ACKNOWLEDGMENT

I am grateful to my research supervisor, Dr. F. D. F. Talbot, for his counsel and encouragement throughout the progress of this work. I wish also to thank Environment Canada and the National Research Council of Canada for providing financial assistance.

I dedicate this thesis to my wife Trinh Khiet and my parents.
ABSTRACT

The removal of copper, lead and cadmium ions from aqueous solution by foam fractionation using sodium dodecylbenzene sulphonate (NaDBS) has been experimentally studied and theoretically predicted for solutions with a pH less than 4. A mathematical model of the system consisting of the equilibrium relations of chemical reactions occurring in the system was solved for the equilibrium concentration of all ions in the solution. Based on this equilibrium concentration and the effective radius of the hydrated ion, a modified theory of the Gouy-Chapman diffuse double layer developed by Jorne and Rubin (9) was used to predict the distribution factor of the metal ions. The work was extended to systems containing two metal ions for the determination of the separability of the ions with respect to each other.

It was found that the distribution factor for solutions containing one metal ion could be predicted theoretically for a bulk solution pH less than four. Deviation of results above this pH was attributed to the limitations of the bulk solution reaction model because it did not include reactions for the formation of poly hydroxyl and poly nuclear hydroxyl complexes. Good agreement was also obtained between experiment and theory in the separability study. The results indicate that the order of removal of the ions from solution is Pb^{2+} > Cd^{2+} > Cu^{2+}. This sequence is the reverse order of the effective radii of the hydrated ions. The results support the fact that the mechanism for removal of the ions from solution is that of electrical attraction and that selectivity depends upon the charge and size of the hydrated ion.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>1</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td>x</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2. LITERATURE SURVEY</td>
<td>3</td>
</tr>
<tr>
<td>3. THEORETICAL BACKGROUND</td>
<td>11</td>
</tr>
<tr>
<td>3.1 Measurement of the Distribution Factor</td>
<td>11</td>
</tr>
<tr>
<td>3.2 Estimation of Bulk Liquid Ionic Composition</td>
<td>13</td>
</tr>
<tr>
<td>3.3 The Gouy-Chapman Diffuse Double Layer Model</td>
<td>21</td>
</tr>
<tr>
<td>4. EXPERIMENTAL INVESTIGATION</td>
<td>36</td>
</tr>
<tr>
<td>4.1 Foam Fractionation</td>
<td>36</td>
</tr>
<tr>
<td>4.2 Equilibrium Constant Determination</td>
<td>40</td>
</tr>
<tr>
<td>4.3 Instrument and Material</td>
<td>43</td>
</tr>
<tr>
<td>5. RESULTS</td>
<td>44</td>
</tr>
<tr>
<td>5.1 Results of Equilibrium Constants</td>
<td>44</td>
</tr>
<tr>
<td>5.2 Results of Foam Fractionation</td>
<td>47</td>
</tr>
<tr>
<td>6. DISCUSSION</td>
<td>67</td>
</tr>
<tr>
<td>6.1 Error Analysis</td>
<td>79</td>
</tr>
</tbody>
</table>
7. CONCLUSIONS 82
8. RECOMMENDATIONS FOR FUTURE WORK 83
REFERENCES 84
GLOSSARY 89
APPENDIX A
  A.1 A Mathematical Model of the System Containing Two Metal Ions 91 92
  A.2 Derivation of Equation (3.7) 92 97
  A.3 Method of Continuous Variation 99 101
  A.4 Derivation of Equation (3.34) 101 103
  A.5 Derivation of Equation (3.42) 103 104
  A.6 Derivation of Equation (3.44) 104 105
  A.7 Determination of the Effective Radii of Hydrated Ions 105 107
APPENDIX B Tables of Experimental and Calculated Data 107
APPENDIX C Computer Programs 137
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A Schematic Representation of the Variation of Interface Concentration With Distance.</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>A Lamina in the Solution, Parallel to An Interface.</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>Surface Adsorption Model for Small Ions of Charge $z_1$ and Large Ions of Charge $z_2$ to Monolayer of Surfactant of Charge $z_s$ at $x = 0$.</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>Schematic Diagram of the Experimental Apparatus.</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>Spectrophotometric Analysis for the Determination of $k_b$ of Cu-NaDBS System.</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>Spectrophotometric Analysis for the Determination of $k_b$ of Pb-NaDBS System.</td>
<td>49</td>
</tr>
<tr>
<td>7</td>
<td>Spectrophotometric Analysis for the Determination of $k_b$ of Cd-NaDBS System.</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>Method of Continuous Variation for the Determination of the value of n in Cd(DBS)$_n$.</td>
<td>53</td>
</tr>
<tr>
<td>9</td>
<td>Effect of pH on the Distribution Factor of Copper, $[\text{Cu}] = 10 \text{ ppm}$, $[\text{NaDBS}] = 0.50 \text{ gm/l}$.</td>
<td>57</td>
</tr>
<tr>
<td>10</td>
<td>Effect of pH on the Distribution Factor of Cadmium, $[\text{Cd}] = 10 \text{ ppm}$, $[\text{NaDBS}] = 0.50 \text{ gm/l}$.</td>
<td>58</td>
</tr>
<tr>
<td>11</td>
<td>Effect of pH on the Distribution Factor of Lead, $[\text{Pb}] = 10 \text{ ppm}$, $[\text{NaDBS}] = 0.50 \text{ gm/l}$.</td>
<td>59</td>
</tr>
<tr>
<td>12</td>
<td>Effect of Bulk Copper Concentration on Distribution Factor, $\text{pH} = 4.70 \pm 0.05$, $[\text{NaDBS}] = 0.50 \text{ gm/l}$.</td>
<td>60</td>
</tr>
<tr>
<td>13</td>
<td>Effect of Bulk Cadmium Concentration on Distribution Factor, $\text{pH} = 5.00 \pm 0.05$, $[\text{NaDBS}] = 0.50 \text{ gm/l}$.</td>
<td>61</td>
</tr>
</tbody>
</table>
Figure

14 Effect of Bulk Lead Concentration on Distribution Factor, \( \text{pH} = 5.15 \pm 0.07 \), \([\text{NaDBS}] = 0.50 \text{ gm/l} \).

15 Comparison of Predicted and Measured Selectivity Coefficients of Pb-Cu-NaDBS System, \( \text{pH} = 4.10 \pm 0.05 \), \([\text{NaDBS}] = 0.50 \text{ gm/l} \).

16 Comparison of Predicted and Measured Selectivity Coefficients of Cd-Cu-NaDBS System, \( \text{pH} = 4.10 \pm 0.05 \), \([\text{NaDBS}] = 0.50 \text{ gm/l} \).

17 Comparison of Predicted and Measured Selectivity Coefficients of Pb-Cd-NaDBS System, \( \text{pH} = 4.10 \pm 0.05 \), \([\text{NaDBS}] = 0.50 \text{ gm/l} \).

18 pH Change of Cu-NaDBS System: \( \text{pH}_{F} \), \( \text{pH} \) of Foamate; \( \text{pH}_{B} \), \( \text{pH} \) of Bulk.

19 pH Change of Pb-NaDBS System: \( \text{pH}_{F} \), \( \text{pH} \) of Foamate; \( \text{pH}_{B} \), \( \text{pH} \) of Bulk.

20 pH Change of Cd-NaDBS System: \( \text{pH}_{F} \), \( \text{pH} \) of Foamate; \( \text{pH}_{B} \), \( \text{pH} \) of Bulk.


**LIST OF TABLES**

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Various Adsorption Bubble Separation Methods Classified on the Basis of Mechanism of Separation and Size of the Material Separated.</td>
</tr>
<tr>
<td>2</td>
<td>Instrumental Parameters for the Analysis of Metal Ions.</td>
</tr>
<tr>
<td>3</td>
<td>Equilibrium Constants $k_a$ and $k_d$ of Three Metal Ions.</td>
</tr>
<tr>
<td>4</td>
<td>Equilibrium Constant of Acetic Acid Measured by Spectrophotometric Analysis.</td>
</tr>
<tr>
<td>5</td>
<td>Equilibrium Constant $k_c$ of HDBS</td>
</tr>
<tr>
<td>6</td>
<td>Slopes and Intercepts of Figures 5 to 7 and the Results of $k_d$</td>
</tr>
<tr>
<td>7</td>
<td>The Effective Radii of Hydrated Ions</td>
</tr>
<tr>
<td>8</td>
<td>Comparison of Selectivity Coefficients Measured from Mixture Systems and That Calculated from Pure Component Systems.</td>
</tr>
<tr>
<td>9</td>
<td>pH Change of Foaming NaDDBS Solution Without Metal Ions.</td>
</tr>
<tr>
<td>A-1</td>
<td>Equilibrium Constants of the Model of Mixture Systems</td>
</tr>
<tr>
<td>B-1</td>
<td>Spectrophotometric Analysis for the Determination of $k_p$ of Cu-NaDDBS System.</td>
</tr>
<tr>
<td>B-2</td>
<td>Spectrophotometric Analysis for the Determination of $k_p$ of Pb-NaDDBS System.</td>
</tr>
<tr>
<td>B-3</td>
<td>Spectrophotometric Analysis for the Determination of $k_p$ of Cd-NaDDBS System.</td>
</tr>
<tr>
<td>B-4</td>
<td>Spectrophotometric Measurements for the Method of Continuous Variation.</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>B-5</td>
<td>Spectrophotometric Measurements of HDES Solution</td>
</tr>
<tr>
<td>B-6</td>
<td>Effect of pH on the Distribution Factor of Cu(^{2+}) and CuOH(^+)</td>
</tr>
<tr>
<td>B-7</td>
<td>Effect of Bulk Copper Concentration on the Distribution Factor of Cu(^{2+}) and CuOH(^+)</td>
</tr>
<tr>
<td>B-8</td>
<td>Effect of pH on the Distribution Factor of Pb(^{2+}) and PbOH(^+)</td>
</tr>
<tr>
<td>B-9</td>
<td>Effect of Bulk Lead Concentration on the Distribution Factor of Pb(^{2+}) and PbOH(^+)</td>
</tr>
<tr>
<td>B-10</td>
<td>Effect of pH on the Distribution Factor of Cd(^{2+}) and CdOH(^+)</td>
</tr>
<tr>
<td>B-11</td>
<td>Effect of Bulk Cadmium Concentration on the Distribution Factor of Cd(^{2+}) and CdOH(^+)</td>
</tr>
<tr>
<td>B-12</td>
<td>Theoretical Prediction of Distribution Factor of Cu(^{2+}) and CuOH(^+) vs. Bulk Concentration</td>
</tr>
<tr>
<td>B-13</td>
<td>Theoretical Prediction of Distribution Factor of Cu(^{2+}) and CuOH(^+) vs. pH</td>
</tr>
<tr>
<td>B-14</td>
<td>Theoretical Prediction of Distribution Factor of Pb(^{2+}) and PbOH(^+) vs. pH</td>
</tr>
<tr>
<td>B-15</td>
<td>Theoretical Prediction of Distribution Factor of Pb(^{2+}) and PbOH(^+) vs. Bulk Concentration</td>
</tr>
<tr>
<td>B-16</td>
<td>Theoretical Prediction of Distribution Factor of Cd(^{2+}) and CdOH(^+) vs. pH</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>------------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>B-17</td>
<td>Theoretical Prediction of Distribution Factor of Cd$^{++}$ and CdOH$^+$ vs. Bulk Concentration</td>
</tr>
<tr>
<td>B-18</td>
<td>Experimental and Predicted Selectivity Coefficient of Cd-Cu-NaDMS System</td>
</tr>
<tr>
<td>B-19</td>
<td>Experimental and Predicted Selectivity Coefficient of Pb-Cu-NaDMS System</td>
</tr>
<tr>
<td>B-20</td>
<td>Experimental and Predicted Selectivity Coefficient of Pb-Cd-NaDMS System</td>
</tr>
<tr>
<td>B-21</td>
<td>Spectrophotometric Measurements of Cu-NaDMS System</td>
</tr>
<tr>
<td>B-22</td>
<td>Spectrophotometric Measurements of Pb-NaDMS System</td>
</tr>
<tr>
<td>B-23</td>
<td>Spectrophotometric Measurements of Cd-NaDMS System</td>
</tr>
<tr>
<td>B-24</td>
<td>Experimental Data of Cu-NaDMS System</td>
</tr>
<tr>
<td>B-25</td>
<td>Experimental Data of Pb-NaDMS System</td>
</tr>
<tr>
<td>B-26</td>
<td>Experimental Data of Cd-NaDMS System</td>
</tr>
<tr>
<td>B-27</td>
<td>Experimental Data of Cu-Cd-NaDMS System</td>
</tr>
<tr>
<td>B-28</td>
<td>Experimental Data of Cu-Pb-NaDMS System</td>
</tr>
<tr>
<td>B-29</td>
<td>Experimental Data of Cd-Pb-NaDMS System</td>
</tr>
</tbody>
</table>
NOMENCLATURE

\( a_i \)  
activity of species \( i \) (moles/l.)

\( A(i) \)  
equilibrium concentration of ions in solution (moles/l.)

\( C_i \)  
Concentration of solute \( i \) in solution (moles/l.)

\( d \)  
diameter of individual bubbles (cm)

\( D \)  
distribution factor of metal ion

\( e_0 \)  
electronic charge = \( 1.602 \times 10^{-19} \) coul.

\( = 4.8029 \times 10^{-10} \) esu,

\( G \)  
volumetric gas rate (cm\(^3\)/min)

\( G(x_i) \)  
equations of the mathematical model

\( k \)  
Boltzmann constant = \( 1.3805 \times 10^{-16} \) erg/molecule.

\( k_1 \)  
equilibrium constant of chemical reaction in solution

\( K \)  
the Debye-Hückel reciprocal length

\( = (8\pi e_0^2 z_i^2 n_i^0 / \epsilon kT)^{1/2} \)

\( l \)  
length of the optical path

\( n \)  
number of capillaries in a bubbler

\( N \)  
bubble emission frequency (bubbles/minute/capillary)

\( n_i \)  
concentration of species \( i \) (moles/l.)

\( n_i^0 \)  
concentration of species \( i \) in bulk liquid

\( P \)  
volume of solution (liter)

\( Q \)  
volumetric rate of foam overflow on a gas-free

(collapsed) basis

\( S \)  
surface generation rate (cm\(^2\)/min)

\( T \)  
absolute temperature (\( ^\circ \)K)

\( v \)  
the Boltzmann correction for ions at potential

\( \varphi = \exp(-e_0 \varphi / kT) \)
\( v_0 \)  
\( v \) at \( z = x_0 \)

uncertainty in the independent variable

\( x \)
distance from interface into the interstitial liquid (cm.)

\( x_i \)
independent variable

\( x_0 \)
distance of closest approach (cm.)

\( y \)
the difference between the optical density found and calculated for no reaction

\( z_i \)
charge of species \( i \)

**Subscripts**

b  
bulk liquid

d  
diffuse layer

f  
foamate

s  
surfactant

**Greek Letters**

\( \Gamma_i \)  
surface excess of species \( i \) (moles/cm\(^2\))

\( \sigma_{AB} \)  
selective separation coefficient of element A to B

\( \epsilon \)  
molar extinction coefficient (cm\(^2\)/mole), or dielectric constant of water = 81 at 18 °C (69)

\( \rho \)  
charge density at distance \( z \) from interface (esu/cm\(^3\))

\( \phi \)  
electrical potential at distance \( z \) from interface (erg/coul.)

\( \sigma \)  
surface charge density (esu/cm\(^2\))
Abbreviations

M^{++} free form of metal ions in solution
DES^- anionic surfactant ion
E experimental result
T theoretical prediction
OD optical density
TM transmittance

Unit

esu electrostatic unit (g m^3 cm^3/2 sec^{-1}) = 3.336 x 10^{-10} coul.
erg g cm^2 sec^{-2} = dyne-cm
CHAPTER 1

INTRODUCTION

The use of foaming as a separation technique is well documented. General references concerning the technique have been published by Sebba (1), Lemlich (2) and Rubin et al (3). The separation of ions from aqueous solution using foam fractionation is based on the fact that surface-active materials accumulate at an air-liquid interface. Finely dispersed air bubbles introduced into such a solution will effectively remove the surface-active substance from the solution into the foam. Surface inactive ions, such as metal ions used in this study, can be removed using an ionic surfactant of opposite charge. The actual mechanism of attachment of the surface inactive ion to the surfactant ion depends on the system. Experimental evidence from metal ion removal studies reported by Walling et al (4), Rubin et al (5,6,7), and Dick and Talbot (8) indicate the mechanism to be one of electrical attraction. That is, the layer of anionic surfactant adsorbed at the air-liquid interface has associated with it a diffuse layer of ions of opposite charge in order to maintain electrical neutrality. The fact that counterions associated with the anion layer could consist of a mixture of all the cation species in solution complicates the matter. Preferential attraction of cations to the layer depends on concentration, physical size, and electrical charge.
Application of foaming to the extraction of non-surface-active species requires a method of predicting the specificity of the foam surface for individual ions in the solution. This specificity may arise from charge interactions between the adsorbed surfactant layer and a diffuse-double-layer of counterions or from bonded interactions of a complex type between surfactant and solution species. Competitive coadsorption of ions of opposite charge to the surfactant based on the diffuse-double-layer theory of Gouy and Chapman and allowing for the difference in the distance of closest approach of ions of different size has been reported by Jorne and Rubin (9). The theory enables one to predict the distribution factor of each species between a solution of mixed electrolytes and a surface layer, and therefore to calculate the selective separation coefficient between two elements. They reported that the diffuse-double-layer theory agreed well with experimental results for solutions containing Sr$^{++}$ or UO$_2$$^{++}$ in the presence of monobutyl biphenyl sodium sulfonate as the collector.

This study consists of the application of the above principles reported by Jorne and Rubin combined with an equilibrium model of the solution to predict the surface specificity of copper, lead and cadmium in dilute aqueous solution using sodium dodecylbenzene sulfonate as collector. The work represents a variety of bulk solution conditions, different metal ion species, and mixtures of metal ions.
CHAPTER 2

LITERATURE SURVEY

It is difficult to separate soluble materials from solutions when their concentrations are relatively small as most of the separation techniques become inefficient. A number of separation methods which appear to be useful for separating any material particularly when its bulk concentration is low, are called adsorptive bubble separation techniques and are discussed by Lemlich (2). These methods are based on the fact that the surface-active materials are preferentially concentrated at air-liquid interface and certain other components that are not surface active are associated with these materials so that they can be enriched in the foam phase. The classification of these techniques based on the particle size of the material and the mechanism by which it is separated are listed in Table 1. If a species is naturally surface active, it can be separated simply by providing enough air-liquid interface and by collecting the resultant foam. Such a separation is called "foam fractionation" for the separation of surface-active molecules, "foam flotation" for that of hydrophobic colloids, "froth flotation" for that of sieve-size particles of crushed naturally hydrophobic minerals such as sulphur and graphite. If the species to be separated is not naturally surface active, a surface active agent that would associate with the species in some manner is added and
Table 1. Various Adsorptive Bubble Separation Methods Classified on the Basis of Mechanism of Separation and Size of the Material Separated (10).

<table>
<thead>
<tr>
<th>MECHANISM</th>
<th>MOLECULAR</th>
<th>MICROSCOPIC</th>
<th>MACROSCOPIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural surface activity</td>
<td>FOAM FRACTIONATION</td>
<td>FOAM FLOTATION</td>
<td>FROTH FLOTATION</td>
</tr>
<tr>
<td></td>
<td>ex: detergent from aqueous solutions</td>
<td>ex: micro-organisms, proteins, dyes</td>
<td>of non-polar minerals ex: sulfur</td>
</tr>
<tr>
<td>In association with surface active species</td>
<td>ION FLOTATION</td>
<td>MICRO FLOTATION</td>
<td>FROTH FLOTATION</td>
</tr>
<tr>
<td></td>
<td>MOLECULAR FLOTATION</td>
<td>ex: particulates in waste, micro-organisms</td>
<td>ex: minerals such as silica</td>
</tr>
<tr>
<td></td>
<td>ex: Sr⁺⁺, Cu⁺⁺, Cd⁺⁺, Pb⁺⁺, Hg⁺⁺, Cyanides, Phosphates</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
then foaming is conducted. This process is called "ion flotation" for the separation of submicro species. The separation of particulates of colloid size by this technique is called "micro flotation" and of sieve-size particles of naturally hydrophilic minerals such as silica and alumina is called "froth flotation".

In the early stage of exploring the foam separation technique, all the experiments reported deal with the separation or purification of naturally surface active substances such as proteins, enzymes, various fatty acids, salts, and detergents. In recent years, the foam separation method has found increasing application in water treatment and the recovery of valuable substances. The former is mainly in the removal of radio-active materials (11,12,13) and organic substances (14) from waste waters; an example of the latter is the uranium and vanadium extraction from carbonate solution (15). A comprehensive review of the materials separated by foam separation techniques was summarized by Rubin and Gaden (3) in 1962 and by Somasundaran (10) in 1972.

Copper, cadmium and lead ions were chosen for this study, and it is appropriate to review all the works that have been done on these elements. Rubin et al (6,7) studied the effect of pH on the separation of copper from dilute aqueous solution using stearylamine or sodium lauryl sulfate (NaLS). The mechanism of ion flotation they proposed was that attraction
between the cation and anionic surfactant must be due to specific ion-pair interaction or complex formation, that is the charge on LS⁻ is neutralized so that electroneutrality in the foam is maintained. Dick and Talbot (8) also worked on the same system but more factors were studied. The optimum conditions of removal were found to be as follows: pH range between 3.8 and 5.7 and surfactant concentration of 0.5 gm/l.

It was also found in this work that as the ratio of molar concentration of sodium ion to cupric ion was increased, the distribution factor of copper decreased. A similar decrease was noted for the hydronium ion. This behavior supports the ion attraction mechanism proposed by Rubin et al (6,7) for the removal of cupric ion from solution using NaLS. The work was extended to study the effect of the addition of an auxiliary ligand and the results indicated that under certain conditions the separation efficiency was improved.

Rubin and Lapp (16) reported the study on the removal of lead from Pb(II)-NaLS system. An attempt was made to relate the mechanism of the process to the hydrolytic behavior of the metal and the solution pH as well as the ionic strength and collector concentration. The results presented in the per cent removal demonstrate the applicability of hydrolysis data to estimating maximum removals by foam separation. It also mentioned that increasing the ionic strength results in a reduction in lead(II) removal at all pH values. This reduction is attributed to a reduction in the activity of the lead species and increased competition between cations for the collector.
There are no reports available in the literature on the separation of cadmium ion, and this is the first work on this element.

Grieves et al. have reported a number of extensive studies on the foam separation process in an effort to establish the effects on the extent of separation of each of the following independent variables: surfactant concentration, temperature, pH and ionic strength etc. The systems they have studied include the separation of orthophosphate (17), phenol (18,19), chromium(IV) (20,21), cyanide complexed by iron (22), colloidal ferric oxide (23), bacteria (24,25), clay (26) and active carbon (27). All the works have been summarized and discussed in the book (2).

Robertson (28) investigated the foam fractionation of rare-earth elements by extraction of their EDTA chelates with a cationic surfactant, and the foam fractionation of an anionic surfactant. The results suggested that appreciable separation improvement was achieved by blocking foam with stacks of screen or plastic bead packings. The published research on ion flotation done by Sebba (1,29,30,31) and others (32,33) has concentrated largely on extraction of individual ion. Little work has been done to investigate interionic separation.

Walling et al. (4) reported a study of the relative adsorption of calcium and sodium ion by N-palmitoyl methyl taurine. The result indicated a strong preferential adsorption of calcium ion by the anionic surface layer. The results among
the univalent ions suggest an order of increasing adsorption
\[ H^+ < Na^+ < K^+ < NH_4^+ \]. A selective extraction of copper from
solution containing zinc by using increased pH has been inves-
tigated by Jacobelli-Turi et al (2a). This is based on the
difference in values of stability constant of the two metallic
complexes. In this case, at pH values above 10.5 the copper
surfactant complex is stable while the zinc complex is less
stable.

From the above experimental evidence of metal ion removal
it can be concluded that the specificity depends on charge
interaction and complex formation that occur at the gas-liquid
interface between the adsorbed surfactant layer and a diffuse-
double-layer of counterions in solution. The adsorption model
was first given independently by Gouy (34) and Chapman (35).
The basic assumptions are that the charged surface is impene-
trable, that the charge is uniformly spread over it, and that
the counterions behave as point charges, being able to approach
right up to the plane of the charges. On the basis of these
assumptions, they solved the Boltzmann equation for the distrib-
ution of cations and anions in terms of a potential near the
charged surface relative to the bulk of the solution.

