the molecule in the gaseous state, by Onsager's theory as

$$\mu\bar{\mu} = \frac{(n^2 + 2)^2}{9} \mu_o^2 \qquad [I\text{-}14]$$

where n is the refractive index of the molecule. In the case of associated molecules like water, the moments μ and $\bar{\mu}$ have to be evaluated from knowledge of the properties and structure of the liquid.

The Onsager and Kirkwood theories were extended by Hasted, Ritson and Collie (2), by Booth (41) and others (42) to give expressions for the integral dielectric constant at high field strengths. These theories are fairly complicated but Grahame (43, 44) was able to show that Booth's relation may be represented very accurately by the empirical relation

$$\mathcal{E}_d = \frac{dD}{dE} = \frac{\mathcal{E}_o - n^2}{1 + b(E^2)} + n^2 \qquad [I\text{-}15]$$

where $\mathcal{E}_o$ is the static dielectric constant at zero field strength (taken as 78.5 at 25°C). The square of the optical refractive index n^2 is equal to 1.78 and the constant b is found to be equal to 1.08×10^{-8} e.s.u.$^{-2}$.

If the integral dielectric constant is desired, equation [I-15] may be integrated (45) to give

$$\mathcal{E}_i = \frac{D}{E} = \frac{[\mathcal{E}_o - n^2]}{b^{1/2}E} \operatorname{Tan}^{-1} b^{1/2}E + n^2 \qquad [I\text{-}16]$$

Therefore, provided the field strength near an ion or polyion is known, the dielectric constant may be obtained as a function of the distance from the ion, e.g. as discussed by Laidler (45, 46).

The validity of these relations for the dielectric saturation effect may be questioned since there is very little experimental evidence to support them. Booth's theory agrees well with Malsch's measurements of dielectric constant as a function of field strength, but the latter determinations were not made at very high fields where the saturation effect is most significant. Also, very close to the ion where the saturation effect is greatest, other interactions, e.g. van der Waals' short range forces, will probably affect the local dielectric constant. However, at field intensities lower than 10^4 e.s.u., Booth's theory is probably quite reliable and, since we are primarily interested here in the relative effect of hydration for different types of electrolytes, it is sufficient to compare the effect of dielectric saturation for different models in the range where Booth's theory is applicable.

THE POISSON-BOLTZMANN EQUATION

The values for the electrical field and potential near an ion are usually obtained from the Poisson equation. Expressed in rectangular coordinates, this relation is

$$\frac{\partial}{\partial x}\left[\varepsilon_1 \frac{\partial \psi}{\partial x}\right] + \frac{\partial}{\partial y}\left[\varepsilon_1 \frac{\partial \psi}{\partial y}\right] + \frac{\partial}{\partial z}\left[\varepsilon_1 \frac{\partial \psi}{\partial z}\right] = -4\pi\sigma \qquad [\text{I-17}]$$

where σ is the charge density or the net charge per unit volume at the distance x, y, z from the reference charged particle or surface. In the case of a simple ion, this expression may be written in polar coordinates as

$$\nabla^2\psi = \frac{1}{r^2}\frac{d}{dr}\left(\varepsilon_i \frac{d\psi}{dr}\right) = -4\pi\sigma \qquad [I\text{-}18]$$

Because of the spherical symmetry around a simple ion, the equation is independent of the two vectorial angles θ and ϕ.

The simplest solution of equation [I-18] is for the case of an isolated ion or an ion in an infinitely dilute solution. The field strength is then simply

$$E = -\frac{z_i\, e}{\varepsilon_i\, r^2} \qquad [I\text{-}19]$$

Whenever the concentration of the electrolyte is finite, then the distribution of ions around a reference ion must be taken into account, since the presence of other ions will affect the field near the reference ion. Equation [I-19] is therefore no longer a good representation of the ionic field. In the case of polyions or colloidal ions, the situation is even worse since, in these cases, one cannot isolate the large ion from its counterions even at high dilution as in the case of simple ions.

If the Boltzmann equation is applicable to the distribution of ionic particles in an electric field of varying intensity, then the time-average number of ions of the ith type and of charge $z_i e$ present in a volume element dv is given by

$$dn_i = n_i^o \exp\left(-\frac{z_i e \psi_i}{kT}\right) dv \qquad [I-20]$$

where n_i^o is the number of ions when $\psi_i = 0$.

From the distribution of the ions, the charge density σ may then be obtained at any distance from the reference ion from the relation $\int \sigma dv = \sum_i e z_i n_i$. Therefore the combination of equation [I-18] and [I-20] constitute the Poisson-Boltzmann equation. The exact form of this equation depends on the symmetry and boundary conditions of the model used. A more detailed discussion of the Poisson-Boltzmann equation for different models of simple, polymeric and colloidal electrolytes will be given in chapter II of this thesis.

The solution of these equations is of great importance since the theories of electrolytes, e.g. for the activity coefficient (47), conductance (48) and degree of ion association (49) are based on the ionic field or potential.

If the dielectric constant is assumed uniform throughout the solution, then the Poisson-Boltzmann equation can be solved exactly in some cases, e.g. for the models of charged plates (50) and charged rods (51, 52). In other cases, the differential equations may be solved only if mathematical approximations are made as in the case of the Debye-Hückel theory (47); otherwise numerical methods have to be used (53).

In this thesis, an attempt will be made to obtain the dielectric constant near charged particles having various forms using the field obtained from the solution to the Poisson-Boltzmann equation. This work will serve a dual purpose. The dependence of the dielectric saturation on the nature of the ion (shape, charge density, radius and concentration) will lead to information about the influence of these effects on hydration. Also the simultaneous solution of the Poisson-Boltzmann equation taking into account dielectric saturation effects should give an estimate of any errors caused by the assumption of a uniform dielectric constant throughout the solution.

It is possible to estimate the dielectric saturation if an isolated ion is considered, simply by combining equations [I-15] or [I-16] with equation [I-19] or by following the method suggested by Laidler (45). However, if the field given by the Poisson-Boltzmann equation is used, then there is no simple way of solving the problem and numerical methods have to be used. Nevertheless, the difficulties involved in the calculations may be overcome by making use of an electronic computer in order to obtain the numerical solutions.

In the present work, we have been primarily interested in polyelectrolytes and, since these molecules can occur in different shapes (depending on the degree of ionization and molecular structure), the different models for which it is possible to write a system of differential equations and boundary conditions soluble with an electronic computer must now be considered. The charged cylinder model is probably the most important one since many polyelectrolytes may be treated as such, at least locally, when the degree of ionization is relatively high. There is a fair amount of evidence to support the validity of this model. For example, the increase in viscosity with increasing degree of ionization is usually explained in terms of change in structure of the polyelectrolyte: the repulsion between the charges on the chain will open up the coil and the polyion becomes effectively a charged rod in solution (54). Also, the observed activities of the counter-ions of many polyelectrolytes can be explained in terms of a linear model for the polyion (55).

In some cases, e.g. for highly branched polyelectrolytes and polyelectrolytes having a low degree of ionization, there is a tendency for the molecules to acquire the configuration of a random coil as in the case of flexible uncharged polymers. In such cases, the model of a charged cylinder is certainly not valid and it is then preferable to consider the polyelectrolyte as a sphere penetrable by small ions and solvent molecules. Finally, if the polymeric ion is large enough, as in the case of colloidal electrolytes, the best representation is a model based on a charged plate, e.g. as discussed in the monograph by Verwey and Overbeek (50), in the work of Levine (56) and Booth (57). Since the principal aim of the work described in this thesis is to compare the solvation of polyelectrolytes with that of simple electrolytes, the dielectric saturation near a simple ion must, of course, be examined by a similar treatment to that used in the case of the polyelectrolytes.

SALTING-OUT AND SALTING-IN

It is well known that the solubility of a non-electrolyte in water is altered by the addition of a salt. Salting-out, the most common effect, corresponds to a decrease in solubility, while salting-in corresponds to the opposite effect. Essentially, salting-out is a result of the preferential attraction of the more polar substance by the ion. Since less water is then effectively available to dissolve the non-electrolyte, its solubility will decrease.

Besides its uses in laboratory technique as a means of purification and separation of compounds, salting-out is important theoretically since it can give information about ion-solvent interactions in relation to interactions between ions and neutral molecules.

The activity coefficient of the non-electrolyte in a salt solution can be obtained directly from solubility measurements. Since, in solubility measurements, an equilibrium is established between the dissolved non-electrolyte and the undissolved pure substance, the chemical potential of the non-electrolyte must be the same in a salt solutions as in the pure corresponding solvent. Therefore, the activities are also equal, or

$$f_n S = f_n^o S_o, \qquad [I-21]$$

where S and S_o refer to the solubilities of the non-electrolyte in salt solution and in pure solvent respectively, and f_n and f_n^o are the corresponding activity coefficients. Since f_n^o is taken by definition as equal to unity, the activity coefficient of a non-electrolyte in a salt solution is given by

$$f_n = \frac{S_o}{S} \qquad [I-22]$$

It is found experimentally that the degree of salting-out is a function of concentration and can be expressed by either of the equations:

$$\ln \frac{S_o}{S} = k_s' m \quad (58)$$

or [I-23]

$$\frac{S_o - S}{S_o} = k_s m \quad (59)$$

where m is the concentration of the salt in moles per liter, k_s' and k_s are the salting-out constants. It can be shown by expanding the logarithm as a power series and retaining only the first term that the equations above are equivalent at low concentrations, and consequently, the two salting-out constants should be approximately equal.

Earlier work on this subject has been reviewed by Randall and Failey (60) and a very good account of the work done up to 1950 has been given in a review by Long and McDevit (61). A critical discussion of the main theories of salting-out covering matters not previously discussed and also the more recent work will be given in chapter III of this thesis. It may, however, be useful to note at this point the general conclusions reached from existing experimental work:

1) Salting-out is an additive property of the ions.
2) Salting-out constants decrease with increasing ionic radii and are even negative (salting-in) with large ions such as alkyl ammonium quaternary salts. The lithium ion seems to be an exception to this rule since, in general, its salting-out constant is approximately equal to that of the potassium ion.
3) The constant k_s increases with the volume of the non-electrolyte and decreases with increasing polarity of the non-electrolyte.

4) At high concentrations, the salting-out relation commences to deviate from linearity.

Salting-out by simple salts has been measured for many non-electrolytes but no work on salting-out by polyelectrolytes has apparently been recorded in the literature. Since, as will be shown, it is possible to relate extent of salting-out to degrees of primary hydration, it was considered that measurements of the salting-out of non-electrolytes by some typical polyelectrolytes would provide a useful approach to obtain experimental evidence on the hydration complementary to that deduced by means of the theoretical dielectric saturation calculations.

The main purpose of the experimental work described in this thesis has been to study the hydration of polyelectrolytes. In the theoretical work on dielectric saturation near a polyion, the case of the analogous corresponding simple ion has been used for purposes of reference since the degree of (primary) hydration at a simple ion is known, at least semi-quantitatively. For similar purposes of comparison, it has been necessary to study salting-out by simple ions which correspond (as closely as possible) to the monomer groups of the polyelectrolytes studied.

PARTIAL AND APPARENT MOLAR VOLUMES

Extensive properties of a system, e.g. volume, 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 solution may be written differentially in terms of the contributions from different constituents as

$$dV = \left(\frac{\partial V}{\partial n_1}\right) dn_1 + \left(\frac{\partial V}{\partial n_2}\right) dn_2 + \left(\frac{\partial V}{\partial n_3}\right) dn_3 + \dots \left(\frac{\partial V}{\partial n_i}\right) dn_i + \dots \quad [I\text{-}24]$$

where n_i is the amount of constituent i. The term $\partial V/\partial n_i$, when all the other parameters are held constant (P, T, n_1, n_2, ...), is called the partial specific, molal or molar volume depending on the units in which n is expressed, and is usually denoted by the symbol $\overline{V}_i$. The partial molar volume $\overline{V}_i$ 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.

It may also be shown mathematically that

$$V = \sum_{i=1}^{r} \overline{V}_i n_i \text{ (T, P constant).} \quad [I\text{-}25]$$

for a solution of r constituents.

The partial molar volume of a solute in solution is usually obtained from the apparent molar volume, which is defined by the relation

$$\phi_v = \frac{V - n_o v_o}{n_s} \qquad [I-26]$$

where n_o is the number of solvent molecules of molar volume v_o and n_s is the number of solute molecules. If n_s is expressed in terms of molarity m it may be easily shown (62) that the apparent molar volume is given quite closely by the relation

$$\phi_v = \frac{M}{d_o} - \frac{(d - d_o)1000}{md_o} \qquad [I-27]$$

where M is the molecular weight of the solute, d_o the density of the solvent and d the density of the solution. ϕ_v can therefore be obtained directly from the density of the solution.

Since, from equation [I-26] $V = n_s\phi_v + n_o v_o$, the partial molar volume is then given by

$$\overline{V}_s = \left(\frac{\partial V}{\partial n_s}\right)_{n_o,T,P} = \phi_v + n_s\left(\frac{\partial \phi_v}{\partial n_s}\right) \qquad [I-28]$$

From this equation it follows that, at infinite dilution, the partial molar volume becomes identical with the apparent molar volume.

The partial molar volumes of neutral molecules in aqueous solutions differ little from their molar volumes but for most polar molecules, and especially electrolytes, the partial molar volume is sometimes quite different from the molar volume. For most salts, the partial molar volume is smaller than the actual molar volume of the salt and this is caused by electrostriction effects near the ions. The volume decrease due to the closer packing of the water molecules in the first hydration shell will make the volume of the ions appear smaller. With some large ions, where the secondary hydration predominates, the partial molar volume may be slightly larger than the actual volume of the ions (18). Therefore, information on the relative values of partial molar or apparent molar volumes of ions should lead to comparative data on the hydration of the ions.

Darmois (63), and later Conway and Bockris (14), have shown that the hydration number of an ion can be evaluated from its apparent molar volume. By similar arguments, we can show an analogous relation for the volume of a hydrated ion.

The total volume of a solution may be written in terms of the volumes of the hydrated salt and of the pure solvent molecules by the relation

$$V = n_s v_h + (n_o - n_s) v_o \qquad [I-29]$$

where n_s is the number of hydrated salt molecules of volume v_h, n_o is the total number of water molecules of volume v_o and n is the number of water molecules associated with each salt molecule. The volume v_h can be written as

$$v_h = v_a + nv_o^h \qquad [I-30]$$

where v_a is the molar volume of the salt and v_o^h is the volume of the compressed water molecule in the first hydration shell. Eliminating n between equations [I-29] and [I-30], and introducing the apparent molar volume from equation [I-26], it follows that

$$v_h = \frac{v_a v_o - \phi_v^o v_o^h}{v_o - v_o^h} \qquad [I-31]$$

Therefore, from density measurements at different concentrations, it is possible to obtain ϕ_v^o, the apparent molar volume at infinite dilution, and consequently v_h. However, it must be remembered that this relation is based on the assumption that the ions will only affect the water molecules in the first hydration shell. This is, of course, incorrect since the secondary hydration also determines the total solvation. Also, the evaluation of reasonable values for v_o^h is difficult and limitingly low or limitingly high values must usually be considered (13). The quantity v_h is therefore an apparent hydration volume. However, the main apparent volume change of the solvent (or the electrostriction) will occur in the primary layer nearest to the ions.

If enough information about the apparent molar volumes of large ions were known, it would be possible, using an extrapolation and interpolation procedure similar to that proposed by Nightingale (11) for ionic mobility data, to relate the true hydration radius to the apparent one evaluated from equation [I-31]. However, there are not enough accurate data for ϕ_v^o for large ions available* at the moment, but the volume v_h is still useful as a basis for comparison of (relative) degrees of hydration of ions in terms of electrostriction of the solvent. In chapter III of this thesis, it will be shown that the hydration radius of a hydrated polyion can be compared with that of simple ions by making use of the relation [I-31].

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* Work is at present in progress by the writer on the determination of such data.

II. DIELECTRIC SATURATION

In this section, a series of original numerical calculations will be presented on the form of the relation between the dielectric constant of the solvent and distance from charged particles of various types: a simple spherical ion, a linear polyion, a spherical freely coiled polyion and an element of the surface of a charged colloidal particle. It will be the purpose of these calculations to give a theoretical basis for assignment of the relative extent of primary hydration of these particles compared with that for corresponding simple ions as a function of symmetry, charge density, concentration, etc., estimated in terms of a distance corresponding to an arbitrarily chosen dielectric constant in the region where the solvent dielectric constant changes rapidly from its minimum value (optical dielectric constant) to its maximum value (static dielectric constant at zero field intensity). These extents of primary hydration will be used in section III in the interpretation of the salting-out constants and apparent molar volumes of these charged particles.

A - NUMERICAL METHOD OF SOLUTION

The Poisson-Boltzmann equation is a differential equation of the second order. Therefore any numerical method capable of solving second order differential equations may, in principle, be used for our problems. Milne's method was used in the present work since it is one of the easiest to program for a digital computer, but is is by no means the only method available. Only a brief outline of this method will be given here since it is described in detail in most text-books on numerical analysis (64).

Essentially, this method will enable a solution of a differential equation to be obtained through a series of successive approximations. Let us consider a first order differential equation of the type.

$$\frac{dy}{dx} + f(x,y,) = 0;$$

the range of values of the variable over which the integration of the differential equation must be carried out is divided into N steps of equal size h. Starting at some initial point x_o, the value of y_1 at the second point $x_o + h$ is estimated from the initial value y_o, the slope $(\frac{dy}{dx})_o$ and $(d^2y/dx^2)_o$. This estimated value for y_1 is then fed into the differential equation and corrected. This is repeated until the estimated value and the corrected one differ only by a very small amount. From the first two points, their slopes and the derivatives of their slopes, a third point is estimated and corrected again by successive approximations. This procedure is repeated until the point $x_o + Nh$ is reached. Then the numerical solution of the differential equation is complete and values of y, dy/dx, d^2y/dx^2 and any functions of these variables may be obtained for each of the N steps. Therefore, provided that at some points the values of y, dy/dx, d^2y/dx^2 are known, the first order differential equation can be solved. A second order differential equation can be solved similarly by letting

$$\frac{dy}{dx} = z, \quad \frac{d^2y}{dx^2} = \frac{dz}{dx}, \quad \frac{d^3y}{dx^3} = \frac{d^2z}{dx^2}$$

and solving the two first order differential equations simultaneously.

In a second order differential equation, the values $(d^2y/dx^2)_o$ and $(d^3y/dx^3)_o$ are usually obtained directly from the differential equation while the values y_o and $(dy/dx)_o$ are obtained from the boundary conditions. In some cases, y and dy/dx cannot be determined simultaneously at one point from the boundary conditions, but either y or dy/dx is known at two points. For example, in our cases, the field strength will be known at two points but the exact value of the potential will not be known anywhere. However, the differential equation can still be solved numerically by guessing at a value for y_o. The equation is then solved in the normal way until the point x_f of the second boundary condition is reached. At this point, the calculated and exact value of $(dy/dx)_f$ are compared and the starting value y_o is corrected accordingly. Then the integration is repeated a second time, and from the two initial values $y_o(1)$ and $y_o(2)$ and the two final values

$(dy/dx)_f(1)$ and $(dy/dx)_f(2)$, a third value for y_o may be obtained by linear interpolation. This procedure is repeated until the correct value for y_o is obtained. It is obvious that the function y must be finite and continuous between the initial boundary value x_o and the final one x_f.

The program for the I.B.M. 650 computer was written in S.O.A.P. III form and was composed of three parts. The main program contained the general form of Milne's method of numerical integration capable of solving most second order differential equations. The second part contained subroutines to calculate square-roots and exponentials and in addition a floating point subroutine which calculates automatically the decimal places in each arithmetical operation. The last part of the program contained the subroutine to adapt the general program to one particular differential equation and set of boundary values. If the program had now to be rewritten, the second part could be omitted completely since these subroutines have since been incorporated in the new computer I.B.M. 650 - 4000 words.

B - SIMPLE ELECTROLYTE

The purpose of the calculations on dielectric saturation is, as we have mentioned, to make a comparison of the degrees of primary hydration of polymeric and corresponding monomeric ions. Accordingly, the first case that will be investigated is that of a simple ion in aqueous solution, so that a basis for comparison will then be available.

Model

An exact solution of the dependence of the dielectric constant of the solvent upon distance near a simple ion has previously been obtained (2, 43, 45, 46) assuming the ion to be an isolated point charge and using the electrostatic field intensity given by equation [I-19]. However, if we obtain numerical estimates of the extent of dielectric saturation of simple ions from the above model and use this data for comparison with the results obtained for the polyion case where the gegen-ion atmosphere of the polyion is normally considered (51, 52), we are in effect comparing the behaviour of a monomeric ion without an atmosphere with that of a polymeric ion with an atmosphere. Hence, in the treatment below we consider a model for the simple ion case in which a central reference ion is surrounded by a quasi-lattice arrangement of ions of the same charge, similar to that discussed by Frank (65, 66). Such a model for moderate concentrations is better than the Debye-Hückel diffuse ionic atmosphere picture which ceases to have any clear significance above 0.001 M. Also, as will be seen in the subsequent quantitative development of the problem, this model is formally exactly analogous in spherical symmetry to that for the polyion in cylindrical symmetry, previously considered (51, 52) for the case of constant solvent dielectric constant.

The Poisson-Boltzmann equation for a simple ion is usually based on the model proposed by Debye and Hückel (47). Unfortunately, this model is difficult to use since one of the boundary conditions is that the field at an infinite distance from the ion is zero. As explained before, a numerical integration cannot be carried out if one of the boundary conditions is infinity. Guggenheim (67) has suggested a method which avoids this problem. He assumed that far from the ion Debye and Hückel's approximate equation is valid; the second boundary condition can then be chosen at a suitably large distance from the ion where the potential and field are given accurately from the Debye-Hückel theory. This would not be satisfactory in our case since the dielectric constant is a function of the field and consequently of the distance from the ion. Another model is also desired since it is preferable to have a model which is quite similar in form to the one used in the case of the polyions (see section C). However, the field function for this new model for a simple ion at finite concentration does not differ to any significant extent from the Debye-Hückel field close to the ion and, consequently, the dielectric saturation effects obtained should be essentially the same for either model. A model which satisfies these requirements is described below and will be used in the subsequent calculation.

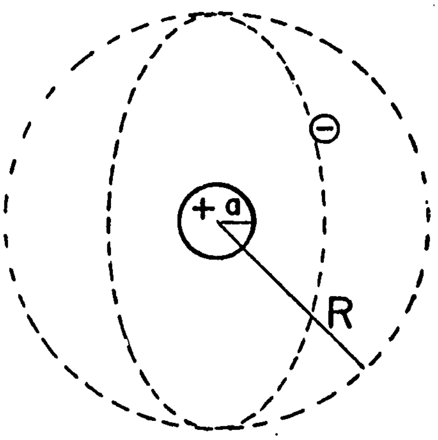
Let us assume that, on a time-average basis, the ions of the same valence z_j are equidistantly spaced (see Fig. 1). The volume of solution available to each ion j is then $(4/3)\pi R^3$ if we assume spherical symmetry. Also, let us assume that the gegen-ion of valency z_i is a point charge free to occupy any position in the volume $(4/3)\pi(R^3 - a^3)$, where "a" is the radius of the ion j or the distance of closest approach. ("a" is to be taken as the radius of the central reference ion when properties like dielectric saturation or salting-out are considered, but it is the distance of closest approach when properties such as the activity coefficient depending on ionic interaction are considered*). The relative average position of ion i with respect to the ion j is determined by the electrostatic energy of interaction and hence by the Boltzmann distribution. Consequently, the charge density in the region bounded by the two radii "a" and R (therefore depending only on the ion i) is given by

$$\sigma = n_{av} z_i e \exp\left(- \frac{z_i e \psi}{kT}\right) \qquad [II-1]$$

---

* The "a" quantities mentioned here are, of course, only identical in the case considered above where the gegen-ions are regarded as "point charges" so that the ionic radius of the central ion is then also the distance of closest approach.

Figure 1. Comparison of models, Poisson-Boltzmann equations and boundary conditions for the three cases considered: simple ion, linear polyion and planar "colloidal" ion.

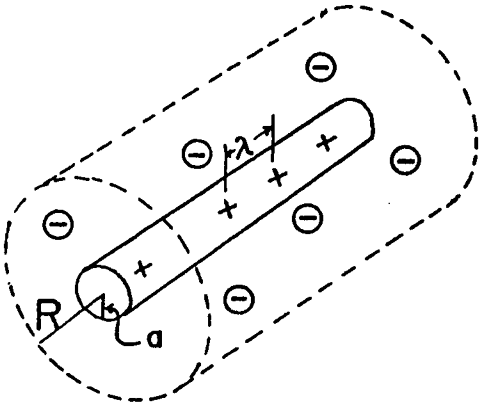


(a) SIMPLE ION

$$\frac{d^2\psi}{dr^2} = \frac{1}{\mathcal{E}d}\left\{Ke^{-\frac{Zie\psi}{kT}} - \frac{2\mathcal{E}_i}{r}\,\frac{d\psi}{dr}\right\}$$

$$\left(\frac{d\psi}{dr}\right)_R = 0\ ;\ \left(\mathcal{E}_i\frac{d\psi}{dr}\right)_a = -\frac{z_je}{a^2}$$

$$R = \left(\frac{3000}{4\pi\, mN}\right)^{1/3}$$

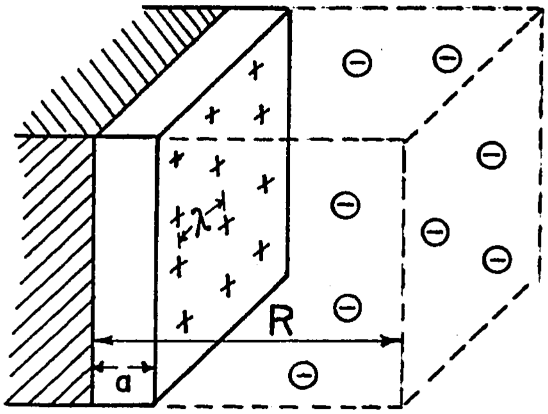


(b) POLYION

$$\frac{d^2\psi}{dr^2} = \frac{1}{\mathcal{E}d}\left\{K'e^{-\frac{Zie\psi}{kT}} - \frac{\mathcal{E}_i}{r}\,\frac{d\psi}{dr}\right\}$$

$$\left(\frac{d\psi}{dr}\right)_R = 0\ ;\ \left(\mathcal{E}_i\frac{d\psi}{dr}\right) = -\frac{2\alpha e}{a\lambda}$$

$$R = \left(\frac{1000}{\pi\, mN\lambda}\right)^{1/2}$$



(C) PLANAR COLLOIDAL ION

$$\frac{d^2\psi}{dr^2} = \frac{1}{\mathcal{E}d}\left\{K''e^{-\frac{Zie\psi}{kT}}\right\}$$

$$\left(\frac{d\psi}{dr}\right)_R = 0\ ;\ \left(\mathcal{E}_i\frac{d\psi}{dr}\right) = -\frac{4\pi e}{\lambda^2}$$

$$R = a + \frac{1000}{mN\lambda^2}$$

where n_{av} is the average concentration of ion i in molecules per c.c.

The two boundary conditions for this model are that the field strength at R is equal to zero

$$\left(\frac{d\Psi}{dr}\right)_R = 0 \qquad [II-2]$$

and that the total charge in the region from "a" to R is equal but opposite in sign to the charge on the ion j.

$$\int_a^R 4\pi r^2 \rho \, dr = -z_j e \qquad [II-3]$$

These two boundary conditions together with equation [II-1] and equation [I-18] constitute the complete Poisson-Boltzmann equation when the dielectric constant is assumed uniform.

The second boundary condition may be simplified in some cases by combining equations [II-2], [II-3] and [I-18]. Then it reduces simply to

$$\left(\varepsilon_1 \frac{d\Psi}{dr}\right)_a = - \frac{z_j e}{a^2} \qquad [II-4]$$

The parameter R can be obtained directly from the relation

$$R = \left(\frac{3000}{4\pi m N}\right)^{1/3} \qquad [II-5]$$

when the concentration m is expressed in moles per liter.

This new model is not without justification. Recently, Frank (65, 66) has shown that the ion-cloud model used by Debye and Hückel ceases to be a valid description of ionic behaviour above concentrations of about 0.001 moles/liter for a 1:1 electrolyte. He also showed that the logarithmic plot of the mean activity coefficient versus the cube-root of concentration gives a linear relation to much higher concentrations (about 0.5 moles/liter for 1:1 electrolytes) than a corresponding square-root plot. He concludes from this that the important parameter is probably the average distance between the ions since this distance varies as the cube-root of concentration (see equation [II-5]). It is well accepted that, at high concentrations, the ionic solution has a fair degree of structure and the properties of such solutions will be determined mainly by the nearest neighbour interactions (6 page 15), i.e. the solution behaves like a disorded ionic lattice.

Essentially the new model proposed takes this partial structure into account. As it will be shown subsequently, this model does in fact predict a cube-root dependence of the logarithm of the activity coefficient on concentration. Therefore, we would expect this model to be valid at intermediate concentrations while the Debye-Hückel model is preferable in more dilute solutions*.

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* Since completion of these calculations and the writing of this section, Fuoss presented closely similar ideas at a lecture at the National Research Council on April 13th, 1961.

The dielectric constant used in the Poisson equation (equation [I-18]) was the integral dielectric constant, since this is the usual one appearing in electrostatic theories. Grahame (43) has stated, however, that the differential dielectric constant should be used whenever the dielectric constant is taken as a variable in the Poisson-Boltzmann equation. If the differential equation [I-18] is solved in this case, a definitely incorrect dependence of the dielectric constant on the distance from the ion is obtained, as will be shown later. Grahame in his treatment expressed the Poisson equation in a different form, as shown below, when the differential dielectric constant was used:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Psi}{dr}\right) = -\frac{4\pi\sigma}{\mathcal{E}_d} \qquad [II-6]$$

The use of this equation can be shown to be correct if the Poisson equation is expressed in one dimension only. Thus, we may write the Poisson equation in one dimension in the two forms

$$\nabla^2(\Psi)_i = \frac{d}{dr}\left(\mathcal{E}_i\frac{d\Psi}{dr}\right) = -4\pi\sigma \qquad (a)$$

$$[II-7]$$

$$\nabla^2(\Psi)_d = \mathcal{E}_d\frac{d^2\Psi}{dr^2} = -4\pi\sigma \qquad (b)$$

By writing $\mathcal{E}_d$ in term of $\mathcal{E}_i$ (equation [I-4]) it may be easily shown that these two differential equations are equivalent. Grahame was interested in the one-dimensional case since his Poisson-Boltzmann equation was applied to the case of the double-layer at a flat electrode. Therefore, in his case, it was possible to use the differential dielectric constant and obtain the same result as if the integral dielectric constant had been used, as in [II-7 (a)]. Unfortunately, this is not true if the Poisson equation is expressed in three dimensions and the difference between the two equations in polar coordinates for spherical symmetry is then

$$\nabla^2(\Psi)_1 - \nabla^2(\Psi)_d = \frac{2}{r}\frac{d}{dr}(\mathcal{E}_1 - \mathcal{E}_d) \qquad [II\text{-}8]$$

Since this term is effectively omitted if the differential dielectric constant is used in equation [II-6], it seems that the only correct way of writing the Poisson equation is to use equation [I-18] with the integral dielectric constant. Recently, Mikulin (68) has attempted to correct the Debye-Hückel theory by taking into account the effect of dielectric saturation. He attempted, in fact, to correct an approximate solution of the Poisson-Boltzmann equation and not an exact solution as we are attempting to do here; however, the important point to be noted concerning his work is that the integral dielectric constant is used and not the differential one.

Computation procedure

From equations [II-1] and [II-6], we may write the Poisson-Boltzmann equation for an ion in an electrolyte solution at finite concentration in the form

$$\frac{d^2\psi}{dr^2} = \frac{1}{\mathcal{E}_d}\left\{-\frac{4\pi e z_i mN}{1000}\exp\left(-\frac{z_i e\psi}{kT}\right) - \frac{2\mathcal{E}_i}{r}\frac{d\psi}{dr}\right\} \qquad [II\text{-}9]$$

The complete differential equation is then given from equations [II-9] using terms defined by [I-15] and [I-16].

We require, for numerical computation, the starting values ψ, $(d\psi/dr)$, $(d^2\psi/dr^2)$ and $(d^3\psi/dr^3)$ at R. From the first boundary condition, $(d\psi/dr)_R = 0$ and consequently from equation [I-15] and [I-16], $\mathcal{E}_i = \mathcal{E}_d = \mathcal{E}_o$. From equation [II-9],

$$\left(\frac{d^2\psi}{dr^2}\right)_R = -\frac{4\pi e z_i mN}{1000\ \mathcal{E}_o}\exp\left(-\frac{z_i e\psi_R}{kT}\right) \qquad [II\text{-}10]$$

Differentiating equation [II-9] with respect to distance r and writing the result at r = R gives

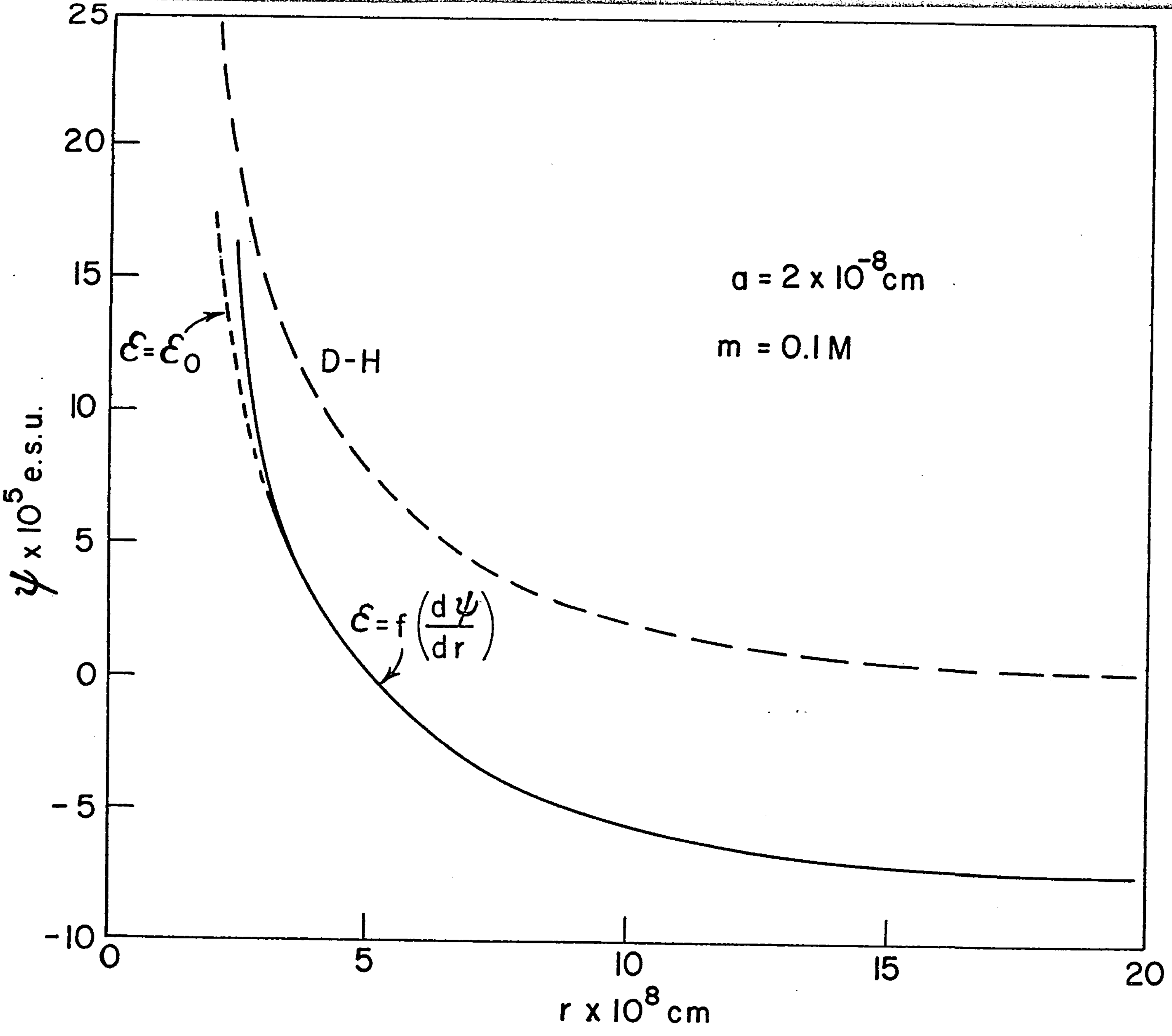
$$\left(\frac{d^3\psi}{dr^3}\right)_R = -\frac{2}{R}\left(\frac{d^2\psi}{dr^2}\right)_R \qquad [II\text{-}11]$$

Hence the only parameter required which is still unknown is ψ_R. As was described above, this value is guessed at and the equation is integrated numerically until the point r = a is reached. The quantity $(\mathcal{E}_i\ d\psi/dr)_a$ is then evaluated and compared with equation [II-4]. From the difference between $(\mathcal{E}_i d\psi/dr)_a$ and the value of the second boundary condition given by [II-4], the initial value ψ_R is corrected and the integration is then repeated. After the second run, a third value for ψ_R is obtained by linear interpolation and the procedure is repeated until the correct starting value is obtained.

The starting value for ψ_R was evaluated by the method indicated above and it was found that ψ_R, when the dielectric constant was assumed uniform throughout the solution, was in fact equal to the value of ψ_R when $\mathcal{E}_1$ was assumed to be a function of the field intensity (see Fig. 2). It was hence sufficient to evaluate the starting values for ψ_R assuming $\mathcal{E}_1 = \mathcal{E}_o$ and use the same values for the regular differential equation. Physically, the reason for this finding is that, except in very strong solutions, the dielectric saturation effects are negligible at appreciable distances (R) from the ions.

The choice of the size of each step in the integration did not cause any difficulties. It was chosen such that the total number of steps would be between 18 and 50. To ensure that the computation error would remain less than one percent, the initial values were calculated to five significant figures and the remaining values to four. A few check runs were made in which the number of steps and the number of significant figures were increased and only the fourth significant figure was affected. The error increases, of course, at each step and, if a large number of steps is used, the

Figure 2. Comparison of potential functions obtained from the Debye-Hückel theory with those obtained from the present modified theory for simple ion solutions.



a = 2 x 10^{-8}cm
m = 0.1 M
D-H
$\mathcal{E}=\mathcal{E}_0$
$\mathcal{E}=f\left(\frac{d\psi}{dr}\right)$
25
20
15
10
5
0
-5
-10
ψ x 10^5 e.s.u.
0
5
10
15
20
r x 10^8 cm

errors on the last steps become appreciable. For this reason, data for very dilute solutions are not very reliable.

Another slight difficulty arose from the rounding off of the parameter R. This was necessary since the distance between "a" and R must be divisible into N equal parts or steps for the computations. By a suitable choice of size of step, it was usually possible to keep this error small. It was realized later that this error could have been avoided completely by fixing R rather than the concentration and calculating the concentration corresponding to a fixed value for R (see equation [II-5]).

The overall accuracy of the numerical results of the computation is estimated to be better than one percent. Very good methods have been devised to estimate the error in numerical integrations (69) but, since the parameters used in our differential equation are often not known to better than one percent (for example b in [I-15]), a rigorous estimation of the error was not made.

The largest source of error in the computations probably arises from the calculation of the integral dielectric constant which involves the evaluation of arctan $b^{1/2}E$. This was achieved by means of a series expansion* of this

---

* We have found, after the computations were terminated, that standard programs have been written to calculate $\tan^{-1} x$ rapidly and precisely with an electronic computer. The use of such subroutines would have eliminated possible errors introduced by the above series.

term as follows:

$$y = \tan^{-1}x = x - \frac{x^3}{3} + \frac{x^5}{5} - \frac{x^7}{7} + \frac{x^9}{9} - \frac{x^{11}}{11} \text{ for } x < 1$$

$$y = \frac{\pi}{2} - \tan^{-1}\frac{1}{x} = \frac{\pi}{2} - \frac{1}{x} + \frac{1}{3x^3} - \frac{1}{5x^5} + \frac{1}{7x^7} - \frac{1}{9x^9} + \frac{1}{11x^{11}}$$

$$\text{for } x > 1$$

This series converges fairly rapidly except in the region where x is close to unity. In the latter case, the error is as large as 5%. Fortunately, this error occurs at rather high field strength and it will be shown below that this error will not affect our results since we will use the dielectric constant at a lower field strength (where the error is evaluating $\mathcal{E}_i$ is small) in the comparison of the relative degree of primary hydration of different types of charged particles.

Results

The Poisson-Boltzmann equation was solved for different values of the parameters "a", m and z_j, using $\mathcal{E}_d$ and $\mathcal{E}_i$ both as constants and as functions of the field intensity. The values for Ψ, $d\Psi/dr$, $\mathcal{E}_i$, and $\mathcal{E}_d$ as a function of r are given in the appendix and some of the results are plotted in Figures 2 to 5.

In Figure 2 the potential is plotted against the distance from a cation of radius 2 Å.* The concentration was taken as 0.1 molar. The potential calculated from the Debye-Hückel theory was compared with our values and it is interesting to note that the derivative of the potential with respect to the distance from the ion, i.e. field intensity, is very similar in both cases if the dielectric constant is assumed continuous (see Fig. 2). The main difference between the two solutions is in the absolute value of the potential; in the Debye-Hückel theory the potential tends to zero far from the ion, while in our case it tends to a constant negative value at R, where $\psi = \psi_R$, between the ions. The appearance of a negative potential is not surprising (it occurs also in the polyion case) and it simply means that the local time-average concentration of the anion is lower in that region than the average concentration. The significance of this change in sign of the potential function will be more obvious when the polyelectrolyte case will be discussed.

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* Here a limiting radius of 2 Å is chosen since it becomes very difficult to solve the Poisson-Boltzmann equation numerically for shorter distances, i.e. $d\psi/dr$ and $d^2\psi/dr^2$ increase exponentially and become very large at short distances from the ion. While most simple ions have a radius less than 2 Å, our results are still significant since we will show that the dielectric saturation does not depend very much on the radii of simple ions.

