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The effect of single electrolytes on the vapor-liquid equilibrium of mixed solvents

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THE EFFECT OF SINGLE ELECTROLYTES ON THE VAPOR-LIQUID EQUILIBRIUM OF MIXED SOLVENTS

by

Peggy Tomasula

Dissertation submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree of
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ABSTRACT

A group-contribution model for the prediction of salt-effects on the vapor-liquid equilibria of multicomponent electrolytic solutions containing a single electrolyte is presented. Coulombic interactions are represented through a Pitzer term. Solvation effects and short-range interactions are represented through a UNIQUAC-type expression. An ion-size, a solvation and three ion-solvent interaction parameters per salt-solvent binary are required for multicomponent predictions.

All parameters are obtained only through the correlation of binary salt-solvent osmotic coefficient and vapor-pressure depression data at 25°C, in most cases, and binary solvent VLE data. The salt-solvent binary data were correlated with an average percent error in Φ of 2.5 and an average percent error in P of 0.35 mm Hg up to a molality of 6 for 1-1 and 2-1 salts. The model is also useful in the prediction of aqueous binary salt data up to a molality of 6 and 200°C and nonaqueous binary salt data up to a molality of 6 and 60°C.

Methods are also presented for the estimation of the ion-solvent interaction parameters needed for multicomponent prediction when the constituent binary data are not available.

25 data sets of isothermal and isobaric salt-alcohol-water and salt-alcohol mixtures were predicted using the binary interaction parameters and gave an average absolute error in the vapor phase composition of 0.019. The model predicts correctly the salting-in of the appropriate component.

Vapor-pressure depression data of NaI, KCH_3COO, NaSCN, and NH_4SCN in methanol at temperatures of 25 and 40°C were measured in the

molality range of 0.1-5.0 m using a static method, where the vapor pressure of the electrolytic solution is compared to that of the pure solvent.

Osmotic coefficients were calculated from the vapor pressure data. This data was used to obtain additional binary interaction parameters which could not be determined from the existing literature data.

PREFACE

The estimation of the effect of a single electrolyte on the vapor-liquid equilibrium of mixed solvents is often necessary in the modeling of chemical reaction equilibria and separation processes. While methods are available to predict nonelectrolytic solution phase-equilibria from little or no experimental data (Derr and Deal, 1969; Fredenslund, et al., 1975), those previously used for electrolytic solutions are usually limited to correlation of existing data. In addition, the lack of salt-nonaqueous solvent data prevented the development of such models.

Recently, two models (Rastogi, 1981; Sander, et al., 1984) have been proposed which have some prediction potential of salt effects on the VLE of mixed solvents. These models represent a significant advance in that the short-range interactions between all solvent species are accounted for through salt-solvent molecule (Rastogi) or ion-solvent molecule (Sander, et al.) parameters and solvent (A)-solvent (B) parameters. The long-range ion-ion interactions are represented through a Coulombic term. However, these models are basically useful for correlation purposes only.

Models in which the parameters are ion-solvent specific require a minimum of experimental data to effect prediction and it is the objective of this work to present such a model for the prediction of the VLE of mixed solvent systems consisting of one

salt. This model combines a Pitzer (1977) expression to represent Coulombic interactions, the Flory-Huggins expression (1941, 1942) to account for differences in the sizes of the solvent species and for the solvation of the ions by the solvents, and the residual term of the UNIQUAC (Abrams and Prausnitz, 1975) equation to account for the short-range interactions between all solvent species. The parameters, which are ion-specific, are evaluated from a binary data base of salts in water and alcohols.

The validity of the model is shown for mixed alcohol-water and mixed-alcohol solutions consisting of one salt.

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INTRODUCTION

Thermodynamic data for solutions containing a single electrolyte in a single solvent, and especially multiple solvents, are often needed in the modeling of separation processes and chemical reaction equilibrium. Osmotic coefficient data at 25°C for binary aqueous electrolytic solutions are available in the extensive compilations of Robinson and Stokes (1959). Vapor pressure depression data for binary aqueous electrolytic solutions at 100°C are tabulated in Weast (1970). Data at temperatures other than 25 and 100°C are very limited. (Snipes, et.al., 1975; Campbell and Bhatnagar, 1979; Holmes, and Mesmer, 1981) Osmotic coefficient and vapor pressure depression data for solvents other than water are scarce. (Janz and Tomkins, 1972; Bixon, et.al., 1979; Tomasula, 1980; Czerwienski, et.al., 1985)

Thermodynamic data for an electrolyte in mixed solvents are even more limited (Ciparis, 1966; Sada, et.al., 1975; Boone, et.al., 1976) and their prediction from binary data would be very useful for industrial applications.

Models for the correlation of nonelectrolytic solution data, such as the Margules (1895) and NRTL (Renon and Prausnitz, 1968) equations, have been applied to the correlation of ternary electrolytic solutions consisting of a salt, water, and an alcohol. (Schuberth, 1974, 1977; Schuberth and Nhu, 1976; Beckerman and Tassios, 1976; Mock, et.al., 1984) These models do not account for the long-range ionic forces, but give recognition to the short-range forces. Binary interaction parameters are evaluated from binary and ternary data.

Recently, three models (Rastogi, 1981; Hala, 1983; Sander, et.al., 1984) for the prediction of salt effects on the VLE of multicomponent electrolytic solutions containing one salt have been developed. Rastogi and Hala assume that the excess Gibbs free energy is the sum of two terms, a long-range Coulombic term to represent ion-ion interactions and a short-range term to represent the interactions between all solution species. Sander, et.al., add an entropic term to the long-range Coulombic term and the short-range term.

The Hala model combines a semi-empirical electrostatic term and the Wilson (1964) equation. The LiCl-water-methanol system at 60°C was predicted from four binary salt-solvent parameters and two solvent-solvent interaction parameters evaluated from binary data at 60°C. The model was not applied to the prediction of other ternary systems.

The Rastogi model combines a modified Debye-Huckel equation and the NRTL equation. This model was used to predict salt-water-alcohol systems from binary salt-solvent and solvent-solvent interaction parameters alone. Prediction of salt-binary mixed solvent data is only possible up to 2m and when the constituent binary data are available. The model cannot be extended to more than two solvents.

Sander, et.al., combine the Debye-Huckel equation and the UNIQUAC equation. (Abrams and Prausnitz, 1975) The UNIQUAC parameters are functions of concentration and are ion-solvent specific. The ion-solvent specific parameters were established through the correlation of electrolytic single and binary mixed solvent data. Prediction was demonstrated for a few mixed solvent systems. However, prediction from ion-solvent parameters determined solely from binary data was not demonstrated.

All these models, however, are limited. The Rastogi model and that of Sander, et.al. are basically applicable to correlation of mixed solvent-single electrolyte systems. The Hala model was applied to one system only.

The difficulty in modeling electrolytic solutions is due to the phenomenon of salting-out. The addition of a salt to a binary or a higher order solvent system increases the vapor phase mole-fraction of the solvent with the smallest dielectric constant. The solvent with the largest dielectric constant is salted-in. While this behavior is not general; for example, in the $HgCl_2$-methanol-water system, methanol is salted-in by $HgCl_2$ and water is salted-out, it is the one of most interest in phase-equilibrium calculations. This effect is most pronounced in electrolytic solutions consisting of water and can be explained by the concept of solvation, where it is assumed that solvent molecules are bound to the ions.

Due to the long-range nature of ion-ion interactions, the addition of a small amount of salt to a solvent results in an increase in the solvent activity coefficient. As the concentration of the salt approaches an ionic strength of unity, short-range forces become important, and the solvent activity coefficient continues to increase until it reaches a maximum. The solvent activity coefficient then continues to decrease with increasing salt concentration.

The decrease in the solvent activity coefficient is a direct result of solvation. Increasing the concentration of the salt increases the number of ions in solution which in turn remove solvent molecules from the bulk solution. As more and more solvent molecules are removed from the solution, the vapor pressure of the solvent decreases.