In the above theory, it is assumed that the ions are
point charges and therefore no selectivity exists between
ions of the same valency. However, a recent paper (4) indicated
that there is selectivity between different ions of the same
valency. It was Jorne and Rubin (9) who first modified the
theory that enables one to predict the distribution factor of each species between a solution of mixed electrolytes and a surface layer. The basis of this modification is that the distances of closest approach of the hydrated ions to the air-liquid interface are different. They reported that the diffuse-double-layer theory agreed well with experimental results for solutions containing Sr$^{++}$ or UO$_2^{++}$ in the presence of monobutyl biphenyl sodium sulfonate as the collector.

Various modes of the foam separation column have been used in research and are summarized by Lemlich (36) and Rubin et al (3). They include foam fractionation in the simple mode with batchwise and continuous flow operation, and in the higher modes with enriching, stripping and combined enriching and stripping. Since the goal of this work was to study the separation mechanism of ions at the air-liquid interface, a reliable one theoretical stage foam fractionating column was chosen. Operating conditions of the column must fulfill the requirements for a theoretical stage as discussed by Lemlich (2b); they are, the liquid pool is well mixed, sparger submergence is over 30 cm, and there is no coalescence in the rising foam. Usually, such coalescence would release adsorbed solute which would run back down through the rising foam as internal reflux, thus enriching the foam overflow beyond that of a single stage of separation. Coalescence of bubbles in the liquid just before they enter the foam can also make for a richer foam.

Foam fractionation of copper, lead and cadmium ions was investigated in this study using sodium dodecylbenzene sulfonate (NaDES) as the collector. For the systems containing one of above elements, distribution factor of that element was measured as function of the
acidity of solution or the concentration of the element. For the systems containing two of above three elements, selective separation coefficient between the two elements was measured. All the experimental results were predicted by the modified diffuse-double-layer theory. Since the effect of ionic interactions is essential to the efficiency of extraction, the chemistry of the solution foamed was examined, that is, the equilibrium composition of species were determined by considering all the equilibrium reactions occurring in the solution.
CHAPTER 3

THEORETICAL BACKGROUND

The original theory of Gouy-Chapman diffuse layer predicts that like-charged ions have like-distribution coefficients. But, this is not usually true, since the relative separability exists between like charged ions. Jorke and Rubin (9) was then the first to modify the theory allowing for the difference of closest approach of ions of different diameter. The physical size of the hydrated ions in a solution depends upon the conditions of the solution such as pH, ionic concentration, etc. Hence, a fundamental investigation on the chemistry of the solution foamed was thought to be essential to the study of foam fractionation. It is known that ionic size increases as solution pH is increased due to the formation of poly nuclear species. A bulk solution reaction model has been developed to estimate the equilibrium concentrations of variously charged ions at different bulk conditions.

3.1 Measurement of the Distribution Factor

The distribution factor of a surfactant or colligend adsorbed on the surface layer is a measure of the degree of separation and is defined as the ratio of the surface excess to the bulk concentration of the species in question. It can be measured experimentally using a single, equilibrium stage foam fractionation column. The method consists of bubbling
prehumidified air through a large volume of solution containing the surfactant and colligend to be studied and collecting a relatively small volume of foam. Assuming no bubble coalescence in the foam and that the interstitial liquid is identical to that of the bulk, a mass balance carried out on the collapsed foam produces the following relationship:

\[ Q \cdot C_f = S \sqrt[3]{\frac{\pi}{\xi}} + Q \cdot C_b \]  

(3.1)

where \( Q \) is the volumetric rate of foam overflow on a gas-free (collapsed) basis, \( S \) is the surface overflow in the foam, \( C_f \) is the concentration of the collapsed foam, and \( C_b \) is the bulk liquid composition. If the air bubble is designed such that the bubbles are spherical and uniform, the surface rate generated from a bubbler of \( n \) capillaries can be estimated by:

\[ S = \pi \frac{\pi}{\xi} n \cdot d^2 \]  

(3.2)

where \( d \) is the bubble diameter, \( \xi \) is the bubble emission frequency and \( \pi d^2 \) is the surface of a sphere. Since the volume of a sphere is \( \frac{4}{3} \pi d^3 \) and the gas rate \( G \) is known, the bubble diameter can be calculated from:

\[ d = \left( \frac{6G}{\pi n^2 \pi} \right)^{1/3} \]  

(3.3)
Rearranging equation (3.1) yields equation (3.4)

\[ \Gamma = \frac{Q (C_x - C_b)}{S} \]  

(3.4)

Thus, from measurements of \( Q \), \( N \), \( G \), \( C_x \) and \( C_b \), \( \Gamma \) can be found. The distribution factor, indicating the possible extent or degree of separation, of the solute is then determined by the relation

\[ D = \frac{\Gamma}{C_b} \]  

(3.5)

A selective separation coefficient of element A to element B is defined as the ratio of their individual distribution factors:

\[ \alpha_{AB} = \frac{(\Gamma / C_b)_A}{(\Gamma / C_b)_B} \]  

(3.6)

3.2 Estimation of Bulk Liquid Ionic Composition

In this study, an attempt has been made to estimate the concentration of all ionic species in the bulk solution by postulating a set of equilibrium reactions and calculating the equilibrium composition. The metal ions, copper, cadmium and lead, used in this study form poly hydroxy complexes and in
the case of lead and copper, polynuclear complexes in basic solution (37). In order to keep the system as simple as possible only acidic solutions with pH < 4 were considered. In this region the equilibrium reactions present in solution were assumed to be:

\[ M^{++} + H_2O \rightleftharpoons MOH^+ + H^+ \]  \hspace{1cm} (a)

\[ M^{++} + 2DBS^- \rightleftharpoons M(DBS)_2 \]  \hspace{1cm} (b)

\[ HDBS \rightleftharpoons H^+ + DBS^- \]  \hspace{1cm} (c)

\[ M^{++} + NO_3^- \rightleftharpoons MNO_3^+ \]  \hspace{1cm} (d)

The equilibrium expressions for the above reactions, including their respective equilibrium constant, \( k_a \), \( k_b \), \( k_c \), and \( k_d \), plus the following material balances constitutes the model assumed in this study.

\[ [M^{++}] + [MOH^+] + [M(DBS)_2] + [MNO_3^+] = C_{M^{++}} \] \hspace{1cm} (e)

\[ [DBS^-] + [2M(DBS)_2] + [HDBS] = C_{DBS^-} \] \hspace{1cm} (f)

\[ [NO_3^-] + [MNO_3^+] = C_{NO_3^-} \] \hspace{1cm} (g)

\( C_{M^{++}}, C_{DBS^-} \) and \( C_{NO_3^-} \) are the total concentration of metal ions, surfactant, and nitrate added to the solution, respectively. Such a mathematical model can be solved on a digital
computer, using an iterative technique, to estimate equilibrium concentration of all the molecular species defined in the model. It is noted that for the systems containing two different metal ions, in addition to equations (a) to (g), four more equations are required for the mathematical model. This is shown in appendix A.1. The equilibrium constants $k_b$ and $k_c$ were not available in the literature and were determined experimentally by the author.

3.2.1 Determination of Equilibrium Constants

Studies of the absorption of visible and ultraviolet radiation have long been used to obtain information about equilibria in solution. Many species undergo electronic transition in the near-ultraviolet and visual regions of the spectrum, and the intensities of the corresponding absorption bands of a solution have been widely used as a measure of the concentration of the various species present. The quantity measured is the optical density which can be expressed as $OD = l \epsilon_s [s]$, where $l$ is the length of the optical path, and $\epsilon_s$ is the molar extinction coefficient of species $s$.

Determination of $k_c$ consider a monobasic acid reaction

$\text{EDBS} \rightleftharpoons \text{H}^+ + \text{DHB}^-$. When the two conjugate forms, EDHB and DHB$, coexist in solution, the observed molar extinction coefficient for the solute at any wavelength is equal to the sum of the products of mole fraction and molar extinction
coefficient of each form. This has provided a convenient means of determining the equilibrium constant of such reaction.

However, the molar extinction coefficients of pure conjugate forms are difficult to determine. A method proposed (38) for the calculation of the equilibrium constant does not require pure conjugate forms. A general equation was derived (see appendix A.2) as:

\[ a_n \epsilon_n (1/k_c) - a_n (\epsilon_p/k_c) - (\epsilon_r) = -\epsilon_n \quad (3.7) \]

where \( \epsilon_p \) is molar extinction coefficient of HDBS, \( \epsilon_r \) is that of DBS\(^{-}\), and \( \epsilon_n \) is that of a mixture at hydrogen ion activity \( a_n \) and containing solute concentration of [HDBS] \( n \) and [DBS\(^{-}\)] \( n \). This is a linear equation in four terms and three unknowns (the latter in parentheses), since \( \epsilon_n \) and \( a_n \) are measurable quantities. Solution for the unknown \( k_c \) requires three simultaneous equations which may be solved with determinants.

\[
k_c = \frac{\begin{vmatrix}
a_1 \epsilon_1 & a_1 & 1 \\
a_2 \epsilon_2 & a_2 & 1 \\
a_3 \epsilon_3 & a_3 & 1 \\
\end{vmatrix}}{\begin{vmatrix}
a_1 & \epsilon_1 & 1 \\
a_2 & \epsilon_2 & 1 \\
a_3 & \epsilon_3 & 1 \\
\end{vmatrix}} \quad (3.8)
\]
Optical density, OD, is the instrumentally measured quantity. If the light path and total concentration of absorbing solute are the same in each measurement, then \([s]\) and \(I\) will cancel out, and OD may then be substituted for \(\varepsilon\) in equation (3.8). This means that the optical densities were measured at a particular wavelength for three solutions with different hydrogen ion concentration and that \(k_c\) can be calculated from equation (3.8).

Determination of \(k_b\)  Equilibrium constant \(k_b\) was determined by using a spectrophotometric method which combines the method of continuous variation (39, 40) with logarithmic analysis similar to that used by Bent et al (41) and Kingery et al (42). The method can be used to demonstrate the existence of metal-DBS complex in a solution and to determine its equilibrium constant.

For the application of the method of continuous variation, consider an equilibrium reaction such as

\[
M_1 + n \text{ DBS} \rightleftharpoons M (\text{ DBS})_n \quad (\Delta)
\]

In general, a series of equimolar mixtures prepared by adding \(p\) liters of DBS to \((1-p)\) liters of \(M\) will have varying optical densities. If the difference between the value of optical density found and the value calculated for no reaction, is plotted against \(p\), a maximum will be obtained. The complex number \(n\) can be calculated using the relationship \(n = p / (1-p)\). (see appendix A.3).
Also in the above equilibrium reaction (h), the mass action expression \( k_b = \frac{[M(DBS)_n]}{[M][DBS]^n} \) can be converted to the logarithmic form:

\[
\log \frac{[M(DBS)_n]}{[DBS]^n} = \log k_b + \log [M] \quad (3.9)
\]

It is seen that a plot of \( \log \frac{[M(DBS)_n]}{[DBS]^n} \) against \( \log [M] \) should yield a straight line with a slope of one and an intercept equal to \( \log k_b \). This method was applied to solutions containing only uncomplexed metal ion.

Once all the equilibrium constants are known, the equilibrium model of the system can be simulated using the modified Reguli-falsi iterative method (45, 75, 76).

3.2.2 Simulation of the Equilibrium Model

Assuming the identities \( A(1) = [M^{2+}] \), \( A(2) = [MOH^+] \), \( A(3) = [M(DBS)_2] \), \( A(4) = [DBS^-] \), \( A(5) = [HDBS] \), \( A(6) = [NO_3^-] \) and \( A(7) = [MNO_3^+] \), the equilibrium expressions for the reactions (a) to (d) plus the material balance (equations (e) to (g)) can be rewritten as:
\[
\begin{align*}
\frac{[H^+]}{A(2)} &= 1.0 \quad (3.10) \\
\frac{A(3)}{A(1) A(4)^2 k_b} &= 1.0 \quad (3.11) \\
\frac{[H^+]}{A(4)} &= 1.0 \quad (3.12) \\
\frac{A(7)}{A(5) k_c} &= 1.0 \quad (3.13) \\
\frac{A(1) + A(2) + A(3) + A(7)}{C_{M^{+++}}} &= 1.0 \quad (3.14) \\
\frac{A(4) + 2A(3) + A(5)}{C_{DBS^-}} &= 1.0 \quad (3.15) \\
\frac{A(6) + A(7)}{C_{NO_3^-}} &= 1.0 \quad (3.16)
\end{align*}
\]

Assuming a function \( G(x_1) \) which is equal to any one of above equations and is defined to satisfy the condition of

\[
\lim_{x_1 \to 0} G(x_1) = 0 \quad (3.17)
\]

For example, the variable \( A(2) \) in equation (3.10) is equivalent to the independent variable \( X_1 \) in the above equation, and in the case of equation (3.11), it is \( A(3) \), etc. The mathematical solution of the model is then obtained when the conditions of \( G(x_1) \) equal to one are met simultaneously.
From the iterative process, the $r^{th}$ approximation is given by

$$x_{r+1} = \frac{x_{r}}{G(x_{r})}$$  \hspace{1cm} (3.18)

To prevent from the divergency of iteration, the following improvement is made.

$$x_{r+1}^{*} = \frac{1}{2} \left( x_{r+1} + x_{r} \right)$$  \hspace{1cm} (3.19)

Substituting equation (3.18) into (3.19), it becomes

$$x_{r+1}^{*} = \frac{1}{2} x_{r} + \frac{1}{2} \frac{x_{r}}{G(x_{r})}$$  \hspace{1cm} (3.20)

Based on this development, the mathematical model can be rewritten for simulation as:

$$\Delta(2)^{r+1} = \frac{1}{2} \Delta(2)^{r} \left( 1.0 + \frac{\Delta(1) k_a}{[H^+] \Delta(2)} \right)^{r}$$  \hspace{1cm} (3.21)

$$\Delta(3)^{r+1} = \frac{1}{2} \Delta(3)^{r} \left( 1.0 + \frac{\Delta(1) \Delta(4)^2 k_b}{\Delta(3)} \right)^{r}$$  \hspace{1cm} (3.22)

$$\Delta(4)^{r+1} = \frac{1}{2} \Delta(4)^{r} \left( 1.0 + \frac{\Delta(5) k_c}{\Delta(4) [H^+] \right)^{r}$$  \hspace{1cm} (3.23)
\[
A(7)^{r+1} = \frac{1}{2} A(7)^r \left( 1 + \frac{A(1) A(6) k_d}{A(7)} \right)^r 
\] (3.24)

\[
A(1)^{r+1} = \frac{1}{2} A(1)^r \left( 1 + \frac{C_{M^{\leftrightarrow}}}{A(1) + A(2) + A(3) + A(7)} \right)^r 
\] (3.25)

\[
A(5)^{r+1} = \frac{1}{2} A(5)^r \left( 1 + \frac{C_{DBS^{-}}}{A(4) + 2A(3) + A(5)} \right)^r 
\] (3.26)

and

\[
A(6)^{r+1} = \frac{1}{2} A(6)^r \left( 1 + \frac{C_{NO_2^-}}{A(6) + A(7)} \right)^r 
\] (3.27)

In summary, the simulation started with the reasonably initial guesses of variables, then followed by successive approximations until the process converged. The final values of the variables are the equilibrium concentration of species in the solution.

3.3 The Gouy-Chapman Diffuse Double Layer Model

A deeper level of understanding of the separation process is gained if the double-layer structure can be predicted on the basis of the properties of the bulk phase. The Gouy and Chapman treatment of the behavior of ions in the vicinity of the charged surface is that the ions are affected by the electrical force arising from the charge on the interface and by thermal jostling. The ionic distribution is known after the equilibrium between electric and thermal forces is attained.
The ions are scattered so much that it is imagined that only scattered particles existed in the interphase and none of the rigidly fixed charges of the simple double-layer model is left (44, 45, 46, 47, 48).

It is noted that the concept of surface excess is different from that of adsorption, though the surface excess may become nearly identical to the total amount adsorbed under certain limiting conditions (i.e., bulk concentration equal to zero). The surface excess of a particular species is the excess of that species present in the surface phase relative to the amount that would be present if the double layer were not there. The surface excess, therefore, represents the accumulation of the species in the entire interphase region.

Application of the diffuse-double-layer theory to foam separation process was first proposed by Jorne and Rubin (9). In the foaming process, if the air is bubbling in water containing surface active material, an excess of this material will generally be present on the air-liquid interface and an equivalent amount of ions of opposite charge will be distributed in the solution near the interface. The charge on the air-liquid interface is treated as a surface charge spread uniformly over the surface. The charge in solution is considered to be composed of an unequal distribution of point-like ions. The solvent influences the double layer only through its dielectric constant. According to the Gouy-Chapman treatment,
the distribution of the ions in the solution is governed by a Boltzmann relation. Positive ions are concentrated at places of negative potential and repelled at places of positive potential. The reverse occurs for negative ions.

Consider a solution of an anionic surfactant and several species of cations and anions. The surfactant adsorbs to the air-liquid interface forming a negatively charged interfacial layer. The ionic atmosphere near the charged interface consisting of an excess of ions of positive charge represents a falling-off, with distance from the interface, of the net charge density in a lamina parallel to the interface and at increasing distances out into the solution.

Gibbs conceived the idea of measuring adsorption in the interface by using the integral of the perturbation in concentration with distance. A schematic representation of these perturbation is shown in figure 1. The surface excess of ions of species 1 of valence \( z_1 \) is given as

\[
\Gamma_1 = \int_{\infty}^{-\infty} n_1(z) \, dz \\
= \int_{\infty}^{-\infty} (n_1^0(z) - n_1^0) \, dz \\
\text{(3.28)}
\]

where \( z_0 \) is the distance of closest approach of ions to the
Figure L. A Schematic Representation of the Variation of Interface Concentration With Distance. (after Brockris and Reddy (47)).
surface. Introducing the Boltzmann relation, equation (3.28) yields equation (3.29).

\[ \Gamma_1 = \int_{-\infty}^{\infty} n_{i_0} (v^{1_m} - 1) \, dx \quad (3.29) \]

where \( v = \exp(-e_0 \phi / kT) \), \( \phi \) is the outer potential difference between a distance \( x \) from the interface and the bulk of the solution (taken as \( \phi_x \to \infty = 0 \)), \( e_0 \) is the electronic charge, \( n_{i_0} \) is the bulk concentration of ions of species \( i \).

Consider a lamina parallel to the interface and at distance \( x \) from it (figure 2). The charge density \( \rho \) in this lamina can be expressed in two ways:

1. in terms of the Poisson equation for the \( x \) dimension in rectangular coordinates

\[ \rho = -\frac{\varepsilon}{4\pi} \frac{d^2\phi}{dx^2} \quad (3.30) \]

where \( \varepsilon \) is the dielectric constant of the medium and is taken to be that of bulk water, and

2. in terms of the Boltzmann equation
\[ \rho = \sum_i n_i z_i e_0 \]

\[ = \sum_i n_i^0 z_i e_0 \exp(-z_i e_0 \phi/kT) \quad (3.31) \]

where the factor \( z_i e_0 \phi/kT \) represents the ratio of the electrical and thermal energies of an ion at the distance \( x \) from the interface. From the two expressions (equations (3.30) and (3.31)) for the charge density, one obtains the Poisson-Boltzmann equation (47a)

\[ \frac{d^2 \phi}{dx^2} = \frac{-4\pi}{\epsilon} \sum_i n_i^0 z_i e_0 \exp(-z_i e_0 \phi/kT) \quad (3.32) \]

Solving for the solution of the nonlinear differential equation (equation (3.32)), a simple transformation can be used. Consider the steps

\[ \frac{1}{2} \frac{d}{dx} \left( \frac{d\phi}{dx} \right)^2 = \frac{1}{2} \frac{d}{dx} \left( \frac{d\phi}{dx} \right) \frac{d\phi}{dx} \]

\[ = \frac{dx}{dx} \frac{d\phi}{dx} \frac{d\phi}{dx} \frac{d\phi}{dx} \]

\[ = \frac{d^2 \phi}{dx^2} \quad (3.33) \]
Thus, the identity, equation (3.33), can be used in the equation (3.32) which can then be integrated (see appendix A.4) to give:

\[
\frac{d\phi}{dx} = \pm \left( \frac{8\pi k T}{\varepsilon} \right)^{\frac{1}{2}} \left[ \sum_{i} z_{i}^{0} \left( \frac{z_{i}^{0}}{\varepsilon} - 1 \right) \right]^{\frac{1}{2}} \tag{3.34}
\]

To decide which root is to be taken, one remembers that, at the positively charged interface, \(\phi > 0\), but \(d\phi/dx < 0\), while, at the negatively charged interface, \(\phi < 0\), and \(d\phi/dx > 0\). Hence, it is clear that only the positive root of equation (3.34) corresponds to the physical situation.

Equation (3.34) represents the field (or gradient of potential) at a distance \(x\) from the interface according to the diffuse-charge model of Gouy and Chapman, and spells out the relation between the electric field and the potential at any distance \(x\) from the interface.

Differentiating \(v\) with respect to \(x\), one obtains a relation

\[
\frac{dv}{dx} = \frac{-e_{0}}{k T} \frac{e_{0}}{e} \frac{\phi}{k T} \frac{d\phi}{dx}
\]

\[
= -\frac{e_{0}}{k T} \frac{\phi}{e} \frac{d\phi}{dx} \tag{3.35}
\]
By change of variables, equations (3.29); (3.34) and (3.35) reduce to equation (3.36).

\[
\left( \frac{\Gamma}{n} \right)_1 = -\left( \frac{kT \varepsilon}{8\pi e_0} \right)^\frac{1}{4} \int_v^1 \frac{(v_1^2 - 1) dv}{v_0 \left[ \sum \frac{z_i}{n_i} - 1 \right]^{\frac{3}{2}}}
\]

(3.36)

This is an equation to calculate the distribution factor \( (\Gamma/n)_1 \) of ions of species \( i \) in a multicomponent solution (9). The lower limit of the above integration, \( v_0 \), can be determined in the later development.

Instead of the field, it is preferable to have an expression for the total charge in the solution in terms of the potential. This diffuse charge is obtained as follows. According to Gauss' theorem assuming that no specific adsorption exists and there is no oriented dipole layer at the boundary or the potential due to such a layer is negligible at \( \pm \approx \),

\[
\alpha = -\int_{-\infty}^{0} \rho \, dx = \frac{\varepsilon}{4\pi} \int_{-\infty}^{0} \left( \frac{d\phi}{dx} \right) \, dx
\]

\[
= -\frac{\varepsilon}{4\pi} \left( \frac{d\phi}{dx} \right)_{x=0}
\]

(3.37)
where \( \sigma \) is the surface charge density at the surface expressed in (esu/cm\(^2\)).

Therefore from equation (3.34) and (3.37)

\[
\sigma = -\left( \frac{k \varepsilon T}{2 \pi} \right)^{\frac{1}{2}} \left[ \sum_i n_i^0 \left( v_i^0 - 1 \right) \right]^{\frac{1}{2}}
\]

where \( v_0 \) is the value of \( v \) when \( \varphi = \varphi_0 \) at distance \( z_0 \) from the interface, or at the outer Helmholtz plane. The negative sign in equation (3.38) is chosen for the case of negatively charged surface (anionic surfactant). The surface charge density can be calculated from knowing surface excess of the ionic surfactant, \( \Gamma_s \):

\[
\sigma = z_s e_0 \Gamma_s
\]

From equation (3.38) and (3.39), \( v_0 \) (or \( \varphi_0 \)) can be calculated by trial and error. Taking \( v_0 \) as the lower limit, equation (3.36) can be integrated to give the distribution factor of ions of species \( i \) in a solution. It is important to note that the summation over all the ionic species includes the cations, the anions, and the surfactant ions.

Assumptions that have been made in the development of the above theory are as follows: (1) the dielectrical constant
is constant over the diffuse double layer, (2) the ions are points of charge. The latter means that no selectivity exists between ions of the same valency. However, it was found experimentally that there is selectivity between different ions of the same valency (4, 49, 50). The modification which enables one to distinguish the selectivity was first done by Jorne and Rubin (9).

3.3.1 Modified Diffuse Model

The concept of difference in the distance of closest approach, \( r_0 \), was incorporated into the diffuse model, because, in general, cations that are strongly solvated have larger \( r_0 \) than those that are weakly solvated. Figure 3 presents a physical picture of the hypothetical interface in which a surfactant monolayer of charge \( z_S \) is formed at \( x = 0 \), a layer of small counterions with charge \( z_1 \) is formed no closer than \( r_0' \), and a layer of larger counterions with charge \( z_2 \) is formed no closer than \( r_0'' \). The diffuse layer can then be divided into two regions: \( r_0'' < x < \infty \), all ions are present; \( r_0' < x < r_0'' \), only smaller ions are present. Therefore, a correction term \( \Delta \Gamma_B \) in addition to the excess of the smaller ion between the limits \( r_0' < x < r_0'' \) is required.