It should be noted also that, although the absolute values of the potentials calculated from the two theories differ appreciably, the values of $\psi_a - \psi_\infty$ from the Debye-Hückel theory and $\psi_a - \psi_R$ from the present calculations compare quite reasonably when "a" is taken fairly large. It is from this difference term that the activity coefficient would be calculated if required. Following the procedure described by Robinson and Stokes (6, page 227) for the calculation of the activity coefficient, the potential at a distance r from an ion may be written as a sum of the two terms.

$$\psi = \psi(I) + \psi(NI)$$

where $\psi(I)$ is the ideal potential due to the central reference ion only and $\psi(NI)$ is the non-ideal potential contribution due to the ionic atmosphere. The total difference in non-ideal potential is therefore given by

$$\psi_a(NI) - \psi_R(NI) = \psi_a - \psi_R - \psi_a(I)$$

since the lower limit of $\psi(I)$ is equal to zero. The change in electrostatic free energy for one mole corresponding to this change in non-ideal potential is

$$\Delta G(NI) = \frac{z_j eN}{2} (\psi_a - \psi_R - \psi_a(I)) \qquad [II-12]$$

The 2 in the denominator is introduced since the ions are effectively counted twice, once as the reference ion and once as part of the atmosphere. The total change in free energy may also be separated into an ideal and a non-ideal part.

$$\Delta G = \Delta G(I) + \Delta G(NI)$$

$$= RT \ln(f_j m) = RT \ln m + RT \ln f_j$$

Therefore,

$$\Delta G(NI) = RT \ln f_j \qquad [II\text{-}13]$$

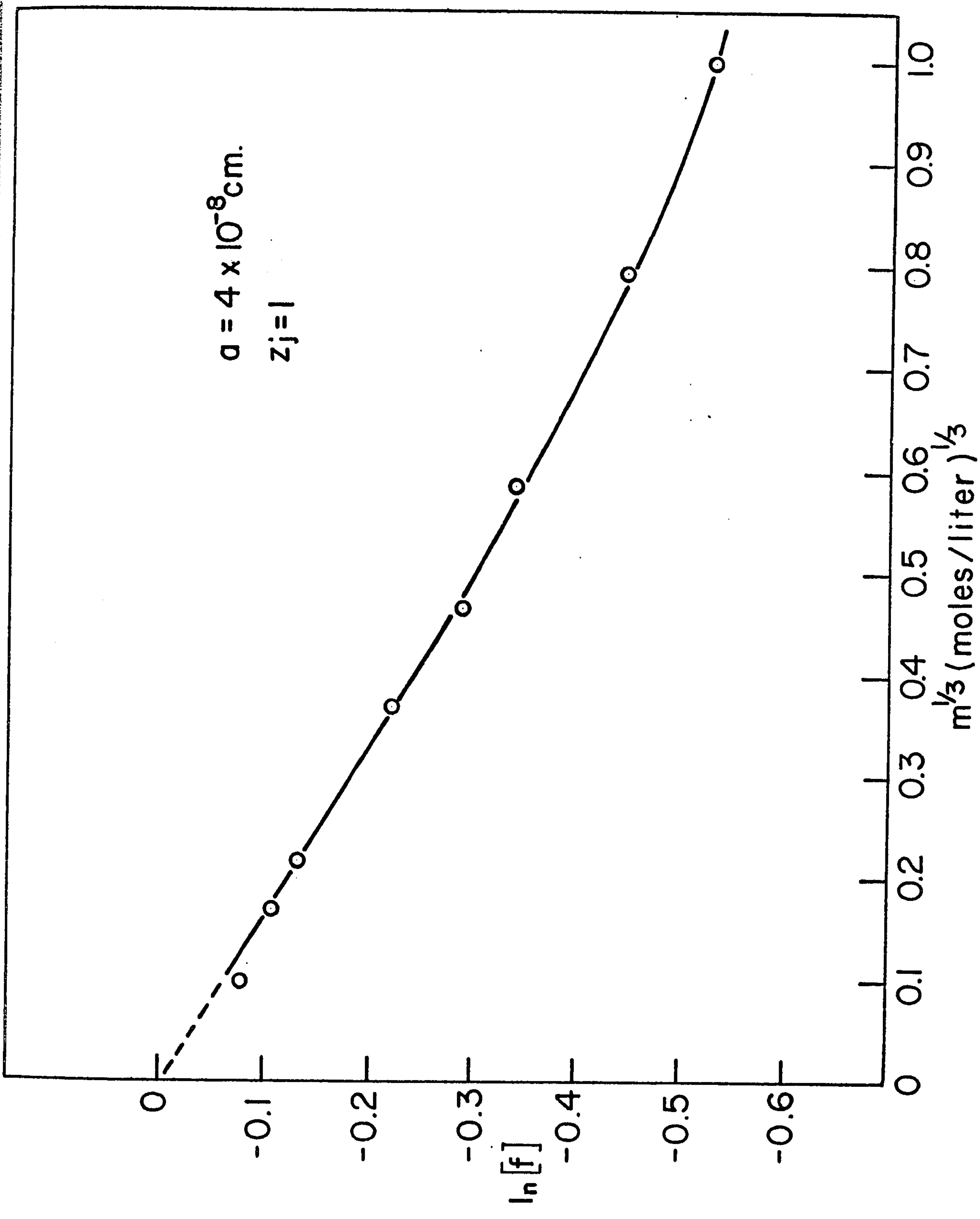
Replacing $\psi_a(I)$ by $z_j e/\mathcal{E}_0 a$, the activity coefficient is then obtained from equations [II-12] and [II-13] as

$$\ln f_j = -\frac{z_j e}{2kT}\left(\frac{z_j e}{\mathcal{E}_0 a} - \psi_a + \psi_R\right). \qquad [II\text{-}14]$$

In order to check our model, the logarithm of the activity coefficient has been plotted against concentration in Fig. 3 for a 1:1 electrolyte taking the distance of closest approach as 4 Å. It is found that a cube-root plot gives a straight line up to about 0.5 molar. Frank (65) has actually shown that this is found experimentally and this confirms our statement that the form of our model is correct for relatively strong solutions. The scatter of points in Fig. 2 is a result of the error introduced by rounding off the parameter R.

In order to demonstrate the consequence of using the wrong form of dielectric constant in the Poisson-Boltzmann equation, the latter equation was solved using the differential

Figure 3. Cube-root dependence of the logarithm of the activity coefficient on concentration.



a = 4 x 10⁻⁸ cm.
zj = 1
ln [f]
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
m1/3 (moles/liter)1/3

dielectric constant instead of the integral dielectric constant as written in equation [I-18] and also in equation [II-6]. These two incorrect solutions (I and III) are compared with the correct solution (II) for a monovalent ion of radius 2 Å and concentration of 0.1 M in Fig. 4. It is therefore obvious from this graph that the choice of the dielectric constant used in a particular equation is very important and the use of the wrong one may lead to erroneous results.

The variation of dielectric constant with distance from the ion is given in Fig. 5 for the case where a = 2 Å and m = 0.1 mole per liter. In this case, it was not possible to solve the differential equation from R to "a" since the values of $d\Psi/dr$ and $d^2\Psi/dr^2$ become too large for the computer to handle at a distance of about 2.5 Å from the ion. The starting values were obtained from a previous run where the dielectric constant was assumed to be equal to $\mathcal{E}_o$ throughout the solution. The integrand was then evaluated numerically at each step until the computer stopped. The low values of the dielectric constant in Fig. 3 are obtained by extrapolation and are represented by broken lines. The exact solutions were compared with the solutions which neglect the distribution of ions i.e. for the case of an isolated ion. The differential and integral dielectric constants were evaluated in this case by the method suggested by Laidler (45).

Figure 4. Comparison of dielectric saturation effects evaluated from different forms of the Poisson-Boltzmann equation (simple ion model).

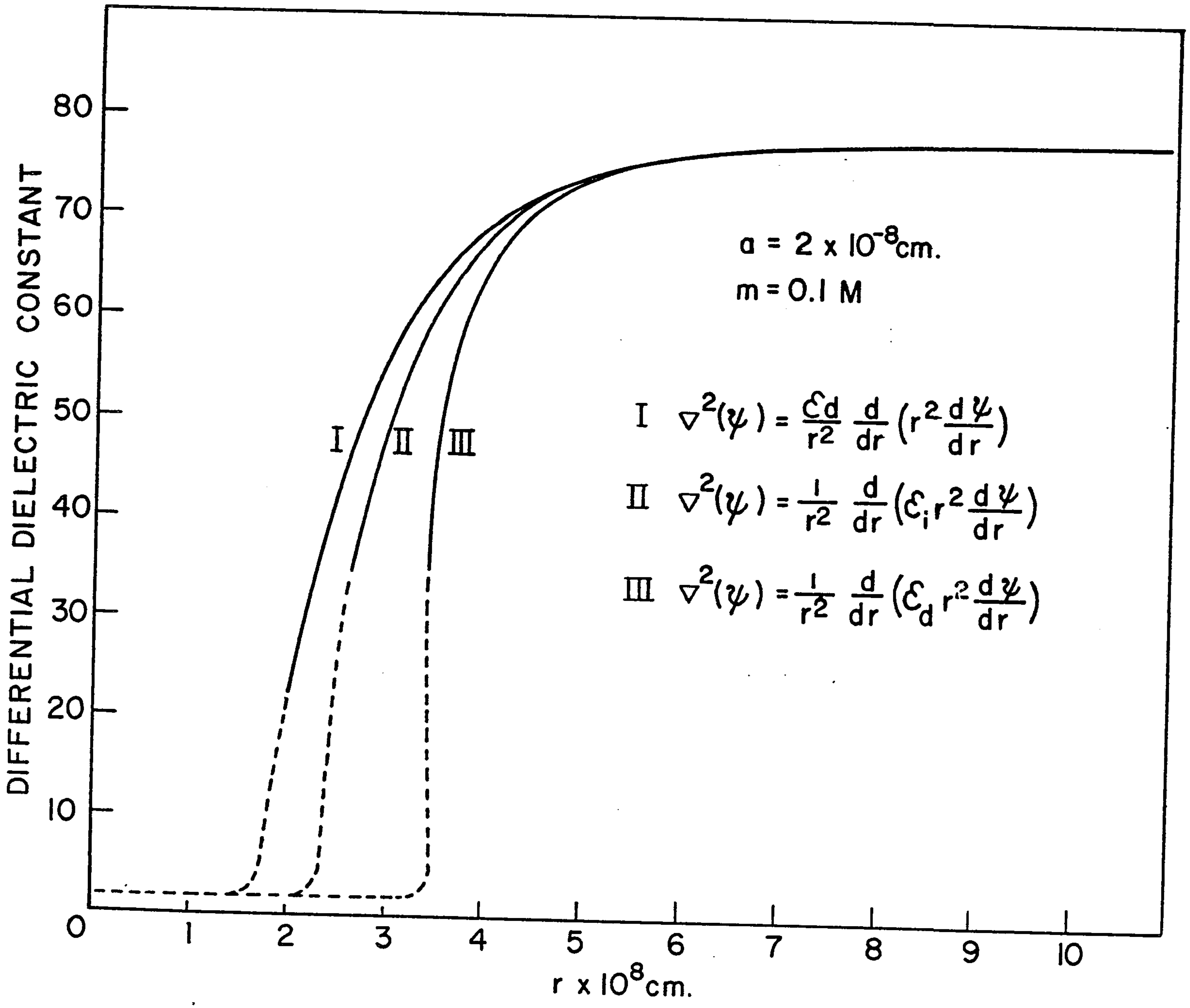
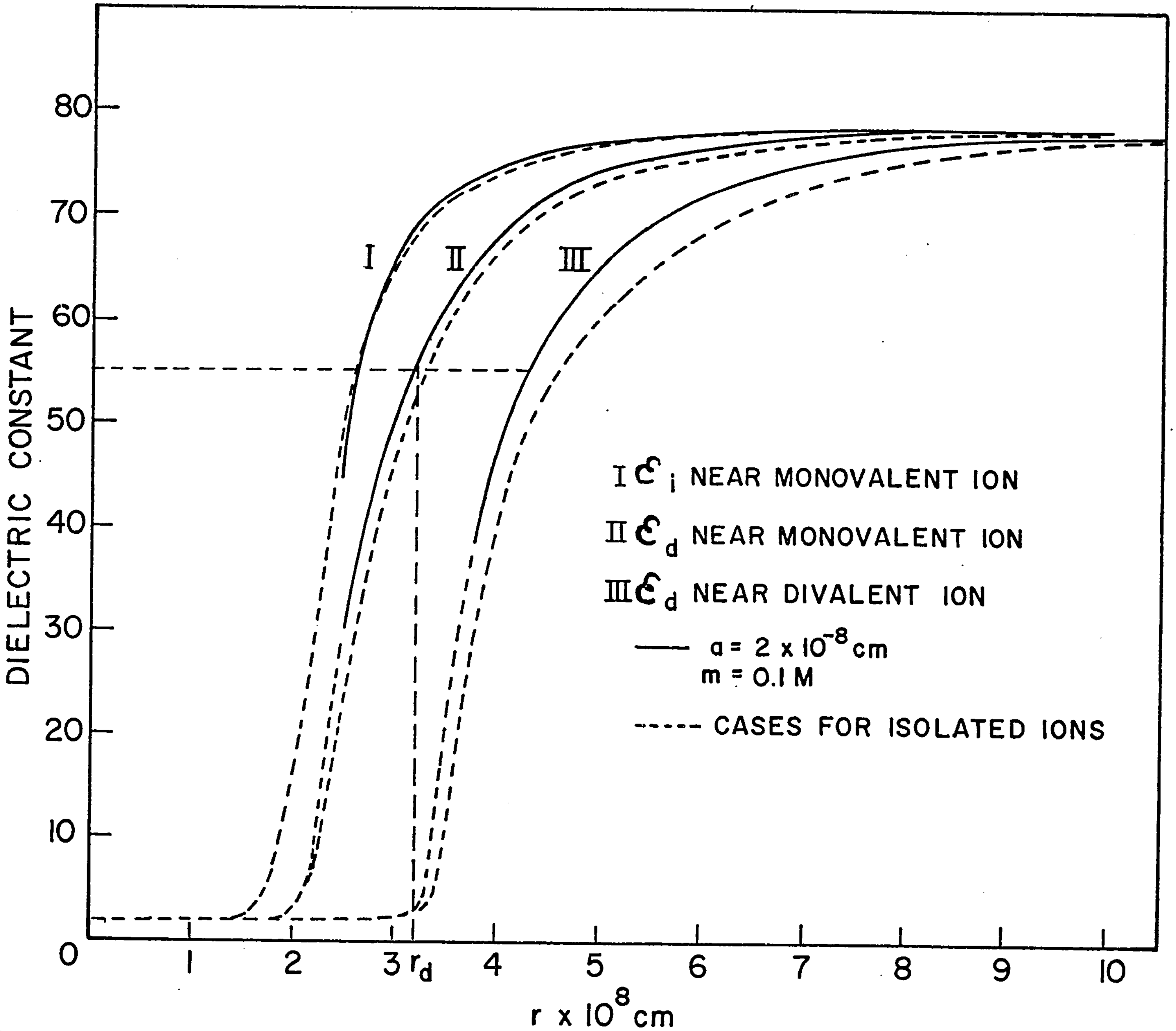

DIFFERENTIAL DIELECTRIC CONSTANT
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7
8
9
10
$r \times 10^8$ cm.
$a = 2 \times 10^{-8}$ cm.
m = 0.1 M
I
II
III
I $\nabla^2(\psi) = \frac{\mathcal{E}_d}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)$
II $\nabla^2(\psi) = \frac{1}{r^2}\frac{d}{dr}\left(\mathcal{E}_i r^2\frac{d\psi}{dr}\right)$
III $\nabla^2(\psi) = \frac{1}{r^2}\frac{d}{dr}\left(\mathcal{E}_d r^2\frac{d\psi}{dr}\right)$

Figure 5. Differential and integral dielectric constants of the solvent near monovalent and divalent ions.


DIELECTRIC CONSTANT
0
10
20
30
40
50
60
70
80
1
2
3
r_d
4
5
6
7
8
9
10
$r \times 10^8$ cm
I
II
III
I ε_i NEAR MONOVALENT ION
II ε_d NEAR MONOVALENT ION
III ε_d NEAR DIVALENT ION
—— $a = 2 \times 10^{-8}$ cm
$m = 0.1$ M
----- CASES FOR ISOLATED IONS

It is interesting to note that the differential dielectric constants calculated by both methods agree fairly well. The small deviation between the two solutions is certainly expected since the field obtained from the Poisson-Boltzmann equation (i.e. with ionic atmosphere) is always smaller than the simple electrostatic field except at "a" where they are equal.

The values of the integral dielectric constant calculated by both methods do not agree as well as those of the differential dielectric constant at shorter distances from the ion. The dielectric constant calculated from the Poisson-Boltzmann equation may be slightly in error in this case since the integral dielectric constant was evaluated by a series expansion of the arctan $b^{1/2}E$. This series converges rapidly everywhere except when $b^{1/2}E$ has a value near unity. This corresponds to a field strength of about 10^4 e.s.u. or a value of ε_i of about 60. The numerical calculations in the region corresponding to a field larger than 10^4 e.s.u. will be in error since the accuracy of the series expansion is only 5% in this region and the error accumulates at each step. This explains why the integral dielectric constant calculated from the Poisson-Boltzmann equation suddenly becomes smaller than the one calculated for the isolated ion.

It should be noted at this point that Azzam (7, 70, 71) has recently suggested a method of evaluating the absolute hydration of a ion taking into account dielectric saturation effects, Essentially, he calculates the number of hydration water molecules ds in the shell between the distance r and r + dr from the equation

$$ds = 4\pi n_o \exp(-W/kT)\, r^2 dr$$

where n_o is the number of solvent molecules in the bulk per unit volume and W is the net potential energy of a solvent molecule in the solvation sheath.

His method is correct in principle and could prove to be very valuable. Unfortunately, Azzam's calculations are not very reliable since in correcting W for dielectric saturation, he has assumed that Webb's theory (72) of dielectric saturation is correct; this theory, being similar to Debye's theory of dielectric saturation is now known to be incorrect (see page 18). He also considers an isolated ion in his theory and we have shown that this approximation for solutions of finite concentration is valid for a monovalent ion but not very satisfactory for higher valency ions which he is also considering. Several of Azzam's conclusions are also doubtful; he claims that all small divalent ions form a "stable hydrate entity" in aqueous solutions, that is, the water molecules are held chemically. This seems to contradict Taube's (3) experimental evidence who found that only a few trivalent ions form stable "chemical" hydrates in solution.

Finally, he suggests that "structure-breaking" effects will not affect the hydration of the ions to any significant extent. This is probably true for small or high-valent ions, but is not true for large ions such as tetra-alkyl ammonium ions which have, for example, apparent molar volumes <u>larger</u> than their actual respective molar volumes (18, 73). This apparent negative electrostriction and hence "hydration" can also be used to explain salting-in which is observed with these ions (see chapter III).

In the present work we are not attempting to predict the absolute values of the extent of the first hydration shell (which would in any case depend to some extent on the definition of this shell) but simply to compare the relative degrees of hydration of different charged species. Therefore, calculations such those used by Azzam are not required. From a theoretical point of view comparison of the degrees of dielectric saturation for analogous models, based on similar assumptions, is sufficient.

Booth's theory (41, 42) for the dependence of the dielectric constant of water on the field intensity takes into account the size and partial structure of water; however, when the dielectric constant is plotted as a function of distance from an ion, the assumption is now made that the solvent is dimensionless, i.e. the finite size of water molecules is neglected. If this model was correct, the radius of a hydrated ion could be predicted easily by considering the distance at which the dielectric constant suddenly falls to its minimum value (at about 2.5 Å from the centre of a simple monovalent ion). However, if the finite size of the water molecules is taken into account, this method would tend to underestimate the primary hydration radius. To illustrate this, we will consider the Li^+ ion which is known to have a relatively strongly bound primary hydration shell. The crystal radius "a" of this ion is about 0.60 Å and that of water, a_w, is 1.38 Å. Therefore $a + a_w$, the distance of closest approach of the water molecule and the ion, is 1.98 Å. Within this distance, both the integral and differential dielectric constants have quite low values and, consequently, the interaction energy between the two particles is strong enough to immobilize completely the water molecule. Therefore, the hydration radius will be, as a first approximation, $a + 2a_w = 3.36$ Å. From these considerations, the hydration radii of simple monovalent ions should have values of about 3 to 3.5 Å and this agrees very well with the values suggested by Nightingale (see table 1).

In order to compare the <u>relative</u> degree of primary hydration of different charged particles, we have defined the distance at which the differential dielectric constant is equal to 55 as r_d. The choice of the value 55 for the dielectric constant is quite arbitrary but, we believe, reasonable as a reference point on account of the following considerations. For a monovalent ion, r_d is equal to about 3.2 Å and we have shown this to be a reasonable value for hydration radii of these ions (see table 1). Also the theoretical calculation of the dielectric constant should be reliable at this distance; at shorter distances, the field intensity becomes quite large and the reliability of Booth's theory becomes more doubtful and at these distances the van der Waals' short range forces may become important. Finally, the error introduced in our calculations by expanding arctan $(b^{1/2}E)$ is small for field values corresponding to $\mathcal{E}_d = 55$. Furthermore, the dielectric constant tends to decrease rather rapidly with decreasing r below this value of $\mathcal{E}_d = 55$.

The dielectric saturation effect was also evaluated for a 2:1 electrolyte and the differential dielectric constant is plotted in Fig. 5 as a function of the distance from the divalent ion. The solution obtained in the present calculations from the Poisson-Boltzmann equation was again compared with the one obtained assuming an isolated ion (45) and the difference between the two solutions is much larger than in the case of monovalent ions. This is expected since the non-ideality of the solution increases with the valency of the ions in solution.

The value of r_d as defined above for a divalent ion is found to be 4.3 Å and this corresponds very closely to the averaged hydration radii of divalent ions on Nightingale's scale (table 1). Therefore, it appears that a comparison of the parameter r_d for different models (and different variables such as concentration, charge density and crystal radius) will give us a direct measure of the relative degree of primary hydration. Therefore, provided there are no specific effects such as hydrogen bonding involved, it should be possible to predict from dielectric saturation calculations the degree of primary hydration of polyions and colloidal ions and evaluate the dependence of hydration on the various parameters mentioned above.

The dependence of the degree of dielectric saturation on concentration was investigated and it was found that r_d for monovalent ions increases slightly with increasing dilution but the effect is rather small. The difference in r_d when the concentration m changes from 1 M to 0.01 M is only approximately 0.05 Å. Therefore, as a first approximation, it may be assumed that the hydration of an ion is independent of concentration below 1 M, and it is then sufficient to choose one concentration, say one molar, and vary the other parameters such as radius of the ion and charge density.

The dependence of the degree of dielectric saturation on the radius of the ion is demonstrated in Fig. 16. These results would predict a small increase in hydration radii with increasing crystal radii. This is actually observed experimentally for ions with a crystal radius larger than 2 Å (11). For smaller ions the opposite effect is observed; the limit of primary hydration increases with decreasing ion size. This is probably due to structural effects or stronger interactions between the ion and the solvent.

The effect of dielectric saturation on the potential function is shown in Fig. 2. The differential equation was solved assuming in one case that the dielectric constant was uniform and assuming in another case that it was a function of the field intensity. The two solutions start to be significantly different at distances less than 5 Å from the ion. Therefore, for theories of electrolytic solutions involving the distance of closest approach, the assumption of a uniform dielectric constant is justifiable provided the distance of closeet approach can be taken as being at least 4 Å.

The deviation between the two solutions for the field function is slightly larger than that for the potential function discussed above and begins to be significant at about the same distance as does the deviation for the potential function.

C - POLYELECTROLYTE

Charged rod model

The charged rod model is probably the most valid one for most simple polyelectrolytes such as, for example, the synthetic vinyl polyelectrolytes, linear polyphosphates, polymines, etc. The Poisson-Boltzmann equation based on this model has been solved exactly independently by Alfrey, Berg and Morawetz (51) and by Fuoss, Katchalsky and Lifson (52) with the assumption that the dielectric constant is uniform throughout the solution. The same model will be used here, except that the dielectric constant will be taken as a function of the field intensity, since we are specifically interested in the behaviour at short distances from the polyions in relation to their hydration.

It is assumed that the polyelectrolyte molecules are long thin rods, uniformly charged and parallel to each other (51, 52), the radius of the cylindrical volume element of solution available to each polyion being R. The gegenions, taken as point charges, are regarded as being distributed statistically in the annular cylindrical region between the radii "a" and R. Again "a" is defined as either the radius of the polyion or the distance of closest approach depending on the function investigated. Comparison of this model with the simple ion case is given in Fig. 1. The

Poisson equation for such a model is

$$\nabla^2(\Psi) = \frac{1}{r}\frac{d}{dr}\left(\mathcal{E}_i r \frac{d\Psi}{dr}\right) = -4\pi\sigma \qquad [II\text{-}16]$$

In the region between "a" and R, the charge density is due to the counterions only, and if the counterions are univalent anions, then from the Boltzmann distribution law

$$\sigma = -\frac{\alpha\ e\ m\ N}{1000}\exp\left(\frac{e\Psi}{kT}\right) \qquad [II\text{-}17]$$

where α is the degree of ionization and m the concentration in moles per liter of the counterions.

Combining equations [II-16] and [II-17] and rearranging, the total differential equation can be written in this case as

$$\frac{d^2\Psi}{dr^2} = \frac{1}{\mathcal{E}_d}\left\{\frac{4\pi e\alpha mN}{1000}\exp\left(\frac{e\Psi}{kT}\right) - \frac{\mathcal{E}_i}{r}\frac{d\Psi}{dr}\right\} \qquad [II\text{-}18]$$

where $\mathcal{E}_i$ and $\mathcal{E}_d$ are defined by equations [I-15] and [I-16].

The first boundary condition is that the field at R is equal to zero, as in the simpler case discussed above:

$$\left(\frac{d\Psi}{dr}\right)_R = 0 \qquad [II\text{-}19]$$

The parameter R can be regarded as defined by the relation

$$R = \left(\frac{1000}{\pi m N \lambda}\right)^{1/2} \qquad [II-20]$$

where λ is the distance between ionizable groups on the polymer chain.

For the second boundary condition, it is assumed that the total charge in the region "a" to R is equal but opposite in sign to the charge on the cylinder, i.e.,

$$\int_a^R 2\pi r \sigma \, dr = - \frac{\alpha e}{\lambda} \qquad [II-21]$$

By substituting the value for σ obtained from equation [II-16] the second boundary condition reduces to

$$\left(\mathcal{E}_1 \frac{d\psi}{dr}\right)_a = - \frac{2\alpha e}{a\lambda} \qquad [II-22]$$

The starting conditions for the numerical integration are

$$\left(\frac{d\psi}{dr}\right)_R = 0 \; ;$$

$$\left(\frac{d^2\psi}{dr^2}\right)_R = \frac{4\pi e m N \alpha}{1000\, \mathcal{E}_0} \exp \left(\frac{e\,\psi_R}{kT}\right)$$

and

$$\left(\frac{d^3\psi}{dr^3}\right)_R = - \frac{1}{R} \left(\frac{d^2\psi}{dr^2}\right)_R \; . \qquad [II-23]$$

The starting value ψ_R is obtained in the same way as described for the case of the simple ion. The computational procedure was also the same and did not present any new difficulties.

Results for the charged rod model

The variable parameters in the problem for rod-shaped particles are the concentration m, the degree of ionization α and the radius of the ion "a". The distance between ionizable groups λ was kept constant throughout the series of calculations and was taken as 2.5 Å (51) the approximate effective value for vinyl polyions. The temperature was taken as 298° K and the dielectric constant at zero field strength as 78.5.

The numerical solution was checked by comparing the results obtained without dielectric saturation with those obtained from the equation of Alfrey, Berg and Morawetz (51) and the results agree within the computational error estimated as one percent.

The calculated values for ψ, $d\psi/dr$, $\mathcal{E}_i$ and $\mathcal{E}_d$ are given as a function of r in the Appendix and some of the results are plotted in Figs. 6 to 10. As in the case of the simple ion, the distance at which the differential dielectric constant is equal to 55 will again be defined as r_d for the purposes of comparing the degree of dielectric saturation and the extent of the primary hydration.

The extent of dielectric saturation increases slightly with dilution. The distance r_d changes from 4.25 Å at 1 M to 4.5 Å at 0.05 M for a molecule for which $a = 3.2$ Å and $\alpha = 0.6$. Solutions of the Poisson-Boltzmann equation for dilute solutions are difficult since it involves taking many integration steps and this increases the error significantly. Since the degree of dielectric saturation does not vary very much with concentration, most of the runs were carried out for unit normality (i.e. for 1 M concentration of the "monomer" units). Figure 6 also indicates that the shape of the potential function is the same for all concentrations. This is not surprising since the two boundary conditions are independent of concentration and the only parameter affected by the concentration is R. Consequently, the field intensity at the two boundary conditions is independent of concentration but the variation of field with distance changes with concentration in the intermediate region. This is the reason for the slight increase in dielectric saturation with dilution. Since the effect of concentration on dielectric saturation is small, we can proceed to make comparisons for different degrees of ionization - a more important and interesting variable.

In Fig. 7, the variation of the differential dielectric constant with distance was plotted for different values of α and this was compared with the results obtained

Figure 6. Functions for variation of potential near a linear polyion for different concentrations.

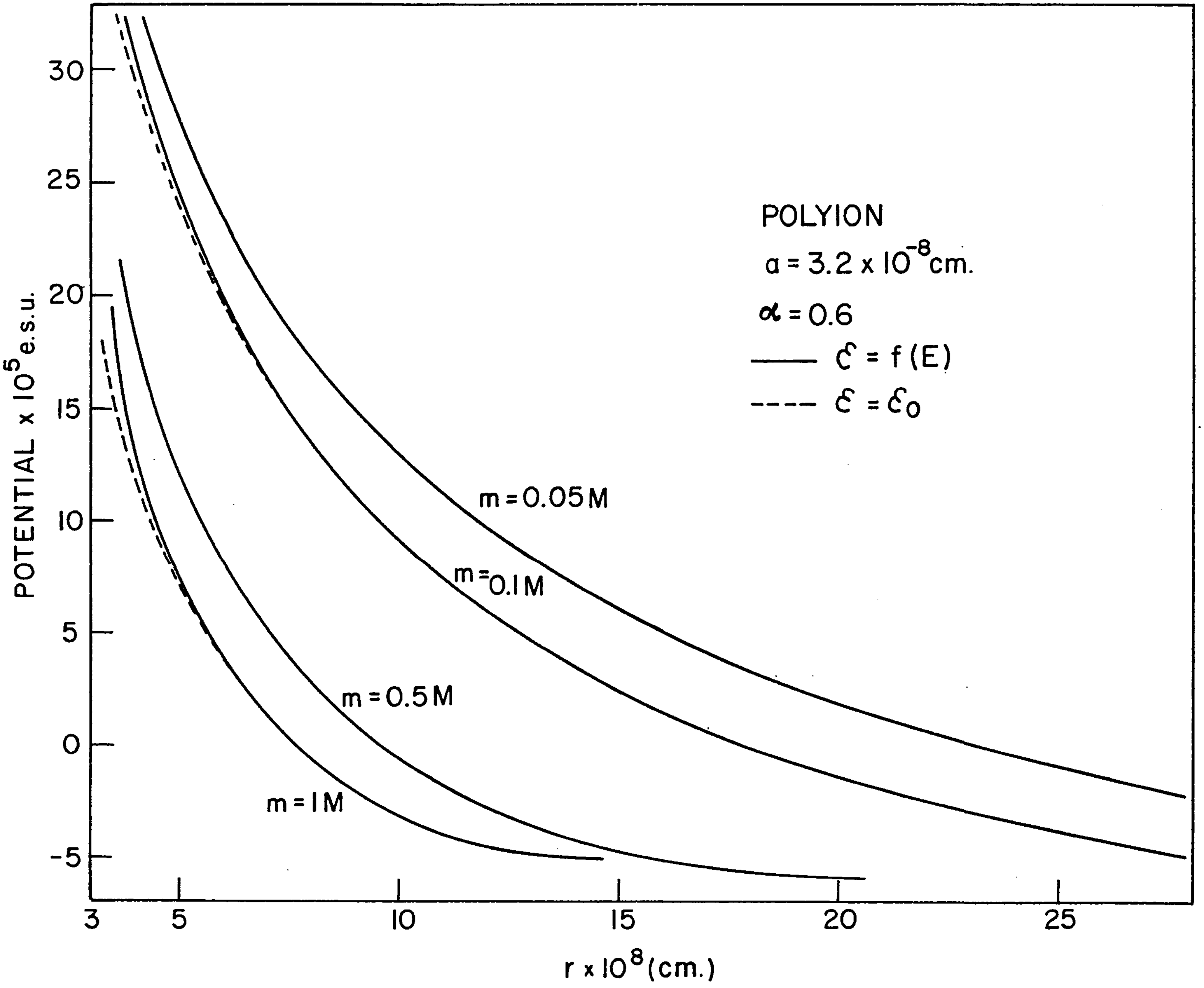
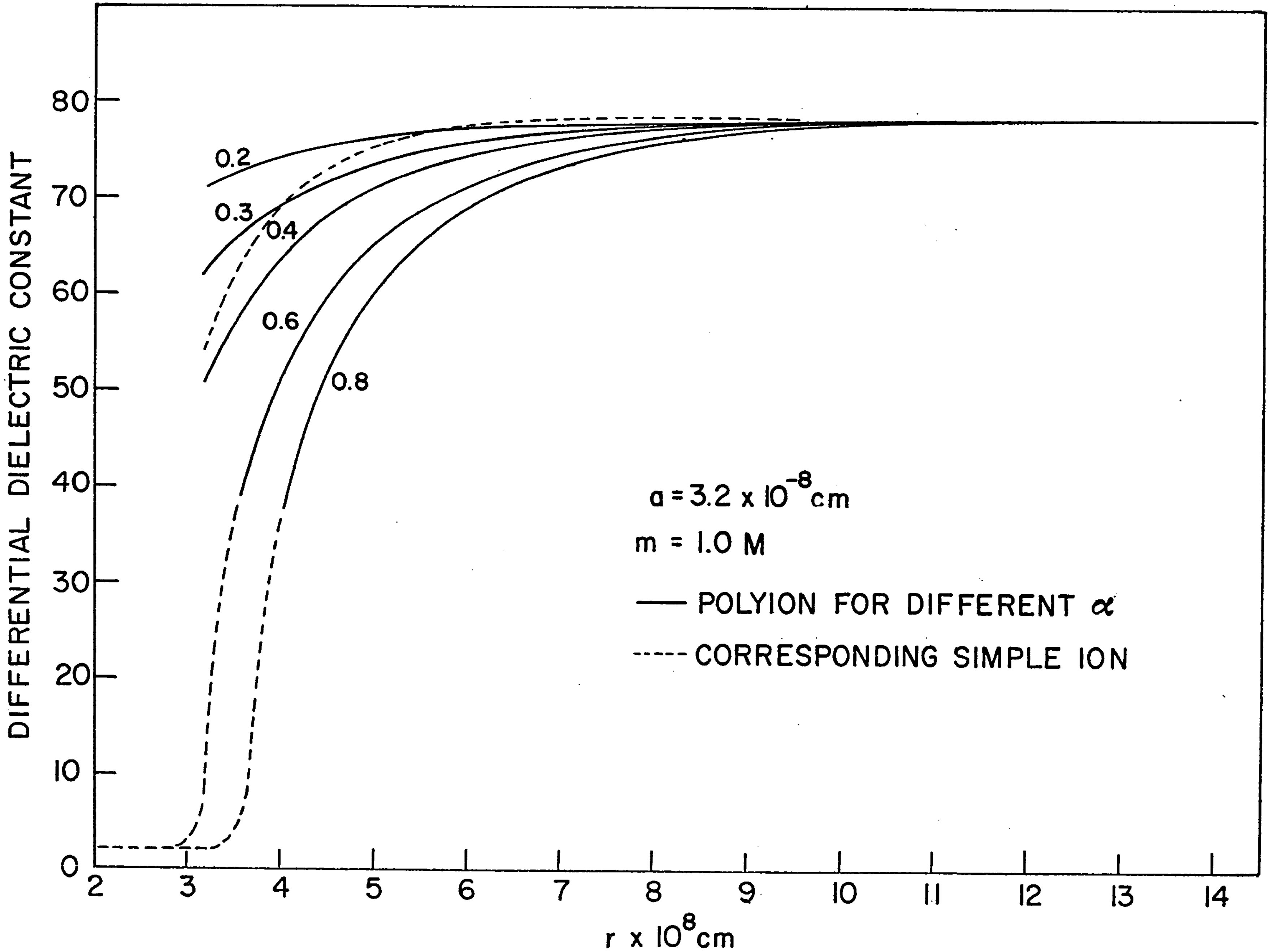

POLYION
a = 3.2 x 10^{-8}cm.
α = 0.6
—— Ɛ = f (E)
---- Ɛ = Ɛ$_0$
m = 0.05M
m = 0.1M
m = 0.5M
m = 1M
POTENTIAL x 10^5 e.s.u.
30
25
20
15
10
5
0
-5
3
5
10
15
20
25
r x 10^8 (cm.)

Figure 7. Dielectric saturation effects near a linear polyion for different degrees of dissociation.


DIFFERENTIAL DIELECTRIC CONSTANT
0
10
20
30
40
50
60
70
80
2
3
4
5
6
7
8
9
10
11
12
13
14
r x 10^8 cm
0.2
0.3
0.4
0.6
0.8
$a = 3.2 \times 10^{-8}$ cm
m = 1.0 M
— POLYION FOR DIFFERENT α
---- CORRESPONDING SIMPLE ION

for the case of the simple electrolyte. The important conclusion to be drawn from this graph is that the dielectric saturation near a polyelectrolyte is similar to that near a simple electrolyte only when the degree of dissociation (or absolute degree of ionization) is about 0.35.

In order to investigate the dependence of the dielectric saturation effect on the degree of ionization, the parameter r_d, as defined previously, was plotted in Fig. 18 as a function of the effective distance between the charges on the charged cylinder. Since the distance between ionizable groups was taken as 2.5 Å, the charge separation is simply $2.5/\alpha$ Å. Therefore, a polyion and a corresponding simple ion with the same radius will have the same value of r_d, and consequently the same hydration radius, when the charge separation on the polyion chain is equal to approximately 7 Å. Fig. 18 and Fig. 7 both indicate that the degree of hydration of a polyion depends to a large extent on this charge separation or on the degree of ionization of the polyelectrolyte; if the charge separation is less than 7 Å, the degree of hydration of the polyion should be much larger than that of the corresponding simple ion and correspondingly, if the charge separation is more than 7 Å, this theory would predict less hydration for a polyion than for a simple ion. It will be shown in chapter III that this dependence of the degree of hydration on α can actually be verified experimentally.

In comparing simple and polymeric ions, it should be noted that the dielectric saturation effect near a polyion with a fairly high degree of ionization is extended much further from the surface of the charged particle than in the case of the corresponding monomeric simple ion. While for simple theories of electrolytic solutions the assumption of a uniform dielectric constant throughout the solution is fairly good if the distance of closest approach is taken as larger than 4 Å, it is not valid for ordinary polyions (α being approximately 0.6) unless the distance of closest approach is taken as being at least 6 Å. The effect of dielectric saturation on the potential and field functions is shown in Figs. 6, 8 and 9. It is easy to see from these graphs that the neglect of this saturation effect could lead to rather serious errors in these functions in some cases.

The effect of the radius of the polyion on the degree of dielectric saturation, as demonstrated in Figs. 10 and 17, shows that a significant increase in the hydration radius of the polyion occurs with increasing "crystal" radius.

In Fig. 10, the differential and integral dielectric constants are compared for different values of "a". As in the case of simple ions (see Fig. 5), the integral dielectric constant is always larger than the differential one but the relative dependence of the saturation effect

Figure 8. Field intensity near a linear polyion for different degrees of dissociation.

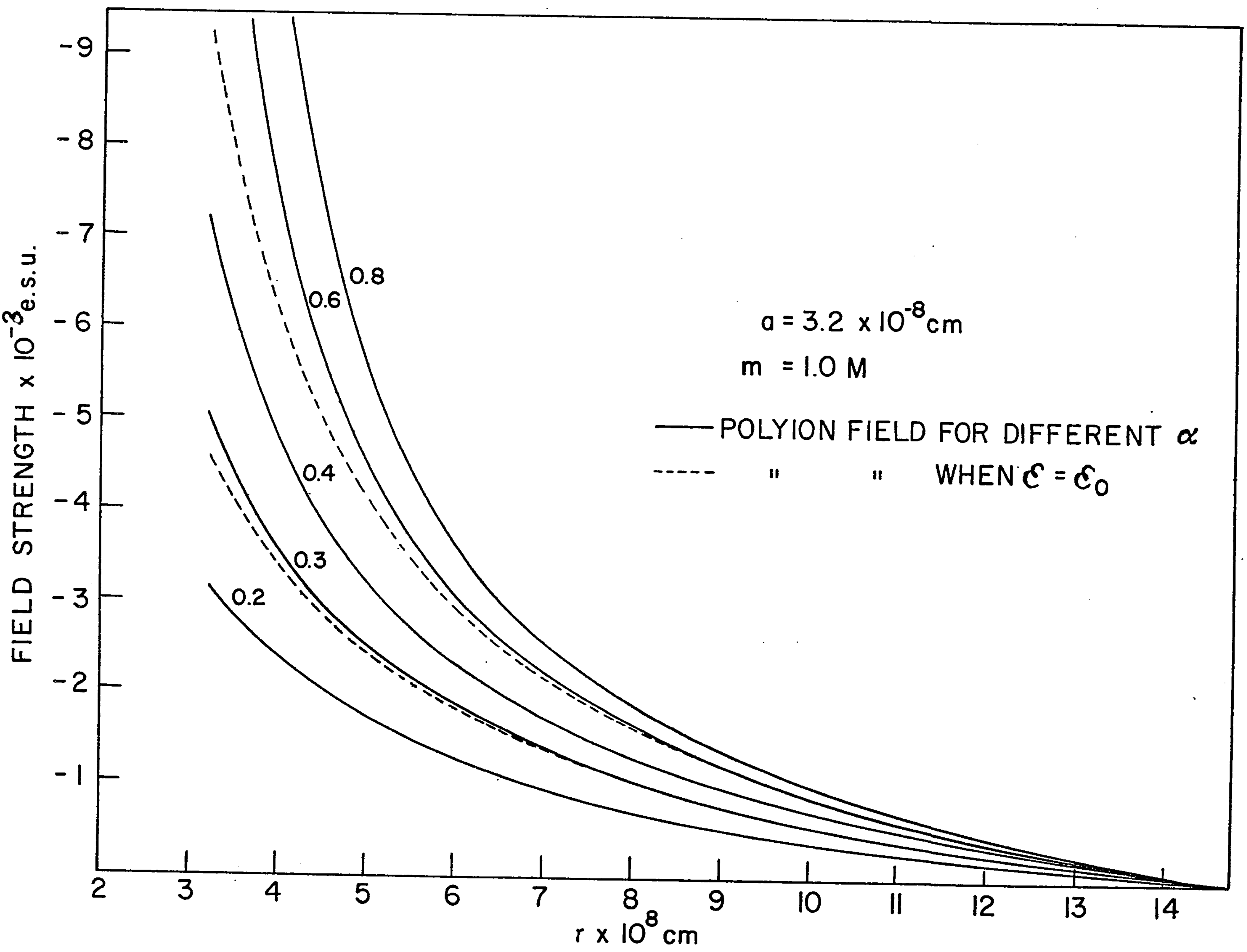

-9
-8
-7
-6
-5
-4
-3
-2
-1
FIELD STRENGTH x 10^{-3} e.s.u.
2
3
4
5
6
7
8
9
10
11
12
13
14
r x 10^8 cm
0.8
0.6
0.4
0.3
0.2
a = 3.2 x 10^{-8} cm
m = 1.0 M
POLYION FIELD FOR DIFFERENT α
" " WHEN $\mathcal{E} = \mathcal{E}_0$

Figure 9. Functions for variation of potential near a linear polyion for different values of "a".