The intermolecular forces which operate in binary electrolytic solutions also operate in salt-mixed solvent systems. Even though the constituent binary salt-solvent systems both exhibit negative deviations from Raoult's law at concentrations above 1 molal, typically only one of the solvents in a salt-mixed solvent system will exhibit a decrease in the solvent activity coefficient relative to its value in the salt-free solution. This phenomenon is often explained by the concept of preferential solvation, where the probability of finding solvent molecules with the higher dielectric constant in the vicinity of the ions is greater than that for the solvent molecules with the lower dielectric constant.

From the above discussion, it is apparent that a semi-empirical model for the representation of salt-effects must not only account for the long and short-range forces which operate in solution, but should also explicitly account for the removal of solvent molecules from the bulk solution by the ions.

While the Rastogi, Hala, and Sander models recognize this phenomenon indirectly through modifications of their respective long-range or short-range terms, solvation effects are not explicitly accounted for in their expressions.

The model presented here combines a Pitzer (1977) expression to account for the long-range and short-range ionic interactions, the athermal Flory-Huggins (1941, 1942) expression to account for the entropic effects of the solvated species, and the residual term of the UNIQUAC equation to account for other short-range interactions not described by the model.

The parameters of the model, which are ion-solvent specific, are evaluated from binary electrolytic solution data. The model is applied to salt-mixed solvent systems to demonstrate its validity.

CHAPTER 1

Thermodynamics of Vapor-Liquid Equilibria

Electrolytes are generally classified into two groups. The first group are known as the strong or non-associated electrolytes and the second as the associated electrolytes. (Robinson and Stokes, 1959; Harned and Owen, 1958)

The strong electrolytes are those which dissociate into their component ions when in solution. While the ions may interact with the solvent; i.e., associate with the solvent, there is no association between the ions of opposite sign. In addition, salts of this type do not vaporize at moderate temperatures and pressures. Salts which are termed strong in aqueous solutions are not necessarily strong in nonaqueous solvents, where the low dielectric constant leads to ion-pairing. Salts such as the alkali halides and the alkaline-earth halides are strong in water.

Associated electrolytes are termed either weak electrolytes or ion-pairing electrolytes. Weak electrolytes exist as ions and molecular species in solution. Acids and bases, with the exception of the alkali metal and quaternary ammonium hydroxides, are weak electrolytes. The molecular electrolyte may enter the vapor phase but dissociates only at high temperatures. (Edwards, et.al., 1975)

Ion-pairing electrolytes are those in which the positive and negative ions associate. Bivalent metal sulphates in water and almost all other salts in nonaqueous solvents at high concentrations form ion-pairs. Salts of this type are not present in the vapor phase.

All electrolytes in this study are assumed to be strong electrolytes; i.e., complete dissociation is assumed in both aqueous and nonaqueous solvents. The electrolyte is not present in the vapor phase.

The condition for equilibrium for any solvent i in an electrolytic solution of N solvents is then:

$$\hat{f}_i^{\,V} = \hat{f}_i^{\,L} \qquad i = 1, 2, \ldots N \qquad (1\text{-}1)$$

where $\hat{f}_i^{\,L}$ is the fugacity of solvent i in the liquid phase and $\hat{f}_i^{\,V}$ is the fugacity of solvent i in the vapor.

The fugacity coefficient, $\hat{\Phi}_i$, of solvent i is used to represent the nonideality in the vapor phase.

$$\hat{f}_i^{\,V} = \hat{\Phi}_i \, y_i \, P \qquad (1\text{-}2)$$

y_i is the mole fraction of solvent i in the vapor and P is the total pressure. $\hat{\Phi}_i$ is unity for the ideal vapor and is approximately unity for systems at low pressures.

The fugacity of solvent i in the liquid phase is given by

$$\hat{f}_i^{\,L} = \gamma_i \, x_i \, f_i^{\circ} \qquad i = 1, 2, \ldots N \qquad (1\text{-}3)$$

where f_i° is the pure-component reference fugacity of solvent i at the temperature, T, and the pressure of the solution. γ_i, is the liquid phase solvent activity coefficient and will be discussed in Chapter 3. x_i, is the mole fraction of i calculated based on the total dissociation of the electrolyte, where, for the solvent

$$x_i = \frac{n_i}{\nu n_s + \sum_k n_k} \qquad (1\text{-}4)$$

$\sum_k n_k$ is the summation over all solvent species. n_s, is the analytical number of moles of electrolyte in the solution and ν is the total number of ions comprising the salt.

f_i° is defined by the following expression:

$$f_i^\circ = \Phi_i^s P_i^s \exp \int_{P_i^s}^{P} v_i \, dP/RT \qquad (1\text{-}5)$$

where Φ_i^s is the fugacity coefficient of pure solvent i evaluated at T and the vapor pressure, P_i^s, of i. v_i, is the molar liquid volume of pure i at T. It is not a function of pressure at low pressures.

The exponential term of equation (1-5), which is the Poynting effect, reduces to equation (1-6) at low pressures

$$\exp \int_{P_i^s}^{P} v_i dP/RT = \exp\,(P - P_i^s)v_i/RT \qquad (1\text{-}6)$$

The Antoine equation is used to calculate the vapor pressures, P_i^s, for the solvents in this study. The Hayden-O'Connell (1975) correlation for the prediction of second virial coefficients is used to calculate $\hat{\Phi}_i$ and Φ_i^s. The constants for the Antoine equation and the Hayden-O'Connell correlation are in Appendix A.

The Hankinson and Thomson (1979) correlation is used to calculate the pure-component liquid volumes, v_i. The method is discussed in Appendix B.

CHAPTER 2

The Gibbs Excess Free Energy, the Activity and the Activity Coefficient

The activity coefficient of solvent i is defined as the ratio of the activity of i to the mole fraction of i.

$$\gamma_i = a_i/x_i \qquad (2\text{-}1)$$

The activity of i is defined

$$a_i = \hat{f}_i/f_i^{\circ} \qquad (2\text{-}2)$$

where $\hat{f}_i$ is the fugacity of i at T, P, and constant composition and f_i° is the fugacity of i at T and a specified P and composition.

The excess Gibbs free energy is the difference between the actual total Gibbs free energy at T, P, and fixed composition and the ideal total Gibbs free energy at the same T, P, and x.

$$G^E = G\begin{bmatrix}\text{real at}\\ \text{T, P, x}\end{bmatrix} - G\begin{bmatrix}\text{ideal at}\\ \text{T, P, x}\end{bmatrix} \qquad (2\text{-}3)$$

Differentiation of equation (2-3) with respect to the number of moles of solvent i, n_i, at constant T, P, and n_j gives

$$\bar{g}_i^E = \bar{g}_i\ (\text{real}) - \bar{g}_i\ (\text{ideal}) \qquad (2\text{-}4)$$

where

$$\bar{g}_i\ (\text{real}) = \partial/\partial n_i\Big[G\ (\text{real})\Big]_{T,\ P,\ n_j} = \mu_i^{\circ} + RT \ln \hat{f}_i\ (\text{real}) \qquad (2\text{-}5)$$

and

$$\bar{g}_i\ (\text{ideal}) = \partial/\partial n_i\Big[(G(\text{ideal}))\Big]_{T,\ P,\ n_j} = \mu_i^{\circ} + RT \ln \hat{f}_i\ (\text{ideal}) \qquad (2\text{-}6)$$

μ_i° is the chemical potential of the standard state. The chemical potentials of the standard state in equations (2-5) and (2-6) are the same since the ideal and real solutions are at the identical T, P, and composition.

Substitution of equations (2-5) and (2-6) into equation (2-4) gives

$$\bar{g}_i^E = RT \ln \hat{f}_i \text{ (real)}/\hat{f}_i \text{ (ideal)} \qquad (2\text{-}7)$$

The activity of solvent i in an ideal solution is equal to the mole fraction of i. From equation (2-2), $\hat{f}_i$ (ideal) is given by

$$\hat{f}_i \text{ (ideal)} = f_i^\circ x_i \qquad (2\text{-}8)$$

$\hat{f}_i$ (real) is obtained directly from equation (2-2).