For \( z=2 \) electrolyte

\[
\Delta \Gamma_B = \int_{r_0'}^{r_0''} \left[ \frac{z \sigma_0 \sigma}{kT} - 1 \right] dx \quad (3.40)
\]
Figure 3. Surface Adsorption Model for small ions of charge $z_1$ and large ions of charge $z_2$ to monolayer of surfactant of charge $z_s$ at $x = 0$ (28).
This integral can be evaluated analytically to give

\[
\Delta \Gamma_B = \left( \frac{k T e B}{2 \pi e_0^2} \right)^{1/2} \left[ (v_0')^{1/2} - (v_0'')^{1/2} \right]
\]  (3.41)

In order to evaluate \( \Delta \Gamma_B \), it is necessary to find that relation between \( \Phi_0' \) and \( \Phi_0'' \) (or equivalently \( v_0' \) and \( v_0'' \)). For \( z-z \) electrolyte, the total diffuse-charge density scattered in the solution under the interplay of thermal and electrical forces is obtained (see appendix A.5) as:

\[
\Phi_0 = \left( \frac{2 k T e B}{\pi} \right)^{1/2} \sinh \left( \frac{z e_0 \Phi}{2 k T} \right)
\]  (3.42)

Again, from equation (3.37) and (3.42), the result is

\[
\left( \frac{d\Phi}{dz} \right)_{\Phi_0} = -\left( \frac{2 k T}{z e_0} \right) K \sinh \left( \frac{z e_0 \Phi}{2 k T} \right)
\]  (3.43)

where \( K \) is the Debye-Hückel reciprocal length and \( K^2 = 8 \pi e_0^2 \\
z^2 n_0 \) \( \epsilon \) \( k T \). The physical meaning of \( K^{-1} \) is the effective
thickness of the diffuse double layer. By integration with the boundary conditions \( x = x_0^* \), \( \varphi = \varphi_0^* \); \( x = x_0^n \), \( \varphi = \varphi_0^n \); we get the desired relationship (see appendix A.6):

\[
\tanh\left( \frac{x \varepsilon_0 \varphi_0^*}{4 k T} \right) = \exp[\kappa (x_0^n - x_0^*)] \tanh\left( \frac{x \varepsilon_0 \varphi_0^n}{4 k T} \right)
\]

(3.44)

where \( x_0^* - x_0^n \) is the difference in closest approach to the surface.

The distribution factors of the two cationic species are:

\[
\left( \frac{\Gamma}{n} \right)_A = \left( \frac{k T \varepsilon_0}{8 \pi \varepsilon_0^2} \right)^{\frac{1}{2}} \int_{v_0^n}^{1} \frac{(v^A - 1) \, dv}{v \left[ \sum_i n_i^0 \left( \frac{z_i^A}{v} - 1 \right) \right]^{\frac{1}{2}}}
\]

(3.45)

\[
\left( \frac{\Gamma}{n} \right)_B = \left( \frac{k T \varepsilon_0}{8 \pi \varepsilon_0^2} \right)^{\frac{1}{2}} \int_{v_0^n}^{1} \frac{(v^B - 1) \, dv}{v \left[ \sum_i n_i^0 \left( \frac{z_i^B}{v} - 1 \right) \right]^{\frac{1}{2}}}
\]

\[+ 2 \left( \frac{1}{n_B} \right)^{\frac{1}{2}} \left[ \left( \frac{v_0^B}{v_0^n} \right)^{\frac{1}{2}} - \left( \frac{v_0^n}{v_0^B} \right)^{\frac{1}{2}} \right] \]

(3.46)

where \( A \) is the larger ion and \( B \) is the smaller ion.
In summary, the above discussion has outlined a method to predict the distribution factor of an ion in a dilute aqueous solution. The procedure is to estimate the equilibrium composition of all ions in the solution, calculate the surface potential, then integrate equations (3.45) or (3.46) to obtain the distribution factor of the ion.
CHAPTER 4

EXPERIMENTAL INVESTIGATION

This chapter consists of two parts; first, the description of apparatus and experimental procedure for foam fractionation, and second, the spectrophotometric analysis for the determination of equilibrium constants of a reaction. The instruments and materials used for the study are also listed.

4.1 Foam Fractionation

The distribution factor of a surfactant or colligend adsorbed on the surface layer can be measured experimentally using a single stage foam fractionation column. The method consists of bubbling prehumidified air through a large volume of solution containing the surfactant and colligend to be studied and collecting a relatively small volume of foam.

Experimental apparatus similar to that developed by Dick and Talbot (8) was used in this study to measure the distribution factor of the various metal ions. A schematic diagram of the equipment is shown in Figure 4.

Description of Apparatus For all runs, oil-free compressed air from cylinders was first reduced to 9 psig and then humidified using a gas wash bottle followed by a saturator
Figure 4. Schematic Diagram of the Experimental Apparatus.
made of a fritted sparger contained in a flask of distilled water. The flow rate of the humidified air was then adjusted with a needle valve, measured with a calibrated flowmeter. The downstream pressure of calibrated flowmeter was recorded using a manometer. The humidified air then passed to the bubbler in the foam column. Because a stroboscope was used to determine the bubble diameters, it was necessary to utilize a bubbler capable of producing bubbles of a uniform size. This requirement was met using a bubbler consisting of five glass capillary tubes 0.240 in. long and 0.007 in. i.d. imbedded in a teflon chamber.

The column was constructed of an inverted 3-liter separatory funnel with the stopcock portion removed and replaced by a foam delivery tube and the bubbler inserted into the bottom. The liquid pool depth was approximately 33 cm. above the bubbler, and the foam/liquid interface height was controlled by means of a 300-ml leveling bulb and adjusting screw. The calibrated air flow rate was controlled by keeping constant readings in both calibrated manometer and flowmeter.

On leaving the column, the foam was directed along a 15-cm long by 0.9-cm i.d. foam delivery tube to a weighed 1000-ml erlenmeyer flask. The foam delivery tube was adjusted so that it had a declination of about 10°. Drainage was therefore toward the flask. The overall foam height in the apparatus, including the vertical portion of the delivery tube, was about 6 cm.
Experimental Procedure

Four liters of feed solution were prepared for each run using deionized distilled water, which was prepared by passing the distilled water through a Barnstead mixed ion exchanger. After addition of the required quantities of chemicals, the pH was then adjusted to the desired value using HNO₃.

Prior to charging the column, the foam receiver was weighed to 0.1 mg. The air was turned on then the column was filled through the leveling bulb. The air flowrate was then adjusted to the exact value desired after the foam-liquid interface height had been set at the mark.

The air flowrate was kept constant during the run. Once steady state had been reached, the foam receiver was placed in position and the timer started. Bubble rate was measured by means of the stroboscope.

On completion of a run (approximately 15 min.), the foam receiver was removed, stoppered, weighed, and allowed to sit so that the foam broke naturally.

Since the solute concentration were so low, a density of 1.0 was assumed so that foam weight was equivalent to foam volume.

Analytical Technique

Surfactant concentration was determined using the methylene blue method (51). This tedious, but reliable, extraction method was used because it was found that the direct measurement of absorption of the solution at ultraviolet wavelength region (52) was interfered by the
presence of metal ions and the pH of solution.

Methylene blue is a cationic dye which, in the form of an inorganic salt such as the chloride or sulfate, does not extract from water into an organic liquid such as chloroform. But if anionic surfactant is present, a salt of much lower water solubility is formed with the surfactant anion, a salt which is readily extractable into organic solvents.

Absorption measurements were made at a wavelength of 652 nm with a Bausch & Lomb precision spectrophotometer. The intensity of blue color in the solvent gives a measure of the amount of anionic surfactant present, one molecule for each molecule of methylene blue. Its intense color makes for adequate sensitivity; 10 μg of surfactant is readily detected, corresponding to a 100 ml sample of 0.1 ppm concentration.

The concentration of heavy metals studied were determined using atomic absorption spectrophotometer, UNICAM SP 90. It was found that the presence of surfactant did not interfere with the absorption readings of the heavy metals. Operating conditions of the analysis are tabulated in table 2.

4.2 Equilibrium Constant Determination

Transmittance measurements were made with a Bausch & Lomb precision spectrophotometer equipped with a digital readout. The same cells were used for all measurements and oriented in the same direction. In all cases, measurements were made with
Table 2. Instrumental Parameters for the Analysis of Metal Ions (53).

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (m(\mu))</th>
<th>Slit Width (mm)</th>
<th>Fuel</th>
<th>Oxidant, Air (l/min)</th>
<th>Sensitivity (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>324.8</td>
<td>0.08</td>
<td>Propane</td>
<td>5.0</td>
<td>0.1 (450)</td>
</tr>
<tr>
<td>Cadmium</td>
<td>228.8</td>
<td>0.10</td>
<td>Propane</td>
<td>5.0</td>
<td>0.04 (400)</td>
</tr>
<tr>
<td>Lead</td>
<td>217.0</td>
<td>0.30</td>
<td>Propane</td>
<td>5.0</td>
<td>0.3 (400)</td>
</tr>
</tbody>
</table>
reference to a blank solution containing all constituents save one, namely, the complex forming constituent in lowest concentration. All measurements were made at room temperature, 20 - 25°C.

**Determination of $k_b$ for Metal-DBS**

Solutions were prepared from mixing 100 ml, 1.0 gm/l NaDBS and 100 ml, 1 M perchloric acid. Different amounts of 0.1 M metal nitrate were added to each of 20 ml of above solution. In order to repress hydrolysis of the metal in the more concentrated solutions, it was necessary to work in 0.5 M perchloric acid, which brought the pH of solution down to 0.5. Perchloric acid is known to have little or no tendency to form complexes and transmits well in the ultraviolet as well as in the visible section of the spectrum.

All measurements were performed at wavelength 260 to 320 m$\mu$. It was found that 300 m$\mu$ was a peak wavelength for the optical density. Therefore, the plot determining the value of $k_b$ is based on the measurements at this wavelength.

**Determination of $k_c$ for HDBS**

The acid HDBS was prepared by passing NaDBS solution through an ion exchanger, REXYN 101(H) resin, to remove sodium ion. Ninety-eight percent removal was obtained. Three HDBS solutions with different pH adjusted by 0.1 N NaOH were examined with a precision spectrophotometer at wavelengths of 300, 320 and 340 m$\mu$. 
Deionized water was used in the reference cell for all the measurements.

4.3 Instruments and Materials

The instruments used in the study were as follows:

1) Precision spectrophotometer; Bausch & Lomb, Cat. No. 33-26-50.

2) Digital readout; AT-20, Bausch & Lomb, Cat. No. 33-26-58, for used with the precision spectrophotometer.

3) Digital pH/mv meter; model 801, Orion Research Inc.


5) Atomic absorption spectrophotometer; Unicam SP 90, Unicam Instruments Ltd.; England.

The material and reagent used were listed as follows:

1) Copper nitrate; 0.1000 ± 0.0005 moles per liter, Orion Research Inc.


4) HNO₃, NaOH; research and analytic grade.

5) Sodium dodecylbenzene sulfonate; K & K Laboratories, Inc., Lot No. 60959.

6) Perchloric acid; analytical grade, The British Drug Houses Ltd., Lot No. 44993.


It is noted that all the chemicals were used directly without further treatment.
CHAPTER 5

RESULTS

This chapter presents all the experimental foaming results and the theoretical predictions of distribution factor, both are plotted on the same figure for easy comparison. The detailed discussion of the results are presented in the next chapter. The complete tabulation of data is shown in appendix B. Computer programs for the pure component and mixture systems are presented separately in appendix C.

5.1 Results of Equilibrium Constants

The equilibrium constants of the model \( k_a \) and \( k_d \) have been reported and are summarized in table 3. The values of \( k_b \) and \( k_c \) were not available in the literature and were determined by the author using spectrophotometric analysis. The quantity measured was the optical density which can be calculated from the transmittance measurement of a solution at wavelengths near ultraviolet region. Experimental details have been given in section 4.2.

In order to verify the applicability of the spectrophotometric analysis for determining \( k_b \) of HDES, an acid with the known value of equilibrium constant was tested. Acetic acid was chosen and the measured data are presented in table 4.
Table 3. Equilibrium Constants $k_a$ and $k_d$ of Three Metal Ions.

<table>
<thead>
<tr>
<th>Element</th>
<th>$k_a$</th>
<th>$k_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>copper</td>
<td>$3.400 \times 10^{-7}$ (54)</td>
<td>$4.237 \times 10^{-17}$ (57)</td>
</tr>
<tr>
<td>cadmium</td>
<td>$4.565 \times 10^{-9}$ (55)</td>
<td>$7.413 \times 10^{-1}$ (58)</td>
</tr>
<tr>
<td>lead</td>
<td>$6.760 \times 10^{-7}$ (56)</td>
<td>$2.291$ (59)</td>
</tr>
</tbody>
</table>
Table 4. Equilibrium Constant of Acetic Acid Measured by Spectrophotometric Analysis.

<table>
<thead>
<tr>
<th>hydrogen ion activity, a</th>
<th>230 mμ</th>
<th>235 mμ</th>
<th>240 mμ (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.811 \times 10^{-4}</td>
<td>0.2233</td>
<td>0.1107</td>
<td>0.0395</td>
</tr>
<tr>
<td>9.638 \times 10^{-5}</td>
<td>0.2055</td>
<td>0.0980</td>
<td>0.0362</td>
</tr>
<tr>
<td>1.037 \times 10^{-5}</td>
<td>0.1409</td>
<td>0.0630</td>
<td>0.0232</td>
</tr>
</tbody>
</table>

| \( k_{HAC} \times 10^5 \) | 1.675 | 2.569 | 1.455 | 1.899 |
The average equilibrium constant is equal to \(1.899 \times 10^{-5}\), which is close to the known value of \(1.800 \times 10^{-5}\) \((60)\). It is therefore assumed that the spectrophotometric analysis method was suitable.

The results for the determination of \(k_b\) and \(k_c\) are presented in figures 5 to 7 and in table 5. In figures 5 to 7, slopes and intercepts of the lines were obtained by the least square correlation and the results are tabulated in table 6. The slope close to one demonstrates the existence of \(M(DBS)_n\) in the solution. The value of \(n\) in the complex species \(M(DBS)_n\) was determined by the method of continuous variation \((39)\). The result is shown in figure 8, from which it is known that the value of \(n\) is equal to 2.

5.2 Results of Foam Fractionation

Experiments for the systems containing one metal ion were carried out to study the effect of solution pH and bulk metal concentrations on the distribution factor of the ions. The systems containing two metal ions were used to study the selectivity between them and to find out what factor controlled the selectivity. The solutions used in the mixture studies were made up in such a way that pH and surfactant concentration was constant. In these solutions the metal concentrations were varied, however, the total concentration was kept constant.

Experiments were performed at room temperature, constant surfactant concentration and constant gas flow rate. A surfactant concentration of 0.50 gm/l was used because it was found to produce a stable foam and the most efficient separation. The
Figure 5: Spectrophotometric Analysis for the Determination of $k_b$ of Cu-NaDES System.
Figure 6. Spectrophotometric Analysis for the Determination of $k_b$ of Pb-NaDBS System.
Figure 7. Spectrophotometric Analysis for the Determination of $k_b$ of Cd-NaDBS System.
Table 5. Equilibrium Constant $k_c$ of HDBS.

<table>
<thead>
<tr>
<th>hydrogen ion activity, a</th>
<th>optical density 300 m$\mu$</th>
<th>optical density 320 m$\mu$</th>
<th>optical density 340 m$\mu$</th>
<th>$k_c \times 10^4$ (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.25 \times 10^{-2}$</td>
<td>0.4101</td>
<td>0.2007</td>
<td>0.1124</td>
<td></td>
</tr>
<tr>
<td>$1.514 \times 10^{-4}$</td>
<td>0.4225</td>
<td>0.2125</td>
<td>0.1175</td>
<td></td>
</tr>
<tr>
<td>$1.14 \times 10^{-6}$</td>
<td>0.4437</td>
<td>0.2219</td>
<td>0.1226</td>
<td></td>
</tr>
<tr>
<td>$k_c \times 10^4$</td>
<td>0.8848</td>
<td>1.9283</td>
<td>1.5068</td>
<td>1.4400</td>
</tr>
</tbody>
</table>
Table 6. Slopes and Intercepts of Figures 5 to 7 and the Results of $k_b$.

<table>
<thead>
<tr>
<th>system</th>
<th>slope</th>
<th>intercept $(\log k_b)$</th>
<th>$k_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-NaDBS</td>
<td>1.059</td>
<td>-1.2412</td>
<td>$5.739 \times 10^{-2}$</td>
</tr>
<tr>
<td>Cd-NaDBS</td>
<td>1.203</td>
<td>-1.1475</td>
<td>$7.121 \times 10^{-2}$</td>
</tr>
<tr>
<td>Pb-NaDBS</td>
<td>1.209</td>
<td>-0.5640</td>
<td>$2.729 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
Figure 8. Method of Continuous Variation for the Determination of the Value of n in Cd(DBS)ₙ.
enrichment ratio, which is defined as the concentration ratio of
the foamate to the bulk of the ion depends upon gas flow rate and
bubble size. However, it has been shown (50) that, for conditions
of stable foams and constant bulk concentration during a run, the
distribution factor of ions is independent of gas flow rate and bubble
size. Thus, it is better to use the distribution factor rather than
enrichment ratio for correlation of experimental results.

All the theoretical predictions were calculated using the same
conditions at which the experiments were performed. The procedure
of calculation started from an estimation of the equilibrium composition
of the ionic species derived from the bulk solution reaction model.
Next, the surface potential of the ions at their distance of closest
approach was calculated followed by the calculation of their distrib-
ution factor using equation (3.45). The surface excess of NaDBS
used in all the calculations is equal to \(3.10 \times 10^{-10}\) moles/cm\(^2\) (61).
The effective radii of hydrated ions are available in the literature (62)
(see appendix A.7) and are summarized in table 7.

A number of experimental runs were performed to obtain data
for comparison with the theoretical predictions. Figures 9 to 11
show the results of distribution factor as a function of solution pH
for the systems containing one metal ion. When bulk concentration is
a variable, the results are shown in figures 12 to 14. Figures 15
to 17 show the results of a set of experiments to measure and predict
the separability of the metal ions with respect to each other.
The experimental results have been shown in a form similar to the
familiar x-y diagram used in vapor-liquid equilibrium studies.
In figures 15 to 17 the ordinate is treated as the mole fraction of the smaller ion in foam (vapor) phase and the abscissa is that in bulk liquid phase. The solid lines in these figures are the theoretical predictions. Selective separation coefficients of both experimental results and theoretical predictions were also determined and are tabulated in tables B-18 to B-20. Comparison of the selective separation coefficients measured in the mixture systems and that calculated from the pure component systems at the same operating conditions is also presented in table 8.
Table 7. The Effective Radii of Hydrated Ions.

<table>
<thead>
<tr>
<th>element</th>
<th>effective radius ($\times 10^8$ cm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>4.7</td>
</tr>
<tr>
<td>Cu$^{++}$</td>
<td>6.8</td>
</tr>
<tr>
<td>Cd$^{++}$</td>
<td>6.4</td>
</tr>
<tr>
<td>Pb$^{++}$</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Figure 9. Effect of pH on the Distribution Factor of Copper,

$[\text{Cu}] = 10 \text{ ppm}, \ [\text{NaDES}] = 0.50 \text{ g/l}$. 
Figure 10. Effect of pH on the Distribution Factor of Calcium,

\([Cd] = 10 \text{ ppm}, \ [NaDBS] = 0.50 \text{ g/L}\).
Figure 11. Effect of pH on the Distribution Factor of Zinc.

$[\text{Pb}] = 10$ ppm, $[\text{NaDTS}] = 0.50$ mm/1.
Figure 12. Effect of Bulk Copper Concentration on Distribution Factor, pH = 4.70 ± 0.05, [NaDEB] = 0.50 M.
Figure 13. Effect of Bulk Cadmium Concentration on Distribution Factor, \( \text{pH} = 5.00 \pm 0.05 \), \([\text{NaDES}] = 0.50 \text{ cm} / \text{L} \).
Figure 14. Effect of Bulk Lead Concentration on Distribution Factor, \( pH = 5.15 \pm 0.07 \), \([\text{NaDES}] = 0.50 \text{ eq/l.}\)
Figure 15. Comparison of Predicted and Measured Selectivity Coefficients of Pb-Cu-NaD2E System, pH = 4.10 ± 0.05, [NaD2E] = 0.50 cm/1.
Figure 16. Comparison of Predicted and Measured Selectivity
Coefficients of Cd-Cu-NaDBS System, pH = 4.10 ± 0.05, [NaDBS] = 0.50 gm/l.
Figure 17. Comparison of Predicted and Measured Selectivity Coefficients of Pb-Cd-NaDES System, pH = 4.10 ± 0.05, [NaDES] = 0.50 gm/l.
Table 8. Comparison of Selectivity Coefficients Measured from Mixture Systems and That Calculated from Pure Component Systems.

<table>
<thead>
<tr>
<th>System</th>
<th>pH</th>
<th>( \alpha_{\text{measured}} )</th>
<th>( \frac{\Gamma_1}{x_1} / \frac{\Gamma_2}{x_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb/Cu</td>
<td>4.1</td>
<td>1.28</td>
<td>3.50</td>
</tr>
<tr>
<td>Pb/Cd</td>
<td>4.1</td>
<td>1.16</td>
<td>1.75</td>
</tr>
<tr>
<td>Cd/Cu</td>
<td>4.1</td>
<td>1.08</td>
<td>2.00</td>
</tr>
</tbody>
</table>
Figures 9 to 11 show the distribution factor of metal ions as a function of bulk solution pH. The concentration of metal ions was kept constant at 10 ppm; the concentration of surfactant was at 0.50 gm/l. It is observed that the theoretically predicted distribution factor is in good agreement with that measured experimentally for pH less than 4.0. At a pH greater than 4.0, deviation of the predicted and experimental results becomes unacceptable. This deviation is due to the fact that the equilibrium model assumed in this study does not account for the complex reactions occurring in this pH region.

Figures 12 to 14 show the results for the changes of distribution factor with respect to bulk metal concentrations at constant pH. In these figures, the theoretical curves were normalized by adjusting the distance of closest approach of metal ions. The data are shown in tables B-12 to B-17, in which the operating pH of each system is also indicated. It is noted that the pH of solution foamed is higher than the applicable pH range of equilibrium model and therefore the radius of hydrated ion is greater. The figures confirm the trend of the theoretical prediction. A similar observation
has been reported by Jorne and Rubin (9) for a different system.

From the results of systems containing one metal ion, it is observed that the magnitude of distribution factor is in the order of \( \text{DF}_{\text{Pb}^{++}} > \text{DF}_{\text{Cd}^{++}} > \text{DF}_{\text{Cu}^{++}} \). The sequence is just the reverse of the order of their effective radii of hydrated ions. It can then be understood that the smaller the hydrated ion, the more the preferential adsorption on the interface, if they have the same ionic charge. This conclusion is supported by equation (5.44) which reveals the fact that the smaller ion possess a higher surface potential. Experimental proof, therefore, was conducted to examine the effect of ionic size on the separation in a system containing two different metal ions.

The results of systems containing two metal ions are shown in figures 15 to 17. Experiments were performed at constant surfactant concentration at 0.50 g/l and pH at 4.10 ± 0.05. The predicted and measured selectivity coefficients agree very well. The experimental results are expressed in a form similar to the familiar x-y diagram used in vapor-liquid equilibrium studies. It is because the similarity of the two separation processes, foam fractionation and distillation, have long been well known. The analogous features of the two processes are worth summarizing (3). For example: (1) the liquid phase in distillation is analogous to the bulk liquid
which the foam is generated in foam fractionation, (2) the vapor phase in distillation is analogous to the interfacial area in foam fractionation, (3) the vapor plus entrained liquid in distillation is analogous to the foam overflow in foam fractionation, (4) the heat input in distillation is analogous to the gas flow in foam fractionation, (5) the pressure in distillation is analogous to the surfactant concentration in foam fractionation (11). In foam fractionation, the concentration of solute in foam (vapor) phase is expressed as the surface excess, and in liquid phase, that is the molar concentration.

If the vapor is richer in the more volatile substance, the curve, on the $x$-$y$ diagram, will be above the diagonal. The greater the distance between the equilibrium curve and the diagonal, the greater is the difference in liquid and vapor compositions and more readily is the separation made. In foam fractionation process, an ion having a smaller ionic size is richer in the foam.