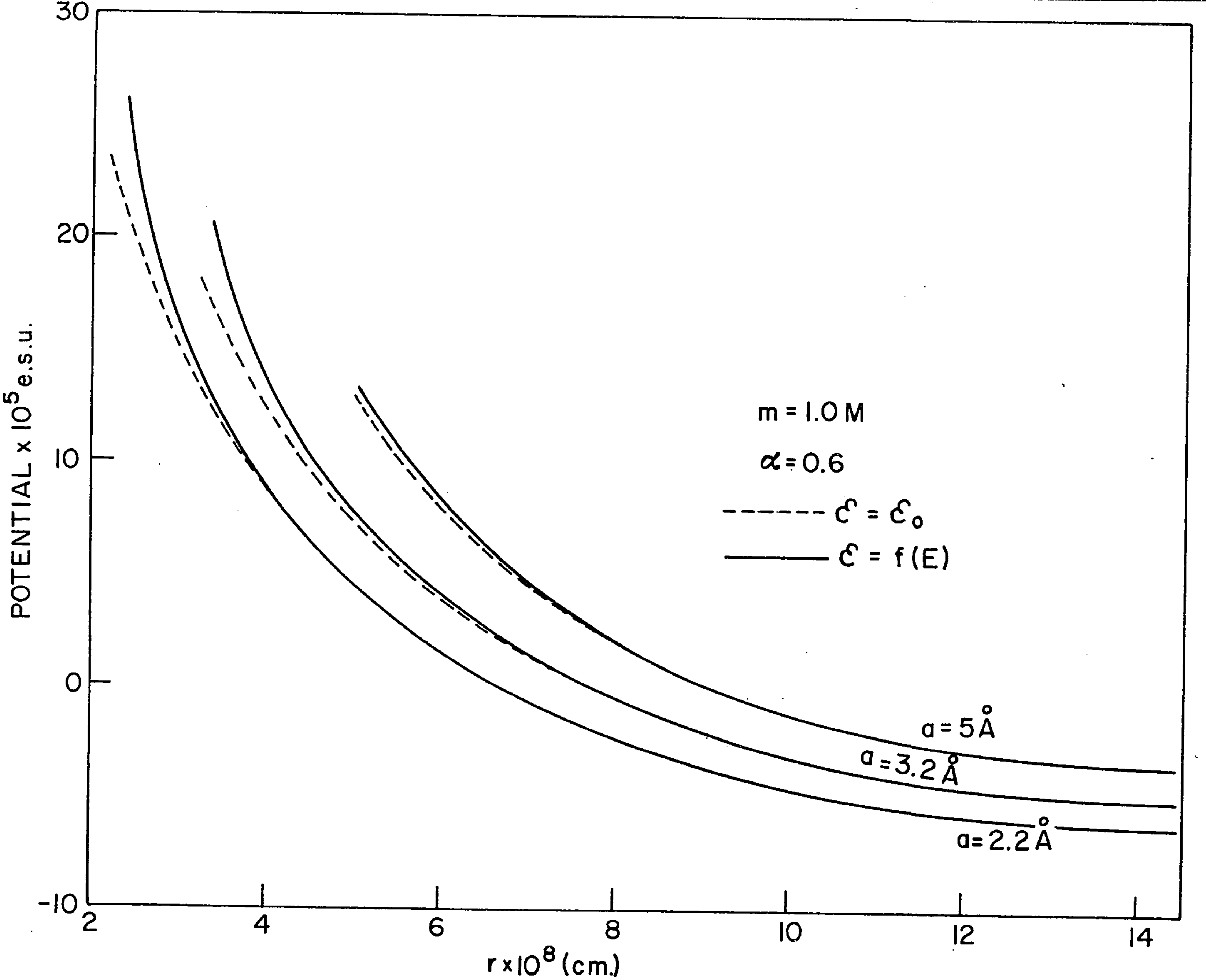
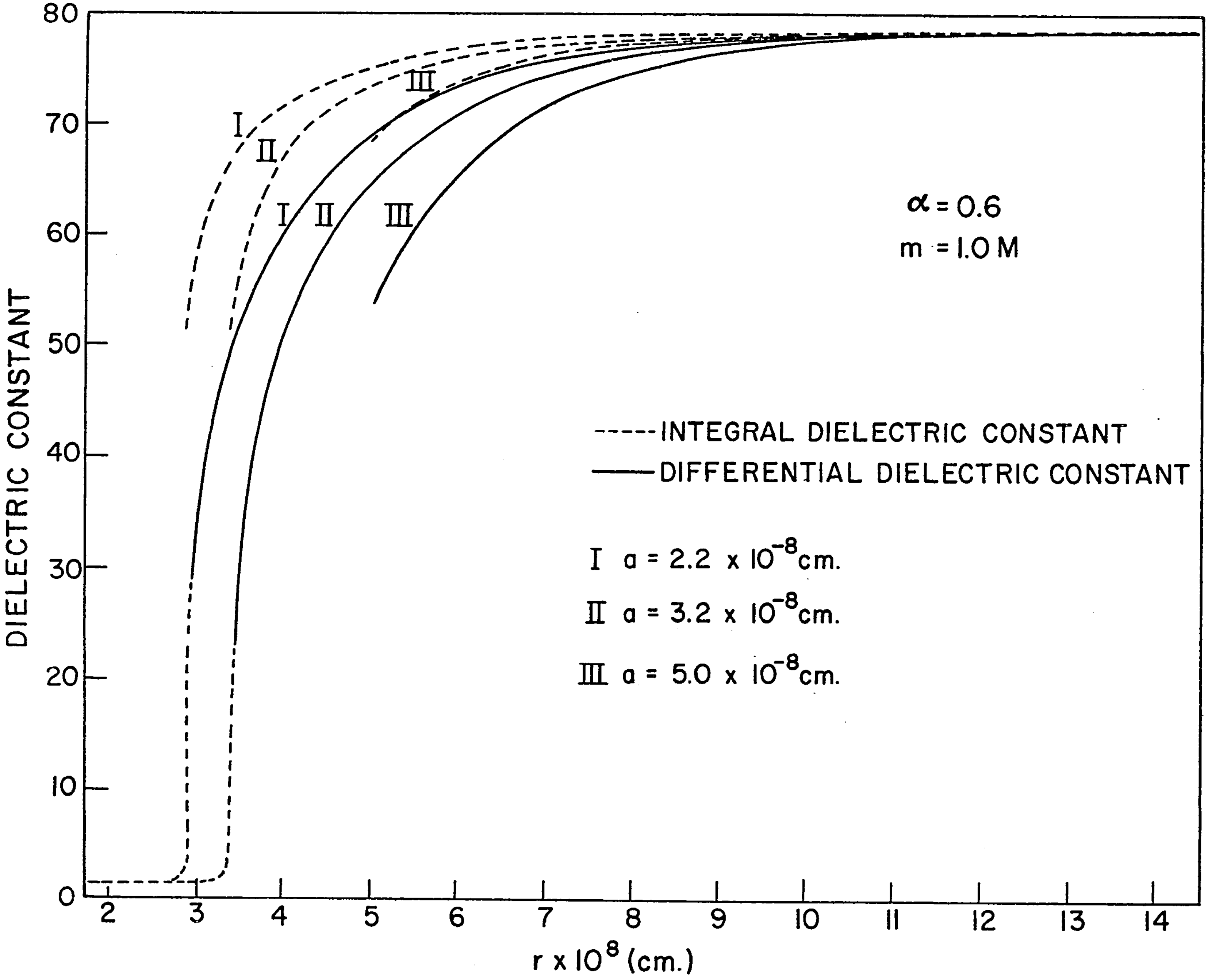

30
20
10
0
-10
2
4
6
8
10
12
14
POTENTIAL x 10^5 e.s.u.
r x 10^8 (cm.)
m = 1.0 M
α = 0.6
$\mathcal{E} = \mathcal{E}_0$
$\mathcal{E} = f(E)$
a = 5 Å
a = 3.2 Å
a = 2.2 Å

Figure 10. Dielectric saturation effects near a linear polyion for different values of "a".


80
70
60
50
40
30
20
10
0
DIELECTRIC CONSTANT
2
3
4
5
6
7
8
9
10
11
12
13
14
r x 10^8 (cm.)
I
II
III
I
II
III
α = 0.6
m = 1.0 M
INTEGRAL DIELECTRIC CONSTANT
DIFFERENTIAL DIELECTRIC CONSTANT
I a = 2.2 x 10^{-8}cm.
II a = 3.2 x 10^{-8}cm.
III a = 5.0 x 10^{-8}cm.

on "a" is the same for both dielectric constants.

Inspection of the literature shows that there is very little experimental evidence which can be used for examination of the above theoretical conclusions on dielectric saturation and hydration. Jacobson (27) appears to be the only worker who has attempted to study the hydration of polyelectrolytes. Unfortunately, he studied mostly natural polyelectrolytes such as nucleic acids and these have such a complicated structure that it is almost impossible to draw any more than very qualitative conclusions about their hydration. He has studied the dielectric constant of aqueous solutions of these macromolecules by a streaming dielectric method and concludes from his results that the hydration shells of some nucleic acids could be as large as one fourth of the length of the macromolecules! Our results definitely show that the field near the polyion can never account for such a large degree of hydration, and it is doubtful if hydrogen bonding between the polyion and the water, as suggested by Jacobson, can increase the structure of water over such a range and to such an extent.

More information could probably be obtained from such experiments if simpler polyelectrolytes were used since the interpretation of the results would be easier. This, in fact, has been done by de Brouckère and Vos (74) who investigated the dielectric properties of solutions of polyacrylic and polymethacrylic acid neutralized with different bases. They, unfortunately, did not attempt to interpret their results in term of extents of hydration. However, it is possible to see qualitatively that their experimental evidence confirms the conclusions reached about the hydration of such polyelectrolytes from density measurements in the present work (see chapter III).

In view of the lack of direct measurements of the degree of hydration of polyions, an important part of this thesis, as we have mentioned previously (see page 13), will be concerned with the experimental evaluation of extents of hydration and the correlation of this extent of hydration with other properties of the polyelectrolytes such as the salting-out behaviour (see chapter III).

Model for a spherical polyelectrolyte

The charged cylinder model is valid for most polyions at appreciable degrees of ionization but there are some cases where this model would be invalid, e.g. for the case of branched polyelectrolytes and linear polyelectrolytes having a low degree of dissociation. In such cases, the penetrable freely-coiled sphere model will be more realistic. The dielectric saturation effect calculated in this case will not be due to the local charge distribution on the polymer molecule as in the case of the charged rod but rather to the overall charge density of the polyion sphere. However, since it is of interest to examine the conditions under which the overall field due to a tightly coiled polyelectrolyte would be large enough to cause electrostriction of the solvent, we have also undertaken the study of this problem.

A numerical solution to the Poisson-Boltzmann equation without dielectric saturation for such a model has been obtained previously by Wall and Berkowitz (53). The same model will be used in the following treatment but with variable field-dependent dielectric constant taken into account.

A system of N polymer molecules are regarded as being dissolved in a total volume V. Hence, each molecule is associated with the volume V/N in the solution defined by the relation

$$\frac{4\pi}{3} R^3 = \frac{V}{N} \qquad [II-24]$$

One spherically coiled polyelectrolyte molecule of radius r_o is regarded as being situated in the center of this spherical element of "available" solution of radius R and surrounded by its counterions, which can penetrate the polyion sphere. The concentration of the counterions at a distance r from the centre of the polyion is given by the Boltzmann distribution. Since the total charge density in the volume of radius R is due not only to the counterions but also to the polyion itself, the Poisson-Boltzmann equation becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(\mathcal{E}_i r^2 \frac{d\psi}{dr}\right) = \frac{4\pi mNe}{1000}\exp\left(\frac{e\psi}{kT}\right) - 4\pi\sigma_0(r) \qquad [II-25]$$

when the counterions are assumed to be anions, and where $\sigma_0(r)$ is the uniform charge density of the polycation and m the average concentration of the counterions.

Wall, in his paper, introduced an extra term $\bar{\Psi}$ in the exponential which he defines as an average potential term. He introduced this term because the numerical solution produced a negative potential at R. By subtracting a constant term $\bar{\Psi}$ from the potential value obtained from the computer, he then obtained a potential function tending to zero at R. He claimed that this was a necessary condition. In reality, the potential must tend to zero only if both simple cations and anions are present in the solution (i.e. the case when a simple electrolyte is added to the polyelectrolyte); otherwise the potential does not tend to zero as, in fact, in the linear rod case at $r = R$. In the model used by Wall, a potential equal to zero at R implies that at all points in the solution the local concentration of counterions is higher than the average concentration m. This follows from the Boltzmann distribution law. Therefore the significance of the term $\bar{\Psi}$ is obscure. Actually, the problem of the significance and importance of this term was avoided by Wall since he used "reduced " values for the potential and distance variables, defined by:

$$x^2 = \frac{4\pi e^2 mN}{1000\,\mathcal{E}_o kT}\; r^2 \qquad [II-26]$$

and

$$u = \frac{e}{kT}\;(\psi - \bar{\psi}) \qquad [II-27]$$

respectively. The Poisson-Boltzmann equation can then be written as

$$\frac{1}{x^2}\,\frac{d}{dx}\left(\mathcal{E}_i x^2 \frac{du}{dx}\right) = \mathcal{E}_o\left(\exp(u) - \frac{1000\;\sigma_o(r)}{mNe}\right) \qquad [II-28]$$

Since the solution will now be obtained in terms of u and not ψ, the removal of the term $\bar{\psi}$ in equation [II-27] will not affect the value of u. It can also be shown from the geometrical properties of the model that

$$\frac{1000\;\sigma_o(r)}{mNe} = \frac{R^3}{r_o{}^3} = \frac{X^3}{x_o{}^3} \qquad [II-29]$$

The two boundary conditions for this differential equation are that the field intensity is equal to zero in the centre of the spherically coiled molecule and at a distance R (or X) from the centre of the coil:

$$\left(\frac{du}{dx}\right)_0 = 0 \qquad \text{(a)}$$

and [II-30]

$$\left(\frac{du}{dx}\right)_X = 0 \qquad \text{(b)}$$

With the above changes of variables, equation [I-15] for the differential dielectric constant must be written as

$$\mathcal{E}_d = \frac{\mathcal{E}_o - n^2}{1 + \mu \left(\frac{du}{dx}\right)^2} + n^2 \qquad [\text{II-31}]$$

where

$$\mu = \frac{4\pi kTbmN}{1000\,\mathcal{E}_o}$$

The dielectric constant used in equation [II-28] should be the integral one. In these computations which were done at the beginning of the work, we had in fact used the differential one by mistake. After this mistake was noticed, the other problems of dielectric saturation (simple electrolyte, rod-shaped polyelectrolyte and colloidal electrolyte) were solved using the correct integral dielectric constant. However, as will be shown later, the degree of dielectric saturation calculated for this present case is very small, and since the solution using the differential dielectric constant instead of the integral one gives an overestimate of the effect of dielectric saturation (see Fig. 5), we did not feel it was necessary to repeat the calculations. We proceed, then, to discuss the method and the form of the results obtained.

The differential equation may be solved by defining only the two parameters X and x_o if the effect of dielectric saturation is neglected. If the dielectric constant is taken as a function of the field intensity, then we must in addition define the concentration m.

The numerical integration may be started at x = X or x = 0. In the first case, there are no difficulties in obtaining the starting values.

$$\left(\frac{du}{dx}\right)_X = 0$$

$$\left(\frac{d^2u}{dx^2}\right)_X = \exp(u_X) - X^3/x_o{}^3$$

and

$$\left(\frac{d^3u}{dx^3}\right)_X = -\frac{2}{X}\left(\frac{d^2u}{dx^2}\right)_X \qquad [\text{II-32}]$$

The starting value u_X is obtained in the way described previously in the simple electrolyte problem.

If the integration is to be started at x = 0 the starting values are obtained as follows. We first write u in terms of a power series in x:

$$u = u_o + 0 + a_2x^2 + a_3x^3 + a_4x^4 + a_5x^5 + 0$$

$$\frac{du}{dx} = 0 + 2a_2x + 3a_3x^2 + 4a_4x^3 + 5a_5x^4$$

$$\frac{d^2u}{dx^2} = 2a_2 + 6a_3x + 12a_4x^2 + 20a_5x^3$$

$$\frac{d^3u}{dx^3} = 6a_3 + 24\ a_4x + 60\ a_5x^2 \qquad [II-33]$$

Now expanding exp (u) gives:

$$\exp(u) = \exp(u_o)\ \left\{1 + a_2x^2 + a_3x^3 + 0\right\} \qquad [II-34]$$

For values of x near zero, $\mathcal{E}$ may be taken as $\mathcal{E}_o$. Therefore, substituting equations [II-33] and [II-34] into the differential equation

$$\frac{d^2u}{dr^2} = \exp(u) - \frac{X^3}{x_o{}^3} - \frac{2}{x}\frac{du}{dx}$$

we obtain

$$2\ a_2 + 6a_3x + 12a_4x^2 + 20a_5x^3 + \frac{2}{x}\left\{2a_2x + 3a_3x^2 + 4a_4x^3 + 5a_5x^4\right\}$$

$$= \exp(u_o)\ (1 + a_2x^2 + a_3x^3) - X^3/x_o{}^3 \qquad [II-35]$$

Equating coefficients of like powers, we then find

$$a_1 = a_3 = a_5 = 0$$

$$a_2 = \frac{1}{6}\,(\exp(u_o) - X^3/x_o^3)$$

$$a_4 = \frac{\exp(u_o)}{120}\,(\exp(u_o) - X^3/x_o^3) \qquad [II-36]$$

Hence, from equations [II-33] and [II-36], the starting values at $x = 0$ are

$$\left(\frac{du}{dx}\right)_o = 0,$$

$$\left(\frac{d^2u}{dx^2}\right)_0 = \frac{1}{3}\,(\exp(u_o) - X^3/x_o^3)$$

and

$$\left(\frac{d^3u}{dx^3}\right)_0 = 0 \qquad [II-37]$$

It can be shown that the same starting value equations are obtained if the assumption that $\mathcal{E} = \mathcal{E}_o$ for values of x near zero is not made. This is done by expressing $\mathcal{E}$ also as a power series and substituting in the differential equation. The value u_o is obtained in the usual way.

As a check on the programming procedure, the differential equation was solved without dielectric saturation using Wall's parameters and starting values. The same results as his were obtained within the computational error, although Wall has used the Runge-Kutta method of numerical integration while the Milne method was used in the present calculations. This is fairly strong evidence that the method used in the present calculations is correct and satisfactory.

The differential equation was solved without difficulty in the cases where the degree of dielectric saturation was small. However, when the saturation effect was significant, the function d^2u/dx^2 became discontinuous at x_o and it became impossible to solve the differential equation completely. Fortunately, it happens that the value u_{x_o} is the same whether dielectric saturation is considered or not. Therefore, using u_{x_o} obtained from the solution of the differential equation assuming a constant dielectric "constant" as a second boundary condition, it was possible to solve the complete differential equation in two steps; first the equation is solved from $x = 0$ to $x = x_o$ and then from $x = X$ to $x = x_o$. The values for $(du/dx)x_o$ and $\mathcal{E}x_o$ were found to coincide also at x_o.

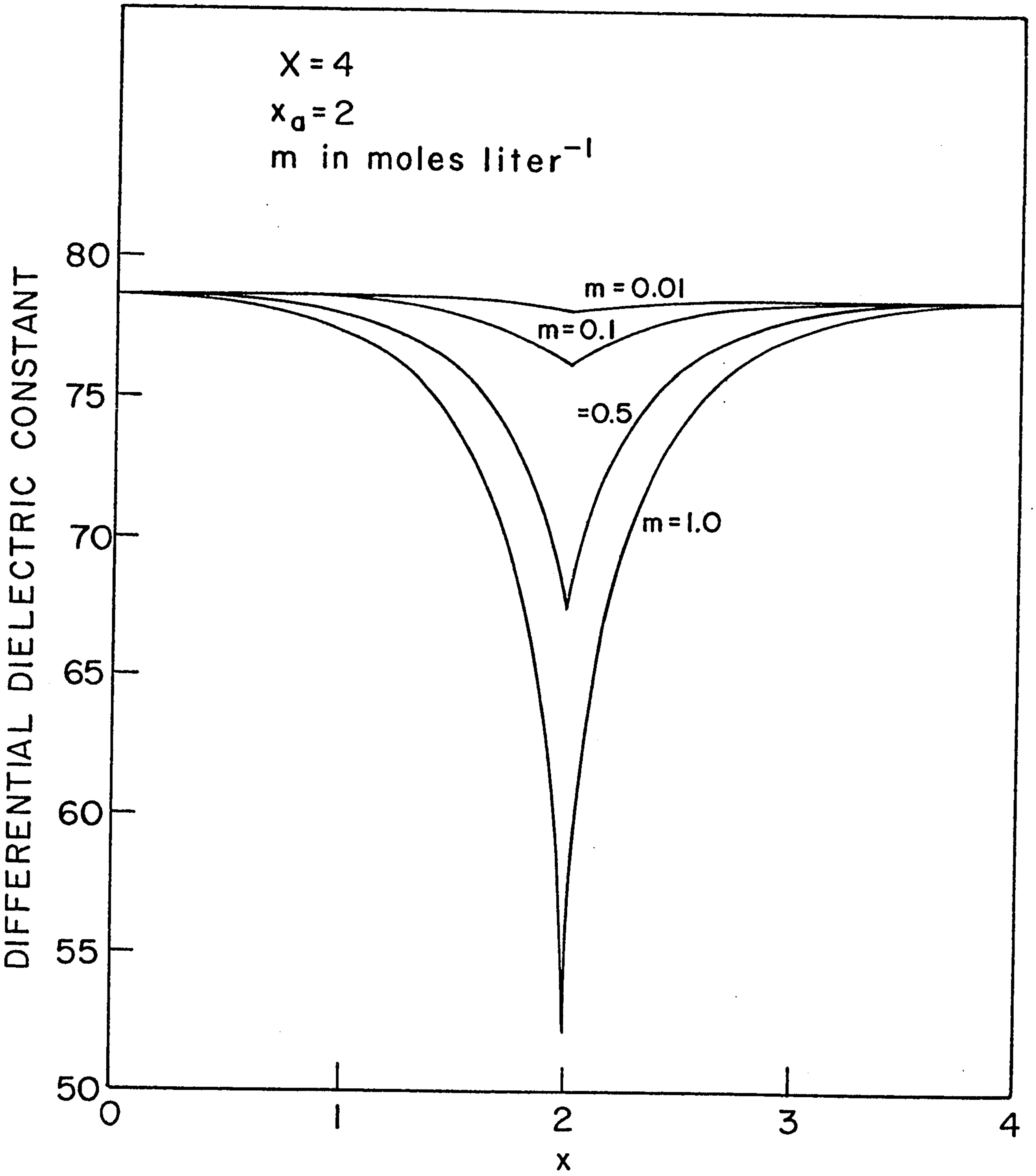
Results for the spherical polyelectrolyte case

Complete tables of u and du/dx as a function of x for different values of X and x_o have been published by Wall (75, 76) for the case where the dielectric constant is assumed uniform throughout the solution. Since the following figures and discussion will show that the functions u and du/dx are not affected to any significant extent by the variation of dielectric constant with field it was not considered necessary to tabulate the results.

The effect of concentration on the degree of dielectric saturation was investigated for the parameters $X = 4$ and $x_o = 2$. Since these parameters are reduced distances, choosing X/x_o as 4/2 simply means that R and r_o are in the ratio 2:1. The absolute value of R can be obtained from equation [II-24] if required. The concentration was varied from 0.01 to 1.0 moles per liter, and the results are plotted in Fig. 11. As stated previously, this model will give the effect of the molecule as a whole on the structure of the solvent near the "surface" of the polyion sphere. It is for this reason that the dielectric constant reaches its minimum value at x_o where the average field is largest. Inside the polyion sphere, the field is probably fluctuating from large positive values to large negative values, the average field being rather small. Therefore, the dielectric constant inside the penetrable polyion sphere is probably much smaller than indicated from this model or assumed in Wall's calculations, since the effective ionic concentration inside the polyion sphere is very high (see below).

From Fig. 11, the effect of dielectric saturation appears to become more important when the concentration approaches 1 M, but since the ratio of X and x_o was taken

Figure 11. Dielectric saturation effects near a spherically coiled polyion for different concentrations as a function of reduced distance x.

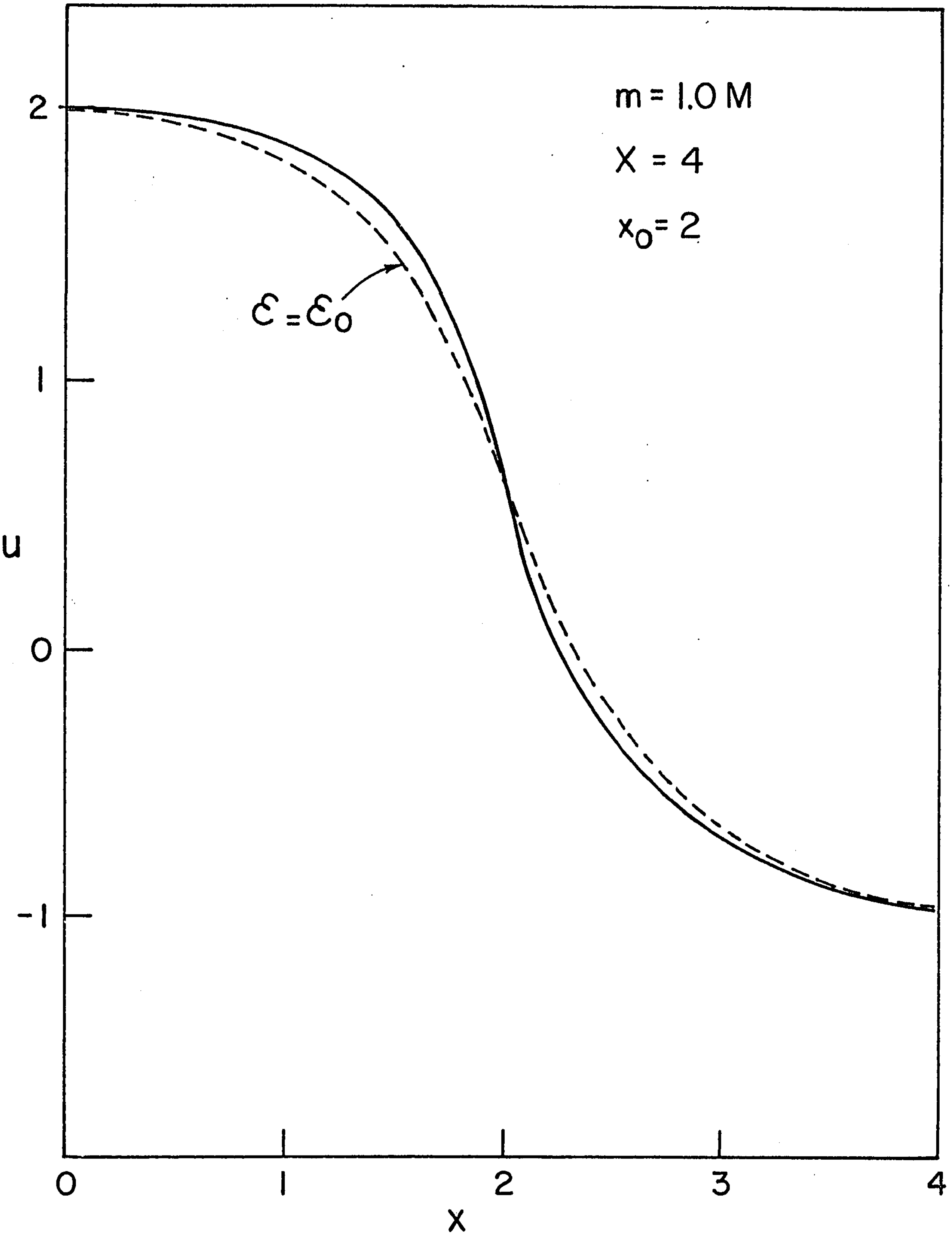

X = 4
$x_a = 2$
m in moles liter^{-1}
DIFFERENTIAL DIELECTRIC CONSTANT
80
75
70
65
60
55
50
0
1
2
3
4
x
m = 0.01
m = 0.1
=0.5
m = 1.0

as 2:1, this implies that the polyion coil occupies only one eighth of the total solution volume available to it. Therefore the local polyelectrolyte concentration in terms of normality should be eight times the average concentration of its counterions. A concentration of 8 M inside the polymer sphere is most improbable since the repulsion of charges would immediately open up the coil or ion binding would reduce the free charge concentration. If we also remember that the type of dielectric constant $\mathcal{E}_d$ used in the Poisson-Boltzmann equation was the wrong one, then the actual degree of dielectric saturation outside the polyion coil would even be smaller. As a first approximation, the error introduced in using the differential dielectric constant instead of the integral one in equation [II-25] can be estimated from Fig. 5. In this figure, we have shown the consequences of using the wrong form of Poisson-Boltzmann equation in evaluating the degree of dielectric saturation near a simple ion. The extent of dielectric saturation near a spherically coiled polyion can be compared to the simple ion problem since both models have spherical symmetry. Therefore, the differential dielectric constant obtained near the spherical polyion would correspond to curve III of Fig. 5, while the correct solution would correspond to curve II. Returning to Fig. 11, the minimum dielectric constant obtained for a concentration of 1 M should therefore not be 52 but rather in the vicinity of 62.

In order to show the manner in which dielectric saturation affects the potential and field functions, these functions are shown in Figs. 12 and 13 for X/x_o equal to 4/2 and m equal to unity, even though this extreme case is in practice rather unrealistic. From these two graphs, it is seen that for a more realistic case (lower concentration or larger value for x_o) the dielectric saturation would practically not affect the potential and field functions.

The next step is to investigate the effect of the ratio x_o/X on the degree of dielectric saturation. X was therefore fixed at 6, the concentration m at 0.1 M and the parameter x_o was varied. The final results are summarized in Fig. 14 where the relative lowering of the dielectric constant $(\mathcal{E}_o - \mathcal{E}_d)/\mathcal{E}_o$ is plotted as a function of the ratio x_o/X where $\mathcal{E}_d$ corresponds to the minimum value of $\mathcal{E}$ at $x = x_o$. The relative lowering of the dielectric constant increases exponentially when x_o/X is equal to 1/3. But, here again, this implies that the polyion occupies only 1/27 of the total volume available to it and the charge concentration in the polyion sphere is then about 2.7 M. However, the conditions chosen for this case are somewhat improbable and for more realistic conditions of more "dilute" coils, the overall saturation effects near the periphery of the polyion sphere will be negligible, although for such dilute

Figure 12. Reduced potential function near a spherically coiled polyion as a function of reduced distance x.



m = 1.0 M
X = 4
x_0 = 2
$\mathcal{E} = \mathcal{E}_0$
u
2
1
0
-1
x
0
1
2
3
4

Figure 13. Reduced field intensity near a spherically coiled polyion as a function of the reduced distance x.

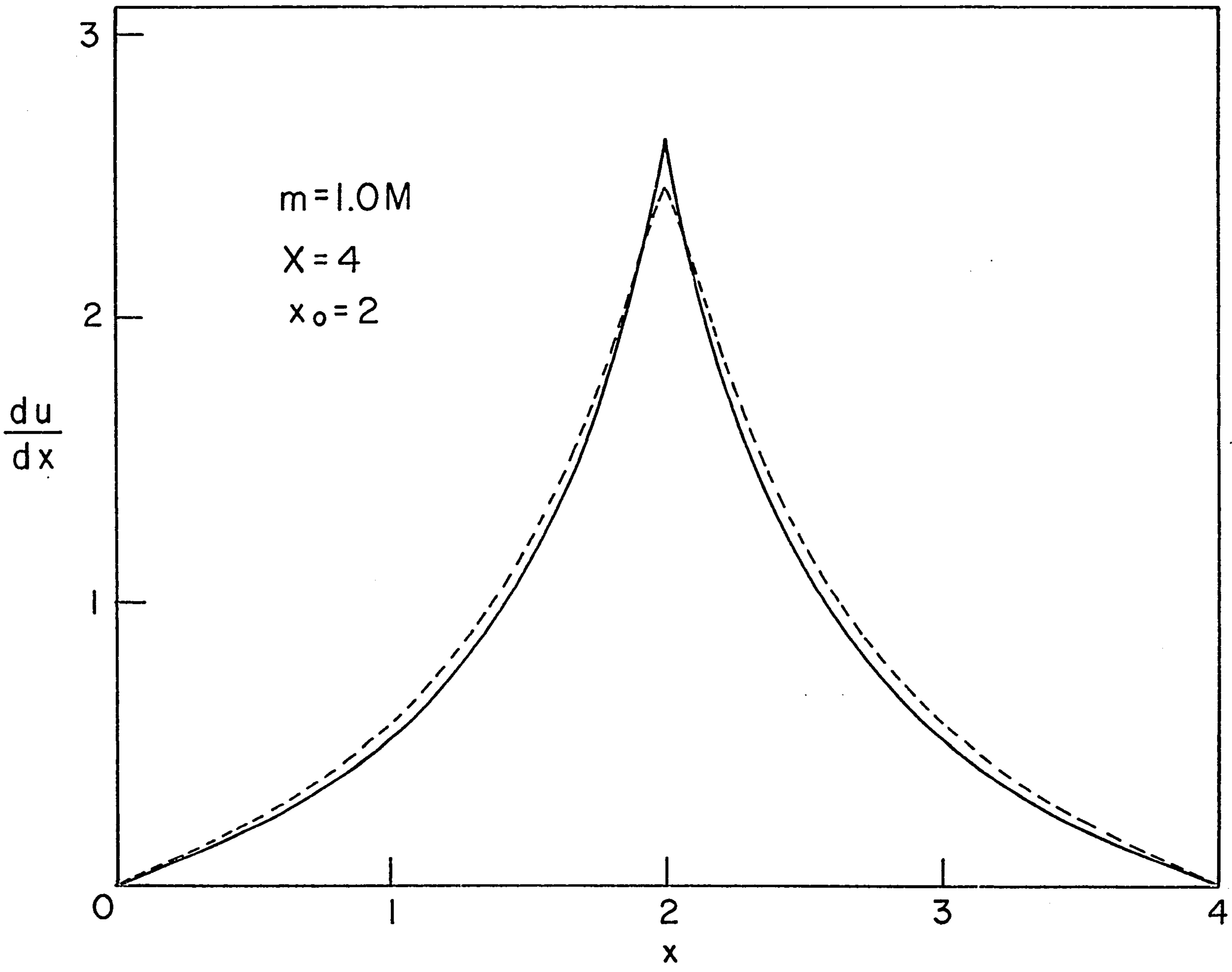
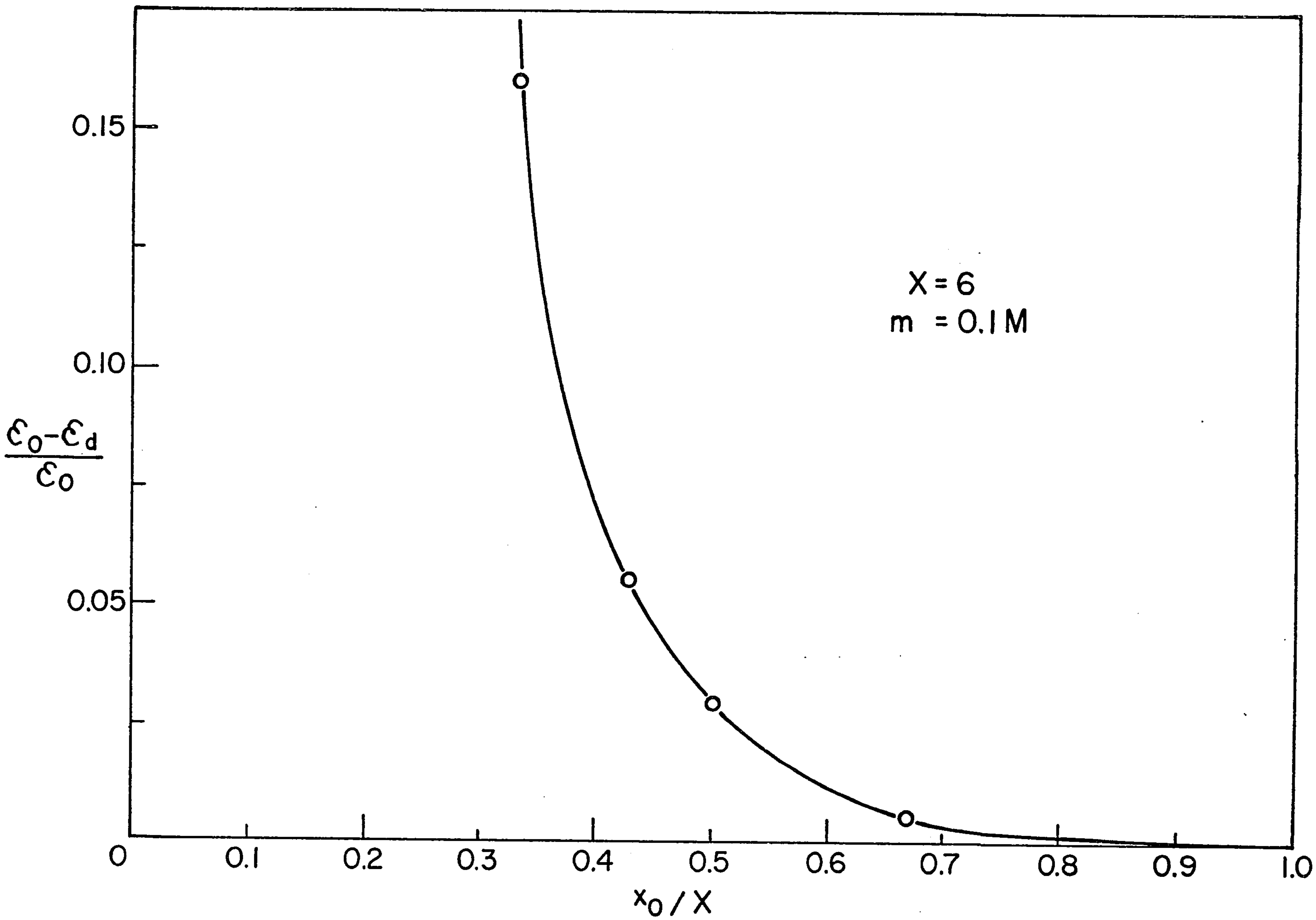

m=1.0M
X=4
x_o=2
du/dx
3
2
1
0
1
2
3
4
x

Figure 14. Lowering of the minimum differential dielectric constant (i.e. for diminishing values of x_o/X) as the coil of a spherical polyion tightens up.


0.15
0.10
0.05
$\frac{\varepsilon_0-\varepsilon_d}{\varepsilon_0}$
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
x_0/X
X = 6
m = 0.1M

spheres the internal saturation effects, i.e. close to the polymer chains, will of course, be significant as in the linear rod model.

We can therefore conclude that whenever a polyelectrolyte occurs as a penetrable sphere, its solvation can be predicted in either of two ways. If the sphere is actually a fairly loose open coil (high degrees of ionization and/or low concentration), then the dielectric saturation should be evaluated by assuming that the polyelectrolyte can be treated locally as a charged rod. If the sphere is actually a fairly tight coil, then one can assume, as a first approximation, nearly total dielectric saturation inside the coil and little on the outside.

D - COLLOIDAL ELECTROLYTE

Model

The last case investigated in this thesis is that of colloidal electrolytes. On account of their large dimensions, these particles may be treated locally (i.e. for short distances from their surfaces) as charged plates. This problem has been studied intensively by Verwey and Overbeek and others (50, 56, 57) since it is possible to solve the Poisson-Boltzmann equation exactly in this case. This problem is also of great interest because of its relation to the problem of the double-layer at colloidal particles and at electrodes. A certain amount of work has already been carried out on the improvement of the Poisson-Boltzmann equation for the double-layer with regard to such effects as dielectric saturation (43, 44, 77), compressibility of solvent etc., in relation to the properties of the double-layer (78, 79). In the present work we are more interested in the factors influencing the extent of dielectric saturation near a charged plate. It is thus possible to use a rather simpler model than those used in the treatment of the double-layer. As in the previous problems, we will examine the influence of the plate charge density, concentration and distance of closest approach, on the solvation of the colloidal ion and dielectric saturation of the solvent near to its surface.

We assume that two charged parallel plates of infinite dimensions are separated by the distance 2R as in the model of Verwey and Overbeek for interaction of two double layers. Between the two plates, there are enough counterions* to neutralise the charges on the two plates (see Fig. 1). The Poisson-Boltzmann equation for this model is

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* This situation might for example arise by ionization of a protein particle, or occur near a large micellar ion.

$$\frac{d}{dr}\left(\mathcal{E}_1 \frac{d\psi}{dr}\right) = -\frac{4\pi z_1 eNm}{1000} \exp\left(-\frac{z_1 e\psi}{kT}\right) \qquad [II-38]$$

where m is the average concentration of the counterions of valency z_1.

The two boundary conditions are similar to the ones in the previous problems:

$$\left(\frac{d\psi}{dr}\right)_R = 0 \qquad [II-39]$$

$$\left(\mathcal{E}_1 \frac{d\psi}{dr}\right)_a = -4\pi\sigma_s = -\frac{4\pi e}{\lambda^2} \qquad [II-40]$$

where "a" is the distance between the point where the charge resides and the surface of the plate (or is the distance of closest approach), σ_s the surface charge density of the plate and λ the nearest neighbour charge separation on the plate. The concentration m is related to R by

$$m = \frac{1000}{N\,\lambda^2 (R-a)}\,. \qquad [II-41]$$

The starting values for this case are

$$\left(\frac{d\psi}{dr}\right)_R = 0,$$

$$\left(\frac{d^2\psi}{dr^2}\right)_R = -\frac{4\pi z_1 eNm}{1000\,\mathcal{E}_0} \exp\left(-\frac{z_1 e\psi_R}{kT}\right),$$

$$\left(\frac{d^3\psi}{dr^3}\right)_R = 0 \qquad [II-42]$$

and ψ_R is obtained by guessing and correcting repetitively by equation [II-40] on the computer as in the previous problems discussed.

The main difference between our model and the ones used in the theory of the diffuse double layer for hydrophobic colloids is that we assume only counterions to be present between the two plates. In the diffuse double-layer theory applicable to non-ionizable colloidal particles in the presence of excess electrolyte, it is necessary to assume that both cations and anions are present, one type of which, being preferentially adsorbed on the particles, stabilises it. In the present calculations, we avoid the problem of assuming that the average concentrations of the remaining anions and cations are the same. In fact, we are assuming in our case that all the cations (or anions) are adsorbed on the plate or colloidal particle and that only the anions are left free to move in the solution (the model is thus analogous to the linear polyelectrolyte case in the absence of added salt). This model is therefore applicable to both colloidal particles stabilized by adsorbed simple ions and to actual colloidal electrolytes in the presence of their counterions only, which have arisen by ionization of the plate or particle.