Substitution of equations (2-2) and (2-8) into equation (2-7) gives

$$\bar{g}_i^E = RT \ln a_i/x_i \qquad (2\text{-}9)$$

From the definition of the activity coefficient of i given in equation (2-1), the partial molar excess Gibbs free energy is

$$\bar{g}_i^E = RT \ln \gamma_i \qquad (2\text{-}10)$$

where

$$\bar{g}_i^E = \left[\partial G^E/\partial n_i\right]_{T,\ P,\ n_j} \qquad (2\text{-}11)$$

n_T is the total number of moles of species in the solution and

$$G^E = n_T g^E \qquad (2\text{-}12)$$

G^E is obtained from Euler's theorem, where

$$G^E = \Sigma_i\, n_i\, \bar{g}_i^E \qquad (2\text{-}13)$$

or

$$G^E/RT = \Sigma_i n_i \ln \gamma_i \qquad (2\text{-}14)$$

The activity coefficient of component i is easily determined from equations (2-10) and (2-11) given an expression for the excess Gibbs free energy, G^E. Conversely, the excess Gibbs free energy may be calculated from equations (2-13) and (2-14) given an expression for the activity coefficient, γ_i, of i.

Any expression for the molar excess free energy of a binary solution must obey the conditions:

$$\begin{aligned} \text{when} \quad x_1 &= 0 \quad g^E = 0 \\ x_2 &= 0 \quad g^E = 0 \end{aligned} \tag{2-15}$$

CHAPTER 3

Model Development

The thermodynamics of an electrolytic solution as of all solutions are determined by the forces which operate between the species of the solution. Assuming that the electrolyte dissociates into its constituent ions, interactions between the ions, between the ions and the solvent molecules, and between the solvent molecules must be considered. These interactions may be loosely categorized as physical or chemical in nature.

The forces between the ions are the long-range Coulombic interactions, which are important only in dilute solutions. The short range ion-solvent molecule interactions, such as dispersion forces, ion-dipole, and ion-induced dipole forces, become important as the concentration of the electrolyte is increased. (Bockris and Reddy, 1977). The molecule-molecule interactions are also short-range in nature. These interactions may be classified as induction forces between a permanent dipole (or quadrupole) and an induced dipole, electrostatic forces between permanent dipoles and higher poles, or dispersion forces between non-polar molecules. (Prausnitz, 1969)

Strong physical forces can lead to the formation of loosely bound species. They are referred to as chemical forces and lead to the phenomena of association and solvation. Association results from the formation of polymers, as in the case of water or methanol which are known to hydrogen bond. Solvation refers to the formation of complexes between unlike molecules. Solvation effects cause negative deviations from Raoults's law.

Solvation effects are evident in electrolytic solutions. They are typical in binary electrolytic solutions where the solvent activity coefficients are less than unity and in multicomponent systems such as, for example, the LiCl-water-methanol system. While the activity coefficient of water is greater than unity in the methanol-water system at 25℃, it is less than unity in the LiCl-water-methanol system at the same temperature.

In this study, it is assumed that the salt completely dissociates into its constituent ions and that the ions are solvated by the solvent molecules. Association effects are neglected. It is further assumed that the apparent solvent activity coefficient, γ_i, is the sum of three terms:

$$\ln \gamma_i = \ln \gamma_i \text{ (Coulombic)} + \ln \gamma_i \text{ (Combinatorial)} + \ln \gamma_i \text{ (Residual)} \qquad (3\text{-}1)$$

The first term accounts for the long-range Coulombic forces, the second for differences in the sizes of the molecules (combinatorial term), and the third for the short range ion-solvent molecule and molecule-molecule interactions. (residual term)

To account for ion-solvation, equation (3-1) is rewritten in terms of γ_i', the true activity coefficient.

$$\ln \gamma_i' = \ln \gamma_i'^{\text{ Coulombic}} + \ln \gamma_i'^{\text{ Combinatorial}} + \ln \gamma_i'^{\text{ Residual}} \qquad (3\text{-}2)$$

For simplicity purposes, it is assumed that all solvation effects are accounted for explicitly through the combinatorial term and implicitly through the Coulombic and the residual terms, i.e.,

$$\ln\gamma_i^{\text{Coul.}} + \ln\gamma_i^{\text{Res.}} = \ln\gamma_i'^{\text{Coul.}} + \ln\gamma_i'^{\text{Res.}} \qquad (3\text{-}3)$$

To relate the apparent solvent activity coefficients, γ_i, to the true solvent activity coefficients, a relationship due to Bjerrum (1920) and discussed by Guggenheim and Stokes (1969) is used. Bjerrum showed that the activity of the solvent is the same whether the solute is solvated or not, i.e.,

$$a_i' = a_i \qquad (3\text{-}4)$$

and

$$\gamma_i' x_i' = \gamma_i x_i \qquad (3\text{-}5)$$

Substitution of equations (3-1), (3-2), and (3-3) into (3-5) yields

$$\gamma_i^{\text{Comb.}} = x_i'\gamma_i'^{\text{Comb.}}/x_i \qquad (3\text{-}6)$$

Introduction of equation (3-6) into (3-2) gives

$$\ln\gamma_i = \ln\gamma_i^{\text{Coul.}} + \ln\gamma_i^{\text{Res.}} + \ln(\gamma_i'^{\text{Comb.}}\ x_i'/x_i) \qquad (3\text{-}7)$$

$\ln\gamma_i^{\text{Coul.}}$, the Coulombic contribution to the solvent activity coefficient is evaluated using the free energy expression developed by Pitzer (1977) for binary electrolytic solutions. The expression is extended in this study to electrolytic solutions consisting of an electrolyte in mixed solvents. (See Appendix D)

$$\begin{aligned}\ln\gamma_i^{\text{Coul.}} &= 2A_\Phi((\text{M.W.})_i/1000)I^{3/2}/1+bI^{\frac{1}{2}} - A_\Phi bI^2(\text{M.W.})_i/(1000(1+bI^{\frac{1}{2}})^2)\\ &\quad - 2(\text{M.W.})/1000\ (I^{3/2}/1+bI^{\frac{1}{2}} - I/b\ \ln(1+bI^{\frac{1}{2}}))\ n_T\ dA_\Phi/dn_i\\ &\quad + 2A_\Phi((\text{M.W.})/1000)((I^2/(1+bI^{\frac{1}{2}})^2) + I/b^2\ln(1+bI^{\frac{1}{2}})\end{aligned}$$

$$- I^{3/2}/b(1+bI^{\frac{1}{2}}))n_T\ db/dn_i + v^2(2\pi a^3/3)(N/1000^2)(m^2(M.W.)n_T\ d(d)/dn_i$$
$$- m^2d(M.W.)_i + m^2d(M.W.)(3/a)n_T\ da/dn_i) \qquad (3\text{-}8)$$

$(M.W.)_i$ is the molecular weight of solvent i. (M.W.) is the molecular weight of the mixed solvent system on a salt-free basis. (° indicates the salt-free basis)

$$(M.W.) = \sum_j x_j{}^{\circ}(M.W.)_j \qquad (3\text{-}9)$$

$$x_j{}^{\circ} = n_j/\sum_k n_k \qquad (3\text{-}10)$$

The molality is defined as the number of moles of salt per kilogram of solvent.

$$m = 1000n_s/(M.W.)\sum_k n_k{}^{\circ} \qquad (3\text{-}11)$$

The ionic strength is given by

$$I = |\nu z_+ z_-| m/2 \qquad (3\text{-}12)$$

where z_+ and z_- are the charges of the positive and the negative ions, respectively. ν is the total number of ions which constitute the salt.

A_Φ, the Debye-Huckel limiting coefficient, is given by

$$A_\Phi = 1/3(2\pi Nd/1000)^{\frac{1}{2}}(e^2/DkT)^{3/2} \qquad (3\text{-}13)$$

where d is the density of the mixed solvent on a salt-free basis and D is the dielectric constant.

b is a function of a, the ion-size parameter, which is the only adjustable parameter in the Coulombic term.

$$b = (\ 8\pi N/1000)^{\frac{1}{2}}(e^2d/DkT)^{\frac{1}{2}}\ a \qquad (3\text{-}14)$$

Differentiation of equation (3-13) and (3-14) yields

$$dA_\Phi/dn_i = A_\Phi/n_T(1/2d\ d(d)/dn_i - 3/2D\ d(D)/dn_i)$$
$$(3\text{-}15)$$

$$db/dn_i = b/n_T(1/a\ da/dn_i + 1/2d\ d(d)/dn_i - 1/2D\ dD/dn_i) \qquad (3\text{-}16)$$

a, in a multiple solvent system is given by

$$a = \sum_j x_j{}^\circ\ a_j \qquad (3\text{-}17)$$

where $x_j{}^\circ$ is given by equation (3-10) and a_j is the ion size parameter for an electrolyte in solvent j.