The results (figures 15 to 17) show that cadmium ion is preferentially separable in Cd-Cu-NaDBS system and the same for lead ion in both Cu-Pb-NaDBS and Cd-Pb-NaDBS systems. The differences in values of selective separation coefficients of the three systems studied could be explained as the relative differences of the effective radii of hydrated ions. It was therefore proved that the ionic size determines the selectivity. Other evidence can be found in the work (4) which reported
that the order of increased selectivity is: \( H^+ < Na^+ < K^+ < NH_4^+ \),
which is the order of decreased hydration number.

Another important finding of the foaming results was
that the pH of foamate was higher than that of the bulk in the
high pH region. This was observed by measuring the pH of both
foamate and bulk solutions and the results are present graphi-
cally in figures 18 to 20 and in tables B-24 to B-29. This
result is not from the hydrolysis of anionic surfactant but
from the preferential removal of MOH\(^+\) ion in solution. For
no pH change in foamate, both DBS\(^-\) hydrolysis and preferential
removal of MOH\(^+\) must have equal weight or both are negligible,
that is no hydrolysis of surfactant and no preferential removal
of MOH\(^+\). But, the experimental evidence shows that it is not
the case. In view of the preferential adsorption of MOH\(^+\) ion,
the pH change will shift to the opposite direction to that
reported by Rubin and Jorne (63). The latter will be discussed
later. The distribution factor of MOH\(^+\) ion of six systems
studied is also calculated based on the pH and the ionic con-
centration of metals and surfactant in both bulk and foamate
solutions. The equilibrium model is applied on both solutions
to obtain the composition of each species. The distribution
factor of MOH\(^+\) can then be calculated and the results are	abulated in tables B-6 to B-17, in which the preferential
adsorption of MOH\(^+\) over hydrated metal ion can be observed. It
is noted that the pH change in the foamate is caused by the
Figure 18. pH Change of Cu-NaDES System: pHF, pH of Foamate; pHB, pH of Bulk.
Figure 19. pH Change of Pb-NaDBS System: pH_F, pH of Foamate; pH_B, pH of Bulk.
Figure 20. pH Change of Cd-NaDBS System: pHF, pH of Foamate; pHB, pH of Bulk.
surplus of hydroxyl ion, in the form of MOH\(^+\), carried over by the foam.

It was found in figures 18 to 20 that at pH below 3.0, no pH change was observed. This is because at conditions of low pH and dilute solution, soluble metal hydroxides are not formed or make up only an insignificant fraction of the total. In this region, it can also be imagined that hydrogen ions dominate the separation role, suppressing the charge density of anionic surfactant on the air-liquid interface and therefore the distribution factor of metal ions (see figures 9 to 11).

However at higher pH, it is well known that the metal ion does not exist in solution as a naked ion, but is surrounded by water dipoles which form the so-called hydration sheath. If the central ion is small, i.e., the charge density is high, these coordinated water molecules can exhibit acidic properties, owing to the charge attraction exerted by the central ion on the electrons of the associated water dipoles. For example, at least one of these waters of \(M(\text{H}_2\text{O})_{n}^{++}\) will tend to lose its proton to a base, i.e., behave as an acid (-Ia), or

\[
\frac{M(\text{H}_2\text{O})_{n}^{++}}{M \left( \frac{\text{H}_2\text{O}}{\text{O}^=} \right)_{n-1}^{+}} + \text{H}^+ \quad (1)
\]
Should there be enough base to accept the protons offered, this type of ionization can continue so that further water molecules ionize to a stage at which the metal hydroxide can be expected to be precipitated. However, before that happens, another effect comes into operation. This is the tendency for the polynuclear species to form through an oxygen bridge.

The degree of bridging is comparatively little and the ions are comparatively small, but with increasing pH they tend to grow until finally such a large molecule is produced that it can no longer remain in solution and precipitates out. It should be noted that the formation of a precipitate can often be considered the final stage in the formation of polynuclear complexes. It has been mentioned (64) that the tendency to form metal-metal bonds increases with increasing atomic number within a family. Ringbom (37a) and Sillén (65) discussed in detail on the behavior and character of polynuclear species.

It is not yet clear that whether, at any fixed pH before precipitation, a specific species of exact formulation exists or whether, given time, a range of different sizes is produced. But it is clear that the formation of polynuclear species, which is so complicated that was not considered in the equilibrium model, causes the deviation between the theoretical prediction and experimental results. In region pH below 4,
the hydrolytic reaction of metal ion is minimised and the agreement is considered reasonably well.

Hydrolytic reaction of the anionic surfactant ion on the air-liquid interface is also an important factor in the foam fractionation process. It has been pointed out by Cook and Talbot (66) that free acid was formed by the surface hydrolysis. They studied the surface hydrolysis of sodium lauryl sulfate (SLS) at different ionic strengths by pH measurements of foamed solutions and by the pH dependence of surface tension. The latter showed that an increase in pH resulted in an increase in surface tension explains that there is adequate surface hydrolysis to account for the observed collector properties of SLS solutions by hydrolytic adsorption. They found that foaming a solution of SLS produced a measurable increase in the pH of the substrate. This can only mean that the ratio of (HLS/LS⁻) at surface was appreciable as a result of which the continuous removal and reforming of the surface phase caused an accumulation of OH⁻ in the bulk solution. This can be accounted for the fact that the reaction is shifting toward the right (due to extraction of (HLS)₉) of the equilibrium

\[(LS⁻)₉ + H₂O ⇌ (HLS)₉ + (OH⁻)₉ \quad (j)\]

Here the subscripts s refers to the surface. Therefore, it
is suggested that, if the ratio \( \text{ELS} / \text{LS} \) were the same in the surface as in the solution, foam extraction would not affect the pH of the solution. In this report, it was found that the degree of surface hydrolysis was 1 to 4%.

Rubin and Jorne (63) also reported the surface hydrolysis effects on foam separation, in which the results indicated that the pH of the foamate was lower than that of the bulk liquid. The system they studied was foaming a solution of NaDBS alone. Hydrolysis implies, for anionic surfactants, the preferential adsorption of hydrogen ions over the counterions (sodium in this system) of the surfactant salt, with or without the formation of un-ionized acid.

Two runs were conducted foaming NaDBS solution alone with the apparatus used in this study. The results shown in table 9 indicate that the pH of foamate is lower than that of bulk solution. This is to support the result of Rubin and Jorne.

It should be noted, however, that the system studied in this work is much more complicated than those mentioned above. Furthermore, the apparatus designed and the systems studied were not for the purpose of investigating the effect of surface hydrolysis of surfactant. But the formation of EDBS on the air-liquid interface does reduce the surface charge density, and according to the diffuse double layer theory, the distribution factor of metal ions is decreased. The phenomenon is important and is worthwhile to be extensively investigated.
Table 9. pH Change of Foaming NaDBS Solution without Metal Ions.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>NaDBS (gm/l.)</th>
<th>pHB</th>
<th>pHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>1.75</td>
<td>7.18</td>
<td>6.95</td>
</tr>
<tr>
<td>44</td>
<td>0.50</td>
<td>6.82</td>
<td>6.63</td>
</tr>
</tbody>
</table>
6.1 Error Analysis

In general, the results of several independently measured quantities are combined to give the desired result of the experiments. Suppose a set of measurements is made and the uncertainty in each measurement may be expressed with the same odds. Therefore, the uncertainty in the calculated result can be estimated on the basis of the uncertainties in the primary measurements. Suppose the result \( R \) is a given function of the independent variables \( x_1, x_2, x_3, \ldots, x_n \). Thus,

\[
R = R(x_1, x_2, x_3, \ldots, x_n) \quad (6.1)
\]

Let \( w_R \) be the uncertainty in the result and \( w_1, w_2, \ldots, w_n \) be the uncertainties in the independent variables. If the uncertainties in the independent variables are all given with the same odds, then the uncertainty in the result having these odds is given (67, 68) as

\[
w_R = \left[ \left( \frac{\partial R}{\partial x_1} w_1 \right)^2 + \left( \frac{\partial R}{\partial x_2} w_2 \right)^2 + \ldots + \left( \frac{\partial R}{\partial x_n} w_n \right)^2 \right]^{\frac{1}{2}} \quad (6.2)
\]

Particular notice should be given to the fact that the uncer-
Uncertainty propagation in the result \( w_R \) depends on the square of the uncertainties in the independent variables \( w_n \). This means that if the uncertainty in one variable is significantly larger than the uncertainties in the other variables, then it is the largest uncertainty which predominates and the others may probably be neglected.

The desired result of the experiments in this study is the distribution factor which has the expression as

\[
DF = \frac{Q ( C_f - C_b )}{C_b S} = \frac{Q ( C_f / C_b - 1 )}{( 36 \pi N G^2 )^{1/3}} \quad (6.3)
\]

The independent variables are \( Q, C_f, C_b, N \) and \( G \). The partial derivatives of distribution factor with respect to each independent variable are as follows:

\[
\frac{\partial (DF)}{\partial Q} = \frac{( C_f / C_b - 1 )}{( 36 \pi N G^2 )^{1/3}} \quad (6.4)
\]

\[
\frac{\partial (DF)}{\partial C_f} = \frac{Q}{C_b ( 36 \pi N G^2 )^{1/3}} \quad (6.5)
\]

\[
\frac{\partial (DF)}{\partial C_b} = \frac{-Q C_f}{C_b^2 ( 36 \pi N G^2 )^{1/3}} \quad (6.6)
\]
\[
\frac{\partial (DF)}{\partial N} = \frac{-Q \left( \frac{C_f}{C_b} - 1 \right)}{3 \left( 36 \frac{n}{d} N^4 G^2 \right)^{1/3}} \quad (6.7)
\]

and

\[
\frac{\partial (DF)}{\partial G} = \frac{-2Q \left( \frac{C_f}{C_b} - 1 \right)}{3 \left( 36 \frac{n}{d} N G^5 \right)^{1/3}} \quad (6.8)
\]

The uncertainties in the independent variables are assumed to be 1 per cent for both concentration measurements, 5 per cent for gas flow rate, 3 per cent for the bubble emission frequency, and 0.1 per cent for the weight of foamate, or

\[
C_o = C_b \pm 1\%
\]

\[
C_f = C_f \pm 1\%
\]

\[
G = G \pm 5\%
\]

\[
N = N \pm 3\%
\]

and

\[
Q = Q \pm 0.1\%
\]

The uncertainty of the distribution factor calculated on these bases is then in the range of 3.5% to 4.8% and the data are presented in tables B-6 to B-11.
CHAPTER 7

CONCLUSIONS

In conclusion, the distribution factor of copper, cadmium and lead ions measured by foam fractionation can be predicted by the modified theory of Gouy-Chapman diffuse double layer for the system studied below a pH of 4. Comparison of the results, when bulk concentration was a variable, was also in a good qualitative agreement.

It may also conclude that the surfactant adsorbed on air-liquid interface partly is in the form of whole molecules rather than complete in ionic form, usually caused by hydrolytic adsorption.

The results of the systems containing two metal ions showed that the ionic size determines the selectivity, i.e., for the same ionic charge, smaller ion is preferentially separable.

Because of the effect of hydronium ions at low pH and the hydrolytic reaction at high pH, the optimum conditions for the foam fractionation of aqueous solutions of metal ions with NaDBS were found to be as follows: pH range between 3.0 and 5.7 for copper, 3.0 and 5.5 for cadmium, 3.0 and 4.5 for lead, and NaDBS concentration of 0.50 g/l.
CHAPTER 8

RECOMMENDATIONS FOR FUTURE WORK

From the fact that the ionic size determines the selectivity between ions, it is practical to separate a particular element from a multicomponent system. This could be achieved by controlling the conditions of the system, i.e., by ways of physical or chemical treatment, to enlarge the relative difference of the ionic size.

A further work is recommended to expand the applicability of the equilibrium model over a wide pH range by taking into account the complex reaction occurring in the high pH region. It is also recommended to explore the extent of surface hydrolysis of anionic surfactant ion either by measuring surface tension versus pH of solution or by designing a new apparatus to measure the composition of species right on the bubble surface.
REFERENCES


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(51) ASTM Standards on Water; Atmospheric Analysis, prepared by ASTM Committee D-2330-68, part 13, American Society for Testing and Materials, Philadelphia (1968); pp. 737.


Sillén, L.G., Quarterly Reviews (London), 13, 146 (1959).


**GLOSSARY**

adsorption = the adhesion of a thin film of molecules to a surface.

anionic surfactant = a surface-active material that ionizes in aqueous solution. The ion that bears a negative charge has a pronounced tendency to concentrate at the interface between two phases.

collector = surfactant or an agent used in ore flotation to promote attachment of solid particles to air bubbles.

counterion (colligend) = an ion with electrical charge opposite to the charge on the surface of an aggregate.

electric double layer = the excess of ions of one charge type present at an interface and the equivalent amount of ions of opposite charge present in one liquid phase, generally water. In the diffuse double layer, it is assumed that the charges in the liquid phase are distributed in accordance with a Boltzmann relation.

foam = bubbles of gas whose walls are thin liquid films.

foam fractionation = the separation of solutes by frothing.

selective adsorption = the tendency for one adsorbable species to concentrate at a surface or interface in preference to another.
surface-active agent = a substance that exhibits a marked tendency to adsorb at a surface or interface.
surface charge density = the excess of ions of one charge type per unit area of surface.
surface excess = the difference between the concentration of solute in the surface region and in the interior of the solution.
surface potential = the charge in the potential difference between a liquid and air arising from the presence of a surface film.
surface tension = a force with the dimensions of dynes/cm. that is a measure of the work required to increase the area of a surface by one square cm.
surfactant = a surface-active agent.
APPENDIX A

A.1 A Mathematical Model of the System Containing Two Metal Ions.

A.2 Derivation of Equation (3.7).

A.3 Method of Continuous Variation.

A.4 Derivation of Equation (3.34).

A.5 Derivation of Equation (3.42).

A.6 Derivation of Equation (3.44).

A.7 Determination of the Effective Radii of Hydrated Ions.
A Mathematical Model of the System Containing Two Metal Ions

Equilibrium reaction of the system containing copper and cadmium ions are presented here. The equilibrium constants, $\text{CONC}$, of the three binary systems studied are tabulated in table A-1. The following notations are made for the system:

$A(1) = [\text{Cu}^{++}]$, $A(2) = [\text{CuOH}^+]$, $A(3) = [\text{Cu(DBS)}_2]$, $A(4) = [\text{DBS}^-]$, $A(5) = [\text{HDBS}]$, $A(6) = [\text{NO}_3^-]$, $A(7) = [\text{CuNOS}^-]$, $A(8) = [\text{Cd}^{++}]$, $A(9) = [\text{CdOH}^+]$, $A(10) = [\text{Cd(DBS)}_2]$, and $A(11) = [\text{CdNO}_3^-]$. It is noted that the larger hydrated ion, copper in this case, is chosen as the numerator ion. The equilibrium model of the system can be obtained as follows:

$$\text{Cu}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$$

$$\frac{A(2) [\text{H}^+]}{A(1) \text{ CONC}(1)} = 1.0 \quad (A.1-1)$$

$$\text{Cd}^{++} + \text{H}_2\text{O} \rightleftharpoons \text{CdOH}^+ + \text{H}^+$$

$$\frac{A(9) [\text{H}^+]}{A(8) \text{ CONC}(2)} = 1.0 \quad (A.1-2)$$

$$\text{Cu}^{++} + 2\text{DBS}^- \rightleftharpoons \text{Cu(DBS)}_2$$
Table A-1. Equilibrium Constants of the Model of Mixture Systems.

<table>
<thead>
<tr>
<th>equilibrium constant</th>
<th>Cu / Cd</th>
<th>Cu / Pb</th>
<th>Cd / Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONC(1)</td>
<td>$3.400 \times 10^{-7}$</td>
<td>$3.400 \times 10^{-7}$</td>
<td>$4.565 \times 10^{-9}$</td>
</tr>
<tr>
<td>CONC(2)</td>
<td>$4.565 \times 10^{-9}$</td>
<td>$6.760 \times 10^{-7}$</td>
<td>$6.76 \times 10^{-7}$</td>
</tr>
<tr>
<td>CONC(5)</td>
<td>$5.390 \times 10^{-2}$</td>
<td>$5.390 \times 10^{-2}$</td>
<td>$6.645 \times 10^{-2}$</td>
</tr>
<tr>
<td>CONC(4)</td>
<td>$6.645 \times 10^{-2}$</td>
<td>$2.208 \times 10^{-1}$</td>
<td>$2.208 \times 10^{-1}$</td>
</tr>
<tr>
<td>CONC(5)</td>
<td>$4.237 \times 10^{-17}$</td>
<td>$4.237 \times 10^{-17}$</td>
<td>$7.413 \times 10^{-11}$</td>
</tr>
<tr>
<td>CONC(6)</td>
<td>$7.413 \times 10^{-1}$</td>
<td>$2.291$</td>
<td>$2.291$</td>
</tr>
<tr>
<td>CONC(7)</td>
<td>$1.136 \times 10^{-5}$</td>
<td>$1.136 \times 10^{-5}$</td>
<td>$1.136 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

CONC(8) = concentration of larger ion
CONC(9) = concentration of smaller ion
CONC(10) = surfactant concentration
CONC(11) = NO$_3^-$ concentration
\[
\frac{A(3)}{A(1) \cdot A(4)^2 \cdot \text{CONC}(5)} = 1.0 \quad (A.1-3)
\]

\[
\text{Cd}^{++} + 2\text{DBS} \rightleftharpoons \text{Cd(DBS)}_2
\]

\[
\frac{A(10)}{A(8) \cdot A(4)^2 \cdot \text{CONC}(4)} = 1.0 \quad (A.1-4)
\]

\[
\text{Cu}^{++} + \text{NO}_3^- \rightleftharpoons \text{CuNO}_3^+
\]

\[
\frac{A(7)}{A(1) \cdot A(6) \cdot \text{CONC}(5)} = 1.0 \quad (A.1-5)
\]

\[
\text{Cd}^{++} + \text{NO}_3^- \rightleftharpoons \text{CdNO}_3^+
\]

\[
\frac{A(11)}{A(8) \cdot A(6) \cdot \text{CONC}(6)} = 1.0 \quad (A.1-6)
\]

\[
\text{HDBS} \rightleftharpoons \text{H}^+ + \text{DBS}^-
\]

\[
\frac{A(4) [\text{H}^+]}{A(5) \cdot \text{CONC}(7)} = 1.0 \quad (A.1-7)
\]

\[
\text{Cu}^{++} + \text{CuOH}^+ + \text{Cu(DBS)}_2 + \text{CuNO}_3^+ = C_{\text{Cu}}
\]
\[
\frac{A(1) + A(2) + A(3) - A(7)}{\text{CONC}(8)} = 1.0 \quad (A.1-8)
\]

\[
\text{Cd}^{2+} + \text{CdOH}^+ + \text{Cd(DBS)}_2 + \text{CdNO}_3^- = C_{\text{Cd}}
\]

\[
\frac{A(8) + A(9) + A(10) + A(11)}{\text{CONC}(9)} = 1.0 \quad (A.1-9)
\]

\[
\text{DBS}^- + 2\text{Cu(DBS)}_2 + 2\text{Cd(DBS)}_2 + \text{HDBS} = C_{\text{DBS}^-}
\]

\[
\frac{A(4) + 2A(5) + 2A(10) + A(5)}{\text{CONC}(10)} = 1.0 \quad (A.1-10)
\]

\[
\text{NO}_3^- + \text{CuNO}_3^+ + \text{CdNO}_3^+ = C_{\text{NO}_3^-}
\]

\[
\frac{A(6) + A(7) + A(11)}{\text{CONC}(11)} = 1.0 \quad (A.1-11)
\]

Manipulating above equations, a set of equations for the use of the Regula-falsi iterative process is obtained as follows:

\[
A(2)^{r+1} = \frac{1}{2} A(2)^r \left[ 1.0 + A(1) \frac{\text{CONC}(1)}{A(2)[H^+]} \right]^r \quad (A.1-12)
\]
\[ a(9)^{+1} = \frac{1}{2} a(9)^{+2} \left[ 1.0 + a(8) \text{conc}(2)/a(9) \right]^{+2} \quad (A.1-13) \]

\[ a(5)^{+1} = \frac{1}{2} a(5)^{+2} \left[ 1.0 + a(1) a(4)^{2} \text{conc}(3)/a(5) \right]^{+2} \quad (A.1-14) \]

\[ a(10)^{+1} = \frac{1}{2} a(10)^{+2} \left[ 1.0 + a(8) a(4)^{2} \text{conc}(4)/a(10) \right]^{+2} \quad (A.1-15) \]

\[ a(7)^{+1} = \frac{1}{2} a(7)^{+2} \left[ 1.0 + a(1) a(6) \text{conc}(5)/a(7) \right]^{+2} \quad (A.1-16) \]

\[ a(11)^{+1} = \frac{1}{2} a(11)^{+2} \left[ 1.0 + a(8) a(6) \text{conc}(6)/a(11) \right]^{+2} \quad (A.1-17) \]

\[ a(4)^{+1} = \frac{1}{2} a(4)^{+2} \left[ 1.0 + a(5) \text{conc}(7)/a(4) \right]^{+2} \quad (A.1-18) \]

\[ a(1)^{+1} = \frac{1}{2} a(1)^{+2} \left[ 1.0 + \text{conc}(8)/(a(1)+a(2)+a(3)+a(7)) \right]^{+2} \quad (A.1-19) \]

\[ a(8)^{+1} = \frac{1}{2} a(8)^{+2} \left[ 1.0 + \text{conc}(9)/(a(8)+a(9)+a(10)+a(11)) \right]^{+2} \quad (A.1-20) \]

\[ a(5)^{+1} = \frac{1}{2} a(5)^{+2} \left[ 1.0 + \text{conc}(10)/(a(4)+2a(5)+2a(10)+a(5)) \right]^{+2} \quad (A.1-21) \]

and

\[ a(6)^{+1} = \frac{1}{2} a(6)^{+2} \left[ 1.0 + \text{conc}(11)/(a(6)+a(7)+a(11)) \right]^{+2} \quad (A.1-22) \]
APPENDIX A.2

Derivation of Equation (3.7)

Consider a monobasic acid reaction $HA \rightleftharpoons H^+ + A^-$, and the two conjugate forms, HA and $A^-$, coexist in the solution. According to the Beer's law, the optical density of the solution can be expressed as:

$$OD = l \varepsilon_n c_n$$  \hspace{1cm} (A.2-1)

where $\varepsilon_n$ is the extinction coefficient of the mixture, a characteristic intensive factor of the absorbing species, and $c_n$ is the sum of the concentrations of the light absorbing species and is equal to

$$c_n = c_{A^-} + c_{HA}$$  \hspace{1cm} (A.2-2)

And if, as seems generally to be the case, each substance absorbs independently of the presence of the other, then the optical density is equal to

$$OD = (\varepsilon_n c_{A^-} + \varepsilon_{HA} c_{HA}) l$$  \hspace{1cm} (A.2-3)

where $\varepsilon_n$ is the extinction coefficient of species $A^-$ and
\( \epsilon_b \) is that of species HA. From above three equations, it follows that

\[
\frac{c_{HA}}{c_{A^-}} = \frac{\epsilon_r - \epsilon_n}{\epsilon_n - \epsilon_p} \quad (A.2-4)
\]

By combination of equation (A.2-4) with the common expression of the reaction

\[
k_c = \frac{a_n c_{A^-}}{c_{HA}} \quad (A.2-5)
\]

the following general equation is then derived.

\[
a_n \epsilon_n \left( \frac{1}{k_c} \right) - a_n \left( \frac{\epsilon_b}{k_c} \right) - (\epsilon_r) = -\epsilon_n
\]

(3.7)
APPENDIX A.3

Method of Continuous Variation

The formation of complex ion can be represented by the equation

$$A + nB \rightleftharpoons AB_n$$  \hspace{1cm} (k)

in which $A$ is a metallic ion and $B$ is an anion. To determine $n$, solution of $A$ and $B$ of the same molar concentration, $M$, are mixed in varying proportions, and optical density of the resulting solutions is measured. Let the mixture be made by the addition of $p$ liter of $B$ to $(1-p)$ liter of $A$ ($p < 1$), with no appreciable volume change on mixing. Let $C_1$, $C_2$ and $C_3$ be the concentration of $A$, $B$ and $AB_n$, respectively. For the mixture the following equations apply

$$C_1 = M(1-p) - C_3$$  \hspace{1cm} (A.3-1)

$$C_2 = Mp - nC_3$$  \hspace{1cm} (A.3-2)

$$C_1C_2^n = KC_3$$  \hspace{1cm} (A.3-3)