Results

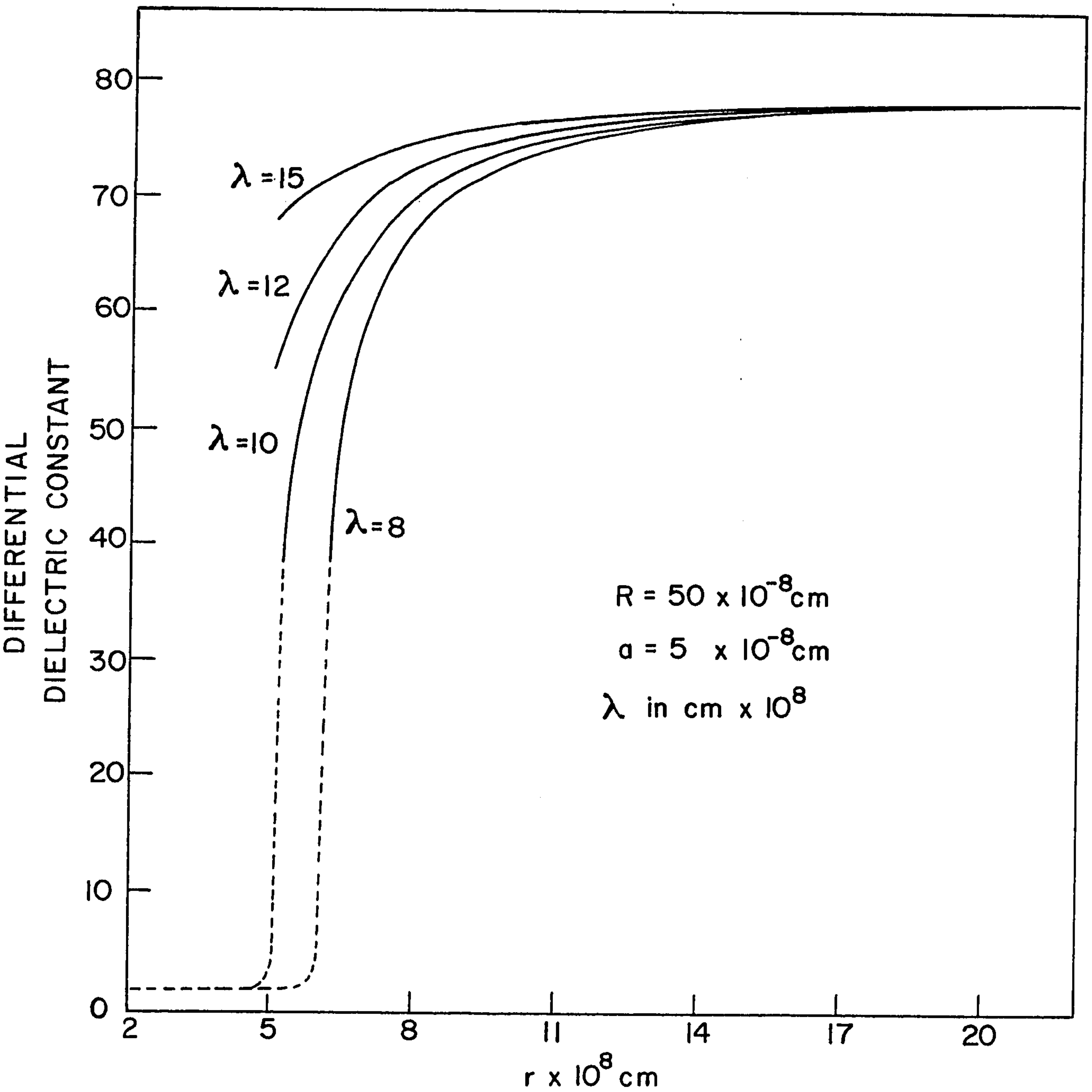
The Poisson-Boltzmann equation was solved for different values of the parameters m, "a" and λ with and without corrections for the effect of dielectric saturation and the numerical results are given in the Appendix. Some of the relevant results have been plotted in Figs. 15 to 18.

The effect of concentration on the degree of dielectric saturation near a colloidal particle is similar to that for the cases of simple and polymeric electrolytes, that is, it increases slightly with dilution, i.e. with distance between the plates.

The dielectric saturation (expressed in terms of r_d, the distance at which $\mathcal{E}_d = 55$) is found to be directly proportional to the parameter "a", i.e. r_d - "a" is independent of "a". This arises from the fact that the second boundary condition at "a" (equation [II-40]) is independent of "a".

The dependence of the dielectric saturation on the charge density on the plate is shown in Fig. 15 where the differential dielectric constant of the solvent near a charged plate is plotted against the charge separation on the plate. In these calculations, R was fixed at 50 Å. In the polyion model, the concentration was constant for a constant R, but this is not so in this case since we are varying the charge separation and the concentration is a

Figure 15. Dielectric saturation effects near a charged plate colloidal ion model for different charge separations on the plate.

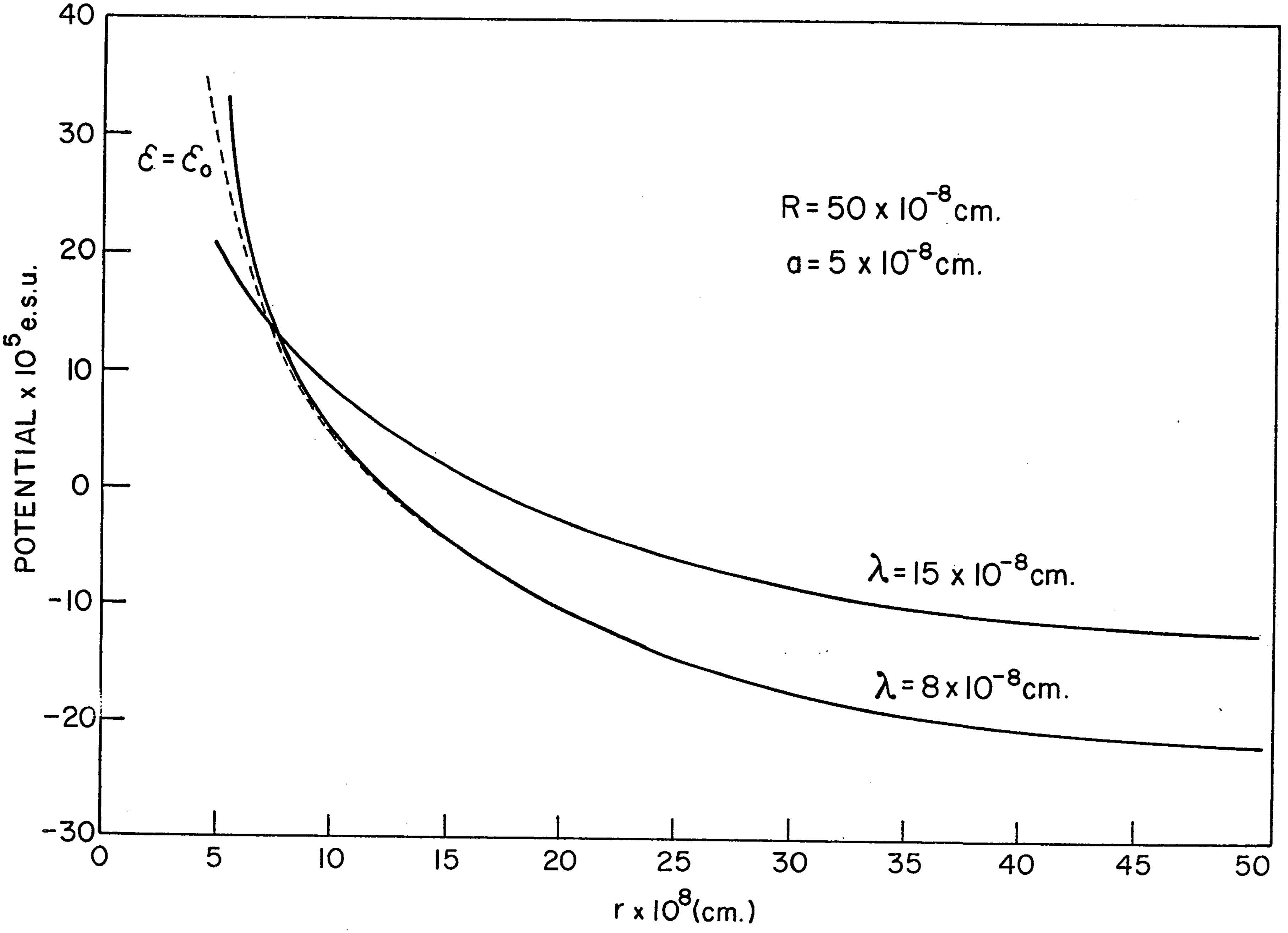


DIFFERENTIAL DIELECTRIC CONSTANT
80
70
60
50
40
30
20
10
0
2
5
8
11
14
17
20
r x 10^8 cm
λ =15
λ =12
λ =10
λ =8
R = 50 x 10^-8 cm
a = 5 x 10^-8 cm
λ in cm x 10^8

function of this charge separation (equation [II-41]). For example, when $\lambda = 15$ the concentration is equal to 0.58 M and when $\lambda = 8$ then m is 0.16 M. However, it was shown by keeping λ constant and varying R, that the concentration has little effect on the degree of dielectric saturation over this range of concentration (as found also for the polyion case). Therefore the comparison made in Fig. 18 of r_d for the three models as a function of the charge separation is valid.

As expected from the comparison with the previous models, the saturation effect can be important in the plate model to distances much further away from the surface of the plate than in the polyion or simple ion cases. Beyond 6 or 7 Å the dielectric constant can be taken as uniform for an average polyion but in the case of colloidal ions the distance beyond which the dielectric constant may be taken as uniform and having its normal value can be much greater. For example, in Fig. 16 the potential is plotted as a function of the distance from the plate ion for $\lambda = 8$ and $\lambda = 15$ with a radius "a" = 5 Å. When $\lambda = 15$ the dielectric constant may be assumed uniform throughout the solution but when $\lambda = 8$ the potential function calculated for $\epsilon = \epsilon_0$ starts to deviate from the more correct solution as far as 13 Å away from the plane of centres of charges on the surface of the colloidal ion.

Figure 16. Functions for variation of potential near a charged plate for different charge separations on the plate.



40
30
20
10
0
-10
-20
-30
POTENTIAL x 10^5 e.s.u.
0
5
10
15
20
25
30
35
40
45
50
r x 10^8 (cm.)
$\mathcal{E} = \mathcal{E}_0$
$R = 50 \times 10^{-8}$ cm.
$a = 5 \times 10^{-8}$ cm.
$\lambda = 15 \times 10^{-8}$ cm.
$\lambda = 8 \times 10^{-8}$ cm.

E - CONCLUSION AND FINAL COMPARISON BETWEEN THE RESULTS FOR THE THREE MODELS

1) New models have been proposed for treating the dielectric saturation near simple and plate-like colloid ions in order to be able to compare the results directly with those calculated for a linear polyion. The models, Poisson-Boltzmann equations and boundary conditions for the three cases have been compared in Fig. 1. The constants K, K' and K'' depend on the concentration and charge density of the charged particles. It is obvious from this figure that the three models are identical in form and differ only in symmetry.

2) It was assumed that the relative extents of primary hydration at different charged particles are proportional to the relative degrees of dielectric saturation of the solvent near the particle. For this purpose, an arbitrary dielectric constant was chosen ($\mathcal{E}_d = 55$) such that the distance corresponding to this value of the dielectric constant would be approximately equal to the primary hydration radius of the charged particle. Therefore, comparison of r_d values for different models and different variables (concentration, crystal radii, charge density) should give information about the relative extents of primary hydration of the three types of charged particles.

3) It was found that in the three cases r_d increases only slightly with increasing dilution; it was therefore concluded that the degree of primary hydration of a particle can be considered independent of concentration (below 1 M), at least as a first approximation.

4) The variation of r_d with "a", shown in Fig. 17, is different for the three models. For a simple ion, the degree of primary hydration should increase slightly with the crystal radius. For a linear polyion, the variation of primary hydration with the polyion radius is much more pronounced than in the simple ion case. For a colloidal ion, the most extreme case of the three, the radius of primary hydration should be directly proportional to the distance "a".

5) The variation of r_d with charge density or charge separation is shown in Fig. 18 for the three models. The variation of r_d, and consequently the extent of primary hydration, with the charge separation is similar for the linear polyion and colloidal particle. For a fixed parameter "a", taken as 3.2 Å, the radii of primary hydration should be approximately the same for the three models when the charge separation is equal to 7 Å for the polyion and 12 Å for the colloidal ion. These values would not be necessarily the same for ions of different sizes since the dependence of r_d on "a" is different for the three models. However, we may conclude that in general the radii of primary hydration should

Figure 17. Comparison of the dependence of r_d on "a" for the three models: simple ion, charged rod and charged plate.

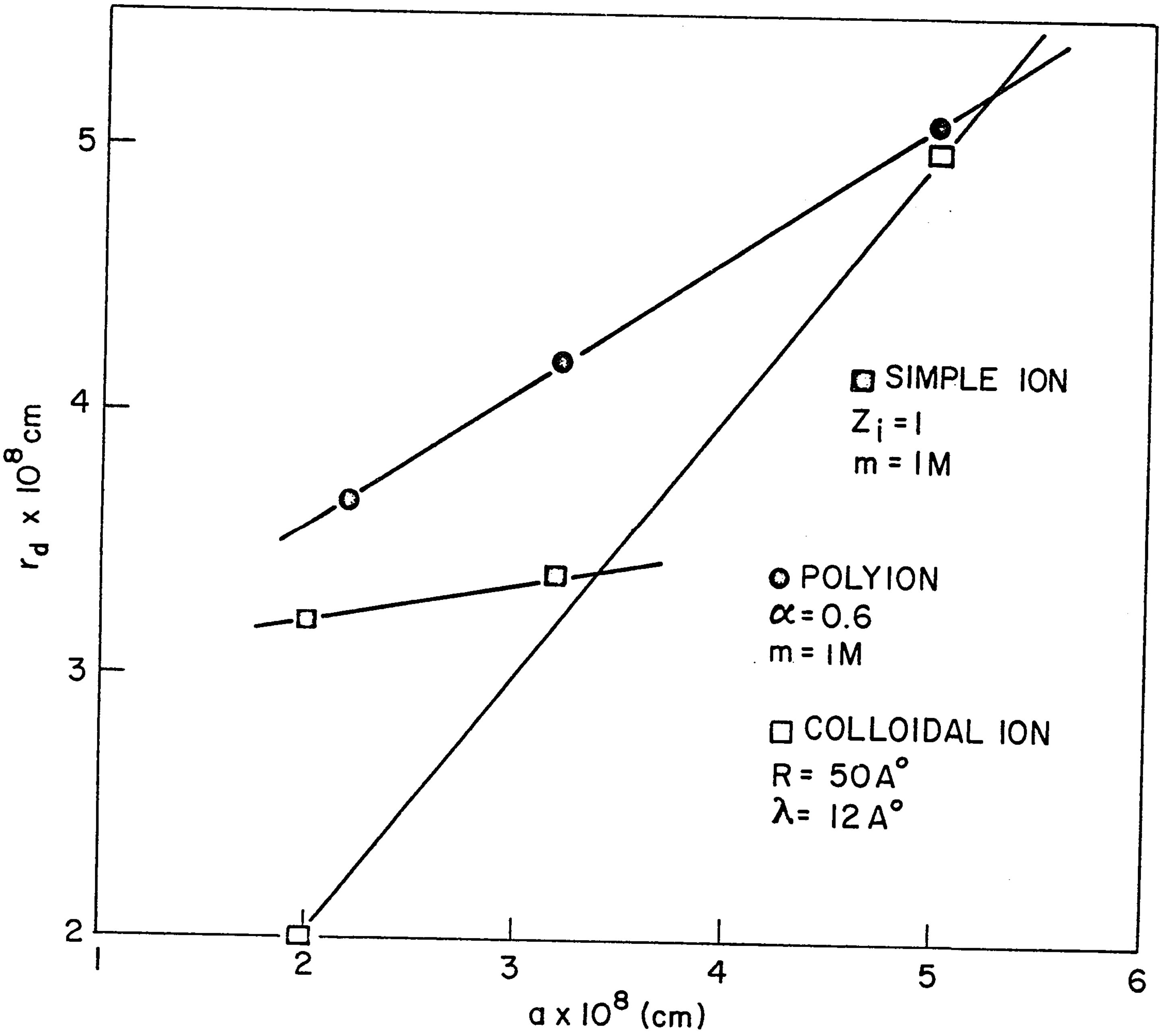
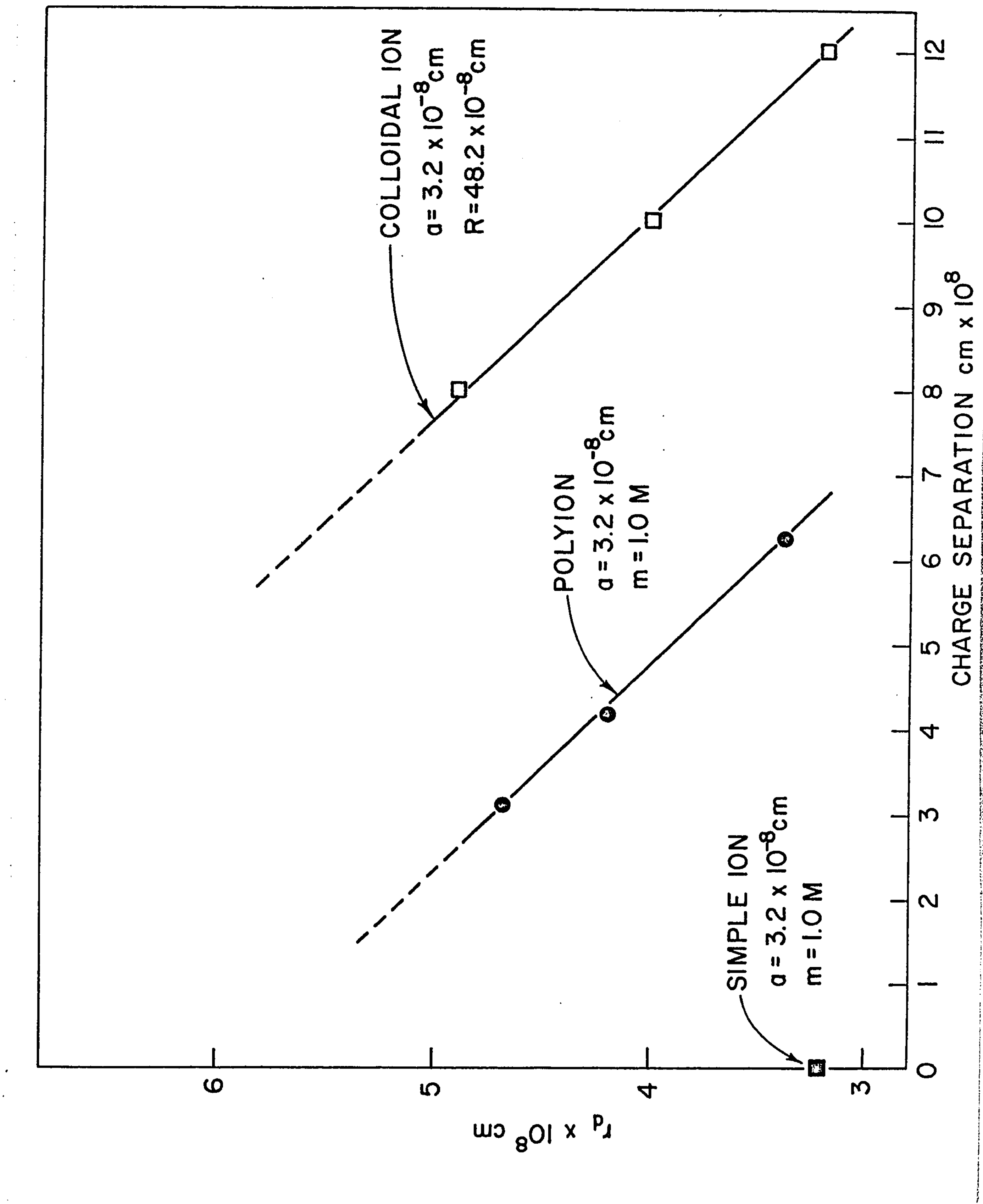

■ SIMPLE ION
$Z_i = 1$
m = 1M
● POLYION
$\alpha = 0.6$
m = 1M
□ COLLOIDAL ION
R = 50A°
λ = 12 A°
$r_d \times 10^8$ cm
$a \times 10^8$ (cm)
1
2
3
4
5
6
2
3
4
5

Figure 18. Comparison of the dependence of r_d on the charge separation for the three models: simple ion, charged rod and charged plate.



COLLOIDAL ION
a = 3.2 x 10⁻⁸cm
R = 48.2 x 10⁻⁸cm
POLYION
a = 3.2 x 10⁻⁸cm
m = 1.0 M
SIMPLE ION
a = 3.2 x 10⁻⁸cm
m = 1.0 M
r_d x 10⁸ cm
3
4
5
6
CHARGE SEPARATION cm x 10⁸
0
1
2
3
4
5
6
7
8
9
10
11
12

increase in the order: simple ion $<$ linear polyion $<$ colloidal ion.

6) The extent of dielectric saturation near a penetrable spherical polyelectrolyte was investigated and it was concluded that the macromolecule as a whole will not affect the solvent structure outside the coil to any significant extent. Depending on the size and charge density of these polyelectrolytes, a crude estimate of the degree of dielectric saturation or primary hydration can probably be obtained in terms of one of the three models discussed previously. If the case does occur that a coiled polyelectrolyte has a fairly high charge density (tight coil or high concentration), it can probably be assumed that complete dielectric saturation occurs inside the coil and none or little on the outside. This case is however improbable since a coil usually opens up when the charge density becomes fairly high.

7) Whenever knowledge of the degree of primary hydration of a charged particle with definite shape and charge density is desired and no experimental evidence is available, a rough estimate of this effect can be obtained by considering the theoretical dielectric saturation effects. From the symmetry, charge density, radius and concentration (important in some cases) it is possible by suitable interpolations to obtain a value for the parameter r_d which, as a first approximation, may be equated to the radius of the primary hydration shell.

III. SALTING-OUT BY POLYELECTROLYTES AND ELECTROSTRICTION OF THE SOLVENT

A - EXPERIMENTAL

In the present work, values of the salting-out constant (equation I-23) have been obtained from measurements of solubilities of gaseous and solid non-electrolytes in solutions of polyelectrolytes. Salting-out measurements were also carried out for reference purposes in solutions of simple electrolytes corresponding to the monomeric unit of each polyelectrolyte used. Since we also wished to relate the salting-out results to the apparent molar volumes of the polyelectrolytes, the densities of the polyelectrolyte solutions were also measured.

i) Choice and Preparation of Substances Examined.

Three polyelectrolytes were used in this work: sodium polyphosphate, potassium polymethacrylate and poly-4-vinyl-N-n-butylpyridinium bromide. The polyphosphates were used since it was possible to obtain various fractions having different molecular weights, thus enabling examination of the effect of increasing chain length on the salting-out constant to be made. The two other polyelectrolytes were chosen since they are typical polyanionic and polycationic salts.

Sodium polyphosphates (NaPP)

The polyphosphates were obtained from Albright and Wilson Ltd. and had the following molecular weights: 800, 2800 and 6800. Higher molecular weight phosphates are difficult to study since their solubility decreases rapidly as the chain length increases.

These polyphosphates were obtained by quenching sodium phosphate melts containing different proportions of P_2O_5 between water cooled rollers. The 6800 molecular weight polymer was obtained by melting anhydrous (cyclic) sodium trimetaphosphate in platinum at 900 - 1000° C in an electric furnace and rapidly quenching the poured melt between steel plates.

The molecular weights of these polymers were determined by "end group" titration. All the above samples are believed to be somewhat polydisperse* linear polyphosphates, although paper chromatography shows that they contain up to 7.5% of cyclic tri- and tetrametaphosphates.

Polymethacrylic acid (PMA)

Practical grade methacrylic acid was obtained from Matheson, Coleman and Bell Co. Inc. A 10% aqueous solution

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* The small degree of polydispersity present is probably unimportant in relation to the salting-out and hydration studies since we will show later that the salting-out constant and apparent molar volume of a monomer unit of a polyelectrolyte are essentially independent of chain length except for very short polymers.

of this monomer containing 0.1 to 0.2% of hydrogen peroxide was kept in a constant temperature bath at 60° C for about three hours. The polymer was precipitated out of solution and fractionated by adding a mixture of hydrochloric acid and acetone to the aqueous solution. The fractionated part of the polymer was then removed from the solution and dried on a steam bath. The polyacid was then purified further by dissolving it in a minimum amount of alcohol and pouring this solution in a fine stream into cool ethyl acetate with vigorous stirring. The fluffy white polyacid was then filtered, washed with ether and dried at 100° C.

It is difficult to determine the molecular weights of the polyacid preparations directly; attempts were made to obtain them from light scattering and osmotic pressure measurements but without too much success. It was found to be more satisfactory to convert the acid into an ester and then estimate the (weight average) molecular weight by the viscosity method. Following Katchalsky's procedure (80), the acid was esterified to polymethylmethacrylate by adding powdered polymethacrylic acid to benzene containing an excess of diazomethane. After the reaction was completed, the ester was precipitated by addition of ether, dissolved in chloroform and reprecipitated with ether. The diazomethane was prepared using Werner's method (81). The molecular weight was then determined using the standard viscosity method (82, chapter 13).

The equation relating the intrinsic viscosity $[\eta]$ to the weight average molecular weight is

$$[\eta] = K M^a$$

For methyl methacrylate in benzene, $K = 0.94 \times 10^{-4}$ and $a = 0.76$ (84) so that from a determination of $[\eta]$, M can be evaluated.

The potassium salt of the polyacid was prepared by titrating the acid against standard alkali until the required degree of neutralization was reached.

The percentage free acid in the PMA samples was evaluated from a potentiometric titration with standard KOH using a glass electrode and was found to vary slightly from sample to sample. On the average 96 to 97% of the PMA was in the pure acid form. The true concentration of the salt in various solutions was determined from the standard alkali titre and the degree of neutralization was calculated relative to the true concentration of free acid groups in the given solution of the polymer.

Poly-4-vinyl-N-n-butylpyridinium bromide (PBPB)

A 5% solution of freshly distilled 4-vinyl-pyridine was prepared in oxygen-free toluene containing 0.2% benzoyl peroxide (83). The solution was then placed in a closed bottle at room temperature. The polymer precipitated out of solution in about a week. The polymer was then removed from the solution, washed with toluene and dried under vacuum. The salt was prepared by dissolving the polymer in nitromethane (3 - 5% solution) and adding an excess of n-butyl bromide. The mixture was heated under reflux to 60-70°C for three days. After cooling, the polysalt precipitated out as an amorphous solid. The excess solvent was removed by decantation and the polyelectrolyte was dissolved in ethanol. The ethanol solution was then poured in a fine stream into vigorously stirred cold ethyl acetate. The fluffy polyelectrolyte was then filtered, washed with ether and dried under vacuum. Different degrees of neutralization were obtained by changing the amount of n-butyl bromide in the procedure.

The molecular weight of the poly-4-vinyl-pyridine preparation was estimated from its intrinsic viscosity in alcohol using the constants $K = 1.51 \times 10^{-5}$ and $a = 0.52$ (84) (see page 112).

The degree of neutralization of the salt was obtained from a potentiometric titration with silver nitrate using a silver-tungsten electrode pair (82 page 198).

Simple electrolytes

The simple electrolytes used were analytical reagent grade salts and were used without further purification. The monomeric salt 4-ethyl-N-n-butylpyridinium bromide, analogous to PBPB, was prepared in the same manner as PBPB.

Non-electrolytes

In the work on salting-out, gaseous and solid non-electrolytes were used. Argon and ethylene were chosen as typical neutral gases because of their structural simplicity and because of their moderate solubilities. The solubility should be large enough so that it can be measured with fair accuracy but still be small enough so that the mole fraction of the non-electrolyte remains small compared with that of the solvent (see section III-C-i). Other gases could have been used, but then more elaborate techniques would have to be used or extra corrections would have to be applied in the theoretical calculations of salting-out constants. The two gases were the bottled reagent materials and were used without further purification since small amounts of impurities or moisture would not affect the salting-out results in the aqueous solutions used to any significant extent.

The two solid non-electrolytes used were d-l leucine and benzamide. Besides their suitable solubilities and structures, these compounds were chosen since they contained nitrogen so that their equilibrium solubilities could be determined directly by analysis for nitrogen by the Kjeldahl method. These two compounds were of reagent grade purity and no further purification was considered necessary.

ii) Solubility of Gases

Many techniques have been developed for measuring solubilities of gases (85) (86) depending on (a) the nature of the gases; (b) their solubility and (c) the accuracy required in the equilibrium measurements. The solubility can be measured either directly from the amount of gas dissolved when equilibrium is reached, or indirectly by analysis of the solution after the two-phase equilibrium has been reached. In the present measurements, the first method has been employed and the apparatus used was similar in principle to that described by Akerlof (87).

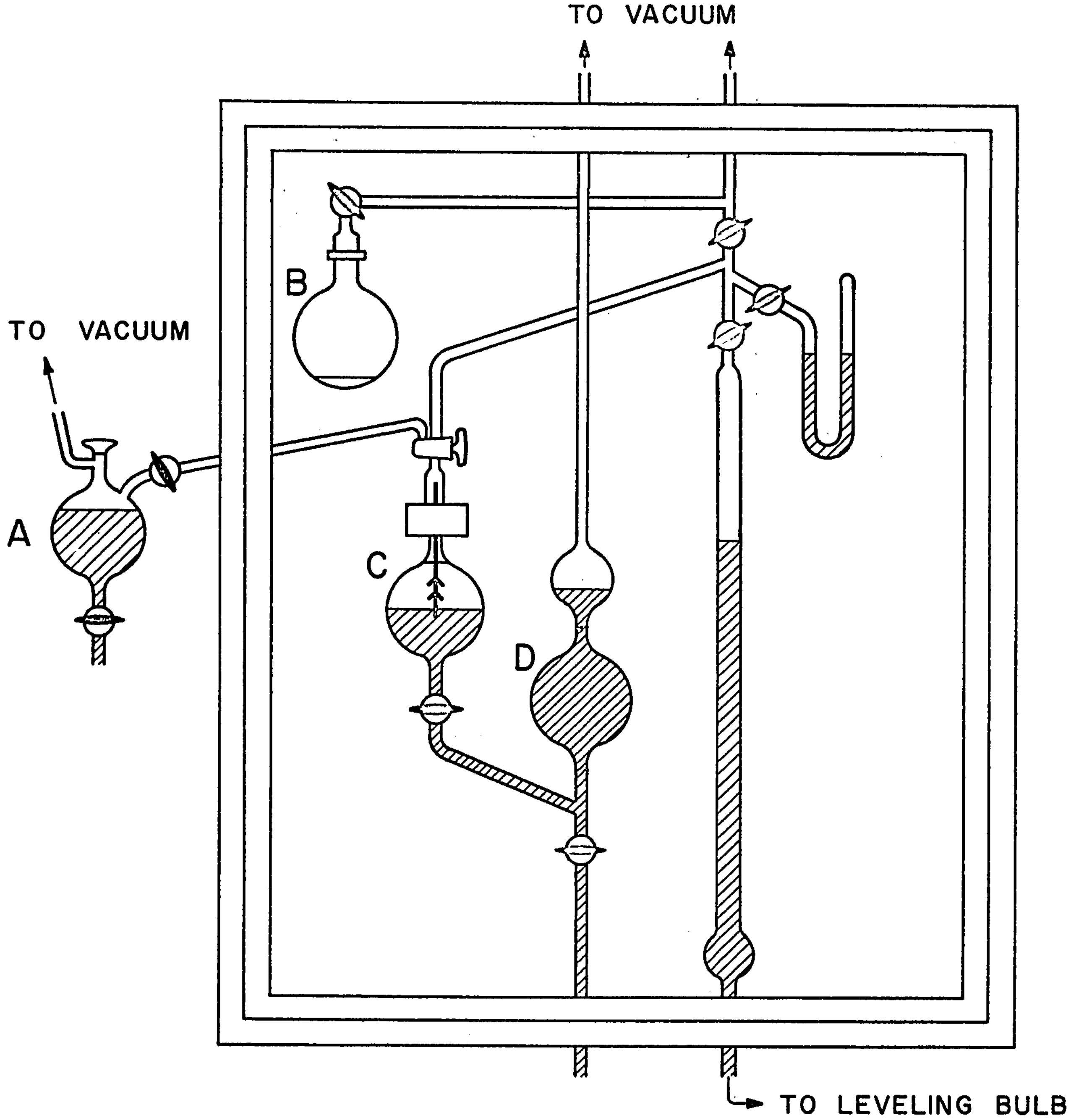
Factors to be considered in solubility measurements

Three main factors have to be considered: temperature, pressure and attainment of equilibrium. The apparatus used, represented schematically in Fig. 19, was thermostated by means of an air bath. The bath was made entirely of "Ten-Test" except for a front leucite window. The heat was supplied from an electric bulb and a fan kept the temperature uniform throughout the bath. A check of the temperature in different parts of the bath showed that its variation in different regions of the box near the solubility vessel did not exceed 0.1° C. The experiments were carried out at 30.0° C.

The pressure of gases used inside the glass vacuum system was kept constant throughout the experiments by adjusting a levelling bulb connected to the gas burette so as to keep the pressure inside the system equal to that in the sealed manometer (see Fig. 19). The measurements of the volume of gas dissolved were corrected to 760 mm. of total pressure.

In solubility measurements, it is of the utmost importance that equilibrium between the dissolved and undissolved gas be reached. Effective agitation of the liquid is therefore essential, and this was achieved by operation of a shaker moving up and down in the solution under the influence of a solenoid outside the glass vessel. The current was supplied to the solenoid from a 12 volt battery and was cut on and off by a rotating switch. The equilibrium was assumed to be reached at such a time when no more dissolution of the gas in the solution could be detected over a further period of two to three hours. This point was usually reached after twenty to thirty hours. The equilibrium point was checked in a few cases by dissolving more gas (by increasing the pressure) and letting the equilibrium be reached again at the same fixed pressure. Very little difference in solubility was detected, thus confirming that equilibrium was reached in the initial solubility measurements. Before final volume measurements were taken in each run, the solenoid was

Figure 19. Apparatus for measuring gas solubilities.


TO VACUUM
TO VACUUM
B
A
C
D
TO LEVELING BULB

switched off in order to avoid possible errors arising from heat conduction from the solenoid to the solution.

Several further factors must be considered in solubility measurements of gases in order to obtain precise data. The pressure of the undissolved gas must be corrected for the vapour pressure of solvent over the solution. Since the vapour pressure of the solvent in the solution changes with the concentration of the dissolved electrolyte, such corrections are difficult. The problem was avoided by saturating the gas with the vapour in vessel B (see Fig. 19) before starting the experiment. The solubility measurements are then obtained in terms of the total pressure of the system, i.e. in terms of the pressure of the gas plus the vapour pressure of the solution. The normal way of expressing solubilities is in terms of the gas pressure only and therefore our measured solubilities are too small. In order to obtain absolute solubilities we should multiply our solubilities by a factor P_t/P, where P_t is the total pressure and P the actual partial pressure of the gas. However, we are only interested in relative solubilities in salting-out measurements and this correction term is cancelled provided, of course, the vapour pressure of the salt solution is close to that of the pure solvent. In general, this is true. Consider, for example, the vapour pressure of a 1 N NaCl solution at 25°C, the difference between the vapour pressure of water p^o and that of the solution p is given by Robinson and Stokes (6 page 476) as 0.785 mm of mercury. Therefore, the true relative solubility of a gas in 1 N NaCl solution should be

$$\frac{S}{S_o} \cdot \frac{P_t/P}{P_t/P_o} = \frac{S}{S_o} \cdot \frac{760-23.75}{760-23.75-0.785}.$$

Therefore, our relative solubility should be multiplied by a factor 1.001 and this correction is well inside experimental error and certainly negligible. Unless the vapour pressure of the polyelectrolyte solutions would be very much different from NaCl solutions at comparable ionic concentrations, which is improbable, our salting-out measurements will not be significantly in error due to neglect of solution vapour pressures.

In order to minimize the error on the measurement of volume change during equilibration, the dead space in the system was kept small by making use of capillary tubing wherever possible. Finally, the solution to be used as a solvent for the gas must be free of any dissolved gases prior to the experiment. The simplest way of degassing a solution is to evacuate it periodically with a vacuum pump and then let it stand under vacuum. This procedure took from four to twelve hours depending on the solution used. A small error could be introduced due to the evaporation of some of the solvent during the degassing process, but this was corrected for by collecting the evaporated solvent, under standardized degassing conditions, in a liquid air trap. In subsequent experiments carried out under the standard conditions an equivalent amount (about 2 mls.) of pure solvent was first added to the solution (250 mls.) prior to degassing to compensate for this loss by evaporation. The amount of solvent lost by evaporation could be estimated to 20% (i.e. 0.4 ml.) so that the error in the final electrolyte concentration was determined by the error of 0.4 ml. in 250 mls., i.e. 0.16% which was considered negligible. Actually, this negligible error could have been avoided completely if the exact concentration of the salt solution had been measured after rather than prior to the solubility measurements. A simple way of doing this would be to measure accurately the density of the solution after the experiment and estimate the concentration from a calibration curve of concentration against density.

Solubility measurements

Essentially, the method used to measure the solubilities of the gases was as follows. The vessel C in Fig. 19 was first filled with mercury and the degassed liquid from vessel A was introduced into vessel C by displacement of mercury into a calibrated vessel D until vessel D was full of mercury. Thus, the volume of solution in vessel C was equal to the calibrated volume of bulb D. The gas, stored in vessel B and saturated with the solution vapour, was now introduced into the gas burette where its volume was measured accurately. The gas was then introduced into vessel C by displacement of mercury as before. The shaking of the solution was started and the pressure adjusted periodically so as to keep it constant. The amount of dissolved gas was obtained by returning the gas to the gas burette by raising the mercury in the vessel C and measuring the difference in volume. This procedure was repeated until equilibrium had been reached.

The gas burette and the vessel D were both calibrated by filling them with mercury at known temperature and weighing this mercury.

Accuracy and reproducibility

The solubilities of the gases in pure water measured in the above apparatus agreed fairly well with those recorded in the literature. The solubilities in cc. of gas per 100 mls. of water at 30.0°C and one atmosphere of gas pressure (corrected for the vapour pressure of water) were found to be equal to 2.90 for argon and 9.86 for ethylene. The corresponding values taken from the literature were 2.89 (88) and 9.04 (88a). Because of the excellent agreement between our results and the literature value in the case of argon and since our results are reproducible within one percent, it seems that the value quoted in the literature for ethylene may be slightly in error. Therefore, the absolute values of our measured solubilities are probably correct within the overall experimental error.

The largest error in the measurement of solubility of gases in a simple salt solution is probably the measurement of the volume in the gas burette. Since the amount of gas dissolved in the solution varied between three and five mls. for argon (about 200 mls. of solution were used in an experiment), the error is of the order of one percent. Other sources of error such as fluctuations in temperature and pressure, uncertainty in the equilibrium between dissolved and undissolved volume of gas and degassing of the solution should contribute about 0.5 percent error. Therefore, the total error in the measurement of solubilities of argon in simple salt solutions is estimated to be about 1.5 percent. Correspondingly, the maximum error in salting-out measurements will be 3 percent if we neglect the error in the concentration of the salt solution.

The experimental errors in the measurements of salting-out by polyelectrolytes are significantly larger than those encountered in the measurements with simple electrolytes. This is a result of the difficulties involved in a) preparing polyelectrolytes of purity comparable with that of simple crystallizable salts; b) degassing the solution since foaming often occurs when a vacuum is applied to the solution and c) attaining equilibrium in dissolving the gas since the high viscosity of the polyelectrolyte solution prevents the stirring of the solution from being very efficient. The exact error introduced by these effects is difficult to evaluate with certainty but the overall error in the measurements of the salting-out constants for polyelectrolytes should not exceed seven percent.

iii) Solubility of Solid Non-Electrolytes

In general, it is easier to measure the solubility of solids than gases, provided there exists some simple method of analysis for the dissolved substance. In the present experiments, amides and amino acids were chosen as non-electrolytes. The solubilities of these non-electrolytes can be determined readily by analysis for nitrogen by the standard Kjeldahl method provided, of course, that the salt does not contain any nitrogen.

Procedure

An insulated constant temperature water bath was used to keep the temperature constant during the measurements of solubilities. The temperature was maintained at $30.4 \pm 0.1^{\circ}C$.

The procedure was as follows: 50 mls. of salt solution were placed in a 100 mls. volumetric flask. An excess of non-electrolyte was added, the flask was stoppered and placed in the water bath. By means of an automatic shaker, the solution and the non-electrolyte were mixed continuously. The equilibration time varied with the solutions, it being found that more time was required for a non-electrolyte to dissolve to equilibrium in a viscous solution of a polyelectrolyte than in a simple salt solution due to the less efficient stirring in the former case. In all cases, the equilibrium was reached after 48 hours of shaking. This was confirmed by repeating some experiments under conditions where the equilibrium was approached from a higher temperature; the mixture of salt solution and non-electrolyte was heated initially to about 45°C and later placed in the thermostat at 30.4°C. Analysis of the solution after 24 hours gave the same result as in the first experiments.

After equilibrium had been reached, the solution was filtered through a sintered glass funnel completely enclosed so that it could be placed inside the constant temperature bath during the filtration, thus maintaining the solution being filtered always at the same temperature.

A 10 mls. sample was then analysed by the standard Kjeldahl method (89) using mercuric sulphate and potassium sulphate as catalysts. Each analysis was carried out at least in duplicate.

Accuracy and reproducibility

The accuracy of the analytical procedure was checked by adding a known amount of non-electrolyte to a polyelectrolyte solution (PBPB could not, of course, be used in this part of the work since it contains nitrogen) and the analysis of the mixture was found to give the correct amount of non-electrolyte present to better than one-percent for both non-electrolytes used (d-l leucine and benzamide).

The absolute values of the solubilities are also reliable to one percent. For example, the solubility of d-l leucine calculated from the data of Cohn and Edsall (90, page 190) is 1.056 grams per 100 mls. of water; Our average value was 1.051. The overall errors in the salting-out measurements (arising from errors in analytical results, concentration of salt used, temperature, etc.) were estimated to be not greater than three percent.

iv) Density of the Polyelectrolyte Solutions

The apparent molar volume ϕ_v of a solute in solution can be obtained directly from the density d of the solution, and accuracy of ϕ_v depends almost entirely on the accuracy of the term $d - d_o$ (see equation [I-27]), where d_o is the density of the pure solvent and d that of the solution. One of the simplest methods available which will give the required accuracy is the differential float or buoyancy method.

Apparatus

The apparatus used was essentially similar to that described by Bauer (62). Two glass floats were suspended from the two pans of an analytical balance by fine platinum wires. The balance was placed over an insulated constant temperature bath such that the vessels containing the floats and the solution of unknown density could be kept at constant temperature during the measurements. The platinum wires were platinized in the regions corresponding to their contact with the air-liquid meniscus of the solutions in order to minimize possible errors due to unequal wetting of the wires and hence to differential surface tension effects. The level of the liquid in the measuring vessels was always kept constant to avoid corrections for different weights and volumes of the platinum wires immersed.

The glass floats had volumes of about 120 mls. and their overall effective densities were adjusted so that they would just sink in the solution of highest density (about 1.1 grams/cc.). Their volumes were measured accurately by weighing them in air and in water. From the accurate knowledge of the density of water, their volumes could be calculated. Two floats were used differentially during the experiments to minimize errors arising from surface tension, wetting and buoyancy. The errors associated with the use of one float and wire are then nearly completely compensated by those arising at the second float and wire in the reference vessel containing pure water.