The change in a with composition is

$$da/dn_i = (da/dx_i)(dx_i/dn_i) \qquad (3\text{-}18)$$

The densities of the mixed solvents and the changes in density with composition are evaluated using the Hankinson and Thomson (1977) correlation. The method is discussed in Appendix B.

The dielectric constants of the mixed solvents and the changes in the dielectric constant with composition are evaluated using the methods discussed in Appendix C.

The residual contribution to the solvent activity coefficient of equation (3-7) is that presented in the UNIQUAC (Abrams and Prausnitz, 1975) development.

$$\ln\gamma_i{}^{Res.} = q_i(1- \ln(\sum_m \Theta_m \psi_{mi}) - \sum_m(\Theta_m \psi_{im}/(\sum_n \Theta_n \psi_{nm})) \qquad (3\text{-}19)$$

q_i is calculated using the procedure of the UNIFAC group contribution method (Fredenslund, et.al., 1975) where

$$q_i = \sum_k v_k{}^{(i)} Q_k \qquad (3\text{-}20)$$

$v_k{}^{(i)}$ is defined as the number of groups of type k in molecule i. Q_k, the group area parameter, is calculated from the van der Waals group surface area, Awk, given by Bondi (1968) and is normalized by factor 2.5 x 10^9 given by Abrams and Prausnitz.

$$Q_k = Awk/2.5 \times 10^9 \qquad (3\text{-}21)$$

The values of Q_k given by Fredenslund and coworkers are used for the solvents in this study.

The Q_k for the positive and negative ions are calculated using the crystallographic radii, $\mathring{r}$, of Pauling. (1960) Awk for the ions is given by

$$Awk = 4\pi \mathring{r}^2 N \qquad (3\text{-}22)$$

where $\mathring{r}$ is in centimeters. Q_1 and Q_2, for the positive and negative ions, respectively, are calculated by equation (3-21).

Θ_i, the area fraction, is given by

$$\Theta_i = q_i x_i / \Sigma_j q_j x_j \qquad (3\text{-}23)$$

x_j is the mole fraction of component j. For the positive (component 1) and the negative (component 2) ions, respectively, x_j is given by

$$x_1 = \nu_1 n_s/(\nu n_s + \Sigma_j n_j) \quad j= 3, 4, \ldots N \qquad (3\text{-}24)$$

$$x_2 = \nu_2 n_s/(\nu n_s + \Sigma_j n_j) \qquad (3\text{-}25)$$

ν_1 and ν_2 are numbers of positive and negative ions, comprising the salt.

The mole-fraction of the solvent is given by

$$x_k = n_k/(\nu n_s + \Sigma_j n_j) \quad k = 3, 4, \ldots N \qquad (3\text{-}26)$$

The binary parameters, ψ_{mi} and ψ_{im}, are evaluated from the experimental binary data. Prediction of ternary systems does not require additional ternary parameters.

$$\psi_{mn} = \exp\left(-(u_{mn} - u_{nn}/RT)\right) = \exp -(A_{mn}/T) \qquad (3\text{-}27)$$

where the u_{mn} represent the energy of interaction between species m and n of the solution. The A_{mn} are determined directly from the experimental data. There are two A_{mn} binary.

The combinatorial contribution to the solvent activity coefficient of equation (3-7) is the activity coefficient expression of Flory and Huggins. (1941, 1942)

$$\ln \gamma_i'^{\text{Comb.}} = \ln\Phi_i'/x_i' + 1-\Phi_i'/x_i' \qquad (3\text{-}28)$$

The primes indicate the solvated basis. Φ_i', the average segment fraction, is given by

$$\Phi_i' = r_i' \, x_i'/\Sigma_j r_j x_j' \qquad (3\text{-}29)$$

x_j' is the true mole-fraction of component j. The true mole-fractions are related to the apparent mole fractions given by equations (3-24), (3-25), and (3-26), by the following:

$$x_1' = x_2/(1- x_1\Sigma_k h+_k - x_2\Sigma_k h-_k) \qquad (3\text{-}30)$$

$$x_2' = x_2/(1- x_1\Sigma_k h+_k - x_2\Sigma_k h-_k) \qquad (3\text{-}31)$$

$$x_j' = (x_j - x_i h+_j - x_2 h-_j)/(1- x_1\Sigma_k h+_k - x_2\Sigma_k h-_k)$$

$$k = 3, 4, \ldots., N \qquad (3\text{-}32)$$

The $h+_j$ and $h-_j$ are the solvation numbers of the positive and negative ions, respectively, and are functions of the apparent solvent mole-fractions.

$$h+_j = ho+_j \, x_j \qquad j = 3, 4, \ldots., N \qquad (3\text{-}33)$$

$$h-_j = ho-_j \, x_j \qquad (3\text{-}34)$$

$ho+_j$ and $ho-_j$ are the solvation numbers of the positive and negative ions, respectively.

The parameter, r_i', for the solvents used in this study, is calculated using the procedure of the UNIFAC method (Fredunslund, et.al., 1975) where

$$r_i' = \Sigma_k v_k^{(i)} R_k \qquad (3\text{-}35)$$

R_k, the group volume parameter, is calculated from the van der Waals group surface volume, Vwk, given by Bondi (1968). Vwk is normalized by the factor 15.17 given by Abrams and Prausnitz (1975), where

$$R_k = \text{Vwk}/15.7 \qquad (3\text{-}36)$$

The values of R_k given by Fredenslund, et.al., are used in this study.

The solvated positive and negative ions may be considered as molecules consisting of a central ion surrounded by $h+_j$ and $h-_j$ solvent molecules, respectively.

For the solvated positive ions, equation (3-35) is

$$r_1' = R_1 + \Sigma_j h+_j r_j' \qquad (3\text{-}37)$$

and for the solvated negative ions

$$r_2' = R_2 + \Sigma_j h-_j r_j' \qquad (3\text{-}38)$$

R_1 and R_2 are calculated using the crystallographic radii, $\overset{\circ}{r}$, of Pauling (1960) for spherical ions or the Yatsimirskii thermochemical radii for nonspherical ions. (Waddington, 1959) Vwk for the ions is given by

$$\text{Vwk}_{ion} = (4/3)\pi \overset{\circ}{r}^3 N \qquad (3\text{-}39)$$

Substitution of equation (3-39) into (3-36) gives R_1 and R_2.

The apparent combinatorial activity coefficient is obtained by introducing equation (3-28) into equation (3-6).

Substitution of equations (3-8), (3-19), and (3-28) into equation (3-7) yields the final expression for the solvent activity coefficient.

$$\begin{aligned}
\ln\gamma_i &= 2A_\Phi((M.W.)_i/1000))(I^{3/2}/(1+bI^{\frac{1}{2}})) \\
&- A_\Phi b\ I^2((M.W.)_i/1000)/(1+bI^{\frac{1}{2}})^2 - 2((M.W.)/1000)(I^{3/2}/(1+bI^{\frac{1}{2}})^2 \\
&- I/b\ \ln(1+bI^{\frac{1}{2}}))n_T\ dA_\Phi/dn_i + 2A_\Phi((M.W.)/1000) \\
&(I^2/(1+bI^{\frac{1}{2}})^2 + I/b^2\ \ln(1+bI^{\frac{1}{2}}) - I^{3/2}/b(1+bI^{\frac{1}{2}}))n_T\ db/dn_i + v^2(2\pi a^3/3) \\
&(N/1000^2)(m^2\ (M.W.)n_T\ d(d)/dn_i - m^2\ d(M.W.)_i + m^2\ d(M.W.)(3/a)n_T \\
&da/dn_i) + q_i(1- \ln(\Sigma_m\Theta_m\psi_{mi}) - \Sigma_m\ (\Theta_m\psi_{im}/\Sigma_n\Theta_n\psi_{nm})) + \\
&\ln\Phi_i'/x_i' + 1-\Phi_i'/x_i' + \ln\ x_i' - \ln\ x_i
\end{aligned} \tag{3-7}$$

The expressions for the mean activity coefficients of the salt in single and mixed solvents are developed in Appendix F.