The condition for a maximum in the curve of $C_3$ plotted against $p$ is that

$$\frac{dC_3}{dp} = 0$$  \hspace{1cm} (A.3-4)
Differentiating equations (A.3-1), (A.3-2) and (A.3-3) with respect to \( p \),

\[
\begin{align*}
\dot{c}_1 &= -M - c_3' \\
\dot{c}_2 &= M - n c_3' \\
\frac{c_2^n c_1'}{c_3} + \frac{c_1 n c_2^{n-1} c_2'}{c_3} &= k c_3'
\end{align*}
\]

and considering the equation (A.3-4), we obtain

\[
\begin{align*}
\dot{c}_1 &= -M \\
\dot{c}_2 &= M \\
\frac{c_2 c_1'}{c_1} + \frac{n c_1 c_2'}{c_2} &= 0
\end{align*}
\]

or

\[
\frac{-c_2 M}{n c_1 M} = 0
\]

Substituting the relation \( c_1 = \frac{c_2}{n} \) into equation (A.3-1) and combining with equation (A.3-2), we immediately deduce the equation (A.3-12).

\[
n = \frac{p}{1 - p}
\]
Derivation of Equation (3.34)

The identity

\[ \frac{d}{d\varphi} \left( \frac{d\varphi}{dx} \right)^2 = \frac{d^2\varphi}{dx^2} \]  

(3.35)

can be used in the differential equation (3.32) to give

\[ \frac{d}{d\varphi} \left( \frac{d\varphi}{dx} \right)^2 = -\frac{8\pi}{\varepsilon} \sum_{i} n_i^0 z_i e_0 \exp(-z_i e_0 \varphi/kT) \]  

(A.4-1)

which can be integrated to give

\[ \left( \frac{d\varphi}{dx} \right)^2 = -\frac{8\pi}{\varepsilon} \int \sum_{i} n_i^0 z_i e_0 \exp(-z_i e_0 \varphi/kT) \, d\varphi \]

\[ = \frac{8\pi kT}{(\varepsilon)} \sum_{i} n_i^0 \exp(-z_i e_0 \varphi/kT) + C \]  

(A.4-2)

The integration constant C can be evaluated by considering that, deep in the bulk of the solution, i.e., at \( x \to \infty \), not only is the volta potential zero, \( \varphi_{x \to \infty} = 0 \), but the field \( d\varphi / dx \) is also zero. Under these conditions,
\[ c = -\frac{8\pi kT}{\varepsilon} \sum_{i} n_{1}^{0} \]  

(A.4-3)

By introducing this value of the integration constant into equation (A.4-2), the result is

\[ \left( \frac{d\phi}{dx} \right)^{2} = \frac{8\pi kT}{\varepsilon} \sum_{i} n_{1}^{0} \left[ \exp(-z_{1}\phi / kT) - 1 \right] \]  

(A.4-4)

or

\[ \frac{d\phi}{dx} = \pm \frac{8\pi kT}{\varepsilon} \left( \sum_{i} n_{1}^{0} \left( \frac{z_{1}}{\varepsilon} \right) - 1 \right) \]  

(3.34)
APPENDIX A.5

Derivation of Equation (3.42)

Equation (3.38) shows that

\[ \alpha = - \left( \frac{kT \varepsilon}{2 \pi} \right)^\frac{1}{2} \left[ \sum n_i^0 \left( e^{-z_i \sigma / kT} - 1 \right) \right]^\frac{1}{2} \]

Consider a z-z electrolyte, and

\[ \alpha = - \left( \frac{kT \varepsilon}{2 \pi} \right)^\frac{1}{2} \left[ n_i^0 \left( e^{z_i \sigma / kT} - 1 + e^{-z_i \sigma / kT} - 1 \right) \right]^\frac{1}{2} \]

\[ = - \left( \frac{kT \varepsilon}{2 \pi} \right)^\frac{1}{2} \left[ n_i^0 \left( e^{z_i \sigma / kT} - 2e^{-z_i \sigma / 2kT} \right) \right] \left( e^{-z_i \sigma / 2kT} + e^{-z_i \sigma / kT} \right)^\frac{1}{2} \]

\[ = - \left( \frac{kT \varepsilon n_i^0}{2 \pi} \right)^\frac{1}{2} \left( e^{z_i \sigma / 2kT} - e^{-z_i \sigma / 2kT} \right) \quad (A.5-1) \]

Since

\[ e^x - e^{-x} = 2 \sinh x \]

equation (A.5-1) then becomes

\[ \alpha = - 2 \left( \frac{kT \varepsilon n_i^0}{2 \pi} \right)^\frac{1}{2} \sinh \left( \frac{z_i \sigma}{2kT} \right) \quad (A.5-2) \]

At \( x = \pi_0 \)

\[ \alpha = - \alpha = \left( \frac{2kT \varepsilon n_i^0}{\pi} \right)^\frac{1}{2} \sinh \left( \frac{z_i \sigma}{2kT} \right) \quad (3.42) \]
Derivation of Equation (3.44)

From equation (3.43), we know that

\[
\frac{d\phi}{dx} \bigg|_{x_0} = -\left(\frac{2kT}{ze_0^2}\right) K \sinh \left(\frac{ze_0\phi}{2kT}\right)
\]

\[
= -\frac{K}{a} \sinh \left( a\phi \right) \quad (A.6-1)
\]

where \( a = \frac{ze_0}{2kT} \). By integration with the boundary conditions \( x = x_0', \phi = \phi_0'; x = x_0'', \phi = \phi_0'' \), we have

\[
\int_{\phi_0'}^{\phi_0''} \frac{d\phi}{\sinh(a\phi)} = -\int_{x_0'}^{x_0''} \frac{K}{a} \, dx \quad (A.6-2)
\]

\[
\frac{1}{a} \ln \left[ \tanh \left( \frac{a\phi}{2} \right) \right] \bigg|_{\phi_0'}^{\phi_0''} = -\frac{K}{a} \left( x_0'' - x_0' \right) \quad (A.6-3)
\]

\[
\ln \left[ \frac{\tanh \left( \frac{a\phi_0'}{2} \right)}{\tanh \left( \frac{a\phi_0''}{2} \right)} \right] = K \left( x_0'' - x_0' \right) \quad (A.6-4)
\]

or

\[
\tanh \left( \frac{ze_0\phi_0'}{4kT} \right) = \exp \left[ K \left( x_0'' - x_0' \right) \right] \tanh \left( \frac{ze_0\phi_0''}{4kT} \right) \quad (3.44)
\]
Determination of the Effective Radii of Hydrated Ions

It has been shown by Brull (70) that the $a_1$ parameter of the Debye-Hückel formula may be regarded as the effective diameter of the hydrated ion. It was also concluded that the $a_1$ parameter has no definite physical significance and is only empirical corrective coefficient to make theoretical results conform to experimental data. On the other hand, the $a_1$ parameter of the theory of Bonino (71) has an unquestionable physical significance, both because on a basis of this physical significance the parameter can be calculated from the fundamental physical constants of the ions, i.e., the true radius and the deformability, and because the same physical significance makes it possible to deduce the parameter from other experiments, e.g., mobility measurements. The expression proposed by Bonino was written as:

$$\frac{10^8 a_1}{z_1} = 0.9 \left( \frac{10^8 r_1}{10^{24} \alpha_1} \right) + 2 \quad (A.7-1)$$

where $z_1$ is ionic valence, $r_1$ is effective ionic radius, and $\alpha_1$ is the deformability. From the ionic mobilities, $a_1$ can be calculated from the equation

$$10^8 a_1 = 182 \frac{z_1}{\mu} \quad (A.7-2)$$
where $l_\infty$ is the equivalent conductivity limit, or its empirical modification given by Brull (72)

$$10^8 a_1 = \frac{216 z_1^{1/2}}{l_\infty} \quad (A.7-3)$$

One can also determine the chemical hydration number by the entropy deficiency method (73,74) and calculate $a_1$ from this and effective radius of the ion. The results have been partly revised, using the recent entropy values of aqueous ions, by Kielland (62) and the values of effective radii of hydrated ions from this work were used in this study.
APPENDIX B

TABLES OF EXPERIMENTAL AND CALCULATED DATA AND

SAMPLE CALCULATION
Table B-1. Spectrophotometric Analysis for the Determination of $k_b$ of Cu-NaDBS System.

<table>
<thead>
<tr>
<th>log$[\text{Cu}^{2+}]_{\text{uncomplexed}}$</th>
<th>log$[\text{Cu(DBS}_2)]/([\text{DBS}^-])^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.050</td>
<td>-3.415</td>
</tr>
<tr>
<td>-1.796</td>
<td>-3.157</td>
</tr>
<tr>
<td>-1.656</td>
<td>-2.996</td>
</tr>
<tr>
<td>-1.606</td>
<td>-2.949</td>
</tr>
<tr>
<td>-1.564</td>
<td>-2.882</td>
</tr>
</tbody>
</table>
Table B-2. Spectrophotometric Analysis for the Determination of $k_b$ of Pb-NaDBS System.

<table>
<thead>
<tr>
<th>$\log[\text{Pb}^{2+}]$ uncomplexed</th>
<th>$\log[\text{Pb(DBS)}_2]/[\text{DBS}^-]^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.643</td>
<td>-3.778</td>
</tr>
<tr>
<td>-2.560</td>
<td>-3.590</td>
</tr>
<tr>
<td>-2.083</td>
<td>-3.081</td>
</tr>
<tr>
<td>-1.932</td>
<td>-2.875</td>
</tr>
<tr>
<td>-1.869</td>
<td>-2.856</td>
</tr>
</tbody>
</table>
Table B-3. Spectrophotometric Analysis for the Determination of $k_0$ of Cd-NaDBS System.

<table>
<thead>
<tr>
<th>$\log[\text{Ca}^{2+}]_{\text{uncomplexed}}$</th>
<th>$\log[\text{Cd(DBS)}_2]/[\text{DBS}^-]^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 2.055</td>
<td>- 3.597</td>
</tr>
<tr>
<td>- 1.711</td>
<td>- 3.260</td>
</tr>
<tr>
<td>- 1.559</td>
<td>- 3.010</td>
</tr>
<tr>
<td>- 1.492</td>
<td>- 2.932</td>
</tr>
<tr>
<td>- 1.442</td>
<td>- 2.870</td>
</tr>
<tr>
<td>- 1.420</td>
<td>- 2.858</td>
</tr>
</tbody>
</table>
Table B-5. Spectrophotometric Measurements of HDBS Solution.

<table>
<thead>
<tr>
<th>solution</th>
<th>pH</th>
<th>300 m(\mu)</th>
<th>320 m(\mu)</th>
<th>340 m(\mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.910</td>
<td>0.389</td>
<td>0.630</td>
<td>0.772</td>
</tr>
<tr>
<td>2</td>
<td>3.820</td>
<td>0.578</td>
<td>0.613</td>
<td>0.763</td>
</tr>
<tr>
<td>3</td>
<td>5.943</td>
<td>0.360</td>
<td>0.600</td>
<td>0.754</td>
</tr>
</tbody>
</table>

\[ [\text{HDBS}] = 5.4 \times 10^{-5} \text{ M} \]
Table B-6. Effect of pH on the Distribution Factor of Cu$^{++}$ and CuOH$^+$.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>pH</th>
<th>DF$_{Cu^{++}}$</th>
<th>*DF$_{Cu^{++}}$</th>
<th>DF$_{CuOH^+}$</th>
<th>*DF$_{CuOH^+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>($10^{-3}$ cm)</td>
<td>($10^{-3}$ cm)</td>
<td>($10^{-3}$ cm)</td>
<td>($10^{-3}$ cm)</td>
</tr>
<tr>
<td>31</td>
<td>5.877</td>
<td>0.916</td>
<td>0.036</td>
<td>0.259</td>
<td>0.012</td>
</tr>
<tr>
<td>32</td>
<td>4.728</td>
<td>0.806</td>
<td>0.032</td>
<td>1.420</td>
<td>0.055</td>
</tr>
<tr>
<td>33</td>
<td>4.141</td>
<td>0.800</td>
<td>0.032</td>
<td>1.610</td>
<td>0.062</td>
</tr>
<tr>
<td>34</td>
<td>3.357</td>
<td>0.802</td>
<td>0.032</td>
<td>0.963</td>
<td>0.038</td>
</tr>
<tr>
<td>35</td>
<td>2.167</td>
<td>0.613</td>
<td>0.025</td>
<td>0.560</td>
<td>0.023</td>
</tr>
<tr>
<td>36</td>
<td>2.467</td>
<td>0.793</td>
<td>0.032</td>
<td>0.763</td>
<td>0.031</td>
</tr>
<tr>
<td>37</td>
<td>1.470</td>
<td>0.244</td>
<td>0.011</td>
<td>0.227</td>
<td>0.011</td>
</tr>
</tbody>
</table>

$[Cu] = 10$ ppm
$[NaDBS] = 0.50$ g/l.
Table B-7. Effect of Bulk Copper Concentration on the Distribution Factor of Cu$^{++}$ and CuOH$^+$.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[Cu] x 10$^4$ (mole/L)</th>
<th>DF$_{Cu^{++}}$ (10$^{-3}$ cm$^3$ cm/mol)</th>
<th>$^{±}$DF$_{Cu^{++}}$ (10$^{-3}$ cm$^3$ cm/mol)</th>
<th>DF$_{CuOH^+}$ (10$^{-3}$ cm$^3$ cm/mol)</th>
<th>$^{±}$DF$_{CuOH^+}$ (10$^{-3}$ cm$^3$ cm/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>1.574</td>
<td>0.806</td>
<td>0.032</td>
<td>1.420</td>
<td>0.055</td>
</tr>
<tr>
<td>38</td>
<td>2.361</td>
<td>0.556</td>
<td>0.023</td>
<td>0.664</td>
<td>0.027</td>
</tr>
<tr>
<td>39</td>
<td>3.935</td>
<td>0.333</td>
<td>0.015</td>
<td>0.624</td>
<td>0.025</td>
</tr>
<tr>
<td>40</td>
<td>0.787</td>
<td>1.500</td>
<td>0.059</td>
<td>2.250</td>
<td>0.086</td>
</tr>
<tr>
<td>41</td>
<td>0.472</td>
<td>2.240</td>
<td>0.086</td>
<td>4.070</td>
<td>0.155</td>
</tr>
<tr>
<td>42</td>
<td>0.157</td>
<td>3.120</td>
<td>0.119</td>
<td>31.900</td>
<td>1.200</td>
</tr>
</tbody>
</table>

$pH = 4.70 ± 0.05$

$[NaDBS] = 0.50$ gm/L
Table B-8. Effect of pH on the Distribution Factor of Pb$^{2+}$ and PbOH$^+$. 

<table>
<thead>
<tr>
<th>Run No.</th>
<th>pH</th>
<th>DF$_{Pb^{2+}}$ $\times 10^3$ cm</th>
<th>$\pm$DF$_{Pb^{2+}}$ $\times 10^3$ cm</th>
<th>DF$_{PbOH^+}$ $\times 10^3$ cm</th>
<th>$\pm$DF$_{PbOH^+}$ $\times 10^3$ cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
<td>3.57</td>
<td>2.010</td>
<td>0.078</td>
<td>2.400</td>
<td>0.093</td>
</tr>
<tr>
<td>83</td>
<td>6.09</td>
<td>0.834</td>
<td>0.034</td>
<td>0.498</td>
<td>0.022</td>
</tr>
<tr>
<td>84</td>
<td>2.76</td>
<td>1.890</td>
<td>0.073</td>
<td>2.080</td>
<td>0.080</td>
</tr>
<tr>
<td>85</td>
<td>2.08</td>
<td>1.620</td>
<td>0.063</td>
<td>1.630</td>
<td>0.063</td>
</tr>
<tr>
<td>86</td>
<td>1.67</td>
<td>1.320</td>
<td>0.052</td>
<td>1.320</td>
<td>0.052</td>
</tr>
<tr>
<td>87</td>
<td>5.44</td>
<td>1.360</td>
<td>0.054</td>
<td>2.240</td>
<td>0.086</td>
</tr>
<tr>
<td>88</td>
<td>4.65</td>
<td>1.340</td>
<td>0.072</td>
<td>2.340</td>
<td>0.090</td>
</tr>
<tr>
<td>89</td>
<td>3.28</td>
<td>2.040</td>
<td>0.079</td>
<td>2.870</td>
<td>0.110</td>
</tr>
<tr>
<td>94</td>
<td>5.21</td>
<td>1.640</td>
<td>0.064</td>
<td>2.090</td>
<td>0.081</td>
</tr>
</tbody>
</table>

[\text{Pb}] = 10 ppm

[\text{NaDBS}] = 0.50 g/l.
Table B-9. Effect of Bulk Lead Concentration on the Distribution Factor of Pb$^{2+}$ and PbOH$^+$.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[Pb]$ = 10^5$</th>
<th>$D_{Pb}^{2+}$</th>
<th>$D_{Pb}^{2+}$</th>
<th>$D_{PbOH}^+$</th>
<th>$D_{PbOH}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mole/l)</td>
<td>$(10^3 \text{ cm})$</td>
<td>$(10^3 \text{ cm})$</td>
<td>$(10^3 \text{ cm})$</td>
<td>$(10^3 \text{ cm})$</td>
</tr>
<tr>
<td>90</td>
<td>2.664</td>
<td>2.650</td>
<td>0.102</td>
<td>3.340</td>
<td>0.128</td>
</tr>
<tr>
<td>91</td>
<td>1.158</td>
<td>3.490</td>
<td>0.153</td>
<td>4.600</td>
<td>0.175</td>
</tr>
<tr>
<td>92</td>
<td>7.480</td>
<td>1.110</td>
<td>0.044</td>
<td>1.500</td>
<td>0.059</td>
</tr>
<tr>
<td>93</td>
<td>12.310</td>
<td>0.699</td>
<td>0.029</td>
<td>0.832</td>
<td>0.034</td>
</tr>
<tr>
<td>94</td>
<td>4.826</td>
<td>1.640</td>
<td>0.064</td>
<td>2.090</td>
<td>0.081</td>
</tr>
</tbody>
</table>

$pH = 5.00 \pm 0.05$

$[\text{NaDBS}] = 0.50 \text{ gm/l}$
Table B-10. Effect of pH on the Distribution Factor of Cd$^{++}$ and CdOH$^+$.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>pH</th>
<th>$\text{DF}_{\text{Cd}^{++}}$ $(10^3 \text{ cm})$</th>
<th>$\pm \text{DF}_{\text{Cd}^{++}} (10^3 \text{ cm})$</th>
<th>$\text{DF}_{\text{CdOH}^+} (10^2 \text{ cm})$</th>
<th>$\pm \text{DF}_{\text{CdOH}^+} (10^2 \text{ cm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>4.982</td>
<td>1.890</td>
<td>0.074</td>
<td>4.510</td>
<td>0.170</td>
</tr>
<tr>
<td>96</td>
<td>4.168</td>
<td>1.860</td>
<td>0.072</td>
<td>3.640</td>
<td>0.137</td>
</tr>
<tr>
<td>97</td>
<td>3.420</td>
<td>1.720</td>
<td>0.067</td>
<td>0.207</td>
<td>0.008</td>
</tr>
<tr>
<td>98</td>
<td>3.007</td>
<td>1.770</td>
<td>0.069</td>
<td>0.262</td>
<td>0.010</td>
</tr>
<tr>
<td>99</td>
<td>2.625</td>
<td>1.650</td>
<td>0.064</td>
<td>0.158</td>
<td>0.006</td>
</tr>
<tr>
<td>100</td>
<td>1.761</td>
<td>1.116</td>
<td>0.044</td>
<td>0.113</td>
<td>0.004</td>
</tr>
<tr>
<td>101</td>
<td>5.400</td>
<td>1.800</td>
<td>0.070</td>
<td>0.268</td>
<td>0.010</td>
</tr>
<tr>
<td>106</td>
<td>5.001</td>
<td>1.890</td>
<td>0.073</td>
<td>1.010</td>
<td>0.038</td>
</tr>
</tbody>
</table>

$[\text{Cd}] = 10 \text{ ppm}$

$[\text{NaDBS}] = 0.50 \text{ g/L}$.
Table B-11. Effect of Bulk Cadmium Concentration on the Distribution Factor of Cd$^{++}$ and CdOH$^+$.  

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[Cd] × 10$^4$ (mole/L)</th>
<th>DF$_{Cd^{++}}$ (10$^3$ cm)</th>
<th>±DF$_{Cd^{++}}$ (10$^3$ cm)</th>
<th>DF$_{CdOH^+}$ (10$^2$ cm)</th>
<th>±DF$_{CdOH^+}$ (10$^2$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>1.379</td>
<td>1.290</td>
<td>0.051</td>
<td>0.542</td>
<td>0.021</td>
</tr>
<tr>
<td>103</td>
<td>2.206</td>
<td>0.816</td>
<td>0.033</td>
<td>1.450</td>
<td>0.055</td>
</tr>
<tr>
<td>104</td>
<td>0.445</td>
<td>3.050</td>
<td>0.116</td>
<td>1.230</td>
<td>0.046</td>
</tr>
<tr>
<td>105</td>
<td>0.165</td>
<td>4.540</td>
<td>0.173</td>
<td>1.370</td>
<td>0.052</td>
</tr>
<tr>
<td>106</td>
<td>0.890</td>
<td>1.890</td>
<td>0.073</td>
<td>1.010</td>
<td>0.038</td>
</tr>
</tbody>
</table>

pH = 5.00 ± 0.05  
[NaDBS] = 0.50 gm/L.
Table B-12. Theoretical Prediction of Distribution Factors of Cu$^{++}$ and CuOH$^+$ vs. Bulk Concentration.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>r$_{eff}$ (10$^8$ cm)</th>
<th>DF$_{Cu^{++}}$ (10$^3$ cm)</th>
<th>DF$_{CuOH^+}$ (10$^3$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>6.8</td>
<td>1.575</td>
<td>2.025</td>
</tr>
<tr>
<td></td>
<td>8.8$^*$</td>
<td>0.990</td>
<td>1.352</td>
</tr>
<tr>
<td>38</td>
<td>6.8</td>
<td>1.098</td>
<td>1.463</td>
</tr>
<tr>
<td></td>
<td>8.8$^*$</td>
<td>0.717</td>
<td>1.016</td>
</tr>
<tr>
<td>39</td>
<td>6.8</td>
<td>0.728</td>
<td>0.957</td>
</tr>
<tr>
<td></td>
<td>8.8$^*$</td>
<td>0.496</td>
<td>0.687</td>
</tr>
<tr>
<td>40</td>
<td>6.8</td>
<td>2.532</td>
<td>3.325</td>
</tr>
<tr>
<td></td>
<td>8.8$^*$</td>
<td>1.487</td>
<td>2.109</td>
</tr>
<tr>
<td>41</td>
<td>6.8</td>
<td>3.633</td>
<td>4.732</td>
</tr>
<tr>
<td></td>
<td>8.8$^*$</td>
<td>2.020</td>
<td>2.864</td>
</tr>
<tr>
<td>42</td>
<td>6.8</td>
<td>6.737</td>
<td>9.118</td>
</tr>
<tr>
<td></td>
<td>8.8$^*$</td>
<td>3.518</td>
<td>5.067</td>
</tr>
</tbody>
</table>

* effective radius of hydrated ion used in the normalization curve in figures 12 to 14.
Table B-15. Theoretical Prediction of Distribution Factors of Cu^{2+} and CuOH^{+} vs. pH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>( r_{\text{eff}} ) (10^8 cm)</th>
<th>( DF_{\text{Cu}^{2+}} ) (10^3 cm)</th>
<th>( DF_{\text{CuOH}^{+}} ) (10^3 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>6.8</td>
<td>2.623</td>
<td>2.776</td>
</tr>
<tr>
<td></td>
<td>8.8*</td>
<td>1.591</td>
<td>1.710</td>
</tr>
<tr>
<td>32</td>
<td>6.8</td>
<td>1.575</td>
<td>2.025</td>
</tr>
<tr>
<td></td>
<td>8.8*</td>
<td>0.990</td>
<td>1.552</td>
</tr>
<tr>
<td>33</td>
<td>6.8</td>
<td>1.169</td>
<td>2.033</td>
</tr>
<tr>
<td></td>
<td>8.8*</td>
<td>0.742</td>
<td>1.442</td>
</tr>
<tr>
<td>34</td>
<td>6.8</td>
<td>0.858</td>
<td>2.969</td>
</tr>
<tr>
<td></td>
<td>8.8*</td>
<td>0.548</td>
<td>2.261</td>
</tr>
<tr>
<td>35</td>
<td>6.8</td>
<td>0.506</td>
<td>8.601</td>
</tr>
<tr>
<td></td>
<td>8.8*</td>
<td>0.325</td>
<td>6.918</td>
</tr>
<tr>
<td>36</td>
<td>6.8</td>
<td>0.607</td>
<td>6.412</td>
</tr>
<tr>
<td></td>
<td>8.8*</td>
<td>0.389</td>
<td>5.108</td>
</tr>
</tbody>
</table>