The insulated water bath was completely covered except for two holes where the vessels containing the solution and pure water were inserted. Heat was supplied to the bath by a partly submerged electric bulb, and the temperature was kept constant by means of a carbon tetrachloride regulator. The temperature was maintained at 30.00°C and did not fluctuate more than 0.02°C near the vessels during the experiments.

Measurements

A first experiment was always made with distilled water in both vessels and the difference in the weights of the two floats was determined (wt_o). The experiment was then repeated with one of the vessels containing the solution of unknown density and the new difference in weight was measured (wt). The difference in density between the solution and pure water is therefore given simply by

$$d - d_o = \frac{wt - wt_o}{V} \qquad [III-1]$$

where V is the volume of the float. The liquid in the reference container does not change, so that the volume of the reference float does not appear in the calculations. Between each run, enough time was allowed to let the temperature inside the vessels become equal to that in the thermostated bath. The point of thermal equilibrium is easily determined by making measurements at different times and is indicated when "wt" ceases to drift any more in any one direction.

Two floats were used for most experiments, but in some cases the viscosity of the polymer solutions was so large that a long time was required for the two pans of the balance to come to equilibrium. In such cases, the advantages of using two floats was neutralized by the uncertainty in the exact determination of the weight "wt". Therefore, for these viscous solutions, only one float was used. That the accuracy was not then affected very seriously was established by measuring the density of some solutions with one and with two floats independently.

The solutions of simple and polymeric salts were made up by volumetric methods. In accurate density measurements (62) it is usually necessary to weigh out the salt and solvent since the molarity of a solution depends on the temperature. Unfortunately, in the present work, limitations arose owing to the fact that the effect of variation of the degree of neutralization of PMA on the partial molar volume was required. Accordingly, solutions of the polysalt were made up by titrating a solution of PMA with standard KOH, so that the accuracy of these titrations limits the accuracy of the concentration of the polysalt.

Accuracy and reproducibility

The density measurements could be obtained to six decimal places although in most cases the last decimal place was rather uncertain. The density of a potassium chloride solution was measured at 30.00°C and compared with the values given in the International Critical Tables for different concentrations. Both sets of values agreed to the fifth decimal place. The apparent molar volume of KCl at infinite dilution was also calculated and was found to be 26.6 mls. per gram-ion at 30.00°C. The value given by Moelwyn-Hughes (91, page 851) is 26.5 mls. per gram-ion at 25°C so that the agreement is quite satisfactory. The density measurements were reproducible to about 5 in the sixth decimal place.

If we neglect small errors in the temperature fluctuations, wetting of the platinum wires, buoyancy etc., the overall error in the estimation of ϕ_v will be the sum of the errors on m and $d - d_o$ (see equation [I-27]). The relative error on these two terms varies with concentration but it is found that above 0.01 M both these terms are reliable inside one percent. Therefore ϕ_v and also ϕ_v^o, the apparent molar volume at infinite dilution, are reliable within two percent. At concentrations lower than 0.01 M, the error increases very significantly and the values ϕ_v in this region are not reliable in the evaluation of ϕ_v^o.

B - EXPERIMENTAL RESULTS

The measured solubilities and salting-out ratios (91) of non-electrolytes are given as a function of concentration of the simple and polymeric electrolytes in Tables 2 to 6. The densities of corresponding salt solutions are given in Tables 7 and 8. All the gas solubilities were corrected to one atmosphere total pressure and are expressed in mls. of gas dissolved at equilibrium per 100 mls. of solution. Normally solubilities are given at one atmosphere gas pressure rather than total pressure but, as we have mentioned previously, the way in which we express solubilities does not affect the calculations of salting-out constants, provided, of course, the vapour pressure of the solution is not too different from that of the solvent (see page 118). The solubilities of the solid non-electrolytes are expressed in grams of non-electrolyte per 100 mls. of solution. The gas solubilities were measured at 30.0°C, the solubility of solids at 30.4°C and the densities at 30.00°C. All the concentrations are expressed in moles per liter (M). In the case of polyelectrolytes, the concentration m is the molarity of the counterions or, in other words, that of the neutralized monomer units on the polymer chain.

Salting-out by NaPP

The salting-out data for ethylene, argon and d-l leucine by sodium polyphosphates are given in Table 2 and sodium dihydrogen phosphate was taken as the reference simple electrolyte corresponding to these polysalts. The salting-out constants k_s were obtained from the slope of the plot of $(S_o - S)/S_o$ against m (see, for example, Fig. 20) and are also listed in Table 2. In Fig. 21 k_s is plotted as a function of the molecular weight of the polyphosphates for the different systems. From this graph the following conclusions can be drawn:

a) The salting-out constant depends on the nature of the non-electrolyte and decreases in the order ethylene, argon and d-l leucine.

b) The dependence of k_s on the molecular weight of the polyelectrolyte seems to be independent of the nature of the non-electrolyte. The constant k_s decreases rapidly at first as the molecular weight increases and beyond a certain molecular weight, approximately 3,000, k_s becomes nearly independent of the molecular weight.

c) The polyelectrolyte (NaPP) salts-out <u>less</u> than the corresponding simple electrolyte (NaH_2PO_4).

Salting-out by KPMA and by PBPB

The salting-out data for argon and benzamide by potassium polymethacrylate and for argon by poly-4-vinyl-N-n-butylpyridinium bromide are given in Tables 3, 4 and 5. Potassium isobutyrate was chosen as the reference simple electrolyte for KPMA, and both 4-ethyl-N-n-butylpyridinium

Table 2

SALTING-OUT BY POLYPHOSPHATES

Salt	m moles/liter	S mls. gas/100 mls. solution	$\frac{S_o - S}{S_o}$	k_s liters/mole
Argon by NaPP* at 30.0°C: S_o = 2.81 ± 0.03 mls./100 mls. water				
NaH_2PO_4	0.50	2.19	0.220	
	1.00	1.55	0.448	
	2.00	0.97	0.656	0.44 ± 0.01
800 M-W	0.50	2.36	0.160	
	1.00	1.99	0.296	0.31
2800 M-W	0.50	2.47	0.121	
	1.00	2.22	0.210	0.22
6800 M-W	0.50	2.58	0.082	
	1.00	2.16	0.231	0.22
Ethylene by NaPP* at 30.0°C: S_o = 9.42 ± 0.05 mls./100 mls. water				
NaH_2PO_4	0.50	7.08	0.258	
	1.00	4.81	0.496	
	2.00	3.31	0.654	0.50 ± 0.01
2800 M-W	0.50	8.24	0.136	
	1.00	7.07	0.259	
	2.00	5.08	0.468	0.26

Table 2 (Cont'd.)

Salt	m moles/liter	S mls. gas/100 mls. solution	$\frac{S_o - S}{S_o}$	k_s liters/mole
d-1 leucine by NaPP at 30.4°C: $S_o = 1.051 \pm 0.007$ gms./100 mls. water				
NaH_2PO_4	0.257	0.987	0.061	
	0.514	0.913	0.131	
	1.029	0.779	0.258	0.251 ± 0.005
800 M-W	0.267	1.018	0.031	
	0.533	0.989	0.059	
	1.067	0.900	0.144	0.118
2800 M-W	0.245	1.024	0.026	
	0.489	1.003	0.046	
	0.979	0.945	0.101	0.095
6800 M-W	0.229	1.038	0.013	
	0.459	1.016	0.033	
	0.917	0.976	0.071	0.075

---

* These experimental salting-out constants of argon and ethylene by NaPP were presented as part of a thesis for the final B.Sc. year at this University.

Figure 20. Salting-out ratio for d-l leucine by NaPP, as a function of concentration.

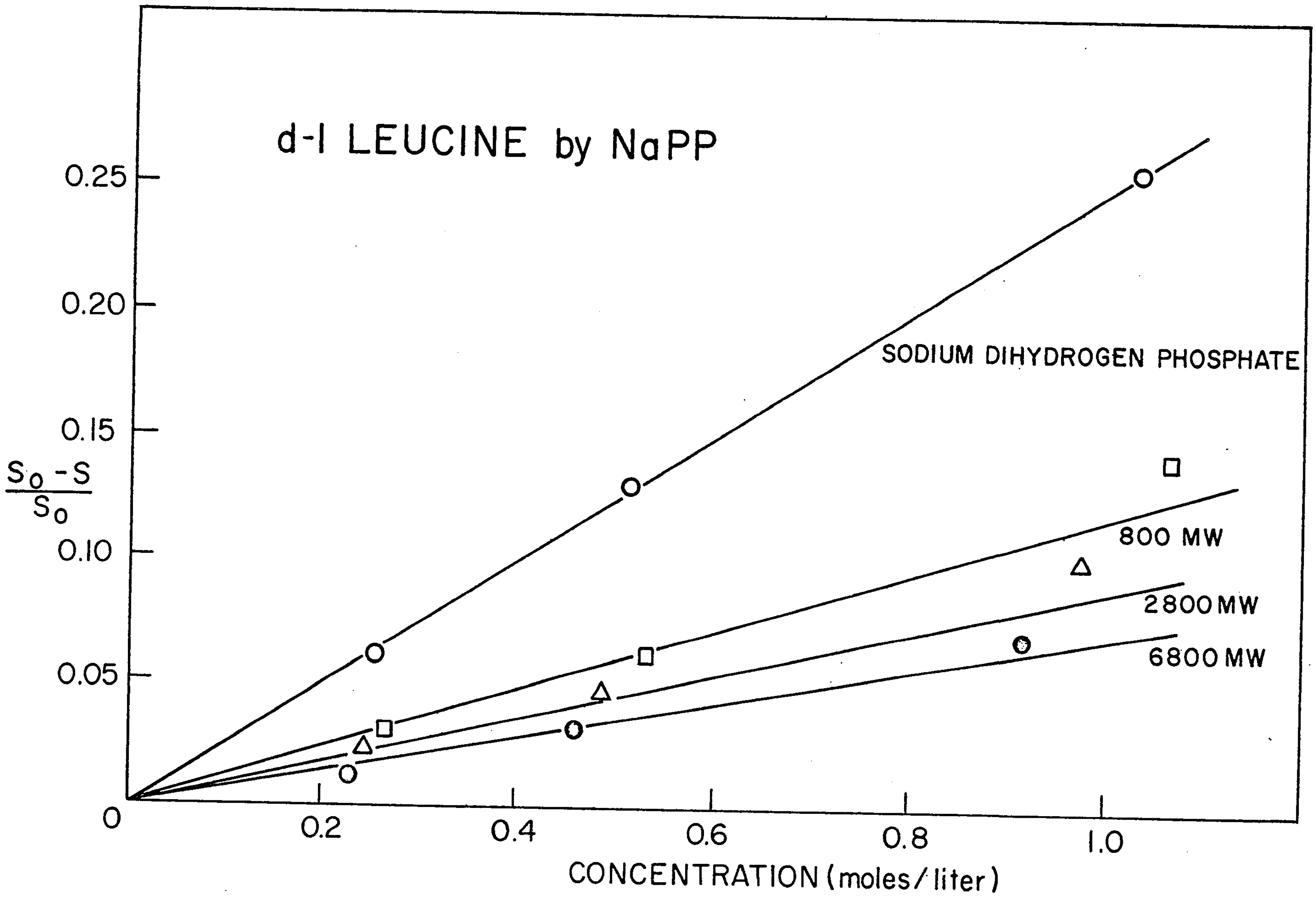

d-l LEUCINE by NaPP
$\frac{S_o - S}{S_o}$
0.25
0.20
0.15
0.10
0.05
0
0.2
0.4
0.6
0.8
1.0
CONCENTRATION (moles/liter)
SODIUM DIHYDROGEN PHOSPHATE
800 MW
2800 MW
6800 MW

Figure 21. Salting-out constants for three different non-electrolytes as a function of the polymer (NaPP) molecular weight.

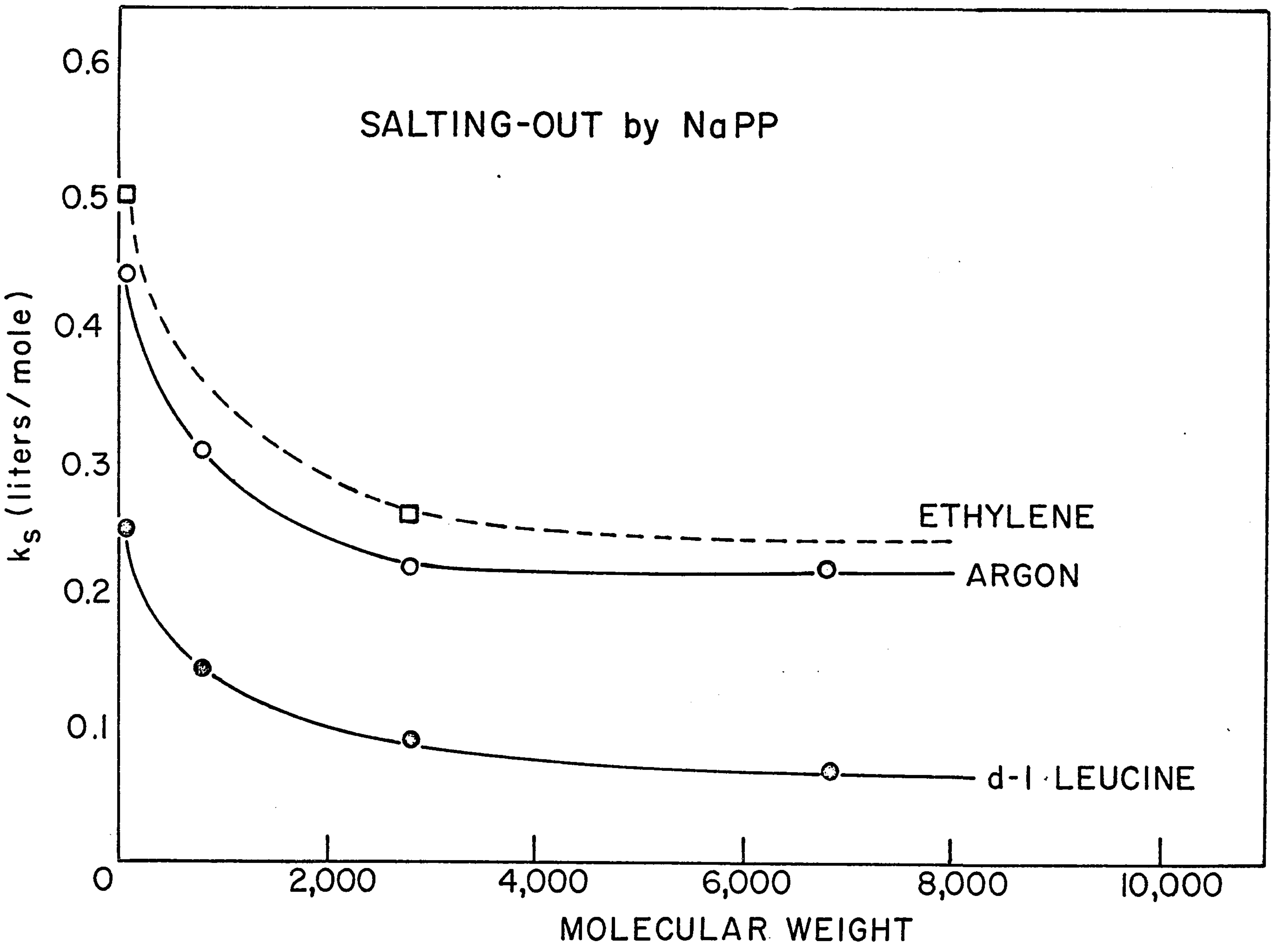

SALTING-OUT by NaPP
k_S (liters / mole)
0.6
0.5
0.4
0.3
0.2
0.1
0
2,000
4,000
6,000
8,000
10,000
MOLECULAR WEIGHT
ETHYLENE
ARGON
d-l · LEUCINE

Table 3

SALTING-OUT OF ARGON BY KPMA AT 30.0°C

Molecular weight of PMA is 56,000: $S_o = 2.81 \pm 0.03$ mls./100 mls. water.

Salt	m moles/liter	S mls. gas/100 mls. solution	$\frac{S_o - S}{S_o}$	k_s liters/mole
Potassium isobutyrate	1.01	1.88	0.331	
	0.50	2.30	0.181	
	0.25	2.52	0.103	
	0.24*	2.55	0.093	0.35 ± 0.01
100% neutralized	0.03	1.74	0.381	
	0.80	1.97	0.299	
	0.47	2.22	0.211	
	0.40	2.38	0.153	
	0.23	2.58	0.082	
	0.20	2.57	0.085	0.41 ± 0.03
73.3% neutralized	0.66	1.73	0.384	
	0.33	2.22	0.210	
	0.165	2.55	0.092	0.58
61.0% neutralized	0.555	1.86	0.340	
	0.275	2.30	0.182	
	0.14	2.54	0.076	
	0.275≠	2.35	0.166	0.63

Table 3 (Cont'd.)

Salt	m moles/liter	S mls. gas/100 mls. solution	$\frac{S_o - S}{S_o}$	k_s liters/mole
44.5% neutralized	0.40	1.78	0.367	
	0.20	2.39	0.150	
	0.10	2.57	0.085	
	0.30[≠]	2.07	0.263	0.86 ± 0.03
26.7% neutralized	0.24	2.31	0.178	
	0.12	2.56	0.089	0.71
17.8% neutralized	0.12[≠]	2.63	0.064	0.50

---

[*] 1 M w.r.t. isobutyric acid and 0.24 M w.r.t. KOH.

[≠] PMA isolated and fractionated by addition of ethyl methyl ketone to an aqueous solution of PMA.

Table 4

SALTING-OUT OF BENZAMIDE BY KPMA AT 30.4°C

Molecular wt. of PMA is 78,000: $S_o = 1.560 \pm 0.007$ gms./100 mls. water.

Salt	m moles/liter	S gms./100 mls. solution	$\frac{S_o - S}{S_o}$	k_s liters/mole
Potassium isobutyrate	0.916	1.29	0.171	
	0.458	1.43	0.092	
	0.229	1.50	0.037	0.185 ± 0.005
92.0% neutralized	0.507	1.20	0.231	
	0.254	1.39	0.109	
	0.127	1.48	0.051	0.43 ± 0.015
76.4% neutralized	0.372	1.28	0.174	
	0.186	1.41	0.096	
	0.093	1.50	0.039	0.48
66.0% neutralized	0.372	1.32	0.154	
	0.186	1.43	0.083	
	0.093	1.49	0.045	0.45
54.6% neutralized	0.372	1.40	0.102	
	0.186	1.46	0.051	
	0.093	1.51	0.032	0.28
46.0% neutralized	0.304	1.48	0.051	
	0.152	1.53	0.019	0.16

Table 5

SALTING-OUT OF ARGON BY PBPB AT 30°C

Salt	m moles/liter	S mls. gas/100 mls. solution	$\frac{S_o - S}{S_o}$	k_s liters/mole
4 vinyl-N-n-butyl pyridinium bromide	0.690	2.40	0.146	
	0.345	2.56	0.089	
	0.170	2.68	0.046	0.25 ± 0.03
4 ethyl-N-n-butyl pyridinium bromide	0.97	1.98	0.295	
	0.485	2.46	0.124	
	0.24	2.63	0.062	0.25
91% neutralized	0.37	2.37	0.156	
	0.185	2.63	0.064	
	0.14	2.68	0.046	0.36
63% neutralized	0.37	2.42	0.138	
	0.185	2.61	0.071	0.36
49% neutralized	0.23	2.53	0.100	
	0.115	2.69	0.043	0.38

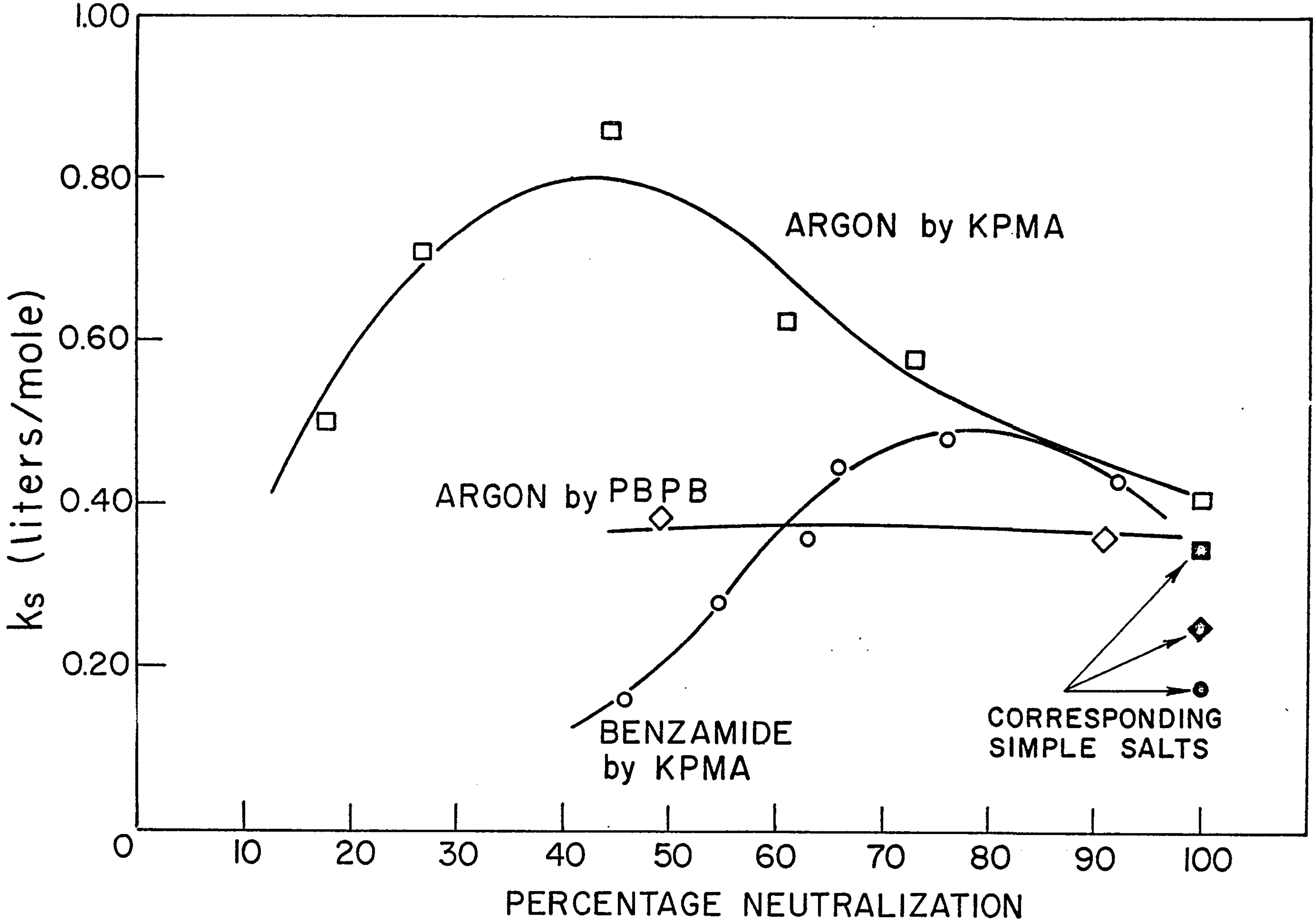
bromide and 4-vinyl-N-n-butylpyridinium bromide were used as reference simple electrolytes for PBPB. The salting-out constants k_s were again obtained by plotting $(S_o - S)/S_o$ against m. The values of k_s as a function of degree of neutralization are compared in Fig. 22 for the different systems. The main conclusions that can be drawn from these experiments are the following:

a) The constant k_s depends significantly on the degree of neutralization. In the case of KPMA, k_s for the polyelectrolyte is approximately equal to or lower than that of the corresponding simple salt when the degree of neutralization is low, is much larger at intermediate degrees of neutralization, and finally decreases again at high degrees of neutralization (approaching unity). The limited data available for PBPB indicate that the salting-out constant in this case is independent of the degree of neutralization.

b) The dependence of k_s on the degree of neutralization appears to be also dependent on the non-electrolyte. The maximum value of k_s for argon occurs when PMA is approximately 40 to 50 percent neutralized while in the case of benzamide the maximum occurs when the polyelectrolyte is about 80 percent neutralized.

c) At intermediate degrees of neutralization the degree of salting-out by both KPMA and PBPB at a given nomality is larger than that observed with the corresponding simple salt; this result is the opposite of that found in the NaPP case.

Figure 22. Salting-out constants for argon and benzamide by KPMA and PBPB as a function of the percentage neutralization of the polyacid or polybase.


1.00
0.80
0.60
0.40
0.20
0
ks (liters/mole)
10
20
30
40
50
60
70
80
90
100
PERCENTAGE NEUTRALIZATION
ARGON by KPMA
ARGON by PBPB
BENZAMIDE
by KPMA
CORRESPONDING
SIMPLE SALTS

d) Argon is salted-out more than benzamide.

e) The two simple salts chosen as corresponding to PBPB have the same value for k_s. Therefore, as might be expected, the presence of the double bond in the vinyl salt does not seem to influence the degree of salting-out caused by the monomeric ion.

In order to examine the possible effect of the undissociated part of the polyacid in determining k_s the salting-out by potassium isobutyrate was determined in the presence of an excess of isobutyric acid (see Table 3); it appears that the undissociated organic acid has little effect on the degree of salting-out. This was also confirmed for the polyacid itself in another experiment in which the salting-out of argon by pure polymethacrylic acid was measured, and the value of the salting-out constant was found to be less than 0.02, i.e. much less than that due to the polysalt derived from the acid.

Three experiments were carried out with KPMA in which the acid used was purified and fractionated further by dissolving the polymethacrylic acid used in previous experiments in water and then reprecipitating out the polymer by adding small amounts of methyl ethyl ketone. The fractionated polyacid was then dried in the way described previously. The salting-out data obtained with this sample of KPMA agreed, within the experimental error, with the results obtained in experiments using the sample previously referred to (see Table 3). This therefore indicates that the degree of fractionation is not critical for experiments in which salting-out constants are determined. The same conclusion was reached in the case of polyphosphates since we have shown that the molecular weight does not have much effect on the degrees of salting-out observed beyond a certain chain length.

Salting-out by KF at high concentrations

In order to study the dependence of k_s on concentration, the salting-out of argon and ethylene by KF was measured up to fairly high concentrations of salt (4.7M) and the results are recorded in Table 6. In Fig. 23 $(S_o - S)/S_o$ is plotted against m and in Fig. 24 log S_o/S is plotted against m. The main conclusions that can be drawn from these experiments are:

a) As expected, the limiting slopes in both plots are almost identical.

$$\left(\frac{S_o - S}{S_o\ m}\right)_{m \rightarrow 0} \simeq \left(\frac{2.3}{m} \log \frac{S_o}{S}\right)_{m \rightarrow 0}$$

b) Using the normal way of expressing the degree of salting-out in terms of $(S_o - S)/S_o$, the salting-out is a linear function of concentration at low concentrations, and at higher concentrations, the function deviates from linearity until an upper limiting value of unity is reached

Table 6

SALTING-OUT OF GASES BY KF AT 30.0°C

Gases	m moles/liter	S mls. gas/100 mls. Soln.	$\frac{S_o - S}{S_o}$	k_s liters/mole	$\ln \frac{S_o}{S}$	k_s' liters/mole
Argon	4.72	0.54	0.807		1.65	
	3.51	0.73	0.740		1.35	
	2.50	1.03	0.634		1.002	
	1.75	1.37	0.513		0.718	
	1.18	1.72	0.375		0.492	
	0.875	2.00	0.288		0.341	
	0.59	2.28	0.188		0.209	
	0.30	2.50	0.110	0.34	0.115	0.39 ± 0.01
Ethylene	3.51	2.20	0.770		1.47	
	2.50	3.37	0.647		1.025	
	1.75	4.46	0.532		0.759	
	1.25	5.63	0.410		0.527	
	0.875	6.48	0.321		0.386	
	0.625	7.42	0.222		0.251	
	0.428	8.06	0.155		0.168	
	0.214	8.83	0.074	0.36	0.076	0.43

Figure 23. Salting-out ratio for argon and ethylene by potassium fluoride at high concentrations.

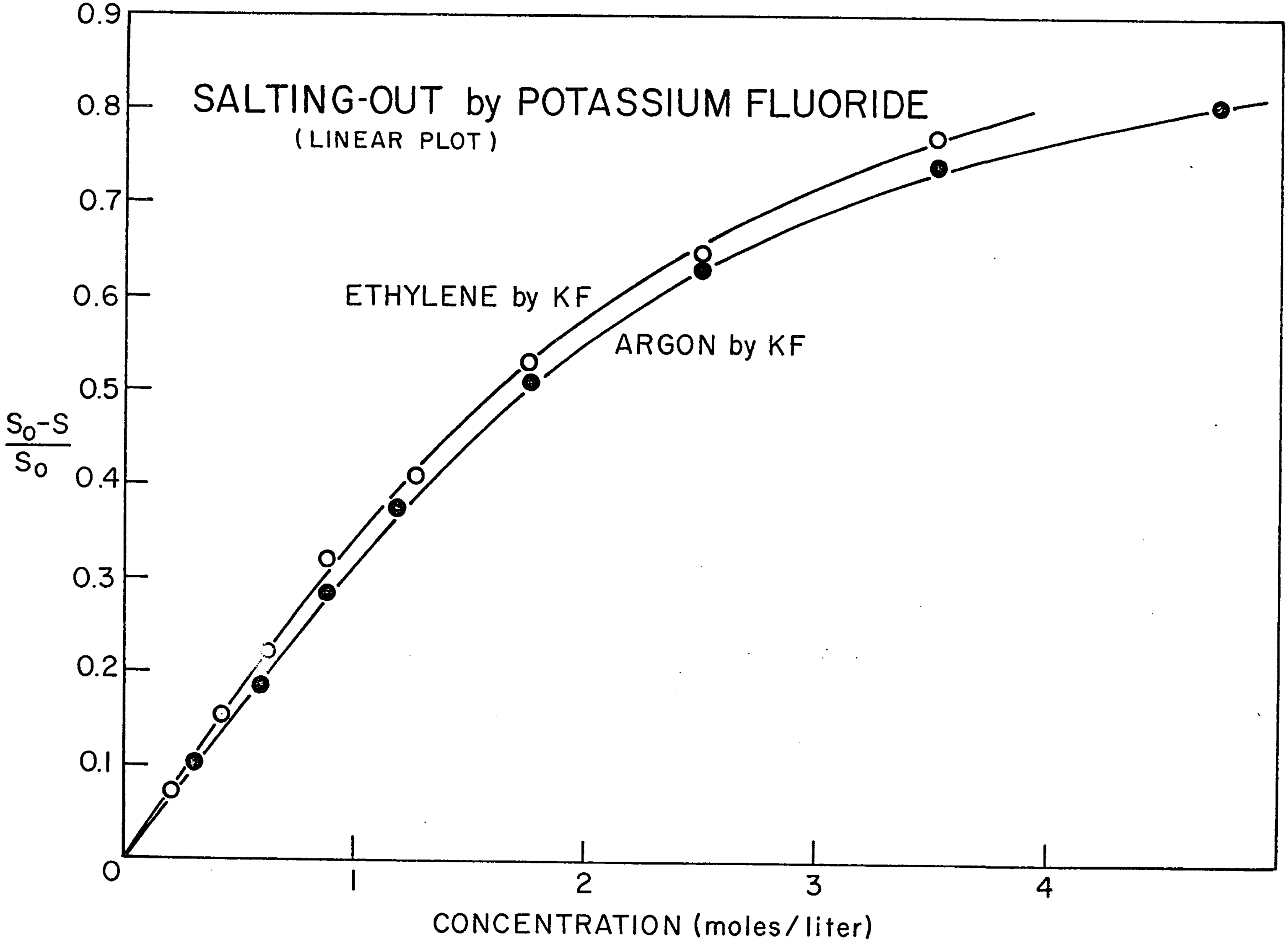
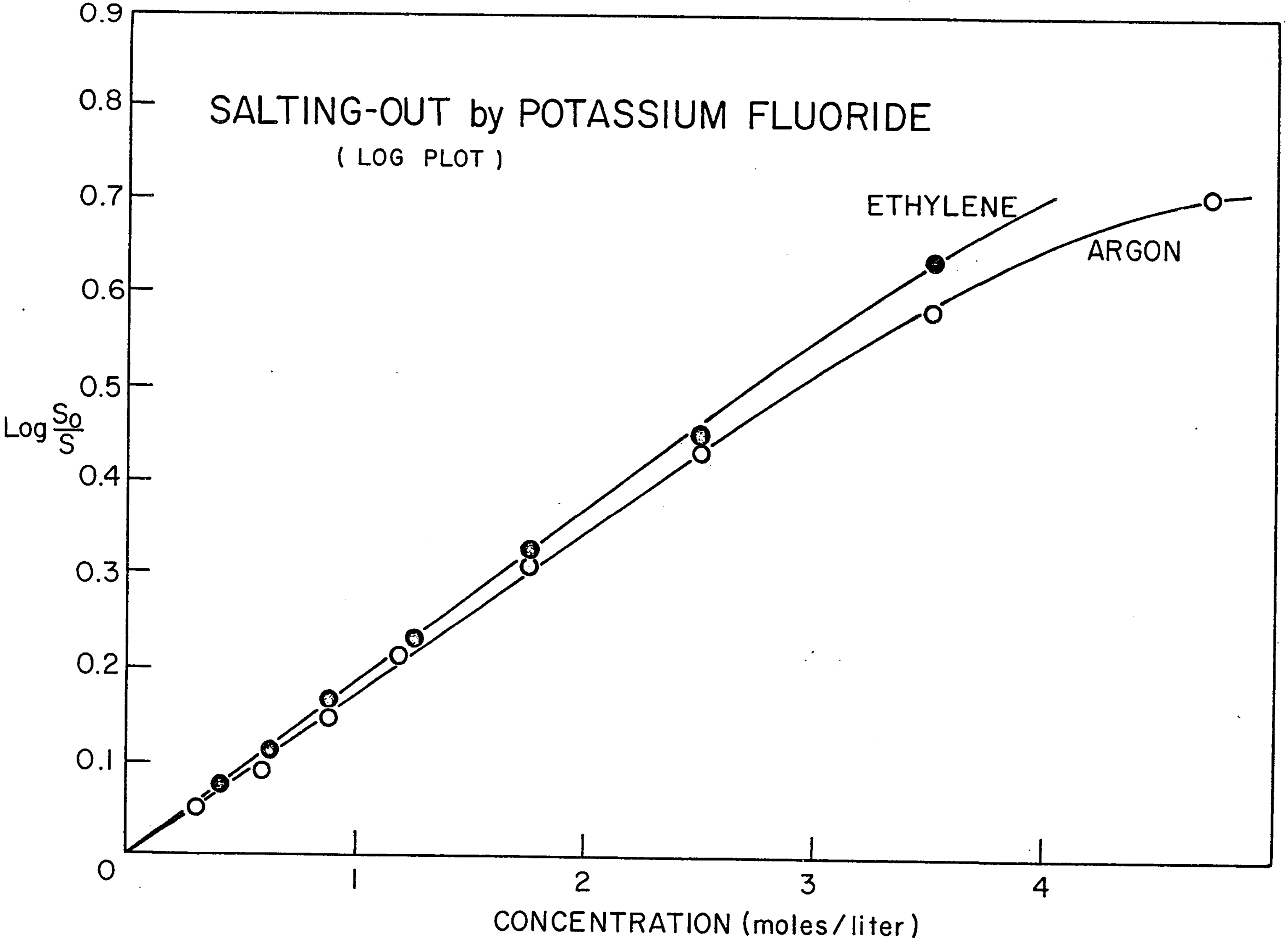

SALTING-OUT by POTASSIUM FLUORIDE
(LINEAR PLOT)
ETHYLENE by KF
ARGON by KF
$\frac{S_o-S}{S_o}$
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
CONCENTRATION (moles/liter)

Figure 24. Salting-out (logarithmic plot) of argon and ethylene by potassium fluoride at high concentrations.



SALTING-OUT by POTASSIUM FLUORIDE

(LOG PLOT)

as $S \rightarrow 0$. At very high concentrations the salting-out should become independent of salt concentration, that is, the non-electrolyte is completely salted-out.

c) The logarithmic form of expressing the degree of salting-out (equation I-23) gives a straight line to much higher concentrations but eventually deviates from linearity to some extent.

Apparent molar volumes of KPMA and NaPP

The densities of the NaPP and KPMA salts were measured in aqueous solution and the results are given in Tables 7 and 8. The apparent molar volumes of the simple and polymeric electrolytes were evaluated from equation [I-27]. For the range of NaPP oligomers studied (see Experimental section), the apparent molar volume contribution ϕ_v per monomer unit was evaluated from the observed densities of the solutions using the molecular weight of the repeating unit $[NaPO_3]$, end effects due to OH instead of O groups thus being neglected in the calculations.

In the case of KPMA, the apparent molar volume of the neutralized monomer unit on the chain was evaluated. This was done by assuming additivity of contributions from the neutralized and unneutralized monomer units with respect to change of density resulting from the presence of the polysalt in solution, i.e. the total change in density $d - d_o$ due to

Table 7

DENSITIES AND APPARENT MOLAR VOLUMES OF NaPP AT 30.00°C

d_o = 0.995646 gms./ml.

Salt	m moles/liter	d gms./ml.	ϕ_v mls./gram-ion	ϕ_v^o mls./gram-ion
NaH_2PO_4	0.10086	1.005927	17.9	
	0.03839	0.999587	17.4	
	0.01321	0.997002	17.4	
	0.00674	0.996336	17.7	
	0.00569	0.006225	18.2	16.4 ± 0.2
NaH_2PO_3	0.16400	1.006835	35.9	
	0.08833	1.001699	35.6	
	0.04521	0.994043	35.6	35.2
NaH_2PO_2	0.07178	0.999516	36.2	
	0.03437	0.997499	36.2	
	0.02031	0.996741	36.2	
	0.01164	0.996296	34.2	36.2
800 M-W NaPP	0.13665	1.006514	22.5	
	0.07361	1.001475	22.9	
	0.03084	0.998126	21.7	
	0.01618	0.996938	22.2	
	0.00809	0.996300	20.9	20.2

Table 7 (Cont'd.)

Salt	m moles/liter	d gms./ml.	ϕ_v mls./gram-ion	ϕ_v° mls./gram-ion
2800 M-W NaPP	0.15235	1.007396	25.0	
	0.04790	0.999384	24.0	
	0.02842	0.997906	22.8	
	0.02277	0.997439	23.3	
	0.01776	0.997047	23.2	
	0.01517	0.996852	22.5	21.8 ± 0.2
6800 M-W NaPP	0.13766	1.006207	25.4	
	0.07064	1.001083	25.1	
	0.01525	0.996839	23.8	22.8

Table 8

DENSITIES AND APPARENT MOLAR VOLUMES OF KPMA AT 30.00°C

Molecular weight of PMA is 43,000: $d_o = 0.995646$ gm./ml.

Salt	m(acid) moles/liter	m(base) moles/liter	d gms./ml.	ϕ_v mls./gram-ion	ϕ_v^o mls./gram-ion
Potassium isobutyrate	0.20979	0.20979	1.005422	79.9	
	0.17398	0.17398	1.003790	79.7	
	0.08291	0.08291	0.999586	78.9	
	0.04590	0.04590	0.997862	78.3	76.0 ± 0.5
Isobutyric acid	0.06326		0.995813	85.8	
	0.04822		0.995710	87.2	
	0.02588		0.995695	87.4	89.0
95% Neutralization	0.10124	0.08160	1.002194	52.5	
	0.06098	0.05795	1.000021	50.7	
	0.03689	0.03504	0.998373	48.8	
	0.01980	0.01827	0.997041	50.9	47.8

Table 8 (Cont'd.)

Salt	m(acid) moles/liter	m(base) moles/liter	d gms./ml.	ϕ_v mls./gram-ion	ϕ_v^o mls./gram-ion
75% Neutralization	0.14941	0.11207	1.004823	55.1	
	0.08339	0.06256	1.000795	53.7	
	0.05469	0.04102	0.999011	53.8	
	0.03159	0.02369	0.997632	50.4	50.0
60% Neutralization	0.18298	0.10978	1.005476	61.6	
	0.09564	0.05740	1.000821	59.6	
	0.04495	0.02696	0.998068	57.7	54.0
40% Neutralization	0.14164	0.05653	1.001851	74.9	
	0.05519	0.02208	0.998076	70.8	
	0.03037	0.01214	0.996982	66.8	61.8
20% Neutralization	0.17266	0.03543	1.001232	132.6	
	0.08944	0.01790	0.998682	120.4	
	0.06294	0.01259	0.997728	114.9	
	0.04883	0.00976	0.997296	107.9	85.5

Table 8 (Cont'd.)