CHAPTER 4

Experimental

The vapor pressure depression measurements were performed using the differential manometer described by Oliver (1969) and further modified by Tomasula (1980). The differential manometer is shown in Figure 4.1. Each flask, equipped with a magnetic stirrer to facilitate stirring, has a capacity of 100 cc.

The vapor pressure depression, ΔP, where

$$\Delta P = P^s - P \qquad (4\text{-}1)$$

is determined directly by measuring the difference in vapor pressure between two flasks. One flask contains pure methanol (P^s) and the other contains the electrolytic solution (P). The direct determination of ΔP provides improved accuracy over measurements of the vapor pressure of the electrolytic solution alone since it eliminates the effects of small temperature variations. These effects are more pronounced at low molalities where ΔP is very small.

The salts used in this study were reagent grade quality KCH_3COO, NaI, NaSCN, and NH_4SCN, were used without further purification. Each was dried under vacuum for 48 hours prior to use. J.T. Baker methanol of spectroquality (99.9 weight percent minimum purity) was used with no further purification. A Karl-Fischer titration indicated that the amount of water was less than 0.03 mole percent.

Solutions were prepared by adding the appropriate salt to a preweighed flask. The flasks were weighed again to determine the amount of salt added. Approximately 30 ml of methanol were then added to each flask and the flask was reweighed.

Briefly, the experiment consisted of degassing the pure methanol

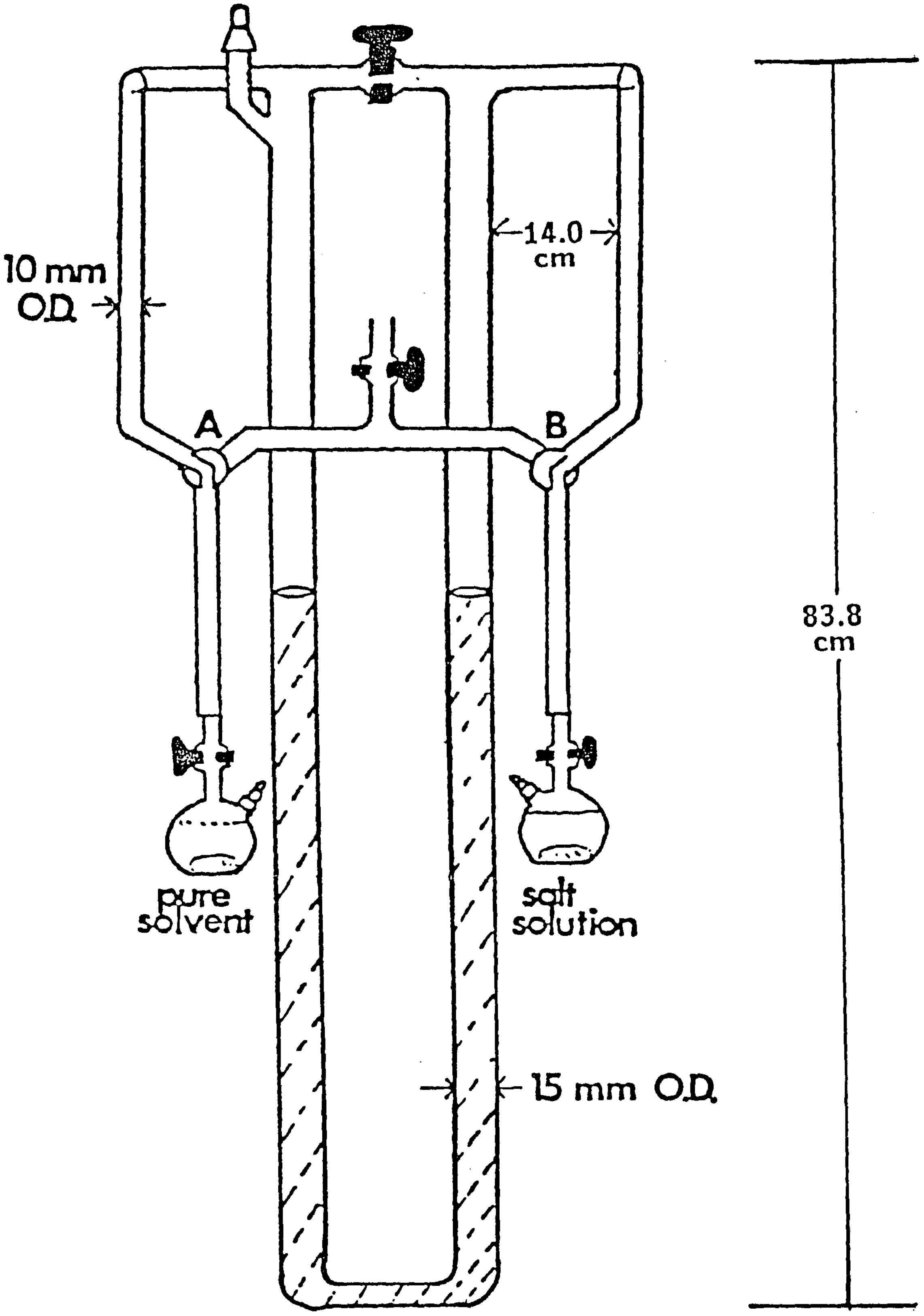


Figure 4.1 Differential Manometer

and the methanol salt solutions before attaching to the differential manometer. This was accomplished by immersing the flasks in a methanol bath at -67°C while boiling at high vacuum. After the methanol solutions subcool and a residual pressure of 10^{-2}mm Hg was indicated on a McLeod gauge, the flasks were removed from the bath and the contents warmed to room temperature. This procedure was repeated until air bubbles no longer rose from the solvent.

The entire differential manometer was immersed in a well stirred constant temperature bath. The vapor pressure depression measurements were performed at 25 and 40°C ± 0.03°C. The vapor pressure depression, ΔP, was measured with the aid of a cathetometer to ±0.06 mm Hg. After a typical run, the manometer was removed from the bath and the flask containing the electrolytic solution was reweighed to determine any loss of solvent. The molality, m, of the solution was then calculated.

The performance of the experimental system is demonstrated in Figure 4.2 where the results for aqueous solutions of KCL used as a test system are compared with the very accurate results reported by Robinson and Stokes (1959).

The results for the electrolytes used in this study are reported in Appendix E. Values of ΔP, P, and Φ, the osmotic coefficient, are given. The vapor pressure data are obtained by subtracting the measured ΔP values from the vapor pressure of pure methanol reported in each table under a molality of zero.

The osmotic coefficient is given by

$$\Phi = -1000 \ln P/P^S/\nu m(\mathrm{M.W.}) \qquad (4\text{-}2)$$

where M.W. is the molecular weight of the solvent and ν is the total number of ions comprising the electrolyte.