* as noted before
Table B-14. Theoretical Prediction of Distribution Factors of Pb$^{++}$ and PbOH$^+$ vs. pH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$r_{\text{eff}}$ (10$^8$ cm)</th>
<th>$DF_{\text{Pb}^{++}}$ (10$^{-3}$ cm)</th>
<th>$DF_{\text{PbOH}^+}$ (10$^{-3}$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
<td>5.9</td>
<td>2.365</td>
<td>5.481</td>
</tr>
<tr>
<td></td>
<td>11.7*</td>
<td>0.536</td>
<td>2.112</td>
</tr>
<tr>
<td>84</td>
<td>5.9</td>
<td>1.659</td>
<td>9.033</td>
</tr>
<tr>
<td></td>
<td>11.7*</td>
<td>0.387</td>
<td>4.172</td>
</tr>
<tr>
<td>85</td>
<td>5.9</td>
<td>1.062</td>
<td>16.26</td>
</tr>
<tr>
<td></td>
<td>11.7*</td>
<td>0.256</td>
<td>8.211</td>
</tr>
<tr>
<td>86</td>
<td>5.9</td>
<td>0.834</td>
<td>24.44</td>
</tr>
<tr>
<td></td>
<td>11.7*</td>
<td>0.209</td>
<td>12.92</td>
</tr>
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<td>87</td>
<td>5.9</td>
<td>11.71</td>
<td>12.22</td>
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<td>11.7*</td>
<td>2.155</td>
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<td>4.739</td>
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<td>11.7*</td>
<td>0.999</td>
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<td>2.146</td>
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<td>11.7*</td>
<td>0.487</td>
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<td>94</td>
<td>5.9</td>
<td>8.405</td>
<td>8.984</td>
</tr>
<tr>
<td></td>
<td>11.7*</td>
<td>1.630</td>
<td>1.895</td>
</tr>
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</table>

* as noted before
Table B-15. Theoretical Prediction of Distribution Factors of Pb$$^{2+}$$ and PbOH$$^+$$ vs. Bulk Concentration.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$r_{\text{eff}}$ ($10^8$ cm)</th>
<th>$DF_{\text{Pb}^{2+}}$ ($10^3$ cm)</th>
<th>$DF_{\text{PbOH}^+}$ ($10^3$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>5.9</td>
<td>12.62</td>
<td>13.60</td>
</tr>
<tr>
<td></td>
<td>11.7*</td>
<td>2.075</td>
<td>2.493</td>
</tr>
<tr>
<td>91</td>
<td>5.9</td>
<td>25.65</td>
<td>27.46</td>
</tr>
<tr>
<td></td>
<td>11.7*</td>
<td>3.234</td>
<td>3.919</td>
</tr>
<tr>
<td>92</td>
<td>5.9</td>
<td>5.468</td>
<td>5.878</td>
</tr>
<tr>
<td></td>
<td>11.7*</td>
<td>1.213</td>
<td>1.411</td>
</tr>
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<td>93</td>
<td>5.9</td>
<td>3.313</td>
<td>3.594</td>
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<tr>
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<td>11.7*</td>
<td>0.850</td>
<td>0.995</td>
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<tr>
<td>94</td>
<td>5.9</td>
<td>8.405</td>
<td>8.984</td>
</tr>
<tr>
<td></td>
<td>11.7*</td>
<td>1.630</td>
<td>1.893</td>
</tr>
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</table>

* as noted before
Table 3-16. Theoretical Prediction of Distribution Factors of Cd$^{2+}$ and CdO$^{2-}$ vs. pH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$r_{\text{eff}}$ ($10^8$ cm)</th>
<th>$D_{\text{Cd}^{2+}}$ ($10^3$ cm$^2$ cm$^{-1}$)</th>
<th>$D_{\text{CdO}^{2-}}$ ($10^3$ cm$^2$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>6.4</td>
<td>3.132</td>
<td>7.616</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
<td>1.722</td>
<td>5.176</td>
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<td>96</td>
<td>6.4</td>
<td>1.896</td>
<td>13.29</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
<td>1.065</td>
<td>9.860</td>
</tr>
<tr>
<td>97</td>
<td>6.4</td>
<td>1.354</td>
<td>22.26</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
<td>0.768</td>
<td>21.54</td>
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<tr>
<td>98</td>
<td>6.4</td>
<td>1.176</td>
<td>44.34</td>
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<td></td>
<td>8.6</td>
<td>0.668</td>
<td>34.01</td>
</tr>
<tr>
<td>99</td>
<td>6.4</td>
<td>0.997</td>
<td>--</td>
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<tr>
<td></td>
<td>8.6</td>
<td>0.568</td>
<td>--</td>
</tr>
<tr>
<td>100</td>
<td>6.4</td>
<td>0.578</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
<td>0.335</td>
<td>--</td>
</tr>
<tr>
<td>101</td>
<td>6.4</td>
<td>3.841</td>
<td>6.627</td>
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<td></td>
<td>8.6</td>
<td>2.091</td>
<td>4.232</td>
</tr>
<tr>
<td>106</td>
<td>6.4</td>
<td>3.166</td>
<td>7.554</td>
</tr>
<tr>
<td></td>
<td>8.6</td>
<td>1.740</td>
<td>5.120</td>
</tr>
</tbody>
</table>

* as noted before
Table 3-17: Theoretical Prediction of Distribution Factors
of Cd$^{++}$ and CdOH$^+$ vs. Bulk Concentration.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$r_{eff}$ (10$^8$ cm)</th>
<th>$D_F$Cd$^{++}$ (10$^3$ cm)</th>
<th>$D_F$CdOH$^+$ (10$^3$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>6.4</td>
<td>2.234</td>
<td>5.133</td>
</tr>
<tr>
<td></td>
<td>8.6*</td>
<td>1.293</td>
<td>3.567</td>
</tr>
<tr>
<td>103</td>
<td>6.4</td>
<td>1.394</td>
<td>3.801</td>
</tr>
<tr>
<td></td>
<td>8.6*</td>
<td>0.853</td>
<td>2.777</td>
</tr>
<tr>
<td>104</td>
<td>6.4</td>
<td>5.830</td>
<td>12.66</td>
</tr>
<tr>
<td></td>
<td>8.6*</td>
<td>2.920</td>
<td>8.017</td>
</tr>
<tr>
<td>105</td>
<td>6.4</td>
<td>11.96</td>
<td>26.01</td>
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<td></td>
<td>8.6*</td>
<td>5.216</td>
<td>15.22</td>
</tr>
<tr>
<td>106</td>
<td>6.4</td>
<td>3.166</td>
<td>7.554</td>
</tr>
<tr>
<td></td>
<td>8.6*</td>
<td>1.740</td>
<td>5.120</td>
</tr>
</tbody>
</table>

* as noted before
Table B-18. Experimental and Predicted Selectivity Coefficient of Cd-Cu-NaDBS System.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>([\text{Cd}] / [\text{Cd}]+[\text{Cu}])</th>
<th>(\Gamma_{\text{Cd}} / (\Gamma_{\text{Cd}} + \Gamma_{\text{Cu}}))</th>
<th>((\alpha_{\text{Cd,Cu}})_{E})</th>
<th>((\Gamma_{\text{Cd}} / (\Gamma_{\text{Cd}} + \Gamma_{\text{Cu}}))_{T})</th>
<th>((\alpha_{\text{Cd,Cu}})_{T})</th>
</tr>
</thead>
<tbody>
<tr>
<td>107</td>
<td>0.113</td>
<td>0.150</td>
<td>1.370</td>
<td>0.121</td>
<td>1.073</td>
</tr>
<tr>
<td>108</td>
<td>0.210</td>
<td>0.245</td>
<td>1.217</td>
<td>0.222</td>
<td>1.072</td>
</tr>
<tr>
<td>109</td>
<td>0.310</td>
<td>0.360</td>
<td>1.247</td>
<td>0.326</td>
<td>1.072</td>
</tr>
<tr>
<td>110</td>
<td>0.410</td>
<td>0.499</td>
<td>1.425</td>
<td>0.428</td>
<td>1.071</td>
</tr>
<tr>
<td>111</td>
<td>0.512</td>
<td>0.552</td>
<td>1.168</td>
<td>0.530</td>
<td>1.071</td>
</tr>
<tr>
<td>112</td>
<td>0.580</td>
<td>0.664</td>
<td>1.430</td>
<td>0.597</td>
<td>1.072</td>
</tr>
<tr>
<td>113</td>
<td>0.683</td>
<td>0.738</td>
<td>1.303</td>
<td>0.700</td>
<td>1.072</td>
</tr>
<tr>
<td>114</td>
<td>0.783</td>
<td>0.838</td>
<td>1.430</td>
<td>0.796</td>
<td>1.072</td>
</tr>
<tr>
<td>115</td>
<td>0.783</td>
<td>0.838</td>
<td>1.430</td>
<td>0.796</td>
<td>1.072</td>
</tr>
<tr>
<td>116</td>
<td>0.312</td>
<td>0.366</td>
<td>1.267</td>
<td>0.328</td>
<td>1.072</td>
</tr>
<tr>
<td>117</td>
<td>0.512</td>
<td>0.575</td>
<td>1.284</td>
<td>0.530</td>
<td>1.071</td>
</tr>
<tr>
<td>118</td>
<td>0.683</td>
<td>0.740</td>
<td>1.317</td>
<td>0.700</td>
<td>1.072</td>
</tr>
</tbody>
</table>

\[pH = 4.10 \pm 0.05\]

\[[\text{NaDBS}]] = 0.50 \text{ gm/l.}\]
Table B-19. Experimental and Predicted Selectivity Coefficient of Pb-Cu=NaDBS System.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>(\frac{[\text{Pb}]}{[\text{Pb}]+[\text{Cu}]})</th>
<th>(\frac{\Gamma_{\text{Pb}}}{\Gamma_{\text{Pb}} + \Gamma_{\text{Cu}}}_E)</th>
<th>((\alpha_{\text{Pb,Cu}})_E)</th>
<th>(\frac{\Gamma_{\text{Pb}}}{\Gamma_{\text{Pb}} + \Gamma_{\text{Cu}}}_T)</th>
<th>((\alpha_{\text{Pb,Cu}})_T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>121</td>
<td>0.804</td>
<td>0.844</td>
<td>1.324</td>
<td>0.836</td>
<td>1.254</td>
</tr>
<tr>
<td>122</td>
<td>0.661</td>
<td>0.748</td>
<td>1.527</td>
<td>0.709</td>
<td>1.253</td>
</tr>
<tr>
<td>123</td>
<td>0.492</td>
<td>0.580</td>
<td>1.436</td>
<td>0.546</td>
<td>1.251</td>
</tr>
<tr>
<td>124</td>
<td>0.304</td>
<td>0.368</td>
<td>1.338</td>
<td>0.352</td>
<td>1.251</td>
</tr>
<tr>
<td>125</td>
<td>0.174</td>
<td>0.193</td>
<td>1.146</td>
<td>0.207</td>
<td>1.251</td>
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<tr>
<td>126</td>
<td>0.304</td>
<td>0.337</td>
<td>1.170</td>
<td>0.352</td>
<td>1.251</td>
</tr>
<tr>
<td>127</td>
<td>0.492</td>
<td>0.586</td>
<td>1.470</td>
<td>0.546</td>
<td>1.251</td>
</tr>
<tr>
<td>128</td>
<td>0.661</td>
<td>0.749</td>
<td>1.539</td>
<td>0.708</td>
<td>1.253</td>
</tr>
</tbody>
</table>

\[\text{pH} = 4.10 \pm 0.05\]

\[[\text{NaDBS}] = 0.50 \text{ gm/l.}\]
Table B-21. Spectrophotometric Measurements of Cu-NaDBS System.

<table>
<thead>
<tr>
<th></th>
<th>260</th>
<th>270</th>
<th>280</th>
<th>290</th>
<th>300</th>
<th>310</th>
<th>320</th>
<th>[Cu]$^{\dagger}$ $(10^2 \text{ M})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TH</td>
<td>0.930</td>
<td>0.928</td>
<td>0.850</td>
<td>0.776</td>
<td>0.737</td>
<td>0.770</td>
<td>0.873</td>
<td>0.91</td>
</tr>
<tr>
<td>OD</td>
<td>0.0315</td>
<td>0.0232</td>
<td>0.0706</td>
<td>0.1102</td>
<td>0.1325</td>
<td>0.1135</td>
<td>0.0590</td>
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</tr>
<tr>
<td>TH</td>
<td>0.860</td>
<td>0.860</td>
<td>0.737</td>
<td>0.632</td>
<td>0.576</td>
<td>0.622</td>
<td>0.778</td>
<td>1.67</td>
</tr>
<tr>
<td>OD</td>
<td>0.0655</td>
<td>0.0655</td>
<td>0.1325</td>
<td>0.1993</td>
<td>0.2396</td>
<td>0.2062</td>
<td>0.1090</td>
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<tr>
<td>TH</td>
<td>0.742</td>
<td>0.770</td>
<td>0.638</td>
<td>0.517</td>
<td>0.449</td>
<td>0.502</td>
<td>0.691</td>
<td>2.31</td>
</tr>
<tr>
<td>OD</td>
<td>0.1296</td>
<td>0.1135</td>
<td>0.1952</td>
<td>0.2865</td>
<td>0.3478</td>
<td>0.2993</td>
<td>0.1605</td>
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<tr>
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<td>0.745</td>
<td>0.605</td>
<td>0.480</td>
<td>0.410</td>
<td>0.462</td>
<td>0.662</td>
<td>2.59</td>
</tr>
<tr>
<td>OD</td>
<td>0.1549</td>
<td>0.1278</td>
<td>0.2182</td>
<td>0.3188</td>
<td>0.3672</td>
<td>0.3354</td>
<td>0.2791</td>
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<tr>
<td>TH</td>
<td>0.620</td>
<td>0.653</td>
<td>0.529</td>
<td>0.413</td>
<td>0.353</td>
<td>0.411</td>
<td>0.618</td>
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<tr>
<td>OD</td>
<td>0.2076</td>
<td>0.1851</td>
<td>0.2766</td>
<td>0.3840</td>
<td>0.4522</td>
<td>0.3862</td>
<td>0.2090</td>
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</tr>
</tbody>
</table>

$[\text{NaDBS}] = 1.436 \times 10^{-3} \text{ M}$

$[\text{HClO}_4] = 0.50 \text{ M}$

Asymptotic limit at 300 mμ: OD = 0.495, $\varepsilon = 344.706$
Table B-23. Spectrophotometric Measurements of Cd-NaDBS System.

<table>
<thead>
<tr>
<th></th>
<th>260</th>
<th>270</th>
<th>280</th>
<th>290</th>
<th>300</th>
<th>310</th>
<th>320</th>
<th>[Cd]</th>
<th>(10^2 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM</td>
<td>1.000</td>
<td>0.975</td>
<td>0.878</td>
<td>0.790</td>
<td>0.741</td>
<td>0.770</td>
<td>0.870</td>
<td>0.91</td>
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</tr>
<tr>
<td>OD</td>
<td>0.0000</td>
<td>0.0110</td>
<td>0.0565</td>
<td>0.1024</td>
<td>0.1302</td>
<td>0.1135</td>
<td>0.0605</td>
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<td></td>
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<tr>
<td>TM</td>
<td>1.000</td>
<td>0.920</td>
<td>0.733</td>
<td>0.598</td>
<td>0.522</td>
<td>0.570</td>
<td>0.740</td>
<td>2.00</td>
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</tr>
<tr>
<td>OD</td>
<td>0.0000</td>
<td>0.0362</td>
<td>0.1349</td>
<td>0.2233</td>
<td>0.2823</td>
<td>0.2441</td>
<td>0.1308</td>
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</tr>
<tr>
<td>TM</td>
<td>0.726</td>
<td>0.658</td>
<td>0.498</td>
<td>0.375</td>
<td>0.314</td>
<td>0.362</td>
<td>0.545</td>
<td>2.86</td>
<td></td>
</tr>
<tr>
<td>OD</td>
<td>0.1391</td>
<td>0.1818</td>
<td>0.3028</td>
<td>0.4260</td>
<td>0.5031</td>
<td>0.4413</td>
<td>0.2636</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TM</td>
<td>0.658</td>
<td>0.573</td>
<td>0.415</td>
<td>0.301</td>
<td>0.250</td>
<td>0.296</td>
<td>0.477</td>
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<tr>
<td>OD</td>
<td>0.1952</td>
<td>0.2418</td>
<td>0.3819</td>
<td>0.5215</td>
<td>0.6021</td>
<td>0.5287</td>
<td>0.3215</td>
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</tr>
<tr>
<td>TM</td>
<td>0.600</td>
<td>0.533</td>
<td>0.365</td>
<td>0.253</td>
<td>0.202</td>
<td>0.243</td>
<td>0.413</td>
<td>3.75</td>
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<tr>
<td>OD</td>
<td>0.2219</td>
<td>0.2733</td>
<td>0.4377</td>
<td>0.5969</td>
<td>0.6946</td>
<td>0.6144</td>
<td>0.3840</td>
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<tr>
<td>TM</td>
<td>0.600</td>
<td>0.533</td>
<td>0.360</td>
<td>0.245</td>
<td>0.193</td>
<td>0.235</td>
<td>0.412</td>
<td>3.94</td>
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</tr>
<tr>
<td>OD</td>
<td>0.2219</td>
<td>0.2733</td>
<td>0.4437</td>
<td>0.6108</td>
<td>0.7144</td>
<td>0.6289</td>
<td>0.3851</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ [\text{NaDBS}] = 1.436 \times 10^{-3} \text{M} \]
\[ [\text{HClO}_4] = 0.50 \text{M} \]

Asymptotic limit at 300 m\(\mu\) : OD = 0.740, \(\epsilon = 515.3203 \)
### TABLE B-24  EXPERIMENTAL DATA OF Cu - NADBS SYSTEM

<table>
<thead>
<tr>
<th>RUN COLLECTION NO.</th>
<th>TIME, MIN</th>
<th>GAS RATE, HL/HN</th>
<th>WEIGHT OF FOAMATE, GH</th>
<th>BUBBLE RATE, PP</th>
<th>BULK CONC.</th>
<th>FOAMATE CONC., PPM</th>
<th>OBS. BULK PHB</th>
<th>PHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>15.00</td>
<td>66.67</td>
<td>7.9975</td>
<td>2574.0</td>
<td>10.00</td>
<td>37.30</td>
<td>0.50</td>
<td>5.88</td>
</tr>
<tr>
<td>32</td>
<td>15.00</td>
<td>66.67</td>
<td>9.3819</td>
<td>2564.0</td>
<td>10.00</td>
<td>34.40</td>
<td>0.50</td>
<td>4.73</td>
</tr>
<tr>
<td>33</td>
<td>15.00</td>
<td>66.67</td>
<td>9.2615</td>
<td>2562.0</td>
<td>10.00</td>
<td>34.20</td>
<td>0.50</td>
<td>4.14</td>
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### Table D-29: Experimental Data of Cd – Pb – NADBS System

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Sample Calculation of the Predicted Value of Distribution Factor in Figures 10, 13 and 16.

Runs 96, 102 and 109, representing one point in each of figures 10, 13 and 16, are chosen for the sample calculation of cadmium ion.

The following constants were used for all the calculations.

- **XK**: Boltzmann constant. \(1.38 \times 10^{-16}\) erg/molecule·°K
- **XT**: Absolute temperature. 298 °K
- **XA**: Dielectric constant of water. 81
- **XE**: Electronic charge, 4.803 \(\times 10^{-10}\) esu
- **XN**: Avogadro number. 6.023 \(\times 10^{23}\) molecules/g-mole
- **XG**: Surface excess of NaDBS. 3.10 \(\times 10^{-10}\) moles/cm²

**Step 1** Solve for equilibrium concentration of all ions in the solution.

From the known equilibrium constants of the reactions and the total amount of metal ions and surfactant used, the equilibrium concentration of all ions in the solution were calculated from the equilibrium model. The results are presented in table B-30.

**Step 2** Solve for surface potential of the smallest ion in the solution.

Based on the above equilibrium concentration and equation (3.38) and (3.39), the surface potential of \(Na^+\) was calculated. The values are tabulated in table B-31 as \(\psi_{Na^+}\).

**Step 3** Solve for the surface potential for other metal ions.

Since we are only interested in the separation of metal ions, the surface potential of other larger size of metal ions were calculated based on equation (3.44). The results are shown in table B-31 as \(\psi_{Cd^{++}}\) and \(\psi_{Cu^{++}}\). The term \((kT e/ 8 N e_0^2) = 758.1\)

**Step 4** Integrate for the distribution factor.

The distribution factor of cadmium ion was calculated by using the value of its surface potential, the equilibrium composition of all ions and equation (3.45). For the smaller metal ion, equation
(3.46) was used. The results are presented in table B-31 as

\[
\text{DTF}_{\text{Cd}^{++}} \quad \text{and} \quad \text{DTF}_{\text{Cu}^{++}}
\]

Since the surface excesses of cadmium and copper ions are needed in figure 16, they are calculated and shown as

\[
\Gamma_{\text{Cd}^{++}} \quad \text{and} \quad \Gamma_{\text{Cu}^{++}}
\]
Table B-30. Equilibrium Concentration of all ions in the solution.

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Run 109

Cu$^{++}$ = 2.171x10$^{-4}$  \quad Cd$^{++}$ = 9.796x10$^{-5}$  \quad CuOH$^+$ = 9.291x10$^{-7}$  \quad Na$^+$ = 1.436x10$^{-3}$

Cu$^{+}$ = 5.630x10$^{-9}$  \quad H$^+$ = 7.943x10$^{-5}$  \quad NO$_3^-$ = 4.769x10$^{-4}$  \quad CuNO$_3^+$ = 4.387x10$^{-24}$

DBS$^-$ = 9.255x10$^{-4}$  \quad CdNO$_3^+$ = 3.463x10$^{-8}$
Table B-3L. Sample Calculation. \([\text{NaDBS}] = 0.50 \text{ gm/L}\)

<table>
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</tr>
<tr>
<td>([\text{Cd}] \ (\text{Cu}))</td>
<td>10 ppm</td>
<td>(1.379 \times 10^{-4} \text{M})</td>
<td>(9.80 \times 10^{-5} \text{M})</td>
</tr>
<tr>
<td>(\text{V}_{\text{Na}})</td>
<td>523.7</td>
<td>422.3</td>
<td>280.3</td>
</tr>
<tr>
<td>(\text{V}<em>{\text{Cd}^{++}} \ (\text{V}</em>{\text{Cu}^{++}}))</td>
<td>18.48</td>
<td>13.79</td>
<td>14.26 (13.78)</td>
</tr>
<tr>
<td>(\text{DTF}<em>{\text{Cd}^{++}} \ (\text{DTF}</em>{\text{Cu}^{++}}))</td>
<td>(1.892 \times 10^{-3})</td>
<td>(1.290 \times 10^{-3})</td>
<td>(7.540 \times 10^{-4}) (7.035 (\times 10^{-4}))</td>
</tr>
<tr>
<td>(\Gamma_{\text{Cd}^{++}} \ (\Gamma_{\text{Cu}^{++}}))</td>
<td>---</td>
<td>---</td>
<td>(0.739 \times 10^{-10}) (1.527 (\times 10^{-10}))</td>
</tr>
<tr>
<td>(X_{\text{Cd}^{++}} \ (X_{\text{Cu}^{++}}) \ (\text{cm}))</td>
<td>(6.40 \times 10^{-8})</td>
<td>(8.60 \times 10^{-8})</td>
<td>(6.40 \times 10^{-8}) (6.80 (\times 10^{-8}))</td>
</tr>
<tr>
<td>pH</td>
<td>4.168</td>
<td>5.00</td>
<td>4.10</td>
</tr>
</tbody>
</table>
Two computer programs for the calculation of distribution factor are presented here separately; one is for the system containing one metal ion, the other is for that containing two metal ions. The notation and the method of use are interpreted as the comment in the computer program.
PURPOSE OF THIS PROGRAM

Calculates the theoretical and experimental values of distribution factor of ionic species for the systems containing one metal ion. The independent variables are the pH and total metal concentration.

The theoretical background is based on the Gouy-Chapman diffuse double layer theory.

DESCRIPTION OF PARAMETERS

PH: PH of the solution for which, preset value
Z: Valance of species I in the solution
B: Correlation constants for the amount of HNO3 vs PH
XK, XK, XA, XE, XN, and XG: Boltzmann constant, absolute temperature, dielectric constant, electronic charge, average atomic number and surface excess of surfactant, NAD
CNC: Equilibrium constants for the simultaneous equations

GOVERNING THE EQUILIBRIUM RELATION IN THE SOLUTION.