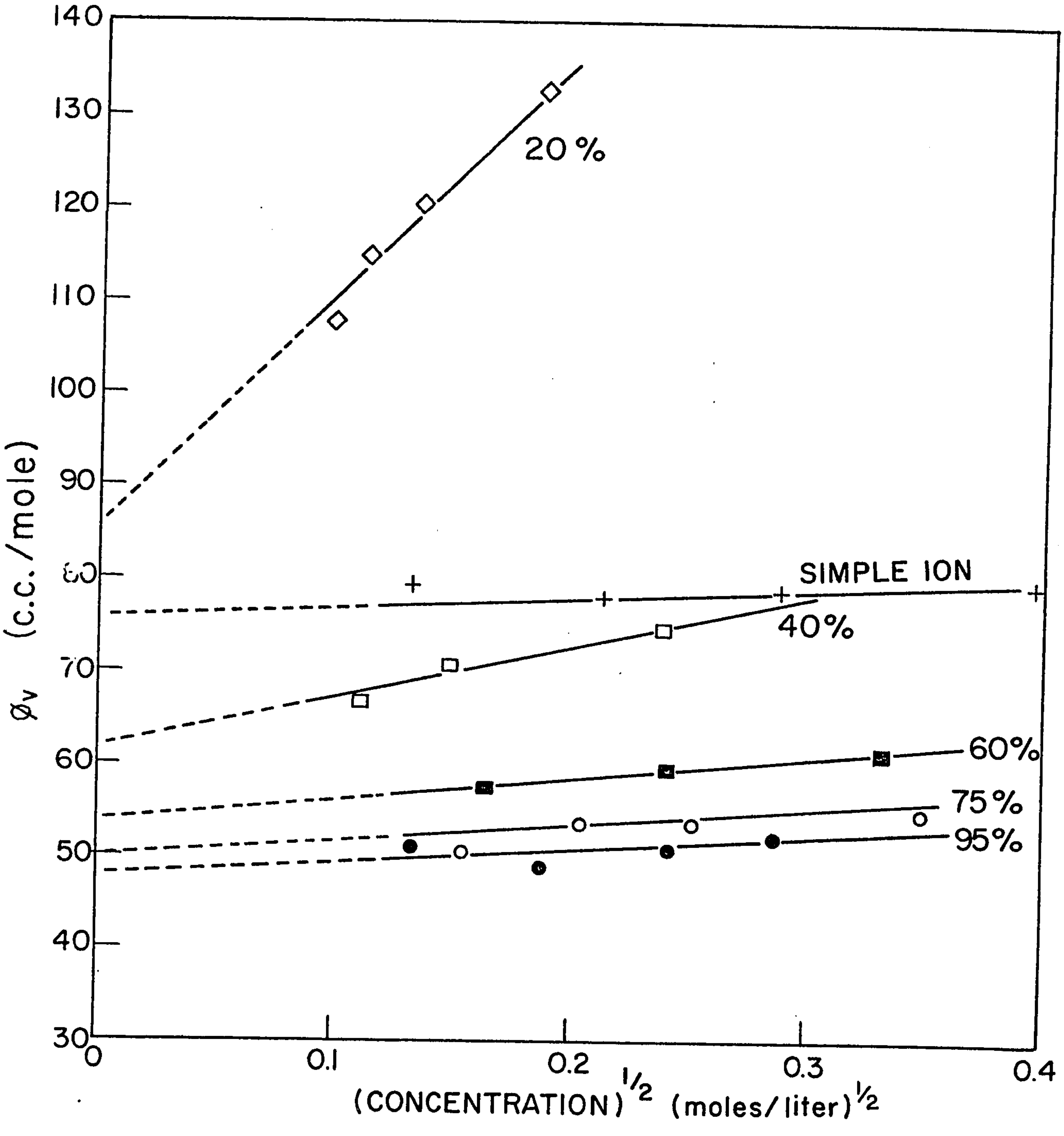
Salt	m(acid) moles/liter	m(base) moles/liter	d gms./ml.	ϕ_v mls./gram-ion	ϕ_v^o mls./gram-ion
0% Neutralization	0.18773		1.000118	62.7	
	0.07370		0.997158	66.0	
	0.03413		0.996235	69.0	
	0.02025		0.995992	69.4	72.5

In these tables, extra significant figures were carried for the concentration and density measurements in order to minimize the error in calculating ϕ_v. The concentrations are actually reliable to four decimal places and the densities to five.

introduction of polysalt into the solvent water was corrected for the presence of neutral groups in the polymer chain in the evaluation of the ϕ_v contribution for the ionic groups in the chains. This correction term can be obtained by plotting $d - d_o$ as a function of concentration for the unneutralized PMA. The densities of the corresponding simple salt solutions were also evaluated, again to serve as reference data for the purpose of comparing the electrostriction effects (in terms of ϕ_v values) of the polysalts with those of corresponding monomeric salts. The apparent molar volumes of KPMA at different degree of neutralization are plotted as a function of the square-root of concentration (62) in Fig. 25 in order to evaluate by extrapolation the limiting apparent molar volumes ϕ_v^o at infinite dilution; these ϕ_v^o volumes were then plotted as a function of the degree of neutralization in Fig. 26. The apparent molar volumes at infinite dilution of NaPP are also plotted in Fig. 27 as a function of their molecular weight. Again, the corresponding values for the simple electrolytes are given for reference. The following conclusions can be drawn from these results:

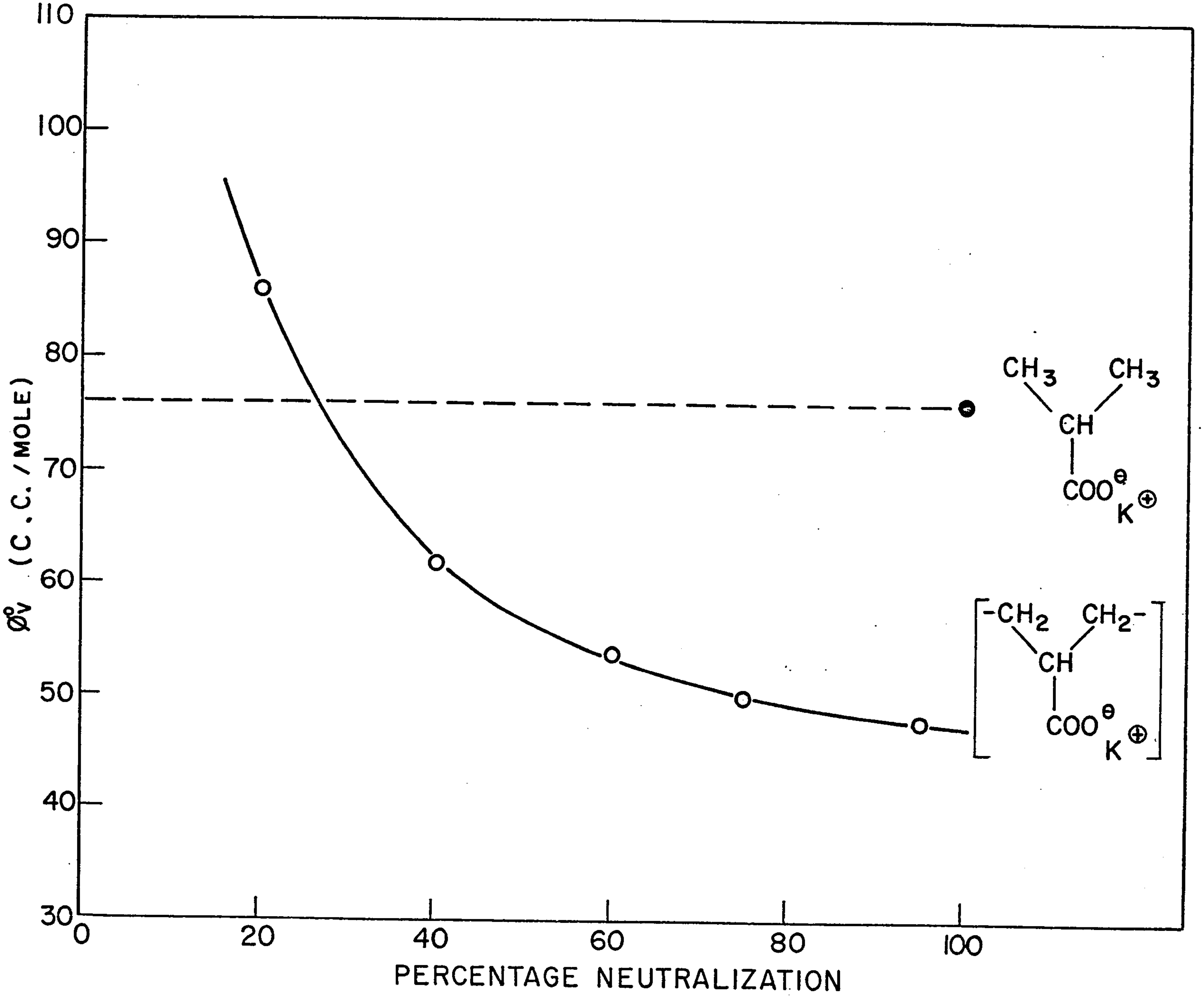
a) From Fig. 27 it is obvious that there is a close relationship between the density of the polyelectrolyte solutions and the salting-out constants for these salts. The dependence of ϕ_v^o on the molecular weight of NaPP is the reverse of that of values of k_s on molecular weight. ϕ_v^o

Figure 25. Square-root dependence of the apparent molar volumes ϕ_v of KPMA on concentration for different percentage neutralization.



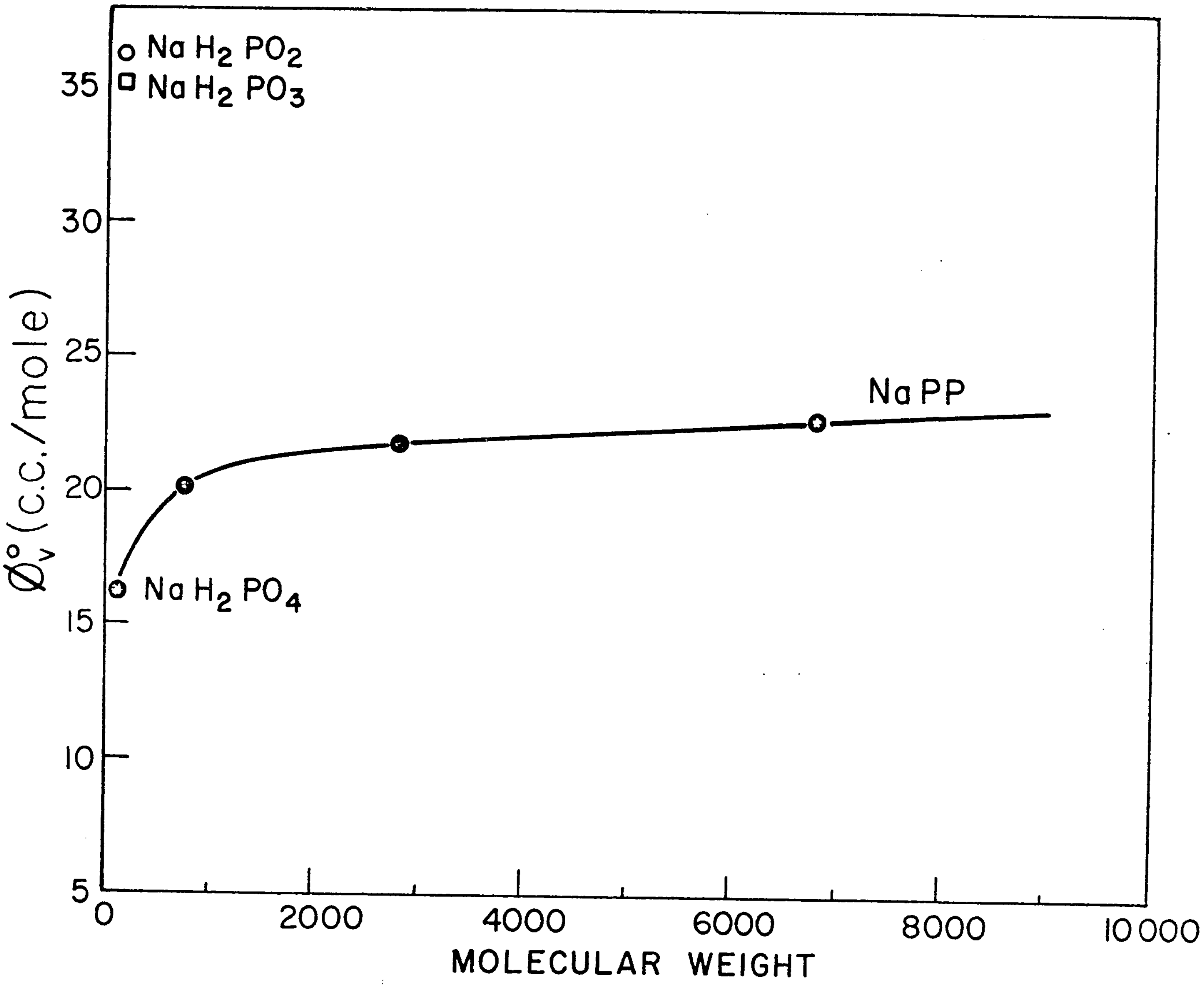
140
130
120
110
100
90
80
70
60
50
40
30
0
0.1
0.2
0.3
0.4
ϕ_v (c.c./mole)
(CONCENTRATION)$^{1/2}$ (moles/liter)$^{1/2}$
20%
SIMPLE ION
40%
60%
75%
95%

Figure 26. Apparent molar volumes of KPMA at infinite dilution as a function of the percentage neutralization.



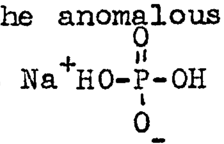
110
100
90
80
70
60
50
40
30
ϕ_v^0 (C.C./MOLE)
0
20
40
60
80
100
PERCENTAGE NEUTRALIZATION
CH_3
CH_3
CH
$COO^{\ominus}$
$K^{\oplus}$
$-CH_2$
CH_2-
CH
$COO^{\ominus}$
$K^{\oplus}$

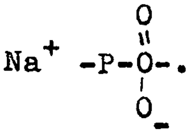
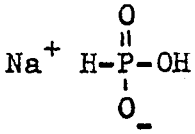
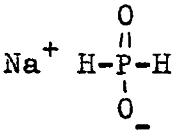
Figure 27. Apparent molar volumes of NaPP at infinite dilution as a function of molecular weight.



$Na\,H_2\,PO_2$
$Na\,H_2\,PO_3$
$Na\,H_2\,PO_4$
Na PP
ϕ_v^o (c.c./mole)
35
30
25
20
15
10
5
0
2000
4000
6000
8000
10000
MOLECULAR WEIGHT

increases fairly rapidly at first with molecular weight and for higher molecular weight ϕ_v^o becomes very nearly independent of the average chain length of the polyelectrolyte. This may be compared with the variation of k_s with molecular weight in the NaPP series as shown in Fig. 21.

It can be seen from Fig. 21 for k_s values and from Fig. 27 for the ϕ_v^o values that the relationship of these values for the polysalt NaPP to those for the corresponding simple salt NaH_2PO_4 is anomalous compared with the analogous relationship for ϕ_v^o and k_s values for KPMA and PBPB. However, the trends of both k_s and ϕ_v^o with molecular weight in the NaPP series are mutually consistent; thus the smaller electrostriction associated with the larger ϕ_v^o values as the molecular weight increases is consistent with the diminishing k_s values which are observed with increasing molecular weight. In order to find the cause of the abnormally high degree of hydration of sodium dihydrogen phosphate which, as we shall see, it is necessary to assume in order to explain these experimental results, the apparent molar volumes of sodium hydrogen phosphite and of sodium hypophosphite were also measured. The choice of these two compounds was dictated by the following factors: it was suspected that the anomalous results, referred to above, arose because the salt  $Na^+HO\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}\text{-}OH$ was being compared with NaPP whose repeating group is, in fact,

 $\mathrm{Na^+}\ -P-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O_-}{|}}{O}}-$. Hence, the salts  $\mathrm{Na^+}\ H-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O_-}{|}}{P}}-OH$ and  $\mathrm{Na^+}\ H-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O_-}{|}}{P}}-H$ may be a preferable basis for reference. As expected by comparison with the case of KPMA and theoretically (see Discussion), the apparent molar volumes of these two salts (see Table 7) are larger than that of polymeric salt NaPP. Therefore, anomalous results are obtained only with the simple salt NaH_2PO_4 and we will see later that this is probably a result of hydrogen bonding which plays an important rōle in the hydration of the low molecular weight polyphosphates, through end-group effects.

The apparent molar volumes of the salts investigated vary linearly with the square-root of concentration down to about 0.01 M. At lower concentrations the experimental points begin to scatter significantly, and the density measurements are not accurate enough to test the dependence of ϕ_v on concentration beyond this concentration of 0.01 M. However, the extrapolations of the values to infinite dilution are fairly reliable as we can see from Fig. 25.

The experimental values for the $\phi_v{}^o$ of potassium isobutyrate and KPMA are the same when the degree of neutralization is about 30 percent (Fig. 26) even though the dependence of ϕ_v of both salts on concentration is different (Fig. 25).

At a low degree of neutralization (20%), $\phi_v{}^o$ for KPMA is larger than that of the unneutralized PMA but for degrees of neutralization larger than approximately 30 percent ϕ_v^o is always smaller than that of the neutral acid molecule.

C - DISCUSSION

The main purpose of the work recorded in this Chapter III of the thesis was to study experimentally and theoretically the salting-out effect and electrostriction with polyelectrolytes and compare these results with those obtained for corresponding simple electrolytes. Since (as in the problem of dielectric saturation treated in Chapter II) we will use the simple electrolyte as a basis of reference for discussing the effects of salting-out by corresponding polyelectrolytes, it is of the utmost importance that we first examine critically the existing theories of salting-out by simple electrolytes before undertaking the more difficult problem of developing a treatment for polyelectrolytes. The following discussion will show that the existing salting-out theories are incomplete; we will therefore attempt to obtain an improved theory and then use the same theory for the problem of salting-out by polyelectrolytes, except that a cylindrically symmetric model will be used instead of a spherically symmetric one. The problem of electrostriction near simple and analogous polymeric ions will be discussed in part (ii) of this Discussion.

i) Salting-out by Simple Electrolytes

Many approaches have been made to the problem of salting-out (60, 61), but electrostatic theories have, of course, received most attention. Debye and McAulay (93) have calculated the work necessary to discharge an ion in pure solvent and in a solution containing a non-electrolyte. The salting-out effect is then related to the change in dielectric constant caused by the presence of the non-electrolyte. Their final relation is

$$\ln \frac{S_o}{S} = \frac{z^2 e^2 mN}{1000\,\mathcal{E}_o} \frac{\beta}{kT} \frac{1}{a} \qquad [\text{III-2}]$$

where β, the dielectric increment, is defined in terms of

$$\mathcal{E} = \mathcal{E}_o (1 - \beta C_2) \qquad [\text{III-3}]$$

where $\mathcal{E}$ is the dielectric constant of the solution containing a concentration C_2 of non-electrolyte and $\mathcal{E}_o$ is the dielectric constant of the pure solvent.

Later, Debye (94) modified this theory to take into account the distribution of water and non-electrolyte molecules around the ions. This theory was a significant improvement over Debye and McAulay's treatment but was still expressed in terms of the dielectric increment as defined in equation [III-3]. This was a serious drawback since such information is not always available. However, Butler (95) has shown that it is possible to relate the salting-out effect to the polarizabilities and volumes of the non-electrolyte and water molecules. He also showed that his theory becomes identical with that of Debye and McAulay if certain assumptions are made about the relation between the dielectric constant and the polarizability of a molecule. Most of the theories that have appeared since then are modifications or improvements of these three principal treatments (96, 97, 98, 99, 61) but none is entirely satisfactory.

The equation derived below will also be essentially based on Debye's treatment but important improvements will be made by taking into account the following factors not previously examined or treated in quantitative detail:

a) Dielectric saturation effects,

b) Molecular "structure" of the primary hydration shell of the ions, and

c) Relation between dielectric constant and molecular parameters (dipole moment, polarizability, molar volume) using Kirkwood's theory of dielectrics.

Theory of salting-out by simple ions

The energy U stored in an element of volume dV of a medium of dielectric constant $\mathcal{E}$, subject to the action of an electrical field E is given by (34, page 110)

$$dU = (\mathcal{E}E^2/8\pi)dV \qquad [III-4]$$

In a system containing n_1 molecules of component 1 and n_2 molecules of component 2, the corresponding mole fractions are given by

$$N_1' = \frac{n_1}{n_1 + n_2} \text{ and } N_2' = \frac{n_2}{n_1 + n_2} \qquad [III-5]$$

The introduction of ions into the system will redistribute the two components; the component with the highest dielectric constant will crowd around the ions and the other one will be displaced from regions near the ions.

If the local mole fractions of components 1 and 2 in the presence of the ions are N_1 and N_2 at a distance r from the ion in a volume element dV, the changes of configurational free energy in this volume element will be given by

$$\begin{aligned} \Delta G_1 dV &= n_1 kT \ln(N_1/N_1')\ dV \\ \Delta G_2 dV &= n_2 kT \ln(N_2/N_2')\ dV \end{aligned} \qquad [III-6]$$

The total integral free energy change over unit volume of the system, including the electrical energy given by [III-4] is therefore

$$\Delta G = n_1 kT \ln(N_1/N_1') + n_2 kT \ln(N_2/N_2') + \mathcal{E}E^2/8\pi \qquad [III-7]$$

where the field E, due to the ion, is a function of the distance from the ion.

If component 2 is taken as the non-electrolyte, then the change in free energy is a minimum when $d\Delta G/dn_2 = 0$. Now, if we assume that a small change dn_2 in the concentration of 2 will not significantly affect the mole fractions N_1 and N_1' of the solvent (i.e. for dilute solutions of the non-electrolyte), then differentiating equation [III-7] with respect to n_2, we obtain

$$kT \ln N_2/N_2' + \frac{d}{dn_2}\left(\frac{\mathcal{E} E^2}{8\pi}\right) = 0 \qquad [III-8]$$

if the distribution of non-electrolyte is independent of concentration at low concentration. Replacing E by the electrostatic field $-ze/\mathcal{E} r^2$ and rearranging gives

$$\int_0^{n_2} \ln\,[N_2/N_2']\,dn_2 = -\int_{\mathcal{E}_0}^{\mathcal{E}} \frac{z^2e^2}{8\pi kTr^4}\;d\left(\frac{1}{\mathcal{E}}\right) \qquad [III-9]$$

Integrating

$$\ln N_2/N_2' = -\frac{z^2e^2}{8\pi kTr^4}\left(\frac{1}{\mathcal{E}} - \frac{1}{\mathcal{E}_0}\right)\frac{1}{n_2} \qquad [III-10]$$

where $\mathcal{E}_0$ is the dielectric constant of the pure solvent and $\mathcal{E}$ the dielectric constant of the solution containing n_2 molecules of non-electrolyte. Since N_2' is small compared with unity, equation [III-10] may be written as

$$N_2/N_2' = C_2/C_2^{\circ} = \exp\,[-\frac{\Delta U}{kT}] \qquad [III-11]$$

where C_2 and C_2° are the concentrations of non-electrolyte now expressed in moles per liter with and without ions present, and $\Delta U/kT$ is given by

$$\frac{\Delta U}{kT} = \frac{1000\ z^2e^2}{8\pi kTNr^4}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_o}\right)\frac{1}{C_2} \qquad \text{[III-12]}$$

where ΔU is expressed in ergs molecule^{-1}.

If the concentration of the non-electrolyte is not small, it is possible to correct equation [III-11] by adding extra terms in the energy relation (equation [III-12]) (98).

Equation [III-11] may be written as

$$dn_2 = C_2^{\,o} \exp\left[-\frac{\Delta U}{kT}\right] dV\ . \qquad \text{[III-13]}$$

For spherical symmetry ($dv = 4\pi r^2 dr$)

$$n_2 = C_2^{\,o}\int \exp\left[-\frac{\Delta U}{kT}\right] 4\pi r^2 dr \qquad \text{[III-14]}$$

where n_2 is the number of non-electrolyte molecules in the spherical annular element of thickness dr at a distance r from the ion. Similarly, the number of non-electrolyte molecules $n_2^{\,o}$ in the same annular volume element in the pure solvent is given by

$$n_2^{\,o} = C_2^{\,o}\int 4\pi r^2 dr \qquad \text{[III-15]}$$

The limits of integration are the radius of the ion "a" and the parameter R, which is defined as the radius of the volume of solution available for each ion. R can be evaluated from

$$R = \left(\frac{3000}{4\pi Nm}\right)^{1/3} \qquad [III-16]$$

where m is the molar concentration of the ions. This equation is in fact identical with equation [II-5].

Combining equations [III-14] and [III-15], we obtain

$$\frac{n_2}{n_2^{o}} = \frac{\int_a^R \exp(-\Delta U/kT)\, 4\pi r^2 dr}{\int_a^R 4\pi r^2 dr} \qquad [III-17]$$

Since $\int_a^R 4\pi r^2 dr$ is the volume available for one ion, the reciprocal of this term gives the concentration of the electrolyte in terms of the number of ions per unit volume. Expressing the concentration of the ions in moles per liter, equation [III-17] can be written as

$$\frac{n_2}{n_2^{o}} = 1 - \frac{mN}{1000} \int_a^R (1 - \exp\ (-\Delta U/kT))\ 4\pi r^2 dr \qquad [III-18]$$

Since $1 - n_2/n_2^{o} = 1 - S/S_o = (S_o - S)/S_o$,

$$\frac{S_o - S}{S_o} = \frac{4\pi mN}{1000} \int_a^R (1 - \exp(-\Delta U/kT))r^2 dr \qquad [III-19]$$

This equation is identical with the one derived by Debye (94) and very similar to those of Belton (97) and

Albright and Williams (98) except for the limits of integration. These authors use ∞ instead of R. In the more approximate equations for the salting-out constant, the exponential in equation [III-19] is expanded as a power series and only the first term is retained. The equation can then be integrated easily (95, 99). The approximate salting-out equations are not very useful since for small ions the energy ΔU is usually larger than kT and the expansion of the exponential may cause the predicted salting-out to be seriously in error as we will show later.

The term $\Delta U/kT$ in the Debye theory is difficult to evaluate since it is expressed in terms of the change in dielectric constant due to the presence of the non-electrolyte. Butler (95) has shown that this change in dielectric constant may be related to the polarizability of the non-electrolyte and of the water molecule and other authors have since used similar transformations (98, 99). In the present derivation, we shall follow the method discussed by Long and McDevit (61) but will use Kirkwood's theory of the dielectrics rather than Onsager's as they suggested.

Equation [III-12] may be written as

$$\Delta U/kT = \frac{1000\ z^2 e^2}{8\pi kTNr^4}\left(\frac{\varepsilon_o - \varepsilon}{\varepsilon_o\ \varepsilon}\right)\frac{1}{C_2} \simeq \frac{1000\ z^2 e^2}{8\pi kTNr^4}\left(\frac{\varepsilon_o - \varepsilon}{\varepsilon_o{}^2}\right)\frac{1}{C_2} \quad [III-20]$$

This is essentially the same as regarding the electrical field at some point near the ion as not being affected by the presence of the non-electrolyte. This is of course a correct assumption only if the concentration of the non-electrolyte is small. Hence

$$\Delta U/kT = \frac{1000\ E^2}{8\pi kTN} \ (\mathcal{E}_o - \mathcal{E})\ \frac{1}{C_2} \qquad [III-21]$$

When the dielectric constant $\mathcal{E}$ of a solution is high compared with the optical dielectric constant of the solvent $\mathcal{E}_\infty$, Kirkwood's equation for the dielectric constant of a solution (100) may be written as

$$\mathcal{E} = 9/2 \sum_k c_k \overline{P}_k \qquad [III-22]$$

where c_k denotes the concentrations in moles per unit volume of the different constituents k, and $\overline{P}_k$ terms are their molar polarizations. These molar polarizations are related to the respective polarizations per unit volume $\overline{p}$, defined by equation [I-13], by the relation $\overline{P} = \overline{Vp}$, where $\overline{V}$ is the partial molar volume. For the system water plus non-electrolyte, equation [III-22] may be written as

$$\mathcal{E} = 9/2\ (c_1\overline{P}_1 + c_2\overline{P}_2) \qquad [III-23]$$

c_1, the concentration of solvent, may be written in terms of c_2 by the relation

$$c_1\bar{V}_1 + c_2\bar{V}_2 = 1$$

where the $\bar{V}$ terms are the corresponding (partial) molar volumes. Therefore, equation [III-22] may be written as

$$\mathcal{E} = 9/2\,\frac{1 - c_2\bar{V}_2}{\bar{V}_1}\,\bar{P}_1 + c_2\bar{P}_2. \qquad \text{[III-24]}$$

Therefore,

$$\frac{d\mathcal{E}}{dc_2} = \frac{\mathcal{E} - \mathcal{E}_o}{c_2} = 9/2\,(\bar{P}_2 - \frac{\bar{P}_1\bar{V}_2}{\bar{V}_1}) \qquad \text{[III-25]}$$

Now $C_2 = 1000c_2$ and $\bar{P}_1/\bar{V}_1 = \bar{p}_1 = 2/9\ \mathcal{E}_o$, so that

$$1000\,\frac{\mathcal{E}_o - \mathcal{E}}{C_2} = \bar{V}_2\,\mathcal{E}_o - 9/2\,\bar{P}_2 \qquad \text{[III-26]}$$

Substituting in equation [III-21], the energy function becomes

$$\Delta U/kT = \frac{E^2}{8\pi kTN}\,(V_2\mathcal{E}_o - 9/2\,\bar{P}_2) \qquad \text{[III-27]}$$

where V_2 is the partial molar volume or the molar volume of the non-electrolyte since these two value are almost identical for non-electrolytes in water.

Therefore, the salting-out of a non-electrolyte by an ion may be predicted if the size of the ion, the molar volume and the polarization of the non-electrolyte are known. However, it must be noted that the approximate form of the Kirkwood theory used in this derivation is only valid when the electric field is low. Hence this equation as it stands cannot be expected to hold in the region close to the ions, as discussed further below.

It should be noted at this point that Kirkwood (101) has derived a salting-out equation which is more complex since he expresses the electrostatic energy of interaction of an ion and a non-electrolyte molecule (actually dipolar ions) in terms of a series. Long and McDevit have shown that his theory actually predicts salting-out values very nearly the same as those given by the Debye theory.

A relation of the form of our equation [III-19], with the energy given by equation [III-27], predicts (see Long and McDevit (61)) the correct dependence of the salting-out constant k_s on the nature of the non-electrolyte but still fails to explain the marked variation in the salting-out constant for different types of ions.

Before the development of quantitative electrostatic theories of salting-out, the usual explanation for the lowering in solubility of a non-electrolyte by a salt was that the water molecules were effectively removed from their solvent rôle due to hydration of the ions (102). These theories were, in general, unsatisfactory since they failed to explain the dependence of the salting-out on the nature of the non-electrolyte. Nevertheless, the "removal" of water (or rather the change of its activity) due to solvation is a leading factor determining the extent of salting-out even if it is not the only effect. The electrostatic theory of Debye, and correspondingly the one described above, is, in fact, concerned to some extent with this hydration effect; it is based on the fact that the more polar component, usually water, is crowded near the ion while the less polar substance is effectively pushed away. This theory represents fairly well the situation existing at intermediate distances and far from the ion but is not reliable in the immediate vicinity of the ion for the following reasons:

a) The dielectric constant near the ion is usually much lower than that of the pure solvent (see Chapter II).

b) The relation used between the dielectric constants of the non-electrolyte solution and the molecular properties of the solvent and non-electrolyte is not valid in the region near the ion where the field intensity is quite high (see page 169).

c) Important interactions in the vicinity of the ion (ion-dipole, dipole-dipole, van der Waals' short range forces, etc.) are not considered in detail (see Chapter II, page 62). A correct theory of salting-out should take all these factors into consideration, i.e. should consider the detailed structure of the solvent near the ion.

Direct solvation effects may be taken into account partially by correcting the field in the salting-out equation for the effect of dielectric saturation. It is possible by graphical methods to examine the effect of the degree of dielectric saturation near an ion on the total salting-out. In the first case, let us assume that $\Delta U/kT$ is small compared with unity. The exponential in equation [III-19] may then be expanded and the salting-out ratio is given approximately by

$$\frac{S_o - S}{S_o} = \frac{4\pi mN}{1000} \int_a^R (\Delta U/kT) r^2 dr \qquad [\text{III-28}]$$

Substituting the electrostatic field $(-ze/\varepsilon r^2)$ for E in equation [III-27], gives the salting-out constant as

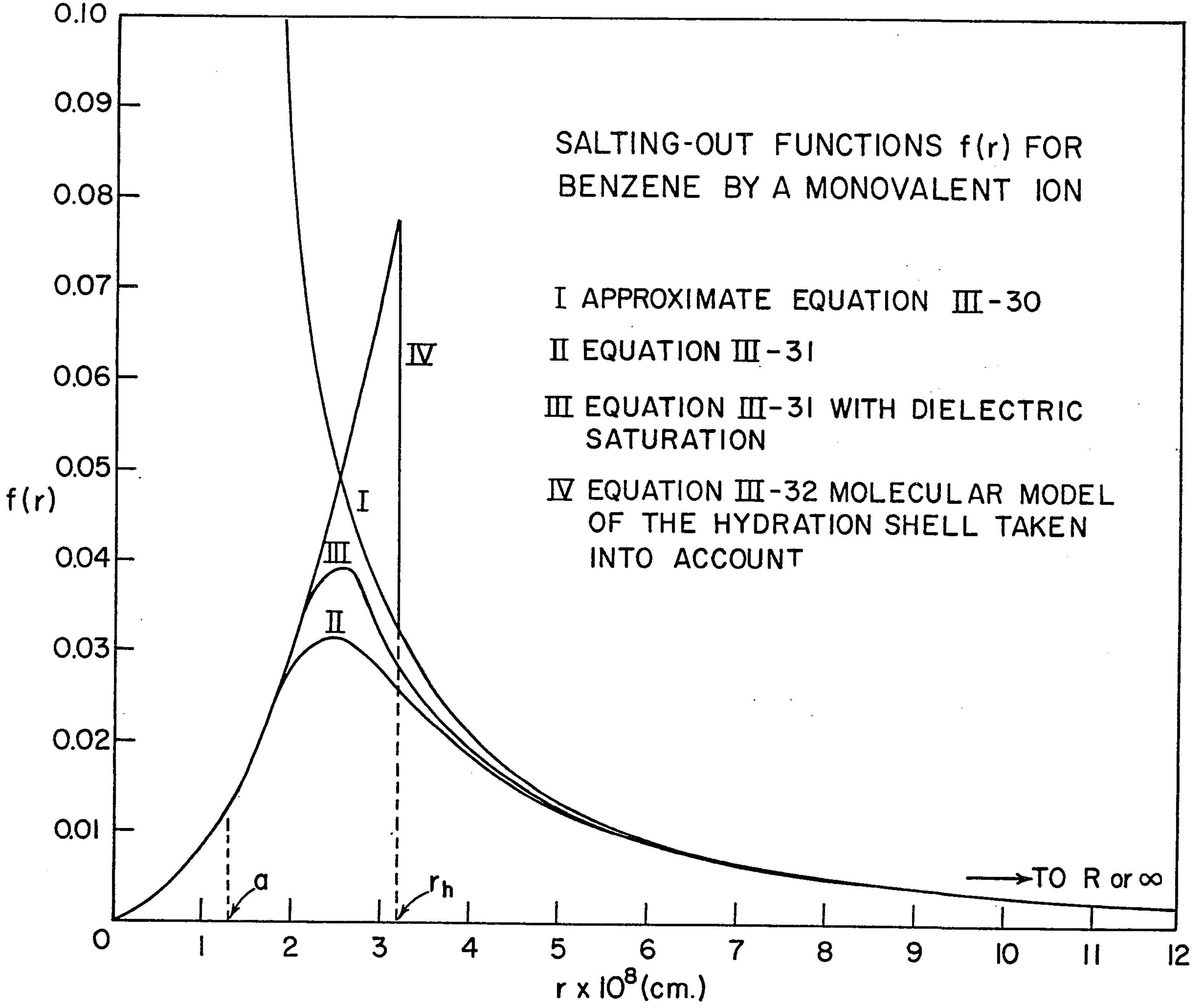
$$k_s = \frac{S_o - S}{S_o m} = \frac{4\pi N}{1000} \int_a^R \frac{z^2 e^2}{8\pi kTN\,\varepsilon^2} (V_2 \varepsilon_o - 9/2\bar{P}_2) \frac{1}{r^2}\, dr \qquad [\text{III-29}]$$

If a graphical solution is required (e.g. in the case of dielectric saturation), then we must plot f(r) against r, where

$$f(r) = \frac{z^2 e^2}{2000\,\varepsilon^2 kT} (V_2\, \varepsilon_o - 9/2\ \bar{P}_2) \frac{1}{r^2}\ ; \qquad [\text{III-30}]$$

f(r) has the units of liters. mole^{-1} cm^{-1}. This function is plotted as curve I in Fig. 28 for the case of salting-out of benzene by a monovalent ion. Benzene was chosen as a typical

Figure 28. Theoretical salting-out functions (see text) for benzene by a monovalent ion.



SALTING-OUT FUNCTIONS f(r) FOR BENZENE BY A MONOVALENT ION non-electrolyte because it is large compared with the solvent, is spherical and non-polar. The molar volume of benzene was taken as 89.4 mls./mole (103) and the polarization term was neglected (since the dipole moment is zero and the polarizability negligible) in comparison with $V_2 \mathcal{E}_o$. The value k_s is then equal to the area under the curve from "a" to R or from "a" to infinity in the limiting case of infinitely dilute solution.

From this graph, it is easy to see why this approximate equation fails with small ions. This equation predicts that an infinitely small ion would be associated with an infinite salting-out constant. If we would correct this equation for the effect of dielectric saturation near the ion, the situation would be even worse since the field would be higher. This equation is thus satisfactory only for large ions and is not valid for small ions.

If we do not expand the exponential in the salting-out equation, the f(r) is given by

$$f(r) = \frac{4\pi N}{1000} (1 - \exp[-\Delta U/kT])r^2 \qquad [III-31]$$

instead of by [III-30]. This function is represented as curve II in Fig. 28, and does not tend to infinity but rather to zero as the distance r tends to zero. Hence, the main objection to the approximate equation is now removed. In addition, if we take the dielectric constant as a function of the field intensity instead of as a constant everywhere, i.e. if we use the integral dielectric constant as a function of distance in the field relation, the maximum in the function f(r) is raised to higher values and shifted to larger values of r (see curve III in Fig. 28). It may therefore be concluded that the effect of taking into account dielectric saturation is to increase the value of k_s. This correction is in the right direction since the theory of Debye usually predicts values of k_s which are too small.

The maximum in the function f(r) is a result of two effects: f(r) increases as the volume around the ion increases, and decreases exponentially due to the Boltzmann distribution assumed. The maximum in curve III of Fig. 28 corresponds to a distance of about 2.6 Å from the centre of the ion. It is apparent from this graph that the region between the radius "a" of the ion and the distance where the maximum in f(r) occurs can contain only solvent molecules, i.e. the non-electrolyte molecules are completely salted-out in this region. It is therefore obvious that the distance where the salting-out function f(r) is a maximum should correspond theoretically to the radius of the (primary) hydration shell of the ion. This would be true, of course, only if all the interactions between the water molecules and the ion would be considered in detail (see page 62). The model and the assumptions made in the derivation of the salting-out equation do not allow us to calculate a priori the extent of hydration (in terms of radius of the primary layer) from salting-out data. However, the reverse is possible; we can improve the salting-out relations by taking into account a molecular model of the hydration shell around the ions.

The region of intense dielectric saturation of the solvent near the ion actually corresponds to a layer of water having a thickness smaller than the actual primary hydration shell. This problem was discussed in detail on p.62 and we have shown that the main reason for the difference between the limiting distance of intense dielectric saturation and the radius of the primary hydration shell lies in the fact that the finite size of the water molecule is neglected in the theory of the dielectric saturation based on a dielectric continuum.

We have shown that the effect of taking into account the dielectric saturation on salting-out is to shift the maximum in f(r) in Fig. 28 to higher values and also to somewhat longer distances from the ion, i.e. the region of strong ion-solvent interaction is extended. If the actual primary hydration is taken into account rather than the effect of dielectric saturation, i.e. if we consider a molecular picture of the hydration, the maximum in f(r) will be even larger and shifted to greater distances from the ion. This can be demonstrated by considering the salting-out equation [III-19] or the relation [III-31]. In the first hydration shell of radius r_h the dielectric constant may be assumed to be low. Consequently, $\Delta U/kT$ is large compared with unity and $\exp[-\Delta U/kT]$ is negligible. Beyond the first hydration shell, $\Delta U/kT$ will be small compared with unity and the exponential can then be expanded, retaining only the first term of the series. Therefore, the integration of the salting-out equation may be carried out conveniently in two parts; from "a" to r_h and from r_h to R (or infinity in the limiting case). Equation [III-31] then becomes

$$f(r) = \frac{4\pi N}{1000}\left\{ [r^2]_a^{r_h} + \left[\frac{\Delta U}{kT} r^2\right]_{r_h}^{R} \right\} \qquad [III-32]$$

This function is also plotted in Fig. 28 from which it can be seen that the salting-out constant will depend to a large extent on the choice of the parameter r_h. In other words, the limit of the "primary" hydration shell may be one of the main effects in determining the salting-out constant and a close relationship should exist between the geometry of the hydration shell and the degree salting-out caused by the ions. In the following calculations, values of the radius r_h will be taken from Nightingale's table (see Table 1), in which the data are based on corrected hydrodynamic Stokes' radii.

If we make the same simplifications to equation [III-19], the salting-out equation becomes

$$\frac{S_o - S}{S_o} = \frac{4\pi mN}{1000}\int_a^{r_h} r^2 dr + \int_{r_h}^{R} (\Delta U/kT) r^2 dr. \qquad [III-33]$$

As a limiting case (m tending to zero), R may be taken as infinity and the field may then be taken as $-ze/\mathcal{E} r^2$. After integrating, the salting-out equation reduces to

$$\frac{S_o - S}{S_o} = \frac{4\pi mN}{1000}\left\{\frac{1}{3}(r_h^3 - a^3) + \frac{z^2 e^2}{8\pi NkT\, \mathcal{E}_o{}^2 r_h}(V_2\, \mathcal{E}_o - 9/2\overline{P}_2)\right\} [III-34A]$$

or

$$\frac{S_o - S}{S_o} = \frac{4\pi mN}{3000}(r_h^3 - a^3) + \frac{z^2 e^2 m}{2000\ kT\, \mathcal{E}_o{}^2 r_h}(V_2\, \mathcal{E}_o - 9/2\overline{P}_2) \qquad [III-34B]$$

Use of this simplified equation also eliminates the difficulty of using Kirkwood's limiting equation in a region of high field intensity where it is, in fact, not valid.

The molecular picture of salting-out is now somewhat clarified. Thus, the first term of equation [III-34] takes into account strong ion-solvent interactions associated with the primary solvation shell of the ion and is, as a first approximation, independent of the nature of the non-electrolyte. For most ions, this term would always contribute a salting-out effect. The second term depends mostly on the nature of the non-electrolyte and may lead either to salting-out or salting-in depending on volume and polarization of the non-electrolyte.

Comparison of theoretical and experimental values of k_s

In order to examine the validity of this equation, we have calculated values of k_s for the salting-out of rare gases and other neutral molecules by the alkali halides, and have compared in Table 9 these values with the experimental k_s data taken from the literature. In the same table are also given the values of k_s estimated by means of the approximate equation [III-29]. The molar volumes of the non-electrolytes were taken from the literature whenever possible (e.g. Hildebrand and Scott (104) give a list of the molar volumes of the rare gases and other neutral molecules in an Appendix). When these values were not available, they were calculated from the molecular weight and density of the compound in the solid state. In the case of helium, the molar volume is not known but can be evaluated from its atomic radius (91, page 25) to be approximately 0.72 mls./mole. This volume is so small compared with that of water (18 mls./mole) that it may be assumed that the helium atoms do not occupy any space in the water solvent, i.e. they are small enough to fit in the spaces between the water molecules in the liquid state. Helium has no permanent dipole moment and its polarizability is small,

Table 9

SALTING-OUT CONSTANTS OF NEUTRAL MOLECULES BY ALKALI HALIDES AT 25°C

		k_s (liters/mole)				
Neutral molecule	Salt	Expt.	Eqn. [III-29]	Eqn. [III-34]	Eqn. [III-35]	Ref.
Helium $V_2 = 0.72$	NaCl	0.186	0.005	0.191	0	(105)
	LiCl	0.115	0.006	0.176	0	
	NaBr	0.200	0.004	0.186	0	
	KCl	0.157	0.004	0.162	0	
	KI	0.191	0.003	0.150	0	
Neon $V_2 = 16.8$	NaCl	0.223	0.096	0.224	0.18	(105)
	LiCl	0.136	0.133	0.210	0.13	
	KI	0.184	0.074	0.185	0.08	
Argon $V_2 = 24.2$	LiCl	0.221	0.192	0.226	0.19	(105)
	NaCl	0.306	0.139	0.240	0.27	
	KI	0.249	0.105	0.201	0.11	
	KF*	0.330	0.129	0.240	0.38	

Table 9 (Cont'd.)

		k_s (liters/mole)				
Neutral molecule	Salt	Expt.	Eqn. [III-29]	Eqn. [III-34]	Eqn. [III-35]	Ref.
Krypton $V_2 = 38.8$	LiCl	0.267	0.308	0.258	0.31	(105)
	NaCl	0.336	0.223	0.270	0.43	
	KCl	0.285	0.181	0.246	0.33	
	KBr	0.276	0.175	0.241	0.27	
	KI	0.276	0.168	0.233	0.15	
	NH_4Cl	0.150	0.158	0.231		
Xenon $V_2 = 48.6$	NaCl	0.343	0.278	0.289	0.53	(105)
	KI	0.260	0.210	0.253	0.22	
Naphthalene $V_2 = 112$	NaCl	0.599	0.643	.424	1.23	(106)
Biphenyl $V_2 = 131$	NaCl	0.636	0.879	.461	1.43	(106)

Table 9 (Cont'd.)