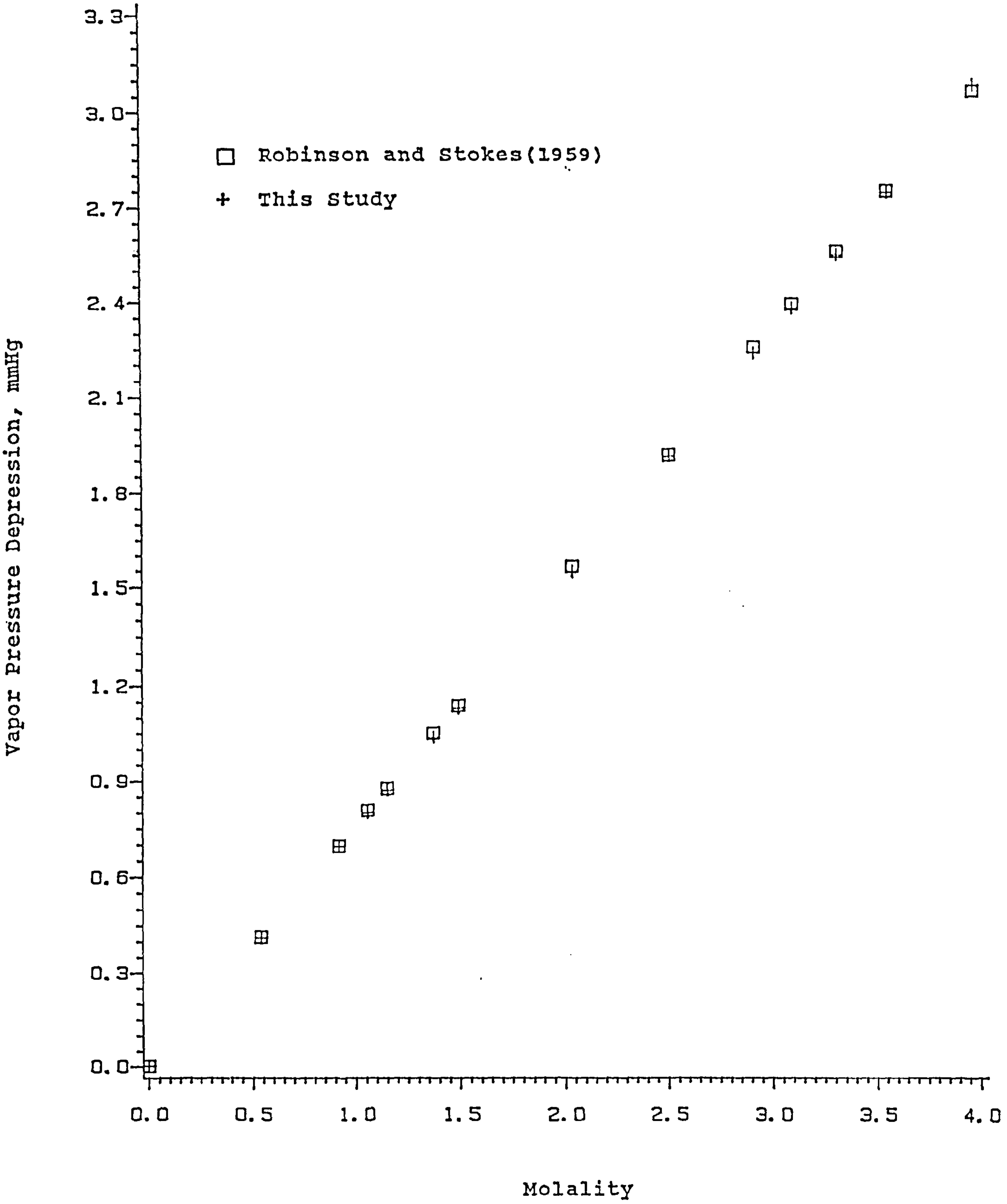


Figure 4.2 Vapor Pressure Depression of Aqueous KCl Solutions at 25 °C

CHAPTER 5

Binary Data Reduction

5.1 The Binary Equations and the Ternary and Binary Data Bases

For a binary electrolytic solution, equations (3-8), (3-19), and (3-28), reduce to: (the subscripts 1, 2, and 3 refer to the positive ion, the negative ion, and the solvent, respectively.)

$$\ln\gamma_3^{\text{Coul.}} = 2A_\Phi((\text{M.W.})_3/1000)(I^{3/2}/1+bI^{\frac{1}{2}}))-A_\Phi bI^2(\text{M.W.})_3/(1000(1+bI^{\frac{1}{2}})^2)$$
$$-v^2(2\pi a^3/3)(N/1000^2)m^2\ d(\text{M.W.})_3 \qquad (5\text{-}1)$$

b is given by equation (3-14).

$$\ln\gamma_3^{\text{Res.}} = q_3(1-\ \ln(\Theta_1\Psi_{13}+\Theta_2\Psi_{23}+\Theta_3\Psi_{33})$$
$$-\ \Theta_1\Psi_{31}/(\Theta_1\Psi_{11}+\Theta_2\Psi_{21}+\Theta_3\Psi_{31})$$
$$-\ \Theta_2\Psi_{32}/(\Theta_1\Psi_{12}+\Theta_2\Psi_{22}+\Theta_3\Psi_{32})$$
$$-\ \Theta_3\Psi_{33}/(\Theta_1\Psi_{13}+\Theta_2\Psi_{23}+\Theta_3\Psi_{33}))$$
$$(5\text{-}2)$$

From equation (3-27), Ψ_{11}, Ψ_{22} and Ψ_{33} are equal to unity. Also, $\Psi_{31} \neq \Psi_{13}$ and $\Psi_{32} \neq \Psi_{23}$.

$$\ln\gamma_3'^{\text{Comb.}} = \ln\Phi_3'/x_3' + 1-\Phi_3'/x_3' \qquad (5\text{-}3)$$

where Φ_3' and x_3' are given by equations (3-29) and (3-32), respectively.

The activity coefficient of the solvent is obtained by substituting equations (5-1), (5-2), and (5-3), into equation (3-7).

The solvent activity coefficient expression for a binary electrolytic solution contains nine parameters.

The Pitzer (Coulombic) term has one adjustable parameter, a, which is the ion-size parameter. a reflects the hard-core volume of the ions and its value may be between the sum of the crystallographic radii or the sum of the solvated radii.

The Flory-Huggins (Combinatorial term) has two fixed parameters, ho_{+j} and ho_{-j}. These values are obtained from Bockris and Reddy (1977) for various ions in water. They are estimated for ions in nonaqueous solvents and the method for estimation will be presented later in this chapter.

The residual term has six adjustable parameters: A_{13}, A_{23}, A_{31}, A_{32}, A_{12}, and A_{21}. Equation (5-2) is simplified further with the assumption

$$A_{12} = A_{21} \qquad (5\text{-}4a)$$

that the interaction energy between two positive ions, u_{11}, is the same as the interaction energy between two negative ions, u_{22}. (See equation 3-27)

The parameters ψ_{13} and ψ_{23} are combined to one parameter, $A_{\pm}$.

$$A_{\pm} = Q_1 \psi_{13} + (\nu_2/\nu_1) Q_2 \psi_{23} \qquad (5\text{-}4b)$$

With the assumptions of equations (5-4a) and (5-4b), equation (5-2) is

$$\begin{aligned} \ln \gamma_3^{Res.} = {} & q_3(1 - \ln \Theta_1 A_{\pm}/Q_1 + \Theta_3) \\ & - \Theta_1 \psi_{31}/(\Theta_1 + \Theta_2 \psi_{21} + \Theta_3 \psi_{31}) \\ & - \Theta_2 \psi_{32}/(\Theta_1 \psi_{12} + \Theta_2 + \Theta_3 \psi_{32}) - \Theta_3/(\Theta_1 A_{\pm}/Q_1 + \Theta_3) \end{aligned} \qquad (5\text{-}5)$$

The number of parameters in the residual term is reduced to four.

The expression for the activity coefficient of the solvent is then given by

$$\ln \gamma_3 = \text{equation (5-1)} + \text{equation (5-3)} + \text{equation (5-5)} + \ln x_3' - \ln x_3 \qquad (5\text{-}6)$$

A_{31} and A_{32} represent the interactions between the solvent and the solvated positive and negative ions, repectively. A_{12} represents the short-range interactions between the solvated positive and negative ions. $A_{\pm}$ combines the interactions between the solvated positive and negative ions and the solvent. To establish these parameters, an extensive data base of salts in various solvents is needed.

The data base for parameter estimation is shown in Table 5.1 and includes osmotic coefficient or vapor pressure data for salts in water, methanol, ethanol, isopropanol, and n-propanol.

This data base was selected since it includes most of the salts and solvents for which ternary salt-mixed solvent data are available. The ternary data base is shown in Table 5.2. In addition, the binary data base includes salts not covered in the ternary data base. The parameters obtained for these systems are applied to the prediction of binary systems at temperatures other than 25°C.

The UNIQUAC surface area (q_i) and volume (r_i) parameters of equation (5-6) were calculated using equations (3-20) and (3-35), respectively, and the group area (Q_k) and group volume (R_k) parameters given by Fredenslund, et.al. (1975). They are tabulated in Table 5.3.