X1 TO X3: Effective radii of species I in the solution

DTF1 TO DTF5: Distribution factor of species I in the solution.

METHOD OF USE

1. THEORETICAL PART:
   Read in all the constants & conditions preset then computer will automatically calculate surface potential of species in the solution. The distribution factor is calculated from the integration of equations using the surface potential as the sole input.

2. EXPERIMENTAL PART:
   Call subroutine LTK right after all the experimental data are read in to give all the results anticipated.
INTEGER Z(20)
M=6
WM(1)=63.54
WM(2)=207.81
WM(3)=112.41
X4=4.7 CCDO-CA
READ(1,50) (Z(I),I=1,7)
REAC(1,49) (PH(I),I=1,3)
READ(1,49) (SH(I),I=1,6)
READ(1,52) XK,XT,XD,XE,XN,XG
READ(1,51) (CCN(I),I=1,N)
DO 2 WK=1,3
READ(1,50) I1
READ(1,51) CAA
DO 1 WK=1,3
READ(1,60) NO(1),PHB(I),PHF(I),TIME(I),CUB(I),CUF(I),GAS(I),HTF(I)
1BUBRAT(I),EBSE(I),EBSF(I)
FORMAT(13,2F5.3,F4.1,3F5.2,F7.4,F6.1,2D10.3)
DIA(I)=6.*GAS(I)/(3.14159*5.*BUBRAT(I))#0.33333
SLRFAS(I)=5.*2.14159*BUBRAT(I)*DIA(I)+DIA(I)
V(I)=HTF(I)/TIME(I)
CUB(I)=CUB(I)/(WH(HK)*1.0D03)
CUB(I)=CUB(I)/(WH(HK)*1.0D03)
CONTINUE
DO 62 N=1,11
CCNC(1)=CUF(N)
CCNC(1)=CUF(N)
CONCD(6)=CLB(N)+G(N)
CALL EQILBM (Z,F,B,CONC,G,A,C,AC,N,1,PCT)
GB1(N)=AC(1)
GB2(N)=AC(2)
CCNC(1)=CUF(A)
CONC(6) = CLF(N) + G1(N)
CALL FCILBM(Z, FC1, N, CONC, G1, A, C, AC, N, 1, PCT)
GF1(N) = AC(1)
GF2(N) = AC(2)
62 CONTINUE
IF(PK-2) 15, 16, 17
15 WRITE(3, 20)
GC TC 4
16 WRITE(3, 21)
GO TO 4
17 WRITE(3, 22)
CALL LTK(G1, GB2, GF1, GF2, IT, WT, GAS, TIME, CIA, CUB, PHB, PFF, CUF, SURFA)
IS, NO, C3S, CL8F, GDES
WRITE(3, 40)
CALL RCH(V, GAS, BUERAT, GB1, GF1, II, NC)
CALL RCH(V, GAS, BUERAT, GB2, GF2, II, NC)
READ(1, 52) X1, X2
WRITE(3, 11) X1, X2, X4
WRITE(3, 9) YX1 = X1
YX2 = X2
DO 250 LL = 1, II
WRITE(3, 97)
CONC(1) = CUB(LL)
CONC(A) = CUB(LL) + G(LL)
CALL FCILBV(Z, FC, 6, CONC, G, A, C, AC, LL, PK, PCT)
CALL RCDT(Z, AC, XK, XT, XX, XF, XA, XG, V114, YK1)
DO 3 LG = 1, 20
WRITE(3, 91) AC(LL), X1, ETF1(LL), ETF2(LL)
CLDX1 = X1
IF(PK .EQ. 2) GC TC 101
CC75  IF (LC .GT. 1) GC TC 10C
CC76  X1=CLDX1+1.4E-08
0077  GO TO 102
CC79  101 IF (LC .GT. 1) GC TC 100
0075  X1=OLDX1+4.0CD-C8
0080  GO TO 102
CC80  100 X1=CLCX1+0.1CF-08
0082  102 X2=X1-0.2CD-C6
0083  3 CONTINUE
CC84  WRITE (3,9)
0085  X1=XY1
0086  X2=XY2
CC87  250 CONTINUE
CCCC  WRITE (3,9)
0089  2 CONTINUE
CC8C  9 FORMAT (/4X,'***',/)
0091  10 FORMAT (5X,10D11.4)
0092  11 FORMAT (/4X,'*** X1 = ',C11.4,2X,'X2 = ',D11.4,2X,'X4 = ',D11.4)
0093  20 FORMAT (1HI1,'**** CEFFER ****',/)
0094  21 FORMAT (/4X,'**** LEAD ****',/)
0095  22 FORMAT (1HI1,'**** DCFNIP ****',/)
0096  40 FORMAT (/4X,'* ERRCR ANALYSIS (CALCULATE THE ABSOLUTE VALUE,OF DF 1)*',/)
CC97  49 FORMAT (12F5.2)
CC98  50 FORMAT (S12)
0099  51 FORMAT (20C10.3)
C1CC  52 FORMAT (20C11.4)
01C1  51 FORMAT (9X,'**',15,3X,5C11.4)
0102  56 FORMAT (5X,'*** RATIO OF DFS/HCBS IN BULK = ',D11.4)
C102  57 FORMAT (9X,'RUN AC',3X,'X1 ',4X,'ETF1',7X,'ETF2','/')
C1C4  RETURN
C1C5  END
SUBROUTINE FCILPP (Z, P, CCAC, C, A, AC, AC, K, L, DCT)

CALCULATES THE EQUILIBRIUM CONCENTRATION OF THE EXISTING SPECIES
IN THE SOLUTION BASED ON THE MODIFIED REGULA-FALSI POSITION METHOD.

A & AC concentrations of species in the solution.

CONC = EQUILIBRIUM CONSTANT

H1 = HYDROGEN CONCENTRATION

IMPLICIT REAL*8(A-H,C-Y)

DIMENSION A(10),B(10),C(10),H(30),AC(10),PH(10),D(10),CCAC(9)
INTEGER Z(20)

A(1) = 1.000-05
A(2) = 1.000-05
A(3) = 1.000-05
A(4) = 1.000-05
A(5) = 1.000-05
A(6) = 1.000-05
A(7) = 1.000-05

DO 300 J=1,100

A(2) = 0.5*A(2)*(((CCAC(3)*A(1)/(A(2)*A(K)+1.0))
A(3) = 0.5*A(3)*(((CCAC(4)*A(1)*A(4)*A(4)/A(3))+1.0)
A(4) = 0.5*A(4)*(((CCAC(5)*A(5)/A(K)*A(4))+1.0)
A(5) = 0.5*A(5)*(((CCAC(6)/A(6)+A(7))+1.0)
A(6) = 0.5*A(6)*(((CCAC(7)/A(7))+1.0)
A(7) = 0.5*A(7)*(((CCAC(8)/A(8)+A(9))+1.0)

CONTINUE

C(1) = A(1)+A(2)+A(3)+A(7)
C(2) = A(4)+2.*A(3)+A(5)
C(3) = A(2)*A(K)/A(1)
C(4) = A(3)/A(1)*A(4)/A(5)
C(5) = A(K)*A(4)/A(5)
C(6) = A(6)+A(7)
C(7) = A(7)/A(1)*A(6)
AC(1) = A(1)
AC(2) = A(2)
AC(3) = 2 * A(3) + A(4) + A(5)

AC(4) = CCAC(2)
AC(5) = H(K)
AC(6) = A(6)
AC(7) = A(7)
AC(8) = A(4)
PCT = A(4) / CONC(2)

1 RETURN
END
SUBROUTINE RCGT (Z, AC, XK, XT, XE, XN, XG, V11C, YK1)

IMPLICIT REAL*8(A-H, O-Z)
DIMENSION AC(10)
INTEGER Z(20)
Z(3) = -Z(3)
Z(6) = -Z(6)

YK = 8.*3.14159*Z(4)*Z(4)*XN*XG*AC(4)/(XA*XK*XT)
YK1 = DSQRT(YK)

H = 1
TT1 = XE*XG*XN
TT = XK*XT*XN*XN*1.0D00/(2.*3.14159)
V1 = 15.0

DO 10 N = 1, 7
SUN1 = SUN1 + AC(N)*(V1**2*(Z(N)-1.0)*1.0D-03
10 SUM2 = SUM2 + AC(N)*((V2**2*(Z(N)-1.0)*1.0D-03

T1 = DSQRT(TT*SUM1)
T2 = DSQRT(TT*SUM2)
F1 = T1 - TT
F2 = T2 - TT
FF = F1*F2
IF(FF) = 1, 13, 13

V2 = V2 + 50.
IF(M .GT. 900) GO TO 19

V = M + 1
GO TO 9

M = 1
Y = (V2 - V1)*CABS(F1)/(CABS(F1) + CABS(F2))

V3 = V1 + Y
SUM3 = 0.0
DO 14 N = 1, 7
14 SUM3 = SUM3 + AC(N)*((V3**2*(Z(N)-1.0)*1.0D-03
T3 = DSQRT(TT*SUM3)
F3 = T3 - TT
AA1=OABS(Y/V3)

IF(AA1 .LT. 1.0E-06) GO TO 15
FF=F1+F3
IF(FF) = 16, 15, 17

16 V2=V3
V2=V3
DO 8 N=1,7
8 SUM2=SUM2+AC(N)**(V2**Z(N)-1.0)**1.0E-03
18 M=N+1
IF(M .LE. 558) GO TO 19

GO TO 11

17 V1=V3
SUM1=0.0
DO 7 N=1,7
7 SUM1=SUM1+AC(N)**(V1**Z(N)-1.0)**1.0E-03
GO TO 18

WRITE(3,47) F
FORMAT(5X,'NO CONVERGENCE, NUMBER OF ITERATION = ',I5)
GO TO 1

V1=V3
Z(3)=Z(3)
Z(6)=Z(6)
RETURN
END
SUBROUTINE INTEG (Z, AC, XK, XT, XA, XF, XK, V222, P, TF, V333, KK)

IMPLICIT REAL*8 (A-H, O-Y)
DIMENSION AC(10), U(5000), C(5000)

INTEGER Z(20)
Z(3) = -Z(3)
Z(6) = Z(6)
L = 1
U111 = 1.0001
DV = (V222 - U111) * 4.0C-03

DO 30 N = 1, 7
H1 = 0.0

30 H1 = H1 + AC(N) * (U111 * Z(N) - 1.0) * 1.0C-03

IF (H1) 10, 10, 11
10 WRITE (3, 9) H1
9 FORMAT (5X, 'THE VALUE OF H1 = ', 1D12.5)

H1 = H1

11 H1 = QSCRT(H1)

Q(L) = (V333 * Z(KK) - 1.0) / (U111 * H1)

IF (U111 .GE. V222) GO TO 40

U111 = U111

L = L + 1

U111 = U111 + DV

GO TO 36

40 CALL QSF (DV, C, L, L)

P = U(L)

1 P = F / QSCRT(XA)

TF = (XK * XK + XA) / (E * 3.14159 * XE + XF)

TF = QSCRT(TF)

Z(3) = -Z(3)

Z(C) = Z(C)

RETURN

END
SUBROUTINE MIKE (YK, XT, XK*XT, X1, X2, XK*XT, V114, V111, V112)

IMPLICIT REAL*8 (A-H, O-Y)
INTEGER Z(26)

FY = -LOG(V114)*XK*XT/XE
TN4 = CTAN(1.4*XK*Y4/(4.*XK+XT))
TN1 = TN4/DEXP(YK1*(X1-X4))

TH2 = TN4/CEXP(YK1*(X2-X4))
FY = DLOG((1+TN1)/(1-TN1))/2.

FY = DLGC((1+TN2)/(1-TN2))/2.
FY1 = FY*64.*XK*XT/(Z(1)*XE)
FY2 = FY*64.*XK*XT/(Z(2)*XE)

V111 = CEXP(-XE*FY1/(XK*XT))
V112 = DEXP(-XE*FY2/(XK*XT))

RETURN
END
CLIPPING files (H, Y, Z, NDIM).

PARAMETERS H-THE INCREASE OF ARGUMENT VALUES, Y-THE INPUT VECTOR
OF FUNCTION VALUES, Z-THE RESULTING VECTOR OF INTEGRAL VALUES. Z
MAY BE IDENTICAL WITH Y.

PETITCE BEGINNING WITH Z(1)=0.0 EVALUATION OF VECTOR Z IS DONE
BY MEANS OF SIMPSONS RULE TOGETHER WITH ASHTGAS 3/8 RULE OR A
COMBINATION OF THESE TWO RULES. TRUNCATION ERROR IS OF ORDER H^3.5
( I.E., FOURTH CRED PASITIVE). ONLY IN CASE NDIM=3 TRUNCATION ERROR
OF Z(2) IS OF ORDER H^4.

HT=.33333333334
IF(INCH=.5) 7,0,1
NDIM IS GREATER THAN 5. PREPARATION OF INTEGRATION LOOP

1 SUM=Y(2)+Y(2)
SUM=SUM+Y(1)
SUP1=Y(1)+Y(3)
ALUX=Y(4)+Y(4)
AUX1=ALUX+ALUX
AUX=ALUX+ALUX
AUX1=ALUX+ALUX
AUX2=SUM*Y(1)+SUM*Y(3)+SUM*Y(5)
SUM2=SUM2+ALUX*ALUX
SUM2=SUM2+ALUX*ALUX
SUM2=SUM2+ALUX
SUM2=SUM2+ALUX
SUM2=SUM2+ALUX
Z(1)=0.0
0010 AUX=ALUX+ALUX
0011 Z(1)=SUM2-Z(1)+Y(2)+Y(2)+Y(2)+Y(2)+Y(2)+Y(2)
0020 Z(3)=SUM2
0021 Z(4)=SUM2
0022 IF(KNCM=6) 5,5,2
0023 GO 4 1=7,NCM,2
0024 SUM1=AUX1
CC25
SUM2 = ALX2

0026
AUX1 = Y(1-1) + Y(1-1)

CC27
AUX1 = ALX1 + ALX1

0028
AUX1 = SUM1 + HT * (Y(1-1) + ALX1 + Y(1))

CC29
Z(1-1) = SUM1

CC30
IF (NDIP < 1) 3, 6, 6

CO31
3
AUX2 = Y(1) + Y(1)

CC32
AUX2 = AUX2 + AUX2

CC33
AUX2 = SUM2 + HT * (Y(1-1) + ALX2 + Y(1+1))

CO34
4
Z(1-1) = SUM2

CC35
5
Z(NCIP - 1) = AUX1

CC36
Z(NDIM - 1) = ALX2

0037
RETURN

CC38
6
Z(NCIP - 1) = SUM2

CC39
Z(NDIM - 1) = AUX1

0040
RETURN

C END OF INTEGRATION LOOP

0041
7
IF (NDIM < 3) 12, 11, 8

CC42
SUM2 = 1.25 * HT * (Y(1) + Y(2) + Y(2) + Y(3) + Y(3) + Y(3) + Y(4))

CC43
SUM1 = Y(2) + Y(2)

CC44
SUM1 = SUM1 + SUM1

CC45
SUB1 = HT * (Y(1) + SUM1 + Y(3))

0046
Z(1) = 0.0

CC47
AUX1 = Y(3) + Y(3)

0048
AUX1 = AUX1 + ALX1

0049
Z(2) = SUM2 + HT * (Y(2) + AUX1 + Y(4))

0050
IF (NCIP < 5) 10, 9, 9

0051
9
AUX1 = Y(4) + Y(4)

0052
AUX1 = AUX1 + AUX1

0053
Z(5) = SUM1 + HT * (Y(3) + AUX1 + Y(5))

0054
10
Z(3) = SUM1

0055
Z(3) = SUM2

0056
RETURN

C NDIM IS EQUAL TO 3

CC57
11
SUM1 = HT * (1.25 * Y(1) + Y(2) + Y(2) - C.25 * Y(3))

CC58
SUM2 = Y(2) + Y(2)

CC59
SUM2 = Y(2) + Y(2)

C
SUBRUTINE LTK (CUEL, CUF2, CLF1, CUF2, 11, HTP, GAS, TIME, DIA, CUF, CBF, PHE, 
SUB, SURFAS, NO, CO8B, COSF, CARN).

CALCULATES THE DISTRIBUTION FACTOR OF SPECIES 1 FROM THE
EXPERIMENTAL RESULTS.

IMPLICIT REAL*8 (A-H, O-Z)
DIMENSION CGAS1(30), CGAS2(30), HTP(30), GAS(30), TIME(30), CUF(30), CUB(30), 
GAMA1(30), GAMA2(30), DIA(30), SURFAS(30), CUB2(30), CUB1(30), GAMA3(30), 
GAMA4(30), C301(30), D30(30), P30(30), CUF(30), CBF(30), 
CGAS1 = HTP*(1 - CGAS1) / (1 + 1.003*GAS*TIME)
CGAS2 = HTP*(1 - CGAS2) / (1 + 1.003*GAS*TIME)
GAMA1 = GAMA1 + 1/2
GAMA2 = GAMA2 + 1/2
GAMA3 = GAMA3 + 1/2
GAMA4 = GAMA4 + 1/2
CUB1 = CUB1 + 1/2
CUB2 = CUB2 + 1/2
DIA = DIA + 1/2
SURFAS = SURFAS + 1/2

DO 84 IT = 1, II
SURFACE CONCENTRATION OF CU++
CGAS1 = HTP*(1 - CGAS1) / (1 + 1.003*GAS*TIME)
CGAS2 = HTP*(1 - CGAS2) / (1 + 1.003*GAS*TIME)
GAMA1 = GAMA1 + 1/2
GAMA2 = GAMA2 + 1/2
GAMA3 = GAMA3 + 1/2
GAMA4 = GAMA4 + 1/2
CUB1 = CUB1 + 1/2
CUB2 = CUB2 + 1/2
DIA = DIA + 1/2
SURFAS = SURFAS + 1/2

THE OH- CCAC IN FHCAATE
DPH = 1.00 - 1.4 + 1.4*(PHI(1)) + GAMA2*TIME*SURFAS / 1.003
CC12
CC13
CC14
CC15

THE D1 TO D5 DISTRIBUTION FACTOR OF SPECIES 1
D1 = GAMA1 + 1.003/CUB
D2 = GAMA2 + 1.003/CUB
D3 = GAMA3 + 1.003/CUB
D4 = GAMA4 + 1.003/CUB
D5 = GAMA5 + 1.003/CUB

WRITE (3, 90)
WRITE (3, 87) NC(1), CGAS1(1), CGAS2(1), GAMA1(1), GAMA2(1), GAMA3(1), D1(1)
0024  FORMAT(14, 10D10.3, 1F7.3)
0025  SC FORMAT(///, 'RUN', 1X, 'CU++ GAS', 2X, 'CLCH+ GAS', 1X, 'GAMA CU++', 1X, '
     1GAMA CUH++, 1X, 'GAMA CUT', 1X, 'GAMA CU+', 2X, 'DSF CUHP+', 1X, 'DSF CLT
     31, PFF, ///)
CC26  RETURN
CC27  END
SUBROUTINE FCF(V,GAS,PCUPPA,T,CUP,C15,NC)

ERROR ANALYSIS (CALCULATE THE ABSOLUTE VALUE OF DISTRIBUTION FACTOR
OF EXPERIMENTAL RESULTS.

IMPLICIT REAL(A-H,O-Z)

DIMENSION V(15),C5(15),BUBRAT(15),CUB(15),CF(15),ERR(15),HF(15)
1,NG(15),KG(15),KG1(15),KN(15),KN1(15),HX(15),HX1(15),HY(15),HY1(15),CF(15)
215),CUB(15),KN1(15),NO(30)

DC 10 1=1,11

CUB1=CC(1)*1.0C*0.03

CUB(1)=CF(1)*1.0C*0.03

HF1=V(1)*0.001

WN1=BUBRAT(1)*40.03

KG1=1.0GAS(1)*0.05

KN1=CF(1)*0.01

HY1=CF(1)*0.01

WF1=(CF(1)/CUB(1)-1.0)/(565.48*BNBRAT(1)*GAS(1)**2.0)**0.3333

WN1=-V(1)*(CF(1)/CUB(1)-1.0)/(1.0*(565.48*BNBRAT(1)*GAS(1)**4.0*GAS(1)
1)**2.0)**0.3333

KG1=-2.0*V(1)*(CF(1)/CUB(1)-1.0)/(3.0*(565.48*BNBRAT(1)*GAS(1)
1)**5.0)**0.3333

HY1-V(1)/(CF(1)*(565.48*BNBRAT(1)*GAS(1)**2.0)**0.3333

HX1=-V(1)*CF(1)/(1*(565.48*BNBRAT(1)*GAS(1)**2.0)**0.3333*CUB(1)
1)**2.0)

ERR1=(WF1*WF1+WF1*HY1+HY1*HY1+HY1*KG1+KG1*KG1+KG1*KN1+KN1*KN1+KN1*HX1
1+HX1*HX1+HX1*HX1)**2.0)

DF1=V(1)*(CF(1)/CUB(1)-1.0)/(1*(565.48*BNBRAT(1)*GAS(1)**2.0)**2.0)

13333)

ERR1=ERROR1/DF1

CONTINUE

WRITE(3,5) (AC(I), I=1,11)

WRITE(3,7) (DF(I), I=1,11)

WRITE(3,6) (ERROR1, I=1,11)

WRITE(3,8) (ERR1, I=1,11)

5 FORMAT(2X,1X,1X,1X,1X,12.10)

6 FORMAT(1X,1X,1X,1X,1X,12.10)

7 FORMAT(2X,1X,1X,1X,1X,12.10)

8 FORMAT(2X,1X,1X,1X,1X,12.10)

RETURN

END
PURPOSE OF THIS PROGRAM
CALCULATES THE THEORETICAL AND EXPERIMENTAL VALUES OF DISTRIBUTION FACTOR OF IONS FOR THE SYSTEMS CONTAINING THE METAL IONS.
THE INDEPENDENT VARIABLE IS THE MOLAR FRACTION OF "LIGHT" METAL.
THE THEORETICAL BACKGROUND IS BASED ON THE GOUY-CHAPMAN DIFFUSE DOUBLE LAYER THEORY.

DESCRIPTION OF PARAMETERS

PH : PH OF THE SOLUTION FIXED, PRESET VALUE
Z : VALANCE OF SPECIES I IN THE SOLUTION
B : CORRELATED CONSTANTS FOR THE ACQUAINT OF HAC3 VS PH
XK,XT, XA, XF, XN AND XG : POULTZMANN CONSTANT, ABSOLUTE TEMPERATURE,
ELECTRIC CONSTANT, ELECTRONIC CHARGE, AVOGADRO NUMBER AND SURFACE EXCESS OF SURFACTANT, NADIR.
CONC : EQUILIBRIUM CONSTANTS FOR THE SIMULTANEOUS EQUATIONS GOVERNING THE EQUILIBRIUM RELATIONS IN THE SOLUTION.
CONC1 & CONC2 : PRESET METAL CONCENTRATIONS
X1 TO X5 : EFFECTIVE RADIUS OF SPECIES I IN THE SOLUTION
DTF1 TO DTF5 : DISTRIBUTION FACTOR OF SPECIES I IN THE SOLUTION.
ALF21 : RELATIVE SEPARATION COEFFICIENT OF METAL 2 TO METAL 1.

METHOD OF USE

1. THEORETICAL PART

2. EXPERIMENTAL PART
CALL SUBROUTINE LTK RIGHT AFTER ALL THE EXPERIMENTAL DATA ARE READ IN TO GIVE ALL THE RESULTS ANTICIPATED.