Neutral molecule	Salt	k_s (liters/mole)				Ref.
		Expt.	Eqn. [III-29]	Eqn. [III-34]	Eqn. [III-35]	
Benzene $V_2 = 89.5$	LiCl	0.325	0.708	0.365	0.701	(107)
	NaF	0.585	0.570	0.397	1.63	
	NaCl	0.449	0.512	0.375	0.98	
	NaBr	0.357	0.499	0.371	0.83	
	NaI	0.219	0.482	0.362	0.63	
	KCl	0.382	0.416	0.354	0.77	
	KBr	0.274	0.403	0.350	0.78	
	RbCl	0.322	0.392	0.351	0.73	
	CsCl	0.203	0.365	0.347	0.58	
	NH_4F	0.237	0.450	0.374		

* present work: measured at 30°C.

Eqn. [III-29]: Approximate salting-out equation where the exponential is expanded.
Eqn. [III-34]: Salting-out equation where the primary hydration of the ion is taken into account.
Eqn. [III-35]: McDevit and Long theory.

The constant k_s is calculated to three decimal places in order to see the theoretical variation of k_s for different salts but the values are certainly not reliable quantitatively to more than two decimal places.

therefore the second term of the salting-out equation [III-34] is negligible since it depends on the magnitude of the term ($\mathcal{E}_o V_2 - 9/2 \overline{P}_2$) and this term is very small. Therefore, the salting-out constant of helium should be given by the first term only of equation [III-34]. Hence, this affords in principle a method of obtaining primary hydration data from salting-out measurements since this first term is determined by the limits of the primary hydration shell.

The crystal radii taken were those given by Pauling (108) and reproduced in Table 1. The hydration radii were taken from Nightingale's table (Table 1) except for the case of lithium; from the apparent molar volumes of the lithium salts it appears that the hydration radius of Li^+ is probably smaller than that of Na^+ although conductance measurements predict a larger hydration radius for Li^+. Therefore, we have chosen a value of 3.4 Å for r_h of Li^+ and this gives a better value for the predicted k_s than Nightingale's suggested value.

Examination of Table 9 shows that the approximate equation [III-29] fails completely to predict the salting-out constants for helium, gives somewhat low values for the other rare gases and predicts too large values for naphthalene and biphenyl. It is also not very good with small ions, e.g. Li^+, or large ions, e.g. I^-. However, for the salting-out of benzene by ions of intermediate sizes, k_s is predicted fairly well. This apparently good agreement is a result of the fact that the error introduced by expanding the exponential in the salting-out equation [III-19] nearly balances out the error caused by the neglect of the primary hydration structure around the ions (see Fig. 28).

Equation [III-34] predicts the dependence of k_s on the size of the non-electrolyte molecule very well, except for very large non-electrolytes where the predicted values are somewhat smaller than the experimental ones. This equation also predicts the dependence of k_s on the size of the ion fairly well for the salting-out of small non-electrolytes but is unsatisfactory in the case of large non-electrolytes. For example, k_s for benzene salted-out by NaCl is found experimentally to be twice that by NaI while equation [III-34] predicts that the two k_s should only differ by about three percent.

Comparison with the theory of McDevit and Long

It would be of interest at this point to compare equation [III-34] with the one obtained by McDevit and Long (103) based on the internal pressure concept. They assumed that the only rôle of the non-electrolyte was to occupy volume. A limiting expression for the relative salting-out was then obtained by assuming that the excess work that must be done against the ion-solvent forces to introduce a volume $\bar{V}_2$ of non-electrolyte into the salt solution was proportional to the volume change which occurs on mixing (liquid) salt and water. Their limiting equation is

$$k_s = \ln \frac{S_o}{S} = \frac{\overline{V}_2(V_s - \overline{V}_s)}{\beta_o RT} \qquad [III-35]$$

where $\overline{V}_2$ and $\overline{V}_s$ are the partial molar volumes of the non-electrolyte and salt, respectively, V_s is the molar volume of the (liquid) salt and β_o is the compressibility of water.

The comparison of predicted values of k_s using McDevit and Long's theory with the experimental values, shows that their theory overestimates the dependence of k_s on the volume of the non-electrolyte (the predicted k_s of Li^+ is negligibly small and that of naphthalene or biphenyl is about two times too large). This relation also fails to take into account the polarization of the non-electrolyte and consequently would not apply to polar non-electrolytes. The advantage of this theory, however, is that it predicts the dependence of k_s on the nature of the salt much better than do other theories. This is not surprising since, as we have shown in the introduction, $V_s - \overline{V}_s$ is related to the degree of hydration of the salt. Also, since $\overline{V}_s$ or ϕ_v^o depend on the primary and also secondary hydration, this theory may account for the salting-in observed with some large ions (99). In the latter case, e.g. with quaternary alkyl ammonium salts, there is a possibility of "negative " hydration, that is, the water molecules near the ion are more mobile (rotationally and librationally more free) than in the bulk. This may arise from structure-breaking effects (8), as discussed in the introduction, or from short range van der Waals' repulsion forces which can, like the attractive forces, become more significant with large ions (104). Independently of the origin of this negative hydration, the result will be a partial molar volume larger than the molar volume for the salt in aqueous solution. Equation [III-35] would then predict salting-in. Among the other possible explanations for this salting-in effect, McDevit and Long (61), Bockris, Bowler-Reed and Kitchener (99) and more recently Huang (109) have suggested that the London dispersion forces between the large ions and non-electrolytes may be important and may account for salting-in. The problem of salting-in by large ions can probably be elucidated by studying the salting-in of different non-electrolytes by large ions. If "negative" hydration is responsible for the effect all non-electrolytes would be salted-in. If dispersion forces were responsible, salting-in should occur only with fairly large non-electrolytes since the dispersion forces are important only between large ions and large non-electrolytes. More work on this problem is desirable.

The failure of our equation [III-34] to explain the small values of the salting-out constants observed with ions like iodide and bromide is possibly a result of not taking into account this suggested "negative" hydration. Hence, an extra term should be added in equation [III-34] to account for cases of salting-in. Unfortunately, not enough is known quantitatively about these structure-breaking effects to permit such calculations to be made at present.

Dependence of k_s on concentration

The only general effect of salting-out which we have not yet attempted to explain is the deviation from linearity of k_s with salt concentration at high concentrations. The salting-out of argon and ethylene by potassium fluoride was measured up to about 5 M and the results were given in Figs. 23 and 24 (see page 143) where the two forms of the salting-out relation were plotted as a function of the salt concentration in moles per liter. In Fig. 23, the salting-out ratio increases linearly with concentration up to about 1 M and then flattens out until it reaches the upper limit of unity. The origin of the upper limiting value of unity is easy to visualize since at high concentrations all the water is held by the ions as water of hydration and no more solvent will be available for the non-electrolyte. At intermediate concentrations, it is more difficult to deal with the problem theoretically since many factors must then be taken into account (110). However, it is possible to show qualitatively that equation [III-34] does, in fact, predict a curve and not a straight line for the relation between salting-out ratio and the concentration of salt. The work on dielectric saturation effects near an ion, described in chapter II, indicates that the effective radius of a hydrated ion does not change very significantly with concentration in solutions less than 1 M. Correspondingly, the first term of equation [III-34] will be assumed to be independent of concentration below 1 M. However, in the second term, it was assumed that 1/R was small compared with $1/r_h$, i.e. in very dilute solutions. If this assumption is not made, then the salting-out constant varies with concentration since R is a function of the concentration of the ion. In Table 10, theoretical values of $(S_o - S)/S_o m$ are given as a function of concentration for the salting-out of benzene by the potassium ion using equation [III-34] with the parameter R.

Table 10

THEORETICAL SALTING-OUT OF BENZENE BY K^+ (EQUATION [III-34])

m moles/liter	$\frac{S_o - S}{S_o m}$ liters/mole	m moles/liter	$\frac{S_o - S}{S_o m}$ liters/mole
0.00	0.190	0.5	0.156
0.05	0.175	1.0	0.148
0.25	0.162		

Equation [III-34] hence leads to non-linearity in the salting-out relation as the concentration of salt increases. These calculations are mostly only of qualitative value since we are neglecting the ion-ion interactions. It is seen however, that the equation gives an adequate account of the concentration dependence of $\Delta S/S_o m$. A slight improvement could be made by making use, in the salting-out equation, of the Debye-Hückel field, or even better, the values of the field calculated numerically in chapter II. In order to predict the salting-out at concentrations higher than 1 M, we would require to know the variation in the thickness of the hydration shell as the concentration increases to large values, and this information is not available, nor could it reasonably be calculated.

In general, examination of equation [III-34], indicates that the salting-out ratio will increase approximately linearly with concentration up to about 1 M (and then non-linearly for higher concentration) for small non-electrolytes. For larger non-electrolytes, the deviation from linearity can be predicted from equation [III-34] with a suitable field function. Above a concentration of about 1 M, simple electrostatic theories of ionic solutions (e.g. for conductance, chemical potential of ions, etc.) fail due to the more complicated structure of the solution and to the strong ion-ion and ion-solvent interactions and the theory of salting-out is no exception.

In Fig. 24, the logarithmic form of the salting-out equation has been used to represent the salting-out of argon by potassium fluoride up to high concentrations. The linearity of the concentration plot is extended to much higher concentrations than in Fig. 23. Although the limiting salting-out constant in this case is about the same as the usual k_s, this form is rather more empirical and the deviations from linearity on the log plot seen at high concentrations are much more difficult to interpret; they, however, are secondary to the effects leading to the concentration dependence of $\Delta S/S^{o}m$ discussed above.

Discussion of recent salting-out theories

We will now attempt to examine briefly, but critically, some of the main theories, or improvements to salting-out theories, that have been proposed since the publication of the review by Long and McDevit (61). Wada (111) and Nakajima (112) have substituted the free ion electrostatic field by the Debye-Hückel field in the Debye and McAulay salting-out theory in their attempt to explain deviations from linearity of log S_o/S plot at high concentrations. Baranoski and Sarnowski (113), in addition to using the above field correction, have tried to explain these deviations at high concentrations by introducing a correction for the extent of hydration of the ions. Their correction is similar to that suggested by Robinson and Stokes (114) in their extension of the Debye-Hückel theory. This type of correction is mostly empirical and is of such a form that it becomes important only at high concentrations; however, we have shown above that the molecular structure of the hydration shell of ions can be important, even at infinite dilution, in explaining salting-out ratio values quantitatively. In addition, the above authors (111, 112, 113) are using the Debye-McAulay theory [III-2] which is similar in form to our approximate equation [III-28]. It was shown (see Table 9) that this equation is seriously in error for small ions. These authors are in fact attempting to correct for the statistical electrostatic distribution of ions while they are neglecting the more basic matter, viz. the distribution of solvent and neutral molecules around the ions. Actually, the reverse should be done; in very dilute solutions, the distribution of ions is not important and the ions may be considered isolated, but the distribution of solvent and non-electrolyte molecules should never be neglected and must be a primary basis for any successful theory.

It was realized by Altshuller and Everson (115) that solvation and the related degree of dielectric saturation may play an important rôle in salting-out. They therefore proceeded to make extensive calculations of k_s applying different corrections to an equation similar to that of Debye and McAulay. In order to remove the difficulty of the prediction of an infinite k_s for very small ions as "a" tends to zero, they proposed that the radius of the ion in the equation should be taken as the hydration radius and not as the crystal ionic radius. This implies that hydration effect would <u>decrease</u> the salting-out, while we have shown that it must increase it and be a <u>primary factor</u> in determining k_s values. They also attempted to correct the theory of Debye and McAulay by taking into account the effect of dielectric saturation near the ion. This is the same as correcting <u>curve I</u> of Fig. 28 for this effect. Since this correction led to even larger values for k_s in the case of very small ions, they concluded that dielectric saturation was <u>not</u> an important effect. We have shown that this conclusion is certainly not correct and that, in fact, consideration of dielectric saturation effects leads to improved theoretical values of k_s and is a necessary factor to be taken into account in any quantitatively successful theory of salting-out.

Some other papers have been written on the theory of salting-out (109, 116), but unfortunately only abstracts* of these papers were available and the value of these theories is difficult to appraise. For example, Huang (109) has taken the "iceberg" effect into account in his salting-out theory;

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* From these abstracts, it is evident that these papers do not cover the theoretical approaches made in the present work.

Frank and Evans (10) have shown qualitatively that this effect may be significant in some cases. It is possible that the many anomalous results recorded in the experimental literature may be due to specific structural effects but quantitative evaluation of these effects is difficult. Samoĭlov and Tikhonev (116) in their theory relate the salting-out effect to the decrease in activation energy in removing water molecules from the layer surrounding the ion. Samoĭlov's theory of hydration (117), also based on consideration of the activation energy for the transfer of a water molecule from the hydration sheath to the bulk, is probably oversimplified but still quite promising and novel in approach.

ii) Apparent Molar Volumes and Salting-out by Polyelectrolytes:

Salting-out equation

An equation for salting-out by polyions may now be derived in a similar fashion to that [III-34] deduced for simple ions if cylindrical symmetry about a linear polyion is considered rather than spherical symmetry about a simple ion. The model used for these calculations is essentially the same as that shown in Fig. 1, discussed previously (see section II-C) in relation to the dielectric saturation calculation. For cylindrical symmetry, equation [III-19] may be written as

$$\frac{S_o - S}{S_o} = \frac{\overline{C}N}{1000}\int_a^R \left\{1 - \exp(-\Delta U/kT)\right\} 2\pi l r dr \qquad [III-36]$$

where $\overline{C}$ is the molar concentration of the polyion of length l; the terms "a" and R have been defined previously in section II-C. Now $l\,\overline{C} = \lambda\,\overline{m}$, where $\overline{m}$ is the concentration of the polymer in terms of the equivalent concentration of monomer mole units, i.e. the molar concentrations of ionizable groups, and λ is the distance between the ionizable groups on the polymer chain; also $\overline{m}\alpha = m$, where m is the gegen-ionic concentration of the polyelectrolyte or the monomer mole concentration of free charges on the polyion chain when the degree of dissociation is α. The equation for the salting-out ratio [II-36] may hence be written as

$$\frac{S_o - S}{S_o} = \frac{2\pi\lambda\, mN}{1000\,\alpha}\int_a^R \left\{ 1 - \exp(-\Delta U/kT) \right\} rdr \qquad [III-37]$$

The energy term can be obtained approximately from equation [III-27]. The choice of a suitable field function in equation [III-27] is somewhat more difficult. Normally, the field obtained from the solution of the Poisson-Boltzmann equation should be used since one cannot separate the central polyion from its atmosphere of gegen-ions even at very high dilution. This can be done by making use, for example, of the field function obtained by Alfrey, Berg and Morawetz (51). It is then possible to predict the salting-out constant of a polyion but, unfortunately, due to the complexity of the field function, such calculations are very tedious. It was found easier in most case simply to use the field intensities obtained numerically (see chapter II) and solve the salting-out equation graphically. However, we will show later that it is difficult to predict the absolute value of k_s for a polyion. Therefore, for the sake of simplicity, we will use the field function of an isolated charged rod in the salting-out equation. It will be shown later that the value of k_s predicted in this case is not too different from the solutions where the ionic atmosphere is taken into consideration. For example, the effect of concentration on k_s is still taken into account to some extent since the parameter R depends on the concentration of the solution. The field intensity at a distance r from an infinitely long charged rod is given by

$$E = - \frac{2\alpha e}{\varepsilon \lambda r} \qquad [III-38]$$

The energy term now becomes

$$\Delta U/kT = \frac{\alpha^2 e^2}{2\pi \lambda^2 \varepsilon^2 NkT} \frac{1}{r^2} (V_2 \varepsilon_o - 9/2 \bar{F}_2) \qquad [III-39]$$

Now if we substitute equation [III-39] into equation [III-37], divide the integral into two parts and integrate in the same way as in the simple ion case, we obtain the salting-out equation

$$\frac{S_o - S}{S_o} = \frac{\pi \lambda m N}{1000 \alpha} \left\{ (r_h^2 - a^2) + \frac{\alpha^2 e^2 (V_2 \mathcal{E}_o - 9/2\bar{P}_2)}{\pi \lambda^2 \mathcal{E}_o^2 NkT} \ln \frac{R}{r_h} \right\} \quad [\text{III-40 a}]$$

or

$$\frac{S_o - S}{S_o} = \frac{\pi \lambda N m}{1000 \alpha} (r_h^2 - a^2) + \frac{\alpha e^2 m}{1000 \lambda \mathcal{E}_o^2 kT} (V_2 \mathcal{E}_o - 9/2\bar{P}_2) \ln \frac{R}{r_h}$$

[III-40 b]

The parameter R in this equation, which is defined as the radius of the cylindrical volume available to each polyion, is given by equation [II-20] and r_h is the radius of the primary hydration shell.

The only unknown parameter in the above equation is r_h and this parameter can either be evaluated from the calculated dielectric saturation curves as discussed in chapter II or from the apparent molar volume of the polyion. The methods of calculating r_h for polyions will be discussed in more detail subsequently.

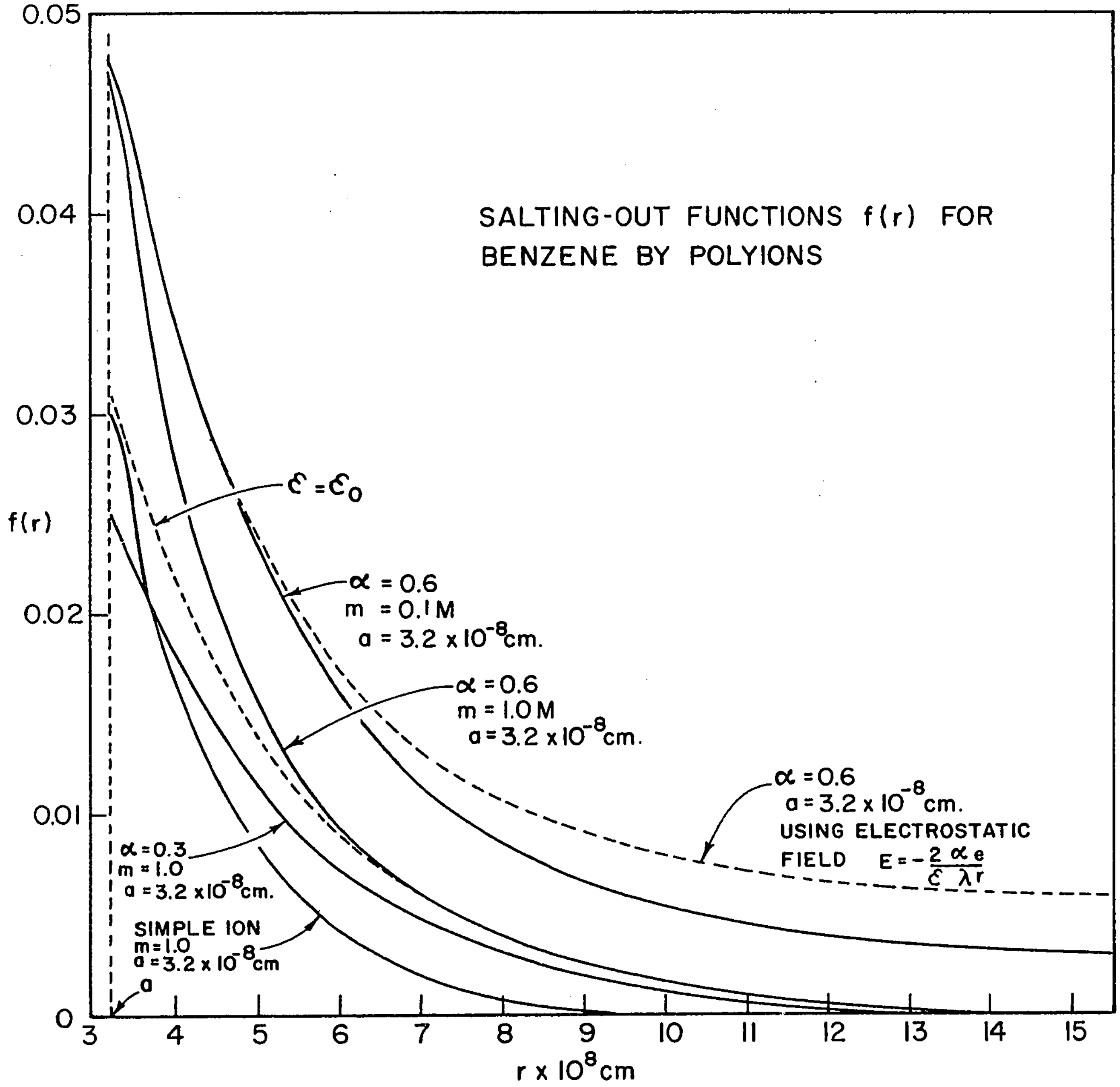
Comparison of salting-out by simple and polymeric ions

In order to compare degrees of salting-out by polyions with the corresponding salting-out by analogous simple ions, we will assume that the simple ion and polyion can both be represented closely by the idealized models discussed in chapter II (see Fig. 1).

We shall first solve the two salting-out equations [III-19] and [III-36] taking the ionic atmosphere and dielectric saturation effects into account, but not considering the molecular structure of the hydration shell (see page 174). This is done by replacing the field function in the salting-out equation by the numerical values obtained with an electronic computer as described in chapter II. The results are summarized in Fig. 29 where f(r), obtained for the polyion in the same way as the corresponding function (equation [III-31]) for the spherically symmetric simple ion, is plotted as a function of the distance from the centre of the polyion for different values of the parameters concentration and degree of ionization, with and without corrections for the effect of dielectric saturation of the solvent.

The equation was solved for the salting-out of benzene by a polyion of radius 3.2 Å, of degree of ionization 0.6 and at a concentration of 1 M. Benzene was chosen as a typical example since effects of changing variables, e.g. concentration, degree of ionization etc., are quite large in this case and can be shown clearly in the comparative plot (Fig. 29). From this graph, it is obvious that dielectric saturation corrections are much more important in the case of salting-out by linear polyions than for the simple ion case for the same non-electrolyte (for comparison see also Fig. 28). These corrections are important out to distances much further from the centre of the polyion than they were for the salting-out equation for the simple ion. Similarly,

Figure 29. Theoretical salting-out functions (see text) for benzene by polyions.



SALTING-OUT FUNCTIONS f(r) FOR BENZENE BY POLYIONS when a detailed molecular model of the primary hydration shell of polyions is taken into account, even larger differences in k_s will result compared to the simple ion case.

The salting-out equation was also solved for the same case as above but taking the concentration as 0.1 M. The salting-out constant k_s increases quite significantly with dilution. The extreme case occurs when the electrostatic field given by equation [III-38] is used and R is taken as infinity (infinite dilution). In this case, f(r) never tends to zero and an infinite value of k_s is obtained at infinite dilution. This can also be seen from equation [III-40]; k_s, being proportional to log R, therefore tends to infinity as R tends to infinity. The same situation would occur if a more exact field function was used, e.g. the field function obtained from the equation of Alfrey, Berg and Morawetz (51), since all these field functions will result in a logarithmic dependence of k_s on R. This mathematical difficulty arises from the fact that the models used all assume the polyions to be infinite in length. If a field function could be used in which the finite length of the polyion would be taken into account, then this anomaly would not arise. It should be realized also that an extrapolation to infinite dilution is not very realistic in the case of polyions, since the minimum concentration for the polyions must be when only one polyion is present in the volume of solvent, and this corresponds to an order of a thousand gegen-ions present in the region of the polyion if the molecular weight is of the order of 10^5. It should also be noted that, even if k_s tends to infinity as the concentration tends to zero, the salting-out ratio still tends to zero since the concentration in the salting-out equation tends to zero much more rapidly than log R tends to infinity. In fact, the dependence of the relative salting-out on concentration of a polyelectrolyte is quite similar to that in the case of a simple ion (see for example Fig. 23) but the deviation from linearity in the plot of $(S_o - S)/S_o$ against m is more pronounced than in the case of simple electrolytes. Therefore, the derived salting-out equation [III-40] can be used to calculate $(S_o - S)/S_o m$ for polyions in the range of experimental results (0.1 ⟶ 1 M) but cannot be used to calculate the limiting k_s, $(S_o - S/S_o m)_{m \to 0}$. We have noticed experimentally a definite deviation from linearity at concentrations higher than 1 M, e.g. in the case of salting-out of argon by NaPP, but at lower concentrations the salting-out ratio appears to be linear with concentration (see Fig. 20) within the limitations set by the small number of points available. Unfortunately, the experimental data are not accurate enough to permit a check of the exact dependence of the salting-out ratio on concentration below 1 M.

Because of the difficulty arising from the large dependence of k_s on R, it is clear that a suitable choice of this parameter R is much more important than the actual choice of the field function. It is for this reason, and for the sake of simplicity, that we have neglected the ionic atmosphere in the present theory of salting-out but have retained the parameter R. This neglect of the ionic atmosphere will introduce an error in the absolute evaluation of k_s (see Fig. 29) but should not effect too much the relative values of k_s with regard to their dependence on α and their comparison with the values for the corresponding simple ions.

It can also be seen from Fig. 29 that k_s depends quite significantly on the degree of ionization of the polyion; while k_s is definitely larger than the value for the corresponding simple ion when α is equal to 0.6, it becomes comparable when α is 0.3. Experimentally, this type of behaviour has been observed in the present work with KPMA (see Fig. 22).

Evaluation of the hydration radius of the PMA ion

The above discussion was for the case of a hypothetical ideal polyion. If we wish to correct the salting-out equation for such a model by taking into account the definite size of the primary hydration shell, we can evaluate r_h in equation [III-40] from the work on dielectric saturation as discussed in chapter II (see page 108). For a given radius "a" and degree of dissociation α we can evaluate the parameter r_d (defined on page 63), by double interpolation; r_d depends on both "a" and α (see Fig. 17 and 18). We can then assume that r_d is approximately equal to r_h. This would be fairly straightforward were it not for the fact that, except for special cases, e.g. polymine salts, any real polyion does not resemble too closely the model described in chapter II (see Fig. 1), the main difference being that the charges in a real macromolecule are not situated in the centre of the cylinder but rather are distributed evenly near the "surface" or outer extremities of the molecule (see diagram, page 12). It is difficult to predict how this distribution of charges on a polyion will affect the degree of hydration; presumably, the hydration radius will not be uniform along the chain and the value of r_h calculated or measured experimentally will be an average value.

The hydration radius of an ionized monomer unit can be evaluated from the apparent molar volume of that group. The method used to obtain ϕ_v^o in this case was discussed on page 147. In these calculations, we have to assume that the degree of ionization is equal to the degree of neutralization. The validity of this assumption is doubtful since it has been found experimentally that the degree of association between the polyion and its counterions is quite significant at high degrees of neutralization (21, 22, 23), but corrections for this association would be rather difficult since the exact nature of this association is still not well established (118, 119). We have shown in the introduction that the volume of a hydrated salt or ion is related to its apparent molar volume by the relation

$$v_h = \frac{v_a v_o - \phi_v^{\,o} v_o^{\,h}}{v_o - v_o^{\,h}} \qquad [\text{I-31}]$$

where the terms have been defined previously. From this volume, the radius of the hydration shell may be obtained as follows. If the volume of a spherical ion is large compared to that of the solvent.

$$r_h = \left(\frac{3v_h}{4\pi N}\right)^{1/3} \qquad [\text{III-41}]$$

where v_h is obviously the volume of the hydrated ion and not of the salt, and for an ion with cylindrical symmetry

$$r_h = \left(\frac{v_h}{\pi \lambda N}\right)^{1/2} \qquad [\text{III-42}]$$

where here λ is the length of the cylinder corresponding to the unit carrying one charge.

The two unknown parameters in equation [I-31] are $v_o^{\,h}$, the molar volume of water in the hydration shell, and v_a, the actual volume of the ion without hydration. Ulich (13) has investigated the problem of allocating a volume to the water molecules in the hydration shell and he suggests two extreme models for the calculation of this volume. The ultimate degree of compression will result in a solvent volume equal to $4/3\pi a^3N$ where "a", the radius of the water molecule, is taken as 1.38 Å. This implies that there is no dead space at all between the water molecules and this is probably not true. Calculations of hydration radii using this value for the molar volume of compressed water molecules lead to unrealistically small values for r_h. Ulich's second suggestion is much more realistic; the water molecules in the hydration sheath are assumed to be cubically close-packed, that is, $v_o^h = (2a)^3N = 12.6$ mls. Therefore, in this case, the term $v_o - v_o^h = 18 - 12.6 = 5.4$ mls. Some evidence for the reliability of this value is given by the calculations of Conway and Bockris (120) who have estimated this term using Webb's data for the pressure set up by the field of an ion and utilizing Bridgemen's data for the compressibility of water at these pressures. They have calculated the effective change in volume of a water molecule at different distances from the ion and the upper limit values obtained close to small ions agree well with the value suggested by Ulich, of 5.4 mls. Eucken (121) has suggested that this change in volume should be between 3.5 to 4 mls. but this value would predict rather high radii of hydrated ions. We have therefore chosen 5.4 mls. for the compressible volume of water molecules since it is a reasonable value theoretically and also predicts reasonable values for r_h, at least for the monomeric ions investigated in this thesis.

The problem of estimating the true volume of ions in solution has been discussed by Stern and Amis (122), Scott (19, 122), Lunden (18), Harned and Owen (124 page 365) and Rosen (125). These volumes can usually be obtained experimentally from density and compressibility measurements of solutions of these salts at high concentrations (18). These values are not available for the salts used in the present work, but these volumes can still be estimated indirectly from the apparent molar volumes of the corresponding unionized acids. The partial or apparent molar volume of a weak acid, e.g. isobutyric acid and PMA, is probably fairly close to its molar volume. Therefore, in order to obtain the actual molar volume of the anion, it is only necessary to use the $\phi_v^{\,o}$ of the pure acid and correct for the contribution to the volume brought about by the presence of a neutral single hydrogen atom, which was found by Traube (126) to be equal to 3.1 mls. Therefore

$$v_a \text{ (isobutyrate ion)} = 89.0 - 3.1 = 85.9 \text{ mls.},$$

and

$$v_a \text{ (PMA-monomer unit)} = 72.5 - 3.1 = 69.4 \text{ mls.}$$

"a" can be obtained from v_a in the same manner as r_h is obtained from v_h (see equations [III-41], [III-42]).

One further correction must be made; in order to find the contribution of the anion to the experimentally determined $\phi_v^{\,o}$, it is necessary to subtract from this value ϕ_v^o for the counterion, K^+ in the present case. The problem of separating the experimentally determined ϕ_v^o into its ionic components has received much attention, but without a successful definition of absolute values due to the difficulty in finding a standard of reference. Owen and Brinkley (127) take ϕ_v^o for hydrogen as zero; Eucken (121) assumes that the volumes of cesium and iodide ions in solution are proportional to the cube of their crystal radii; Fajans and Johnson (128) give extensive arguments to show that ϕ_v^o for ammonium ions and chloride ions should both be equal to that of water (18 mls.) and Couture and Laidler (129) suggest that ϕ_v^o of hydrogen should be taken as -6 mls. It is still not clear which of these procedures is most reliable (122) and we will assume that ϕ_v^o for the potassium ion is equal to 8.5 mls. (-1.7 for Na^+) since this value agrees well with the classification of Owen and Brinkley, and Fajans and Johnson.

Using the method suggested above, we have calculated the volumes and radii of the hydrated PMA and isobutyrate ions and the results are given in Table 11; the corresponding r_h values are plotted as a function of the degree of neutralization of PMA in Fig. 30. Above a degree of neutralization of 0.25 the hydration radius r_h increases rapidly with the degree of neutralization to reach a maximum value of 5.4(5) Å. When the degree of neutralization is below 0.25, r_h becomes

Table 11

IONIC AND HYDRATION RADII OF PMA AND ISOBURYRATE IONS

ISOBUTYRATE ION

v_a = 85.9 mls./gm.-ion (density measurements)

a = 3.2(5) Å

ϕ_v^o = 67.5 mls./gm.-ion.

v_h = 129.0 mls./gm.-ion (density measurements)

r_h = 3.7(2) Å

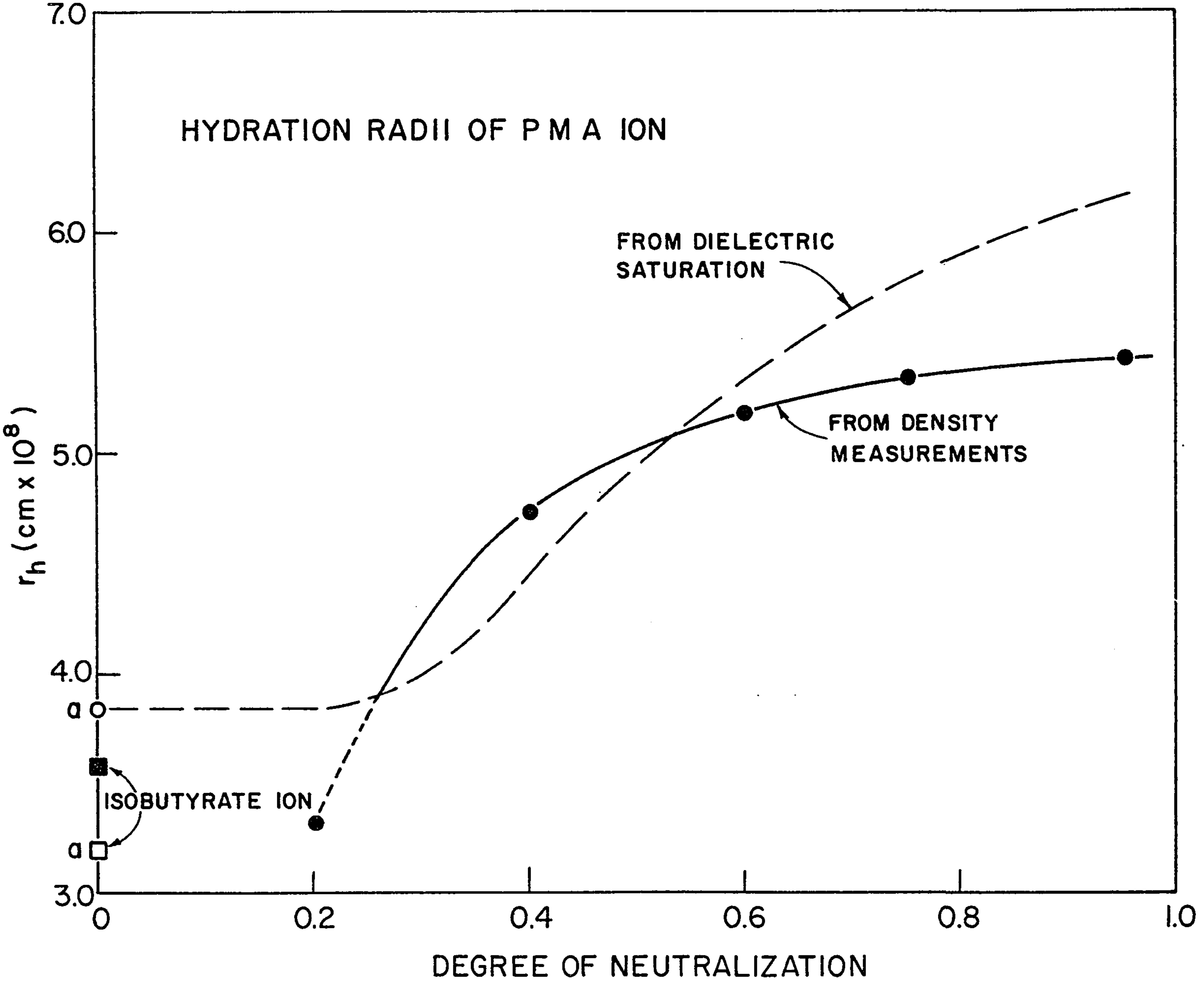
PMA ION

v_a = 69.4 mls./gm. ion (density measurements)

a = 3.8(4) Å

α	ϕ_v^o (mls./gm.-ion)	v_h (dens.) (mls./gm.-ion)	r_h (dens.) Å	r_h (diel. satn.) Å
0.95	39.3	139.8	5.4(5)	
0.80				5.9(0)
0.75	41.5	134.8	5.3(5)	
0.60	45.5	125.3	5.1(5)	5.3(5)
0.40	53.3	107.3	4.7(6)	4.4(5)
0.30				4.0(0)
0.20	77.0	52.0	3.3(2)	3.8(4)

Figure 30. Evaluation of the effective hydration radius of PMA for different degrees of neutralization.


HYDRATION RADII OF P M A ION
FROM DIELECTRIC SATURATION
FROM DENSITY MEASUREMENTS
ISOBUTYRATE ION
a
a
r_h (cm x 10^8)
7.0
6.0
5.0
4.0
3.0
0
0.2
0.4
0.6
0.8
1.0
DEGREE OF NEUTRALIZATION

rather less than "a", which of course is impossible. This is most probably a result of the assumptions and approximations made in the calculation of r_h and to some extent in the evaluation of "a". For example, we have assumed the polyion to be a charged cylinder, but it is well known that this assumption is only valid when the degree of dissociation is fairly large. In addition, we have assumed that there is no interaction between the water molecules in the hydration shell around an ionized group and neighbouring unionized groups on the chain, i.e. we have effectively assumed additivity of partial molar volume contributions from the ionized and unionized groups on the polyion. Again, this assumption may lead to incorrect results for r_h at low degrees of neutralization. These anomalous results should therefore be considered as a consequence of the oversimplified model for the calculations of r_h rather than being considered as having any special physical significance.

For purposes of comparison, we have also given the values of "a" and r_h for the isobutyrate ion in Fig. 30 and it is interesting to note that the differences $[r_h - a]$ for various degrees of neutralization become equal for the simple and polymeric ions when the degree of neutralization is about 0.3. The work on dielectric saturation near polyions (see section II-D) also leads to the conclusion that a polyion and a simple ion, with identical radii "a", should have equal hydration radii when the degree of dissociation is about 0.35 (see Fig. 7). These two approaches, therefore, give very satisfactory agreement and provide a basis for regarding the treatments developed as leading to meaningful conclusions on the degree of hydration of polyions in relation to that of corresponding simple ions.

In order to examine further the relation between the hydration radii predicted by dielectric saturation and deduced from the experimental density measurements, we have attempted to evaluate the value of r_h for PMA by the method suggested in chapter II. We have shown that it is possible, from the comparison of the dielectric saturation effects, to predict the radii of primary hydration of polyions relative to those of simple ions. The parameter r_d obtained in chapter II would represent the primary hydration radius of an "idealized" polyion, i.e. a polyion which can be represented closely by the model of a charged cylinder. PMA cannot be represented too closely by this model, therefore it would not be quite correct to use $\mathcal{E}_d = 55$ as a reference dielectric constant since this value was chosen to give $r_d = 3.2$ Å for a small simple ion. In this case, it is probably preferable to use $\mathcal{E}_d = 65$, since the corresponding value r_d for a simple ion of radius 3.2 Å (isobutyrate ion) is then 3.7 Å, the value found experimentally (see Table 11) for the hydration radius of the isobutyrate ion. In other words, it is preferable to compare the hydration of the PMA ion with the hydration of the isobutyrate ion, which has a similar structure in spherical symmetry, rather than with simple ions such as K^+. Since the dielectric saturation effect near a polyion varies with α and "a", r_h for PMA was obtained from a double interpolation following the method suggested in section II-D; the values obtained are given in Table 11 and in Fig. 30. The agreement between the two methods of evaluating r_h is very good if we consider the assumptions and approximations involved in both types of calculation. The main significant difference between the experimentally and theoretically determined variation of r_h with degree of neutralization is that r_h found from the density measurements becomes effectively constant at high degrees of neutralization while the theoretical curve increases continuously with degree of neutralization or ionization. This difference is, of course, a result of identifying the degree of neutralization with the degree of ionization. In the curve in Fig. 30, for the variation of r_h with degree of neutralization calculated from experimental density measurements, the increase in degree of ionization is not necessarily directly proportional to the increase in degree of neutralization (owing to ion association effects - see page 202) and, for this reason, we obtain an apparent limiting value in the curve based on the experimental data.

Evaluation of the hydration radius of the PP ion

The evaluation of the primary hydration radii of simple and polymeric phosphates is more difficult than with PMA ions since there is no simple experimental method available to evaluate the volume v_a. However, an approximate volume may be obtained from the average radius "a", which can be evaluated from Courtauld models. Still, the problem of finding the appropriate relation between "a" and v_a is difficult; if a spherical ion is large compared with the solvent, $v_a = 4\pi/3\ a^3N$, but, if it is of comparable size, the free volume near the ion in the hydration shell due to the finite size of water molecules must be taken into account and the actual volume is given approximately by $v_a = (2a)^3N$. The average radius "a" of $H_2PO_4^-$ being 2.5 Å, neither formula is appropriate to evaluate v_a, i.e. $H_2PO_4^-$ is larger than a water molecule (a = 1.38 Å) but not quite large enough to neglect the free volume in the hydration shell around the ion. The same problem exists with the polyphosphates since the average radius is again about 2.5 Å. The best that can be done in such cases is to choose a reasonable mean value for v_a between the two extremes volumes. The primary hydration radii were evaluated by the method described previously and were found to be approximately:

r_h (PP$^-$) = 3.7 to 3.8 Å
r_h ($H_2PO_4^-$) = 4 Å
r_h ($H_2PO_3^-$) = 3.4 Å
r_h ($H_2PO_2^-$) = 3.3 Å

The end-effects were neglected in the calculation of r_h (PP$^-$), which therefore represents the hydration radius of the long chain polyphosphates. This value obtained is reasonable. If we predict r_h from the dielectric saturation effect as shown in chapter II, we find r_h = 4.5 Å. However, Wall (23) has shown that the degree of ionic association is very high for polyphosphates and we would therefore expect the average hydration radius to be much smaller than 4.5 Å.

The r_h values for $H_2PO_3^-$ and $H_2PO_2^-$ are also reasonable since they have the same order of magnitude as the hydration radii of monovalent ions given by Nightingale (see Table 1).

Therefore, the only anomalous result is $H_2PO_4^-$ which has a radius of primary hydration much larger than that of most simple monovalent ions, even larger than that of PP$^-$. Correspondingly, k_s for $H_2PO_4^-$ is also anomalously high. It should be noted that the value ϕ_v^o for $H_2PO_4^-$ (130) calculated from recorded density measurements (131) is 29.4 mls./mole compared to 18.1 mls./mole obtained in the present work. This agreement is rather poor but, since these density measurements were made to only four decimal places compared to our six and since they were made more than seventy-five years ago (technique and purity of their salt may be doubtful), it is reasonable to assume that our values are correct.

The obvious explanation for this anomalously high degree of hydration is that hydrogen bonding is enhancing the normal hydration due to the field of the ion. If the molecule is not charged, hydrogen bonding alone is not sufficient to cause any significant hydration, e.g. we found that undissociated PMA and isobutyric acid have little hydration (very small salting-out constant). However, it is quite possible that hydrogen bonding, which can occur at both -OH groups in $H_2PO_4^-$, when added to the normal effect of the electrical field of the ion, may increase the bonding interaction between water and the $H_2PO_4^-$ ion sufficiently to account for the anomalously high degree of hydration.