The UNIQUAC group surface area (Q_1 and Q_2) and group volume (R_1 and R_2) parameters for the positive (1) and negative (2) ions are calculated using the Pauling (1960) crystallographic radii in the case of the spherical ions and the Yatsimirskii thermochemical radii (Waddington, 1959) in the case of the nonspherical ions. The ionic radii (Table 5.4) are then substituted into equations (3-21), (3-22), (3-36), and (3-39), to obtain the ionic Q_k and R_k. These values are tabulated in Table 5.5.

TABLE 5.1

Data Base for Parameter-Estimation from Binary Electrolytic Solution Data

Salt	T°C or PmmHg	Maximum Molality $(\frac{\text{moles salt}}{\text{kg solvent}})$	Reference
Water			
1-1 Chlorides	25°C	6	Robinson & Stokes (1959)
1-1 Bromides		6	
1-1 Iodides		6	
1-1 Chlorates		6	
1-1 Acetates		4	
1-1 Flourides		4	
2-1 Chlorides		6	
2-1 Bromides		6	
2-1 Iodides		6	
1-2 Sulfates		3	
Methanol			
LiCl	25°C	4.6	Tomasula (1985)
LiBr		4.3	This Study
NaI		4.3	
NaSCN		3.4	
NH_4SCN		5.2	
KCH_3COO		2.5	
NaBr	24.88°C	1.6	Bixon et al. (1979)
NaOH		5.9	
$CaCl_2$		2.6	
$CuCl_2$		4.0	
KI	15°C	0.8	Janz & Tomkins (1972)
Ethanol			
LiCl	35°C	4.4	Czerwienski et al. (1985)
LiBr	50°C	4.9	
NaI		2.8	
$CaCl_2$		2.5	

Salt	T°C or PmmHg	Maximum Molality $(\frac{\text{moles salt}}{\text{kg solvent}})$	Reference
Isopropanol			
LiCl	75.1°C	1.8	Sada et al. (1975)
LiBr	75°C	3.9	
$CaCl_2$	760mm	1.8	Nishi (1975)
n-propanol			
$CaCl_2$	760mm	1.8	Nishi (1975)

TABLE 5.2

Ternary Data Base

Salt	Isothermal Data T°C	Isobaric Data mmHg	References
Methanol-Water			
LiCl	25,60	760	Ciparis (1966) Hala (1969) Boone (1976)
NaCl		760	Ciparis
NaBr	25,40	760	Ciparis; Boone
NaF		760	Boone
KCl		760	Boone
$CaCl_2$		760	Nishi (1975)
Ethanol-Water			
LiCl	25	760	Ciparis; Boone
NaCl	30	755	Ciparis
NaI		700	
NaF		700	
KCl		700	
KI		700	
NH_4Cl	30	760	
$CaCl_2$		760	Nishi (1975)
Isopropanol-Water			
LiCl	75		Sada et al. (1975)
LiBr	75		
Methanol-Ethanol			
$CaCl_2$		760	Kato (1971)

TABLE 5.3

UNIQUAC Volume (r_i) and Surface Area (q_i) Parameters

	H_2O	MeOH	EtOH	nPrOH	IsoProp
r_i	0.92	1.4311	2.1055	2.7799	2.7791
q_i	1.40	1.4322	1.9720	2.5120	2.5080

TABLE 5.4

Pauling Crystallographic & Yatsimirskii Thermochemical Radii for the Ions Considered in this Study

Ion	$\overset{\circ}{r}$, Angstroms	Reference
Li^+	0.60	Pauling (1960)
Na^+	0.95	
K^+	1.33	
Rb^+	1.48	
Cs^+	1.69	
Mg^{+2}	0.65	
Ca^{+2}	0.99	
Sr^{+2}	1.13	
Ba^{+2}	1.35	
Co^{+2}	0.74	
F^-	1.36	
Cl^-	1.81	
Br^-	1.95	
I^-	2.16	
SO_4^{-2}	2.30	Yatsimirskii (Waddington, 1959)
NO_3^-	1.89	
ClO_4^-	2.36	
CNS^-	1.95	
CH_3COO^-	1.59	
NH_4^+	1.48	

TABLE 5.5

UNIQUAC Group Volume (R_k) and Group Surface Area (Q_k) Parameters

Ion	R_k	Q_k
Li^+	0.03590	0.10893
Na^+	0.14615	0.27771
K^+	0.39195	0.53607
Rb^+	0.54325	0.66639
NH_4^+	0.54325	0.66639
Cs^+	0.75488	0.82982
Mg^{+2}	0.03773	0.11260
Ca^{+2}	0.16129	0.29657
Sr^{+2}	0.23984	0.38638
Ba^{+2}	0.40898	0.55148
Co^{+2}	0.06736	0.16570
F^-	0.39107	0.53526
Cl^-	0.97915	0.98696
Br^-	1.23253	1.15062
I^-	1.67516	1.41179
SO_4^{-2}	2.02246	1.60073
NO_3-	1.12223	1.08090
ClO_4-	2.18490	1.68534
CNS^-	1.23253	1.15062
CH_3COO^-	0.66817	0.76499

5.2 Parameter Estimation from Binary Electrolytic Solution Data

The 1-1 chlorides at 25°C of Table 5.1, which consist of LiCl, NaCl, KCl, RbCl, NH_4Cl, and CsCl, were chosen as the base systems from which all aqueous ionic parameters of equation (5-6) are evaluated. This means that the values of A_{31} and A_{32} obtained through regression of these systems are the values of A_{31} and A_{32} to be used for all salts containing the same ions. For example, the value of A_{water/Li^+} is the same for LiCl as it is for LiBr. The value of A_{water/Cl^-} is the same for NaCl as it is for $CaCl_2$. (The values of a, A_{12}, and $A\pm$ are discussed under the headings Case 1, Case 2, and Case 3, respectively.)

The 1-1 chlorides were selected over the other aqueous systems of Table 5.1 since ion-pairing between a uni-valent cation and a chloride ion is not observed. (Robinson and Stokes, 1959) In addition, the osmotic coefficient data for these salts is available up to a molality of 6, with the exception of the KCl system which has a maximum molality of 4.5m. A maximum molality of 6 is desirable since the ternary salt-mixed solvent systems of Table 5.2 often extend to this molality.

It is equally valid to use the 1-1 bromides or 1-1 iodides as a base system since these salts also do not ion-pair. However, the osmotic coefficient data for the majority of these salts do not extend to 6m.

The LiCl and LiBr methanol systems at 25°C were chosen as the base systems from which all methanol ionic parameters are evaluated. The data for these systems are available up to a molality of 4.3.

The binary model of equation (5-6) was tested considering the three cases discussed below.

Case 1

a, the ion-size parameter of the Pitzer term, equation (5-1), was set equal to the sum of the ionic radii given in Table 5.4. Therefore, the Pitzer term has no adjustable parameters.

The values of h_{o+j} and h_{o-j} of the Flory-Huggins combinatorial term, equation (5-3), were set equal to zero. This means that the ions are not considered to be solvated.

The residual term, equation (5-5), was used assuming that the value of A_{12} is the same for each salt and a particular solvent along with the values of R_k and Q_k given in Tables 5.4 and 5.5.