IMPLICIT REAL*8 (A-H, I-C, Y)
DIMENSION BUFRAT(30), DTF2(10), CON(10), WM(5), CO(10), SH(10), S(10), F(130), F1(30), G(30), G(30), GB(30), GR(30), GF1(30), GF2(30), CB5(30), D2BSF(30), CLB(30), CUF(30), PHF(30), PHB(30), WTF(30), GAS(30), THF(30), C31A(30), SURFAS(30), NO(30), FO(30), GTF(10), A(15), B(10), C(15), H(30), AC4(15), PH(10), D(10), CCNC(15), GB3(30), GB5(30), GF3(30), GF5(30), CB5(30), CDF(30), CON(10), CON2(10), DTF3(10), DTF5(10), ALF21(10), GAMA21(10), 6CON21(10), V(15), GAMA1(15), GAMA2(15), GAMA3(15), GAMA5(15), GDBS(30)

INTEGER Z(20)
READ(1,3) (Z(I), I=1,10)
READ(1,3) (E(I), I=1,3)
READ(1,1) X, Y, Z, A, X, X, X, X, X
DO 11 J=1,3
READ(1,1) (CONC(I), I=1,7)
READ(1,1) X1, X2, X3, X4, X5
DO 11 X4
READ(1,3) Y
DO 25 I=1,11
READ(1,60) NO(I), PHB(I), PHF(I), WTF(I), TIME(I), GAS(I), BUFRAT(I)
READ(1,1) CUF(I), CUR(I), CDF(I), CDE(I), DBSF(I), DOSB(I)
FORMAT(13,2F5.3,F7.4,2F5.2,F6.1)
DIA(I)=6.*GAS(I)/13.14155*5.*BUFRAT(I)**0.333333
SURFAS(I)=5.*3.14159*BUFRAT(I)**DIA(I)**DIA(I)
V(I)=-TF(1)/TF(1)
25 CONTINUE
DO 61 N=1,11
F(N)=1./(10.*P(HF(N)))
G(N)=10.**(G(N)+A(2)+PHB(N)+E(3)*PHF(N))**2
G(N)=10.**(B(1)+B(2)*PHF(N)+B(3)*PHF(N))**2
61 CONTINUE
DO 62 A=1,11
CONC(10)=CB5(N)
CONC(9)=CDF(N)
CONC(10)=DBSF(N)
CONC(11)=CCNC(8)+CCNC(9)+G(N)
CALL ECILBM(F,CONC,A,C,AC,N,1,PCT)
GB1(N)=AC(1)
GB2(N)=AC(2)
C
C
CC33
GD3(N)=C(3)
CC34
GD3(N)=AC(5)
CC35
CONC(9)=CUB(9)
CC36
CONC(9)=CDF(9)
CC37
CONC(10)=DSF(9)
CC38
CONC(11)=CCNC(A)+CCNC(S)+C1(N)
CC39
CALL EQILBO(F1,CCNC,A,C,AC,K,1,PCT)
CC40
GF1(K)=AC(1)
CC41
GF2(A)=AC(2)
CC42
GF3(N)=AC(3)
CC43
GF5(N)=AC(5)
CC44
62 CONTINUE
CC45
CALL LTK(GD1,GB1,GF1,GF2,II,HTF,GAS,TIME,CLIA,CUB,PHB,PHF,CUF,SURFA)
CC46
WRITE(3,16)
CC47
CALL RCH(V,GAS,EBRAD,GB1,GF1,II,NC)
CC48
WRITE(3,9)
CC49
DO 19 N=1,II
CC50
WRITE(3,97)
CC51
CONC(8)=CUB(N)
CC52
CONC(9)=CUB(N)
CC53
CONC(10)=DSF(N)
CC54
CONC(11)=CCNC(S)+CCNC(9)+G(N)
CC55
CALL EQILBOM(F,CONC,A,C,AC,N,1,PCT)
CC56
IF(PCT .LT. 0.1) GC TO 95
CC57
GOTO 19
CC58
55 WRITE(3,96) PCT
CC59
PCT=0.1
CC60
56 DO 90 L=1,8
CC61
XG=PCT*GERS(L)
CC62
CALL PCEF(2,AC,XX,XT,XA,XE,XA,XG,V114,YK1)
CC63
CALL HIKF(XX,XT,XE,YL,XZ,XF,XS,Z,V114,YK1,V111,Y112,V113,V115)
CC64
CALL INTEG(2,AC,XX,XT,XA,XG,XH,V111,P,TF,V111,1)
CC65
CALL TFP(1)=TF*TF
CC66
CALL INTEG(2,AC,XX,XT,XA,XE,XN,V111,P,TF,V112,2)
CC67
GFO2(L)=TF*(F+2)*F*SC*(1./((1.00-03*AC(2)*XT)*DSQRT(V112)-DSQRT(V111)))
ALF21(L) = CTF2(L) / CTF1(L)

GAMA21(L) = CTF2(L) * AC(2) / (CTF2(L) * AC(2) + DTF1(L) * AC(1))

GAMA1(L) = DTF1(L) * AC(1) * 1.0CD-03

GAMA2(L) = DTF2(L) * AC(2) * 1.0CD-03

WRITE(3,91) NCI(N), GAMA21(L), ALF21(L), GAMA1(L), CTF1(L), GAMA2(L), DTF1(L), PCT

IF(L-2) 100, 101, 102

100 PCT=0.1

GO TO 90

101 PCT=0.20

GO TO 90

GO TO 90

102 IF(L-4) 103, 104, 1C5

103 PCT=0.30

GO TO 90

104 PCT=0.40

GO TO 90

105 IF(L-4) 1C6, 1C7, 1C8

106 PCT=0.50

GO TO 90

107 PCT=0.60

GO TO 90

1C8 PCT=1.00

GO TO 90

GDBS(N)=3,1C6D-10

CONTINUE

WRITE(3,91)

CONTINUE

CONTINUE

FORMAT(20,11.4)

FORMAT(15T2)

FORMAT(/,5X, "ERROR ANALYSIS (CALCULATE THE ABSOLUTE VALUE OF DF")

FORMAT(/,2X, "1")

FORMAT(5X, "1", 15, 1C11.4)

FORMAT(5X, "RATIC CF CES/ERS IN BULK = " , 1D11.4)


1, "GAMA2", 6X, "CTF2", 5X, "PERCENTAGE", )

RETURN

END
SUPPLEMENTARY EQUATIONS (F, C, CAC, K1, L, PCT)

CALCULATES THE EQUILIBRIUM CONCENTRATION OF THE EXISTING SPECIES
IN THE SOLUTION BASED ON THE REGULATED REGULA-FALSI POSITION METHOD.

A & AC = CONCENTRATION OF SPECIES IN THE SOLUTION.
CNC = EQUILIBRIUM CONSTANT
H = HYDROGEN CONCENTRATION

IMPLICIT REAL = 8TA-MC-Z)

DIMENSION A(15), AC(15), C(15), H(15), CCNC(15)

A(1) = 1.000E-05
A(2) = 1.000E-05
A(3) = 1.000E-05
A(4) = 1.000E-05
A(5) = 1.000E-05
A(6) = 1.000E-05
A(7) = 1.000E-05
A(8) = 1.000E-05
A(9) = 1.000E-05
A(10) = 1.000E-05
A(11) = 1.000E-05

CO.1 = 1.000
CO.2 = 0.5*A(2)/((1.0*A(1)*CCNC(1))/A(2)*H(1))
CO.3 = 0.5*A(3)/((1.0*A(2)*CCNC(2))/A(3)*H(3))
CO.4 = 0.5*A(4)/((1.0*A(3)*CCNC(3))/A(4)*H(4))
CO.5 = 0.5*A(5)/((1.0*A(4)*CCNC(4))/A(5)*H(5))
CO.6 = 0.5*A(6)/((1.0*A(5)*CCNC(5))/A(6)*H(6))
CO.7 = 0.5*A(7)/((1.0*A(6)*CCNC(6))/A(7)*H(7))
CO.8 = 0.5*A(8)/((1.0*A(7)*CCNC(7))/A(8)*H(8))
CO.9 = 0.5*A(9)/((1.0*A(8)*CCNC(8))/A(9)*H(9))
CO.10 = 0.5*A(10)/((1.0*A(9)*CCNC(9))/A(10)*H(10))
CO.11 = 0.5*A(11)/((1.0*A(10)*CCNC(10))/A(11)*H(11))
CO.12 = 0.5*A(12)/((1.0*A(11)*CCNC(11))/A(12)*H(12))
CO.13 = 0.5*A(13)/((1.0*A(12)*CCNC(12))/A(13)*H(13))
CO.14 = 0.5*A(14)/((1.0*A(13)*CCNC(13))/A(14)*H(14))
CO.15 = 0.5*A(15)/((1.0*A(14)*CCNC(14))/A(15)*H(15))

1 CONTINUE
C(1) = A(2)*H(1)/A(1)
C(2) = A(4)*H(3)/A(2)
C(3) = A(6)*H(5)/A(4)
C(4) = A(8)*H(7)/A(6)
C(5) = A(10)*H(9)/A(8)
C(6) = A(12)*H(11)/A(10)
C(3) = A(3) / (A(1) * A(6) * A(4))
C(4) = A(10) / (A(8) * A(11) * A(4))
C(5) = A(7) / (A(11) * A(6))
C(6) = A(11) / (A(8) * A(6))
C(7) = A(4) + K / A(5)
C(8) = A(1) * A(2) + A(3) + A(7)
C(9) = A(0) * A(9) * A(10) + A(11)
C(10) = A(4) + A(3) + A(10) + A(10) + A(5)
C(11) = A(6) + A(7) + A(11)
AC(1) = A(1)
AC(2) = A(8)
AC(3) = A(2)
AC(4) = CONC(10)
AC(5) = A(9)
AC(6) = H(K)
AC(7) = A(6)
AC(8) = A(7)
AC(9) = A(4)
AC(10) = A(11)
PCT = A(4) / CONC(10)
RETURN
END
SUBROUTINE ROOT (Z, AC, XK, XT, XE, XN, XG, V1, YK1)

IMPLICIT REAL*8(A-H, L-J, Z, K, M, N)

DIMENSION AC(15)

INTEGER Z(20)

Z(7) = -Z(7)
Z(9) = -Z(9)

YK = 8.4*3.14159*Z(4)*Z(4)*XE*XE*E-1.0D-03*XN*AC(4)/(XN*XK*XT)

YK1 = SQRT(YK)

TT1 = XE*XG*XK

TT = XK*XT*XA*XN*1.0D0/(2.0*3.14159)

V1 = 15.0

V2 = 100.0

SUM1 = 0.0

SUM2 = 0.0

DO 10 N = 1, 10

SUM1 = SUM1 + AC(N) * (V1 * Z(N) - 1.0) * 1.0D0 - 03

10

SUM2 = SUM2 + AC(N) * (V2 * Z(N) - 1.0) * 1.0D0 - 03

T1 = SQRT(TT * SUM1)

T2 = SQRT(TT * SUM2)

F1 = T1 - T11

F2 = 12 - T11

FF = F1 * F2

IF(FF) 12, 13, 13

V2 = V2 + 35

IF(N GT 900) GO TO 19

M = 1

GO TO 9

9

M = 1

Y = (V2 - V1) * C * DS(F1) * (CABS(F1) * CABS(F2))

V3 = V1 + Y

SUM3 = SUM3 + AC(N) + (V3 * Z(N) - 1.0) * 1.0D0 - 03

T3 = SQRT(TT * SUM3)

F3 = T3 - T11
AA1 = CAB5(Y/V3)
IF(AA1 .LE. 1.0E-06) GO TO 1F
FF = F14F.3
IF(FF) 16, 15, 17
16 V2 = V3
SUM2 = 0.0
CO N = 1, 10
8 SUM2 = SUM2 + AC(N)/(V2 + Z(N) - 1.0) - 1.0E-03
10 M = M + 1
1F M .GT. 800) GO TO 19
GO TO 11
17 V1 = V2
SUM1 = 0.0
DO 10 K = 1, 10
7 SUM1 = SUM1 + AG(N)*(V1 + Z(N) - 1.0)*1.0E-03
10 GC, TC 10
19 WRITE (3, 47) K
47 FORMAT (2X, 1 NO CONVERGENCE, NUMBER OF ITERATIONS = ', I6)
GO TO 1F
15 V11 = V3
47 FORMAT (2X, 1 NO CONVERGENCE, NUMBER OF ITERATIONS = ', I6)
RETURN
END
SURGUTIAN. INTEG. (7, AC, X, XT, X', X, XX, V22, P, TF, V33, Z, KK)

C

CPP1

CPP2

IMPLICIT REAL*8 (A-H, O-Y)

DIMENSION AC(15), U(600), C(600)

CPP3

CPP4

CPP5

CPP6

CPP7

CPP8

CPP9

CPP10

CPP11

CPP12

CPP13

CPP14

CPP15

CPP16

CPP17

CPP18

CPP19

CPP20

CPP21

CPP22

CPP23

CPP24

CPP25

CPP26

CPP27

CPP28

CPP29

CPP30

CPP31

CPP32
SUROUNIING MICI*(XK, X1, X2, X3, X4, X5, YK1, YK2, YK3, YK4, YK5, YK6)

0001

0002 IMPLICIT REAL*(A-H, O-Z)

0003 INTEGER Z(20)

0004 FY4=-DLG(1*YK4)*XK*X1/XE

0005 TN4=CTAH((2*(4)*XK*FY4/(4)*(XK*X1))

0006 TN1=TN4/CEXP(YK1*(X1-X4))

0007 TN2=TN4/CEXP(YK1*(X2-X4))

0008 TN3=TN4/CEXP(YK1*(X3-X4))

0009 TN5=TN4/CEXP(YK1*(X5-X4))

0010 FY=DLG((1+TN1)/(1-TN1))/2.

0011 FYY=DLGC((1+TN2)/(1-TN2))/2.

0012 FYYF=DLGC((1+TN3)/(1-TN3))/2.

0013 FYYY=DLGC((1+TN5)/(1-TN5))/2.

0014 FY1=FY*4.*XK*X1/(2(1)*XE)

0015 FY2=FY*4.*XK*X1/(2(1)*XE)

0016 FY3=FY*4.*XK*X1/(2(1)*XE)

0017 FY5=FY*4.*XK*X1/(2(1)*XE)

0018 Y11=DEXP(-XE*FY1/(XK*X1))

0019 Y12=DEXP(-XE*FY2/(XK*X1))

0020 Y13=DEXP(-XE*FY3/(XK*X1))

0021 Y15=DEXP(-XE*FY5/(XK*X1))

0022 RETURN

CC23 END
SUBROUTINE QEF (F,Y,Z,NDIM)
IMPLICIT REAL*4(A-H,Z-1)
DIMENSION Y(6CC),Z(6CC)

PARAMETERS H-THE INCREMENT OF ARGUMENT VALUES, Y-THE INPUT VECTOR
OF FUNCTION VALUES, Z-THE RESULTING VECTOR OF INTEGRAL VALUES. Z
MAY BE IDENTICAL WITH Y

METHOD BEGINNING WITH Z(1)=0.0 EVALUATION OF VECTOR Z IS DONE
BY MEANS OF SIMPSONS RULE TOGETHER WITH NEWTONS 3/8 RULE OR A
COMBINATION OF THESE TWO RULES. TRUNCATION ERROR IS OF ORDER H**5
( I.E., FOURTH ORDER METHOD). ONLY IN CASE NDIM=3 TRUNCATION ERROR
OF Z(2) IS OF ORDER H**4

HT=.33333333*H
IF(NDIM = 5) 7,8,1

1 SUM1=Y(2)+Y(2)
SUM1=SUM1+SUM1

2 SUM1=HT*(Y(1)+SUM1)+Y(3)

3 AUX1=Y(4)+Y(4)
AUX1=AUX1+AUX1

4 AUX1=SUM1+HT*(Y(3)+AUX1+Y(5))

5 AUX2=HT*(Y(1)+3.875*(Y(2)+Y(5))+2.625*(Y(3)+Y(4))+Y(6))

6 SUM2=Y(5)+Y(5)

7 SUM2=SUM2+SUM2

8 SUM2=AUX2+HT*(Y(4)+SUM2)+Y(6))

9 Z(1)=C,C

10 AUX=Y(3)+Y(3)
AUX=AUX+AUX

11 Z(2)=SUM2-HT*(Y(2)+ALX+Y(4))

12 Z(3)=SUM1
13 Z(4)=SUM2
14 IF(NDIM = 5) 5,5,2

INTEGRATION LOOP

2 DO 4 I=7,NDIM+2
SUM1=AUX1

3 4 CONTINUE
0025          SUM2=AUX2
           
0026          AUX1=Y(I-1)+Y(I-1)
0027          AUX1=AUX1+ALX1
0028          AUX1=SUM1+HT*(Y(I-2)+AUX1+Y(I))
0029          Z(I-2)=SUM1
0030          IF(I-NCIM) 3 6 6
0031          3 AUX2=Y(I)+Y(I)
0032          AUX2=ALX2+ALX2
0033          AUX2=SUM2+HT*(Y(I-1)+AUX2+Y(I+1))
0034          4 Z(I-1)=SUM2
0035          5 Z(NDIM-1)=AUX1
0036          Z(NCIM)=AUX2
0037          RETURN
0038          6 Z(NCIM-1)=SUM2
0039          Z(NCIM)=AUX1
0040          RETURN
0041          C END OF INTEGRATION LCCP.
0042          7 IF(NCIM-3) 12 11 8
0043          C NDIM IS EQUAL TC 4 CR 5
0044          8 SUM2=1.25*HT*(Y(I)+Y(2)+Y(2)+Y(2)+Y(3)+Y(3)+Y(3)+Y(4))
0045          SUM1=Y(2)+Y(2)
0046          SUM1=SLPI+SLPI
0047          SUM1=HT*(Y(I)+SUM1+Y(3))
0048          Z(I)=0.0
0049          AUX1=Y(3)+Y(3)
0050          AUX1=AUX1+SUM1
0051          9 Z(2)=SUM2-HT*(Y(2)+AUX1+Y(4))
0052          IF(NDIM-4) 10 6 5
0053          9 AUX1=Y(4)+Y(4)
0054          CC42          AUX1=ALX1+ALX1
0055          AUX1=SUM1+HT*(Y(3)+AUX1+Y(5))
0056          10 Z(3)=SUM2
0057          Z(4)=SUM1
0058          6 RC=VRF(N)
0059          7 NDIM<EQUAL TC 3
0060          8 SUM1=HT*(1.25*Y(I)+Y(2)+Y(2)-0.25*Y(3))
0061          9 SUM2=Y(2)+Y(2)
SUBROUTINE LTK(CU1,CUB2,CU3,CU4,CU5,CU6,CU7,CU8,CU9,H,T,F,G,A,S,T,H,F,CUO,PH,PHF
1,CUF,SURFAS,NO,CDBS,CBSF,CUB3,CUB5,CUF3,CUF5,CCD,CCF,J,GAM/2)

CALCULATES THE DISTRIBUTION FACTOR OF SPECIES FROM THE EXPERIMENTAL RESULTS.

IMPLICIT REAL*8(A-H,L-Z)

DIMENSION CGAS1(30),CGAS2(30),HTF(30),GAS(30),T,H,F(30),CU1(30),CU2(30),
1,2(30),GAM(30),GAHA(30),GAMA2(30),DIA(30),SUPFAS(30),CU2F(30),
3(30),CUB3(30),CUB5(30),CUB6(30),CUB7(30),CUB8(30),CUF3(30),
4D4(30),CUB3(30),CUB5(30),CUB7(30),CUB8(30),CUB9(30),CUB10(30),
DP1(30),CUB11(30),GLA(30),GAMA3(30),GAMA4(30),GAMA5(30),GAM(2(30),D5(
6301,ALF1(30),GAMA21(30),GAM21(30),CC(30)

DO 1 M=1,11

SURFACE CONCENTRATION OF H++ AND H2++ (RADIUS OF H1++ > H2++)

CGAS1(H)+HTF(H)+(CUF1(H)-CU1(H))/6.*1.*CO3*GAS(H)*TIME(H)
CGAS2(H)+HTF(H)+(CUF2(H)-CU2(H))/6.*1.*CO3*GAS(H)*TIME(H)

SURFACE CONCENTRATION OF CH+ AND H2OH+

CGAS3(H)+HTF(H)+(CUF3(H)-CU1(H))/15.*1.*CO3*GAS(H)*TIME(H)
CGAS4(H)+HTF(H)+(CUF4(H)-CU2(H))/15.*1.*CO3*GAS(H)*TIME(H)

GAMA1 TO GAMA5 SURFACE EXCESS OF SPECIES I

GAMA1(H)=CGAS1(H)*DIA(H)
GAMA2(H)=CGAS2(H)*DIA(H)
GAMA3(H)=CGAS3(H)*DIA(H)
GAMA4(H)=CGAS4(H)*DIA(H)
GAMA5(H)=CGAS5(H)*DIA(H)

CC12
CUFCH=CUB1(H)+6.*1.*CO3*GAS(H)+GAMA1(H)+GAMA3(H)*TIME(H)/(DIA(H)
1+HTF(H))

CC14
CC+6.*1.*CO3*GAS(H)+(GAMA2(H)+GAMA5(H))*TIME(H)/(C14(H
1+HTF(H))

CC15
ERROR1(H)=100.*(CCFC(H)-CCF(H))/CCF(H)

ERROR2(H)=100.*(CCFC(H)-CCF(H))/CCF(H)

THE CH+C3AC IN PHASE

DP=1.00-14*(1.00*PHB(H))+(GAMA3(H)+GAMA5(H))*TIME(H)*SURFAS

1/1.00-1/3

DPH(H)=1.00-1/4*CP+H

PHF1(H)=-CLOG10(CP+H)
C C
GAHA7(M)=WTF(M)*(CEF(M)-CEE(M))/(SURFAS(M)*TIME(M)**1.0*COC3)
0024
0025
0026
0027
0028
D3(M)=GAHA3(M)**1.0*COC3/CUB3(M)
D4(M)=GAHA9(M)**1.0*COC3/CBSB(M)
D5(M)=GAHA5(M)**1.0*COC3/CUE5(M)
ALF21(M)=D2(M)/D1(M)
GAMA21(M)=GAMA21(M)/(GAMA21(M)**1.0+GAMA1(M))
CON21(M)=CEE(M)/(CEE(M)**1.0+CUE(M))
D1 TO D5 DISTRIBUTION FACTOR CF SPECIES
1 CONTINUE
IF(J-2)=5,6,7
5 WRITE(3,2)
GO TO 8
6 WRITE(3,9)
GO TO 8
7 WRITE(3,10)
DO 8 P=1,11
8 WRITE(3,4) NO(M),CCE21(M),GAMA21(M),ALF21(M),CI(M),D2(M),D3(M),D5(M)
1H,M1,M2,M3,M4,PFBH(M),PFFH(M),PHF1(M)
WRITE (3,15)
GAMA1(M),GAMA2(M),GAMA3(M),GAMA5(M)
15 FORHA7(37X,11.4)
6 FORMAT(14,9(11.4,3F7.3))
2 FORMAT(1H1,,/,'RUN',1X,'CE/(CD+CU)',2X,'GAMA21',4X,'ALPHA21',4X,'I'
1DTF CU++,3X,'DTF CD++',3X,'DTF CUCH++,2X,'DTF CCH++',3X,'GAMADBS'
2,5X,'CEF CBS',3X,'PFB',4X,'PFF',2X,'CAL PFF',) 2)
9 FORMAT(1H1,,/,'RUN',1X,'PB/(PD+CD)',2X,'GAMA21',4X,'ALPHA21',4X,'I'
1DTF CU++,3X,'DTF PB++',3X,'DTF PUCH++,2X,'DTF PCH++,3X,'GAMADBS'
2,5X,'CEF CBS',3X,'PFB',4X,'PFF',2X,'CAL PFF',) 2)
10 FORMAT(1H1,,/,'RUN',1X,'PB/(PD+CD)',2X,'GAMA21',4X,'ALPHA21',4X,'I'
1DTF CD++,3X,'DTF PB++',3X,'DTF CDOH++,2X,'DTF PDOH++,3X,'GAMADBS'
2,5X,'CEF CBS',3X,'PFB',4X,'PFF',2X,'CAL PFF',) 2)
CC46 RETURN
0047 END
SUBROUTINE PCH(V,GAS,BURAT,CUB,CUF,I1,NC)
C ERROR ANALYSIS (CALCULATE THE ABSOLUTE VALUE OF DISTRIBUTION FACTOR
OF EXPERIMENTAL RESULTS.)
C
DO 10,1=1,2
CUB(I)=CUB(I)*1.00-0.3
CUF(I)=CUF(I)*1.00-0.3
HF(I)=V(I)+C0.01
WN(I)=BURAT(I)*C0.03
WG1(I)=GAS(I)*0.05
HX(I)=CUB(I)*0.01
HY(I)=CUF(I)*0.01
HF(I)=(CUF(I)/CUB(I))**2.0)/(3.0*(565.488*BURAT(I)**4.0*(GAS(I)**2.0)*C0.3333)
WN(I)=V(I)*(CUB(I)/CUB(I)-1.0)/(3.0*(565.488*BURAT(I)**4.0*(GAS(I)**2.0)*C0.3333)
HW(I)=V(I)*(CUB(I)/CUB(I)-1.0)/(3.0*(565.488*BURAT(I)**4.0*(GAS(I)**2.0)*C0.3333)
2*HY(I)**C0.5
133331
CC19
10 CONTINUE
WRITE(3,5) (AC(I),I=1,11)
WRITE(3,7) (CF(I),I=1,11)
WRITE(3,6) (ERPCR(I),I=1,11)
WRITE(3,8) (ERR(I),I=1,11)
5 FORMAT (2X,10X,13110)
6 FORMAT (1X,4F10.9)
7 FORMAT (2X,10X,12C6.3)
8 FORMAT (2X,10X,12C6.3)
END