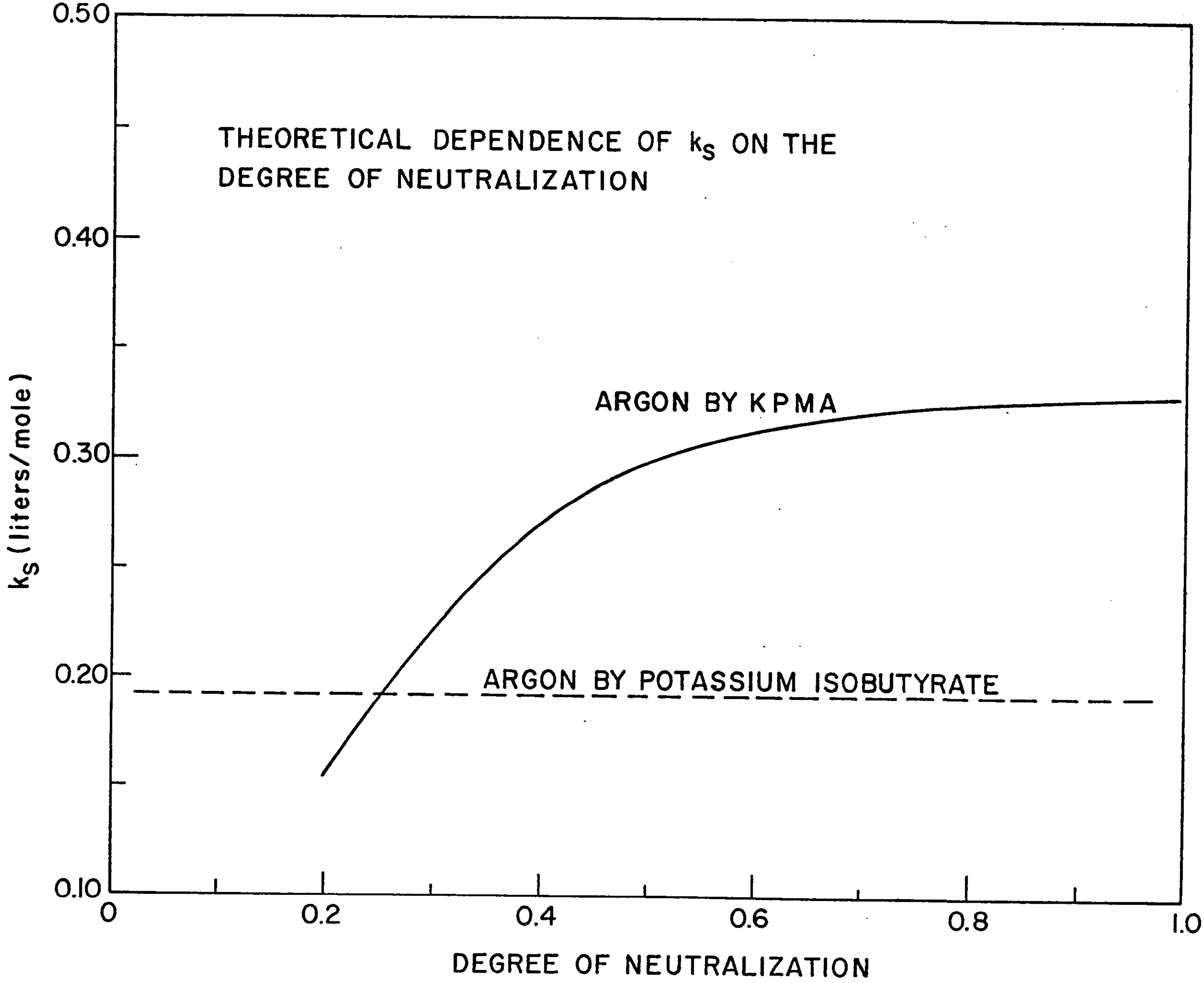
The dependence of ϕ_v^o and k_s on chain length of NaPP can also be explained in terms of hydrogen bonding. The end-groups are more hydrated than the monomer units within the chain because of the presence of -OH groups and the contribution of the end-groups to the hydration properties of total polyion hence decreases with increasing molecular weight or chain length.

We would expect $H_2PO_3^-$ to have an intermediate r_h value between $H_2PO_2^-$ and $H_2PO_4^-$ since $H_2PO_3^-$ has one OH radical capable of forming one hydrogen bond, $H_2PO_4^-$ two and $H_2PO_2^-$ none. The hydration radius of $H_2PO_3^-$ is slightly larger than $H_2PO_2^-$ but not quite as large as we would expect. This may result from structural or symmetry effects; it may also be possible that only one hydrogen bond is not strong enough to increase the primary hydration very significantly.

Interpretation of the present experimental results on salting-out by polyelectrolytes

We are now in a position to examine theoretically the experimental results obtained for the salting-out by polyelectrolytes since we have shown how to evaluate the parameter r_h in equation [III-40]. We have mentioned previously (see page 199) that it is mathematically impossible to evaluate a limiting k_s value exactly from equation [III-40] because of the nature of its dependence on R. However, this equation can still be used to examine relative effects on salting-out by polyelectrolytes. In the following calculations, we will take a fixed value of R (46.2 Å) corresponding to a concentration m = 0.1 M. This concentration was chosen since it represents about the lowest concentration used in the experimental evaluation of k_s. The values of the parameter r_h of PMA ions were evaluated from density measurements (see Table 11 and Fig. 30). Values of k_s for the salting-out of argon by KPMA are plotted as a function of the degree of neutralization in Fig. 31 and compared with k_s for potassium isobutyrate. The salting-out constants for the simple ions

Figure 31. Theoretical dependence of the salting-out constant k_s for argon on the degree of neutralization of PMA by KOH.


THEORETICAL DEPENDENCE OF k_S ON THE DEGREE OF NEUTRALIZATION
ARGON BY KPMA
ARGON BY POTASSIUM ISOBUTYRATE
k_S (liters/mole)
0.50
0.40
0.30
0.20
0.10
0
0.2
0.4
0.6
0.8
1.0
DEGREE OF NEUTRALIZATION

were evaluated from equation [III-34].

The theoretical dependence of k_s on the degree of neutralization is in fair agreement with experiment (see Fig. 22). At low degrees of neutralization, k_s for KPMA is comparable with that of potassium isobutyrate, while at high degrees of neutralization, it is much larger. However, the experimental k_s reaches a maximum value at about 0.45 degree of neutralization while theoretically we predict that k_s should reach a limiting value as the degree of neutralization tends to unity. We suggest that the maximum in k_s is a result of ion association between K^+ and the PMA ion. The first term of equation [III-40] is effectively corrected for ion association since we are using the experimentally determined radii of primary hydration (see page 211), but we are not correcting for any association in the second term. The error introduced by assuming that the degree of neutralization is equal to the degree of dissociation is much more important in the second term of equation [III-40] than in the first, e.g. a loosely bound K^+ may still have a significant amount of primary hydration but its long range influence on the non-electrolyte will be attenuated to a large extent. Therefore, the position and shape of the maximum in k_s will depend on the non-electrolyte salted-out since the second term of equation [III-40] is a function of the volume and polarization of the non-electrolyte. It is for this reason that the maximum in k_s for the salting-out of benzamide by KPMA is lower and occurs at about 0.8 degree of neutralization; it will be shown subsequently that the second term of equation [III-40] is smaller for benzamide than it is for argon.

Although the relative k_s for KPMA can be accounted for, the absolute value of k_s is more difficult to explain. Fig. 31 indicates a maximum k_s of 0.33 while the experimental value is about 0.80. We have shown previously (see page 199) that practically any value of k_s may be predicted depending on the choice of parameter R, but it does not seem reasonable to us to use a value R corresponding to lower concentration than 0.1 M since few experimental results were obtained at lower concentrations. The large discrepancy existing between the experimental and theoretical k_s could be caused by the oversimplified model used in the theoretical calculations of k_s. The electrical charges on the PMA ion are not in the centre of the molecule but distributed near the surface of the hypothetical cylinder (see diagram on page 12). It is therefore possible that the polyion may influence the solvent and non-electrolyte to much further distances since the effective radius of each ionic species on the polymer chain is much smaller than the averaged radius of the molecule and the degree of salting-out is larger for smaller radii. It is difficult to say whether this explanation can account for the large k_s of 0.80 obtained with KPMA; certainly more experimental work on salting-out by polyelectrolytes would be desirable to determine the exact nature of the long range interactions with polyions, e.g. polymine ions should behave more like idealized charged rods.

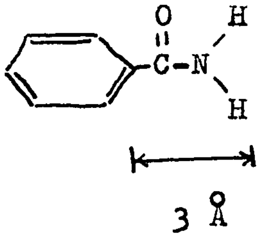
Qualitatively, the dependence of k_s on molecular weight for salting-out by NaPP can be accounted for by considering the end-effects. Quantitatively, equation [III-40] cannot predict this dependence since this equation does not take into account the finite and variable length of a real polyion.

In the case of PBPB, the actual polyion has a local structure so different from that of a charged rod model, that it is very difficult to attempt to predict k_s or its dependence on degree of neutralization. All we can say is that the polyion salts-out more than the corresponding simple ion which is what calculations predict.

Salting-out of polar non-electrolytes

For the purpose of comparing the salting-out of different non-electrolytes by the same salt, we will consider only the simple electrolytes since these are easier to deal with theoretically than the polyelectrolytes. As a typical example, we will consider the salting-out of argon and benzamide by potassium isobutyrate. The theoretical k_s for argon by potassium isobutyrate is 0.187 while the experimental value is 0.35. As in the case of KPMA, the disagreement between these two values probably results from the fact that the isobutyrate is assumed to be a spherical ion with the charge residing at its centre.

If we assume that benzamide is a sphere with a dipole at its centre, it is possible to evaluate k_s, which is then found to be larger than the value of k_s for salting-out of argon by potassium isobutyrate. This arises since benzamide is a much larger molecule than argon and this volume effect is more important than the increase in polarity. Experimentally, benzamide is less salted-out than argon. This disagreement is a result of the failure of the theory to take into account the structure of the non-electrolyte. From the examination of the benzamide molecule



it is obvious that the dipole resides in the amide group and not in the phenyl group. Therefore, the benzamide molecule will tend to be oriented with the polar amide group towards the ion while the phenyl group will be pushed away from the ion. Therefore, the amide group may come as close to the ion as the radius of the primary hydration shell while the phenyl group should not get closer to the ion than the thickness of the primary hydration shell plus the diameter of the amide group (approximately 3 Å). We can take this orientation of the non-electrolyte into account by calculating the second term of equation [III-34] in two steps: by calculating the salting-out of formamide and also of benzene, introducing the distances of closest approach mentioned above and then adding the two contributions together. The first term of equation [III-34] remains the same. For formamide, μ_o was taken as 3.6×10^{-18} e.s.u. (132), the refractive index as 1.6 (133) and the molar volume as 39.7 mls./mole (evaluated from molecular weight and density). The salting-out constant of benzamide by potassium isobutyrate may then be calculated as 0.163 which is smaller than that of argon, 0.187.

The salting-out of ethylene, argon and d-l leucine by NaH_2PO_4 presents no special problem. Ethylene is salted-out more than argon because of its larger volume and d-l leucine is salted-out very little because of its high polarity. In a rigorous calculation of k_s for d-l leucine we would again have to consider orientation effects. A good discussion of the salting-out of amino acids has been given in the monograph "Proteins, Amino Acids and Peptides" (90).

From these calculations and observations, it is obvious that it is difficult to evaluate quantitatively the salting-out constant of organic non-electrolytes by organic salts without consideration of the structure and orientation of these molecules which has been considered here for the first time. Consequently, equations of the type [III-34] and [III-40] should only be expected to hold quantitatively with inorganic simple salts, e.g. alkali halides, very simple polyions, e.g. polymine salts, and simple spherical non-electrolytes.

APPENDIX

Tables of potential, field and differential and integral dielectric constants as function of distance from the centre of the charged particles for the following models: simple electrolyte, linear polyelectrolyte and planar colloidal electrolyte.

Symbols and Units

r: Distance from centre of charged particles - in cm x 10^8

ψ_o: Potential function without corrections for dielectric saturation - in e.s.u. x 10^5

ψ: Potential function with corrections for dielectric saturation - in e.s.u. x 10^5

$(d\psi/dr)_o$: Field function without corrections for dielectric saturation - in e.s.u. x 10^{-3}

$(d\psi/dr)$: Field function with corrections for dielectric saturation - in e.s.u. x 10^{-3}

$\mathcal{E}_d$: Differential dielectric constant

$\mathcal{E}_i$: Integral dielectric constant.

SIMPLE ELECTROLYTE

a = 4 Å

Zj = 1

m = 1.0 M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	$\mathcal{E}_d$	$\mathcal{E}_i$
9.4	-6.71	-6.71	0	0	78.5	78.5
8.8	6.67	6.67	-0.136	-0.136	78.5	78.5
8.2	6.54	6.54	0.295	0.295	78.4	78.5
7.6	6.31	6.31	0.484	0.485	78.3	78.4
7.0	5.95	5.95	0.718	0.720	78.1	78.4
6.4	5.44	5.43	1.015	1.019	77.6	78.2
5.8	4.72	4.71	1.406	1.416	76.9	78.0
5.2	3.72	3.70	1.938	1.965	75.4	77.5
4.9	3.09	3.06	2.28	2.33	74.3	77.1
4.6	2.34	2.30	2.70	2.77	72.6	76.5
4.3	1.46	1.39	3.20	3.33	70.3	75.6
4.0	0.41	0.29	3.82	4.04	67.0	74.4

$a = 3.2$ Å

$Zj = 1$

$m = 1.0$ M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_i
9.4	-7.52	-7.52	0	0	78.5	78.5
8.2	7.37	7.37	-0.268	-0.268	78.4	78.5
7.0	6.83	6.83	0.652	0.653	78.1	78.4
6.4	6.37	6.37	0.921	0.924	77.8	78.3
5.8	5.71	5.71	1.273	1.280	77.2	78.1
5.4	5.15	5.13	1.563	1.588	76.5	77.8
5.0	4.44	4.42	1.950	1.977	75.4	77.4
4.6	3.57	3.54	2.43	2.48	73.7	76.9
4.2	2.48	2.41	3.06	3.16	71.0	75.9
4.0	1.83	1.74	3.45	3.60	69.1	75.2
3.8	1.10	0.97	3.90	4.13	66.6	74.3
3.6	0.27	0.08	4.43	4.75	63.5	73.0
3.4	+0.68	+0.94	5.08	5.49	59.6	71.5
3.2	1.78	2.14	5.97	6.59	54.0	69.0

a = 2 Å

Zj = 1

m = 1.0 M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_1
9.40	-8.05	-8.05	0	0	78.5	78.5
8.66	8.00	8.00	-0.146	-0.146	78.5	78.5
7.92	7.83	7.83	0.323	0.323	78.4	78.5
7.18	7.51	7.51	0.548	0.549	78.3	78.4
6.44	7.00	7.00	0.845	0.847	77.9	78.3
5.70	6.23	6.22	1.258	1.265	77.2	78.1
4.96	5.09	5.07	1.864	1.887	76.7	77.5
4.22	3.39	3.33	2.82	2.90	72.1	76.3
3.85	2.22	2.12	3.52	3.69	68.7	75.0
3.48	0.75	0.57	4.44	4.79	63.3	73.0
3.11	+1.11	+1.49	5.66	6.46	54.7	69.3
2.74	3.53	4.40	7.61	9.67	40.0	58.6
2.37	6.85		10.48			
2.00	11.53		15.36			

a = 2 Å

Zj = 1

m 0.1 M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	$\mathcal{E}_d$	$\mathcal{E}_i$
20.0	-7.32	-7.32	0	0	78.5	78.5
18.0	7.28	7.28	-0.044	-0.044	78.5	78.5
14.0	6.86	6.86	0.179	0.179	78.5	78.5
12.0	6.40	6.40	0.293	0.293	78.4	78.5
10.0	5.64	5.64	0.477	0.477	78.2	78.4
8.0	4.39	4.39	0.811	0.812	78.0	78.3
6.0	2.16	2.13	1.526	1.540	76.9	77.9
5.0	0.30	0.24	2.24	2.28	74.4	77.1
4.0	+2.53		3.56			
3.8		+3.44		4.20	66.2	74.1
3.2		6.55		6.40	55.0	69.4
3.0	7.36		6.49			
2.6		11.62		11.10	34.7	43.5
2.0	17.47		15.30			

a = 2 Å

Zj = 1

m = 0.5 M

r	ψ_0	ψ	$\left(\frac{d\psi}{dr}\right)_0$	$\frac{d\psi}{dr}$	ε_d	ε_i
11.80	-7.81	-7.81	0	0	78.5	78.5
10.82	7.76	7.76	-0.100	-0.100	78.5	78.5
9.84	7.60	7.60	0.222	0.222	78.5	78.5
8.86	7.31	7.31	0.380	0.380	78.4	78.5
7.88	6.84	6.84	0.593	0.593	78.2	78.4
6.90	6.12	6.12	0.895	0.897	77.8	78.3
5.92	5.04	5.03	1.353	1.361	77.0	78.0
4.94	3.37	3.35	2.11	2.14	74.9	77.3
3.96	0.70	0.60	3.49	3.65	68.8	75.1
3.47	+1.27	+1.49	4.61	5.01	62.1	72.5
2.98	3.94	4.52	6.47	7.67	48.7	66.3
2.49	7.80		9.51			
2.00	13.70		15.30			

a = 2 Å

Zj = 2

m = 0.1 M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_i
25.50	-8.87	-8.87	0	0	78.5	78.5
23.62	8.84	8.84	-0.033	-0.033	78.5	78.5
21.74	8.74	8.74	0.073	0.073	78.5	78.5
19.86.	8.56	8.56	0.123	0.123	78.5	78.5
17.98	8.27	8.27	0.186	0.186	78.5	78.5
16.10	7.85	7.85	0.270	0.270	78.4	78.5
14.22	7.24	7.24	0.387	0.387	78.4	78.5
12.34	6.36	6.36	0.559	0.559	78.2	78.4
10.46	5.08	5.07	0.830	0.832	77.9	78.3
8.58	3.12	3.11	1.300	1.308	77.1	78.0
6.70	+0.09	+0.14	2.23	2.27	74.5	77.1
5.76	2.55	2.67	3.08	3.19	70.9	75.9
4.82	6.05	6.36	4.48	4.85	63.0	72.9
3.88	11.35	12.50	7.08	8.82	43.5	62.7
2.94	20.31		12.75			
2.00	39.21		30.83			

a = 4 Å

Zj = 1

m = 0.5 M

r	ψ_o	$\left(\frac{d\psi}{dr}\right)_o$
11.8	-6.99	0
10.6	6.91	-0.138
9.4	6.65	0.317
8.8	6.42	0.431
8.2	6.12	0.568
7.6	5.73	0.737
7.0	5.23	0.948
6.4	4.58	1.219
5.8	3.75	1.579
5.5	3.24	1.805
5.2	2.66	2.07
4.9	2.00	2.39
4.6	1.22	2.77
4.3	0.32	3.23
4.0	+0.72	3.82

a = 4 Å

Zj = 1

m = 0.1 M

r	ψ_o	$\left(\frac{d\psi}{dr}\right)_o$
20	-6.94	0
18	6.89	-0.046
16	6.74	0.105
14	6.46	0.187
12	5.97	0.307
10	5.18	0.500
9	4.61	0.646
8	3.87	0.850
7	2.88	1.147
6	1.52	1.602
5	+0.43	2.37
4	3.45	3.82

a = 4 Å
Zj = 1
m = 0.05 M

r	ψ_o	$\left(\frac{d\psi}{dr}\right)_o$
26	-7.52	0
24	7.49	-0.021
22	7.43	0.046
20	7.31	0.077
18	7.11	0.118
16	6.83	0.172
14	6.41	0.249
12	5.80	0.366
10	4.90	0.557
9	4.27	0.703
8	3.47	0.906
7	2.43	1.202
6	1.02	1.659
5	+0.99	2.42
4	4.04	3.82

a = 4 Å
Zj = 1
m = 0.01 M

r	ψ_o	$\left(\frac{d\psi}{dr}\right)_o$
44	-7.01	0
34	6.89	-0.027
29	6.70	0.050
24	6.37	0.086
20	5.94	0.134
18	5.63	0.171
16	5.24	0.222
14	4.73	0.296
12	4.03	0.409
10	3.05	0.597
9	2.38	0.740
8	1.55	0.941
7	0.47	1.234
6	+0.97	1.683
5	3.00	2.43
4	6.05	3.82

a = 4 Å

Zj = 1

m = 0.005 M

r	ψ_0	$\left(\frac{d\psi}{dr}\right)_0$
55	-6.73	0
45	6.66	-0.013
40	6.58	0.023
35	6.43	0.036
30	6.21	0.055
25	5.86	0.086
20	5.30	0.143
15	4.33	0.262
13	3.73	0.353
11	2.89	0.496
9	1.67	0.746
7	+0.25	1.237
6	1.70	1.689
5	3.73	2.43
4	6.78	3.82

a = 4 Å

Zj = 1

m = 0.001 M

r	ψ_0	$\left(\frac{d\psi}{dr}\right)_0$
94	-6.84	0
84	6.83	-0.002
74	6.79	0.005
64	6.71	0.010
54	6.59	0.016
44	6.38	0.027
34	6.02	0.048
24	5.32	0.100
22	5.10	0.120
18	4.51	0.180
14	3.58	0.299
10	1.90	0.589
8	0.42	0.924
6	+2.06	1.652
4	7.14	3.82

LINEAR POLYELECTROLYTE

$a = 2.2$ Å

$\alpha = 0.6$

$m = 1.0$ M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_1
14.60	-6.20	-6.20	0	0	78.5	78.5
12.70	5.94	5.94	-0.278	-0.278	78.4	78.5
11.75	5.60	5.60	0.440	0.440	78.3	78.4
11.00	5.22		0.584			
10.80		5.10		0.627	78.2	78.4
9.85		4.40		0.847	77.9	78.3
9.80	4.36		0.857			
8.90		3.48		1.114	77.5	78.2
8.60	3.14		1.206			
7.95		2.26		1.452	76.8	77.9
7.40	1.42		1.676			
7.00		0.69		1.874	75.7	77.6
6.60	+0.07		2.06			
6.05		+1.34		2.52	73.6	76.8
5.80	2.02		2.67			
5.10		4.09		3.44	69.8	75.5
5.00	4.52		3.46			

LINEAR POLYELECTROLYTE (Cont'd.)

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_i
4.625		5.91		4.05	67.0	74.4
4.2	7.78		4.63			
4.15		8.00		5.03	62.0	72.5
3.80	9.70		5.55			
3.675		10.74		6.33	55.3	69.6
3.40	12.22		6.51			
3.20		14.18		8.67	44.1	63.2
3.00	14.99		8.07			
2.60	18.73		10.05			
2.20	23.21		13.38			

a = 3.2 Å

α = 0.6

m = 1.0 M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_i
14.60	-5.06	-5.06	0	0	78.5	78.5
12.70	4.77	4.77	-0.318	-0.318	78.4	78.5
10.80	3.80	3.80	0.719	0.720	78.1	78.4
9.85	3.00	3.00	0.973	0.977	77.7	78.2
8.90	1.93	1.93	1.285	1.293	77.1	78.0
7.95	0.54	0.52	1.662	1.679	76.2	77.7
7.00	+1.26	+1.31	2.23	2.28	74.4	77.1
6.525	2.40	2.48	2.49	2.56	73.4	76.8
6.05	3.66	3.77	2.95	3.06	71.5	76.1
5.575	5.19	5.38	3.36	3.53	69.4	75.3
5.10	6.89	7.17	4.02	4.29	65.8	73.9
4.625	9.02	9.48	4.72	5.19	61.2	72.1
4.15	11.43	12.20	5.78	6.68	53.5	68.8
3.675	14.55	15.96	7.10	9.04	42.5	61.8
3.20	18.29		9.18			

$a = 5$ Å

$\alpha = 0.6$

$m = 1.0$ M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	$\mathcal{E}_d$	$\mathcal{E}_1$
14.6	-3.50	-3.50	0	0	78.5	78.5
13.0	3.25	3.25	-0.317	-0.317	78.4	78.5
12.2	2.93	2.93	0.497	0.497	78.3	78.4
11.4	2.45	2.45	0.699	0.700	78.1	78.4
10.6	1.80	1.80	0.932	0.935	77.8	78.3
9.8	0.95	0.95	1.204	1.210	77.3	78.1
8.2	+1.54	+1.58	2.10	2.14	74.9	77.3
7.4	3.39	3.47	2.63	2.71	72.9	76.6
6.6	5.74	5.91	3.35	3.51	69.5	75.4
6.2		7.44		3.98	67.3	74.5
5.8	8.76	9.13	4.35	4.71	63.6	73.1
5.4	10.68		4.97			
5.0	12.78	13.63	5.88	6.86	52.6	68.3

$a = 3.2$ Å

$\alpha = 0.8$

$m = 1.0$ M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_i
14.60	-6.63	-6.63	0	0	78.5	78.5
12.70	6.30	6.30	-0.353	-0.353	78.4	78.5
10.80	5.23	5.22	0.802	0.804	78.0	78.3
9.85	4.34	4.33	1.091	0.095	77.5	78.2
8.90	3.14	3.12	1.445	1.456	76.8	77.9
7.95		1.53		1.925	75.5	77.5
7.00	+0.49	+0.57	2.45	2.52	73.6	76.8
6.05	3.32	3.53	3.36	3.55	69.3	75.3
5.575		5.54		4.40	65.2	73.7
5.10	7.18	7.70	4.70	5.22	61.1	72.1
4.625		10.41		6.77	53.1	68.6
4.15	12.71	14.25	7.02	9.03	42.6	61.8
3.675	16.36		9.07			
3.20	21.46		12.00			

$a = 3.2$ Å

$\alpha = 0.4$

$m = 1.0$ M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	$\mathcal{E}_d$	$\mathcal{E}_i$
14.60	-3.38	-3.38	0	0	78.5	78.5
12.70	3.14	3.14	-0.257	-0.257	78.4	78.5
10.80	2.36	2.36	0.579	0.579	78.2	78.4
9.85	1.72	1.72	0.779	0.780	78.0	78.3
8.90		0.87		1.024	77.6	78.2
7.95	+0.16	+0.24	1.268	1.302	77.1	78.0
7.00		1.68		1.709	76.2	77.7
6.05		3.57		2.26	74.5	77.1
5.575		4.71		2.65	73.1	76.6
5.10	5.97	6.09	2.96	3.06	71.4	76.1
4.625	7.46	7.65	3.50	3.67	68.8	75.1
4.15	9.30	9.59	4.11	4.40	65.2	73.7
3.675	11.41	11.89	4.99	5.52	59.5	71.4
3.2	14.08	14.92	6.11	7.19	51.0	67.5

a = 3.2 Å

α = 0.3

m = 1.0 M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_i
14.60	-2.77	-2.77	0	0	78.5	78.5
12.70	2.58	2.58	-0.207	-0.207	78.5	78.5
10.80	1.95	1.95	0.462	0.462	78.3	78.4
8.90	0.77	0.77	0.797	0.798	78.0	78.3
7.95	+0.06	+0.07	1.008	1.015	77.7	78.2
7.00	1.23	1.25	1.413	1.433	76.8	77.9
6.05	2.75	2.80	1.813	1.847	75.8	77.6
5.575	3.67	3.73	2.07	2.12	75.0	77.3
5.10	4.72	4.82	2.37	2.44	73.9	76.9
4.625	5.93	6.06	2.74	2.84	72.3	76.3
4.15	7.34	7.54	3.21	3.36	70.2	75.6
3.675	9.00	9.28	3.81	4.06	66.9	74.4
3.20	10.99	11.40	4.60	5.04	62.0	72.5

$a = 3.2$ Å

$\alpha = 0.2$

$m = 1.0$ M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_1
14.60	-1.61	-1.61	0	0	78.5	78.5
12.70	1.46	1.46	-0.157	-0.157	78.5	78.5
10.80	0.99	0.99	0.350	0.350	78.4	78.5
8.90	0.15	0.15	0.535	0.536	78.3	78.4
7.00	+1.25	+1.25	1.008	1.012	77.7	78.2
6.05	2.32	2.33	1.281	1.289	77.1	78.0
5.10	3.69	3.71	1.653	1.670	76.3	77.7
4.625	4.53	4.56	1.877	1.903	75.6	77.5
4.15	5.49	5.53	2.19	2.23	74.6	77.2
3.675	6.62	6.69	2.55	2.62	73.2	76.7
3.20	7.94	8.05	3.06	3.17	71.0	75.9

$a = 3.2$ Å

$\alpha = 0.6$

$m = 0.5$ M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	$\mathcal{E}_d$	$\mathcal{E}_i$
20.6	-6.03	-6.03	0	0	78.5	78.5
18.2	5.82	5.82	-0.177	-0.177	78.5	78.5
17.0	5.55	5.55	0.278	0.278	78.4	78.5
15.2	4.90	4.90	0.455	0.455	78.3	78.4
13.4	3.89	3.89	0.675	0.676	78.1	78.4
11.6	2.43	2.42	0.965	0.968	77.7	78.2
9.8	0.35	0.33	1.364	1.373	77.0	78.0
8.6	+1.52	+1.56	1.823	1.852	75.8	77.6
7.4	3.96	4.05	2.36	2.42	74.0	76.9
6.2	7.20	7.38	3.16	3.30	70.5	75.7
5.6		9.59		3.89	67.7	74.7
5.0	11.66	12.12	4.46	4.85	63.0	72.8
4.4	14.70	15.49	5.43	6.19	56.0	69.9
3.8	18.29	19.79	6.96	8.73	43.9	63.0
3.2	23.19		9.23			

a = 3.2 Å

α = 0.6

m = 0.1 M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_1
46.2	-7.36	-7.39	0	0	78.5	78.5
40.2	7.14	7.17	-0.071	-0.076	78.5	78.5
31.2	5.81	5.84	0.231	0.230	78.5	78.5
25.2	3.98	4.01	0.390	0.389	78.4	78.4
19.2	0.93	0.97	0.654	0.652	78.1	78.4
14.2	+3.29	+3.23	1.093	1.088	77.5	78.2
10.2	8.82	8.75	1.780	1.784	75.9	77.6
8.2	12.96	12.92	2.43	2.46	73.8	76.9
7.2	15.67	15.67	2.91	2.98	71.8	76.2
6.2	18.86	18.96	3.62	3.77	68.3	74.9
5.2	23.01	23.36	4.65	5.02	62.1	72.5
4.2	28.39	29.44	6.40	7.58	49.1	66.5
3.2	36.36		9.80			

$a = 3.2$ Å

$\alpha = 0.6$

$m = 0.05$ M

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d	ε_i
65.2	-7.97	-7.95	0	0	78.5	78.5
53.2	7.54	7.52	-0.074	-0.074	78.5	78.5
41.2	6.06	6.04	0.181	0.181	78.5	78.5
29.2	2.88	2.85	0.371	0.373	78.4	78.5
21.2	+0.99	+1.03	0.621	0.625	78.2	78.4
17.2	3.90	3.97	0.847	0.854	77.9	78.3
13.2	7.98	8.09	1.230	1.244	77.2	78.1
11.2	10.73	10.87	1.542	1.565	76.5	77.8
9.2	14.25	14.46	2.01	2.05	75.2	77.4
7.2	18.96	19.31	2.79	2.89	72.1	76.3
5.2	25.89	26.69	4.31	4.73	63.6	73.1
3.2	38.12		8.70			

PLANAR COLLOIDAL ELECTROLYTE

R = 50 Å
a = 5 Å
λ = 15 Å

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ϵ_d
50.0	-11.87	-11.87	0	0	78.5
45.5	11.70	11.70	-0.077	-0.077	78.5
41.0	11.17	11.17	0.158	0.158	78.5
36.5	10.26	10.26	0.246	0.246	78.5
32.0	8.94	8.94	0.346	0.346	78.4
27.5	7.12	7.12	0.466	0.466	78.3
26.0	6.39	6.39	0.512	0.513	78.3
23.0	4.70	4.69	0.620	0.621	78.2
20.0	2.64	2.64	0.753	0.755	78.0
17.0	0.14	0.12	0.922	0.926	77.8
14.0	+2.94	+2.97	1.158	1.166	77.4
11.0	6.90	6.97	1.522	1.539	76.6
9.5		9.48		1.806	75.9
8.0	12.29	12.44	2.15	2.20	74.7
6.5	15.91	16.17	2.67	2.77	72.6
5.0	20.47	20.97	3.54	3.77	68.3

$R = 50\ \mathring{A}$

$a = 5\ \mathring{A}$

$\lambda = 12\ \mathring{A}$

r	ψ_0	ψ	$\left(\frac{d\psi}{dr}\right)_0$	$\frac{d\psi}{dr}$	ε_d
50.0	-15.08	-15.08	0	0	78.5
45.5	14.89	14.89	-0.083	-0.083	78.5
41.0	14.33	14.33	0.170	0.170	78.5
36.5	13.35	13.35	0.265	0.266	78.4
32.0	11.92	11.91	0.375	0.375	78.4
27.5	9.94	9.94	0.509	0.509	78.3
23.0	7.28	7.27	0.684	0.685	78.1
20.0		4.99		0.842	77.9
18.5	3.67	3.65	0.937	0.940	77.8
17.0	2.18	2.16	1.050	1.055	77.6
14.0	+1.31	+1.36	1.271	1.283	77.2
11.0	5.87	6.97	1.755	1.784	75.9
9.5	8.73	8.89	2.17	2.22	74.6
8.0	12.43	12.70	2.68	2.78	72.6
6.5	16.98	17.50	3.62	3.87	67.8
5.0	23.66		5.30		

$R = 50$ Å

$a = 5$ Å

$\lambda = 10$ Å

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	$\mathcal{E}_d$
50	-17.88	-17.88	0	0	78.5
45.5	17.69	17.69	-0.086	-0.086	78.5
41	17.10	17.10	0.177	0.177	78.5
36.5	16.09	16.08	0.276	0.277	78.4
32	14.59	14.58	0.391	0.392	78.4
27.5	12.52	12.51	0.533	0.535	78.3
23	9.73	9.71	0.721	0.723	78.1
20	7.32	7.29	0.891	0.895	77.8
17	4.32	4.28	1.125	1.132	77.5
14	0.47	0.40	1.445	1.463	76.8
11	+4.47	+4.64	2.00	2.05	75.2
9.5	7.83	8.10	2.41	2.51	73.6
8	11.90	12.37	3.20	3.39	70.0
6.5	17.65	18.65	4.44	5.03	62.0
5	26.15		7.54		

$R = 50$ Å
$a = 5$ Å
$\lambda = 8$ Å

r	ψ_0	ψ	$\left(\frac{d\psi}{dr}\right)_0$	$\frac{d\psi}{dr}$	ε_d
50.0	-21.42	-21.42	0	0	78.5
45.5	21.22	21.22	-0.089	-0.089	78.5
41.0	20.61	20.61	0.183	0.183	78.5
36.5	19.56	19.56	0.286	0.287	78.4
32.0	18.02	18.00	0.406	0.407	78.4
27.5	15.86	15.84	0.556	0.557	78.2
23.0	12.93	12.92	0.756	0.758	78.0
20.0	10.40	10.38	0.940	0.945	77.8
17.0	7.22	7.18	1.198	1.206	77.3
14.0	3.08	3.00	1.592	1.611	76.4
11.0	+2.50	+2.65	2.10	2.19	74.7
9.5		6.39		2.92	72.0
8.0	10.90	11.59	3.66	4.01	67.2
6.5	17.57	19.43	5.68	7.14	51.3
5.0	30.02		11.87		

$R = 50$ Å

$a = 2$ Å

$\lambda = 12$ Å

r	ψ_0	ψ	$\left(\frac{d\psi}{dr}\right)_0$	$\frac{d\psi}{dr}$	ε_d
50.0	-16.12	-16.16	0	0	78.5
45.5	15.96	15.95	-0.074	-0.074	78.5
41.0	15.45	15.45	0.150	0.150	78.5
36.5	14.59	14.59	0.233	0.233	78.5
32.0	13.34	13.34	0.327	0.327	78.4
27.5	11.63	11.62	0.438	0.439	78.3
23.0	9.35	9.34	0.579	0.580	78.2
18.5	6.34		0.771		
17.0		5.10		0.856	77.9
14.0	2.27	2.24	1.061	1.066	77.6
11.0	+1.24	+1.30	1.271	1.284	77.2
8.0	5.81	5.92	1.751	1.782	76.0
6.5		8.83		2.22	74.6
5.0	12.35	12.64	2.67	2.77	72.6
3.5	16.87	17.41	3.60	3.86	67.9
2.0	23.52	24.89	5.25	6.29	55.6

R = 35 Å

a = 5 Å

λ = 12 Å

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	$\mathcal{E}_d$
35	-12.00	-12.00	0	0	78.5
32		11.83		-0.114	78.5
29		11.31		0.232	78.5
26		10.43		0.360	78.4
25	10.05	10.05	-0.406	0.406	78.4
23		9.14		0.506	78.3
20	7.37	7.37	0.679	0.680	78.1
17		5.01		0.903	77.8
15	3.03	3.01	1.091	1.100	77.5
13		0.53		1.324	77.1
11		+2.49		1.953	75.5
10	+4.05	4.57	1.805	1.997	75.3
9	6.00	6.64	1.99	2.50	73.6
8	8.43	9.48	2.35	2.72	72.8
7	10.78	12.28	322	3.52	69.4
6	14.69	16.51	3.73	4.27	65.9
5	20.47	21.23	5.32	6.28	55.6

$R = 75$ Å

$a = 5$ Å

$\lambda = 12$ Å

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d
75	-18.93	-18.93	0	0	78.5
69	18.79	18.79	-0.047	-0.047	78.5
63	18.36	18.36	0.096	0.096	78.5
57	17.63	17.63	0.148	0.148	78.5
51	16.57	16.57	0.206	0.206	78.5
45	15.14	15.14	0.273	0.273	78.4
39	13.27	13.27	0.354	0.354	78.4
33	10.85	10.84	0.457	0.459	78.3
27	7.70	7.69	0.602	0.605	78.2
23	5.03	5.01	0.736	0.742	78.0
19	1.73	1.70	0.929	0.939	77.8
15	+2.62	+2.67	1.292	1.310	77.1
13	5.42	5.19	1.487	1.508	76.7
11	8.68	8.82	1.844	1.884	75.7
9	12.87	13.14	2.31	2.38	74.1
7	18.22	18.73	3.22	3.43	69.9
5	26.45	28.06	5.20	6.28	55.6

R = 105 Å

a = 5 Å

λ = 12 Å

r	ψ_o	ψ	$\left(\frac{d\psi}{dr}\right)_o$	$\frac{d\psi}{dr}$	ε_d
105	-21.97	-21.97	0	0	78.5
95	21.77	21.77	-0.039	-0.039	78.5
85	21.18	21.18	0.081	0.081	78.5
75	20.14	20.14	0.126	0.126	78.5
65	18.63	18.63	0.179	0.179	78.5
55	16.53	16.53	0.244	0.244	78.5
45	13.68	13.68	0.331	0.331	78.4
35	9.77	9.76	0.460	0.461	78.3
33	8.82	8.81	0.494	0.495	78.3
29	6.69	6.68	0.576	0.577	78.3
25	4.18	4.16	0.684	0.685	78.1
21	1.16	1.14	0.833	0.835	77.9
19	+0.62	+0.65	0.965	0.971	77.7
17	2.76	2.81	1.190	1.206	77.3
15	5.30	5.38	1.285	1.300	77.1
13	8.03	8.15	1.575	1.602	76.4
11	11.57	11.76	1.825	1.863	75.7
9	15.54	15.84	2.39	2.48	73.7
7	21.29	21.87	3.19	3.41	70.0
5	29.15	30.85	5.24	6.43	54.8

CLAIMS TO ORIGINAL RESEARCH

The hydration of polyions in relation to that of related simple monomeric ions has been studied quantitatively for the first time. Three approaches have been employed; the radius of the primary hydration shell of polyions has been predicted from theoretical studies of dielectric saturation effects, evaluated experimentally from density measurements and related to the salting-out constant of these ions. In particular;

1) Models have been proposed for simple electrolytes and planar colloidal electrolytes for which it is possible to write a Poisson-Boltzmann equation. The two models are similar in form but differ in symmetry to the models for linear polyelectrolytes proposed independently by Alfrey, Berg and Morawetz and by Fuoss, Lifson and Katchalsky.

2) These Poisson-Boltzmann equations were solved numerically using an I.B.M. 650 computer with and without corrections for the effect of dielectric saturation of the solvent for the following models: simple electrolyte, linear polyelectrolyte, spherically coiled polyelectrolyte and planar colloidal electrolyte.

3) The dependence of dielectric saturation effects on the radius of the charged particle, concentration and charge density was quantitatively investigated.

4) The relative degrees of primary hydration were related to the degrees of dielectric saturation of the solvent near the various kinds of charged particles considered.

5) From the dielectric saturation calculations the following conclusions regarding hydration were reached:

- Below an ionic concentration of 1 M, the degree of primary hydration of a charged particle increases slightly with decreasing concentration.
- The radius of primary hydration should increase with size and charge density of the particle.
- In general, the radius of primary hydration of a charged particle should increase in the following order: simple ion < linear polyion < planar colloidal ion.
- For any reasonable spherically coiled polyelectrolyte, the macromolecule as a whole should not affect the solvent structure outside the periphery of the coil to any significant extent.

6) Debye's theory of salting-out by simple ions was modified to take into account the finite thickness of the primary hydration shell of the ions and was related to the molecular properties of the non-electrolyte (molar volume, molar polarization, refractive index) using Kirkwood's theory of dielectrics.

7) A new theory was derived for salting-out by polyions based on that developed, in relation to Debye's theory, for simple ions in section 6.

8) The salting-out constants of some non-electrolytes (argon, ethylene, d-l leucine and benzamide) by polyelectrolytes (NaPP, KPMA and PBPB) and by the corresponding simple electrolytes have been measured. In general, it is found that k_s of polyions is larger than those of the corresponding simple ions; NaH_2PO_4 is an exception since its k_s value is larger than that of NaPP and this can be accounted for by the anomalously high hydration of NaH_2PO_4 arising from hydrogen bonding. The constant k_s of polyions is independent of chain length except for low molecular weight oligomers. It increases with <u>degree of ionization</u> but at high <u>degrees of neutralization</u> k_s decreases due to ionic association between the polyion and gegen-ions. The maximum in k_s depends on the nature of the non-electrolyte and of the salt. These experimental observations were interpreted in the light of the derived theory (section 7).

9) The apparent molar volumes of KPMA, NaPP and their corresponding simple salts have been measured and related to the radii of primary hydration r_h of simple and polymeric ions. The radius r_h of polyions is larger than that of corresponding simple ions (NaH_2PO_4 being again an exception), varies very little with chain length of polyions except for low molecular weight oligomers and increases with degree of ionization (at high degrees of neutralization it becomes effectively constant because of ionic association).

10) The radius r_h was related to k_s and was compared to the theoretical radius of primary hydration predicted from dielectric saturation studies. Good agreement was obtained in both cases.

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