The 1-1 chlorides in water at 25°C and the LiCl and LiBr systems in methanol at 25°C were used to obtain the model parameters. The model parameters were calculated by minimization of the objective function:

$$F = (\Phi_{exp} - \Phi_{cal})/\Phi_{exp}{}^2 \qquad (5\text{-}7)$$

Φ_{exp} is the experimental osmotic coefficient from the data of Table 5.1. Φ_{cal} is the calculated osmotic coefficient and is obtained from equation (5-6) using the relationship

$$\Phi_{cal} = -1000 \ln(\gamma_3 x_3)/\nu(\mathrm{M.W.})m \qquad (5\text{-}8)$$

The results for Case 1 are shown in Table 5.6. The results for the 1-1 chlorides were obtained by simultaneously solving for A_{12}, A_{31}, A_{32}, and $A_{\pm}$. The value of A_{32}, which represents the interaction between a water molecule and a chloride ion, is the same for each of the chloride salts. The value of A_{31}, which represents the interaction between a water molecule and a positive ion, differs from salt to salt, since it depends on the type of positive ion. A_{12}, which represents

TABLE 5.6

Case 1. Test of the Binary Model (Eq. 5.6) with $a = \Sigma r_c$ and ho_{+j} and ho_{-j} Set Equal to Zero

System	$\underline{A}_{12}$	$\underline{A}_{31}$	$\underline{A}_{32}$	Avg. % Error ϕ
Water				
LiCl	-3624.1	-5925.1	-12224.1	22.7
NaCl		-5643.8		7.3
KCl		-2824.7		1.5
RbCl		-2670.6		2.4
CsCl		-2505.6		5.1
		Average % error ϕ =		7.8
Methanol				
LiCl	15820.6	-4633.0	-14788.1	56.0
LiBr			-9077.4	52.5
		Average % error ϕ =		54.3

the interaction between a positive and negative ion, was assumed to be the same for each salt. The value of $A_{\pm}$, which was assumed to be the same for all salts, was found to be approximately zero.

The overall average percent error in Φ for the 1-1 chlorides is 7.8. The performance of the model is especially poor for the LiCl system where the average percent error in Φ is 22.7.

The LiCl and LiBr methanol systems could not be correlated by the model. The overall average percent error in Φ is 54.3. The reasons for the poor performance of Case 1 will be discussed after the presentation of Case 3. The other salt-methanol systems of Table 5.1 also could not be correlated by the model.

Although not shown, the value of $A\pm$ was also found to be zero in the regression of the 1-1 bromides and the 1-1 iodides. The other aqueous systems of Table 5.1 were not tested using Case 1.

Case 2

Case 2 is the same as Case 1 with the exception that a, the ion-size parameter is now an adjustable parameter. The 1-1 chlorides and the LiCl and LiBr methanol systems were again used to obtain the model parameters. The regression procedure used in Case 1 to obtain the model parameters was also used in Case 2.

The results for Case 2 are shown in Table 5.7. The overall average percent error in Φ for the 1-1 chlorides is 2.1 while that for the LiCl and LiBr methanol systems is 1.9. These results are a significant improvement over those in Table 5.6. Again, $A_{\pm}$ was found to be approximately zero for the aqueous and the methanol systems.

The values of A_{31} and A_{12} obtained from the regression of the 1-1 chlorides were used to obtain the values of a and A_{32} for the 1-1

TABLE 5.7

Case 2. Test of the Binary Model (Eq. 5.6) with a an Adjustable Parameter and ho_{+j} and ho_{-j} Set Equal to Zero

System	$\underline{a}$	$\underline{A}_{12}$	$\underline{A}_{31}$	$\underline{A}_{32}$	Avg. % Error in ϕ
Water					
LiCl	3.98	-591.7	-341.6	-2907.8	0.9
NaCl	3.24		-302.7		0.6
KCl	3.14		188.1		1.5
RbCl	3.29		337.1		2.4
CsCl	3.46		494.8		5.1
LiBr	4.24		-341.6	-232.5	1.8
NaBr	3.55		-302.7		0.4
KBr	3.28		188.1		2.4
RbBr	3.44		337.1		3.0
CsBr	3.61		494.8		4.7
Methanol					
LiCl	5.53	-364.7	-166.1	762.1	2.2
LiBr	5.88		-166.1	919.7	1.5
NaBr	5.32		-353.1	919.7	3.7

bromides, where A_{32} is the water-bromide ion interaction parameter. The values of A_{32} and A_{12} obtained from the regression of the LiCl and LiBr methanol systems were used to obtain the values of A_{31}, the methanol-sodium ion interaction parameter, and a for the NaBr-methanol system. $A\pm$ was assumed to be zero. These results will be utilitized in Chapter 6.

Case 3

a, the ion-size parameter of the Pitzer term of equation (5-6) was set equal to the sum of the ionic radii given in Table 5.4. This was done in Case 1 also.

The solvation numbers of the positive, h_{o+j}, and the negative ions, h_{o-j}, in water were set equal to the values of the primary hydration numbers given by Bockris and Reddy (1977). These values are listed in the second column of Table 5.8. The wide variation in the values of h_{o+j} and h_{o-j} for each ion arose since the hydration numbers were determined by five different methods. Since the values of h_{o-j} are 1±1 for the Cl^-, Br^-, and I^- ions, h_{o-j} was set equal to zero for these ions. h_{o-j} was also set equal to zero for the other anions encountered in this study for simplicity purposes.

Since no solvation numbers are available for ions in nonaqueous media, it was assumed that h_{o+j} for a positive ion in a nonaqueous solvent is given by

$$h_{o+j}\binom{\text{nonaqueous}}{\text{solvent}} = h_{o+j\ \text{water}}\ D\binom{\text{nonaqueous}}{\text{solvent}}_{25°C} / D_{H_2O_{25°C}} \tag{5-9}$$

where $D\binom{\text{nonaqueous}}{\text{solvent}}$ is the dielectric constant of the nonaqueous solvent at 25°C and D_{H_2O} is the dielectric constant of water at 25°C.

TABLE 5.8

Hydration Numbers for Some of the Ions Used in This Study

Ion	ho_{+j} or ho_{-j} (Bockris & Reddy, 1977)	ho_{+j} or ho_{-j} (This Study)
Li^+	5±1	5
Na^+	4±1	3
K^+	3±2	2
Rb^+	2±1	1
Cs^+	0	0
Ca^{+2}	7.5-10.5	9
Mg^{+2}	13-16	10
F^-	4±1	0
Cl^-	1±1	0
Br^-	1±1	0
I^-	1±1	0

$h_{o+j\ water}$ is the hydration number of the ion from the values of Table 5.8.

Again, the aqueous 1-1 chlorides and the LiCl and LiBr methanol systems were used to evaluate the model parameters using the procedure outlined under Case 1. A preliminary run indicated that a should be an adjustable parameter for the methanol systems and that the hydration numbers of the aqueous positive ions should be adjusted to the values shown in the third column of Table 5.8. These values are within the experimental error indicated by Bockris and Reddy.

The regression results for the aqueous 1-1 chlorides and the LiCl and LiBr methanol systems are shown in Table 5.9. The average percent error in Φ for the 1-1 chlorides is 1.4. This is an improvement over the value of 7.8 obtained in Case 1 and the value of 2.1 obtained in Case 2.

The average percent error in Φ for the methanol systems is 1.9. This is an improvement over the value of 54.3 obtained in Case 1 and is the same as the value obtained in Case 2.

A comparison of the results of Cases 1, 2, and 3 indicates that the model fails overall for the choice of parameters of Case 1. (a was set equal to the sum of the crystallographic radii and h_{o+j} and h_{o-j} were set equal to zero). The results for the KCl, RbCl, and CsCl systems are comparable to those of Cases 2 and 3.

The Pitzer, Flory-Huggins, and residual terms for the LiCl-water and the LiCl-methanol systems of Table 5.6 are plotted in Figures 5.1 and 5.2, respectively.

Figure 5.1 indicates that the contributions of the Pitzer, Flory-Huggins, and residual terms to the calculated solvent activity

TABLE 5.9

Case 3. Test of the Binary Model (Eq. 5-6) with $a = \Sigma r_c$ for the Aqueous Systems and Adjustable for the Nonaqueous Systems

System	a	ho_{+j}	A_{12}	A_{31}	A_{32}	Avg. % Error in ϕ
Water						
LiCl	2.41	5.	-828.7	-368.2	-87.5	1.6
NaCl	2.76	3.		-442.3		0.9
KCl	3.14	2.		-13.7		1.7
RbCl	3.29	1.		-142.0		1.4
CsCl	3.47	0.		-89.7		1.5
			Average % Error ϕ =			1.4
Methanol						
LiCl	5.35	2.	-253.1	620.8	782.3	2.3
LiBr	5.70	2.			938.4	1.5
			Average % Error ϕ =			1.9

Figure 5.1 Case 1. The Contribution of the Pitzer, Flory-Huggins, and Residual Terms in the Calculation of $\ln\gamma_{H_2O}$ for the LiCl-Water System at 25°C.
(The parameter values are found in Table 5.6)

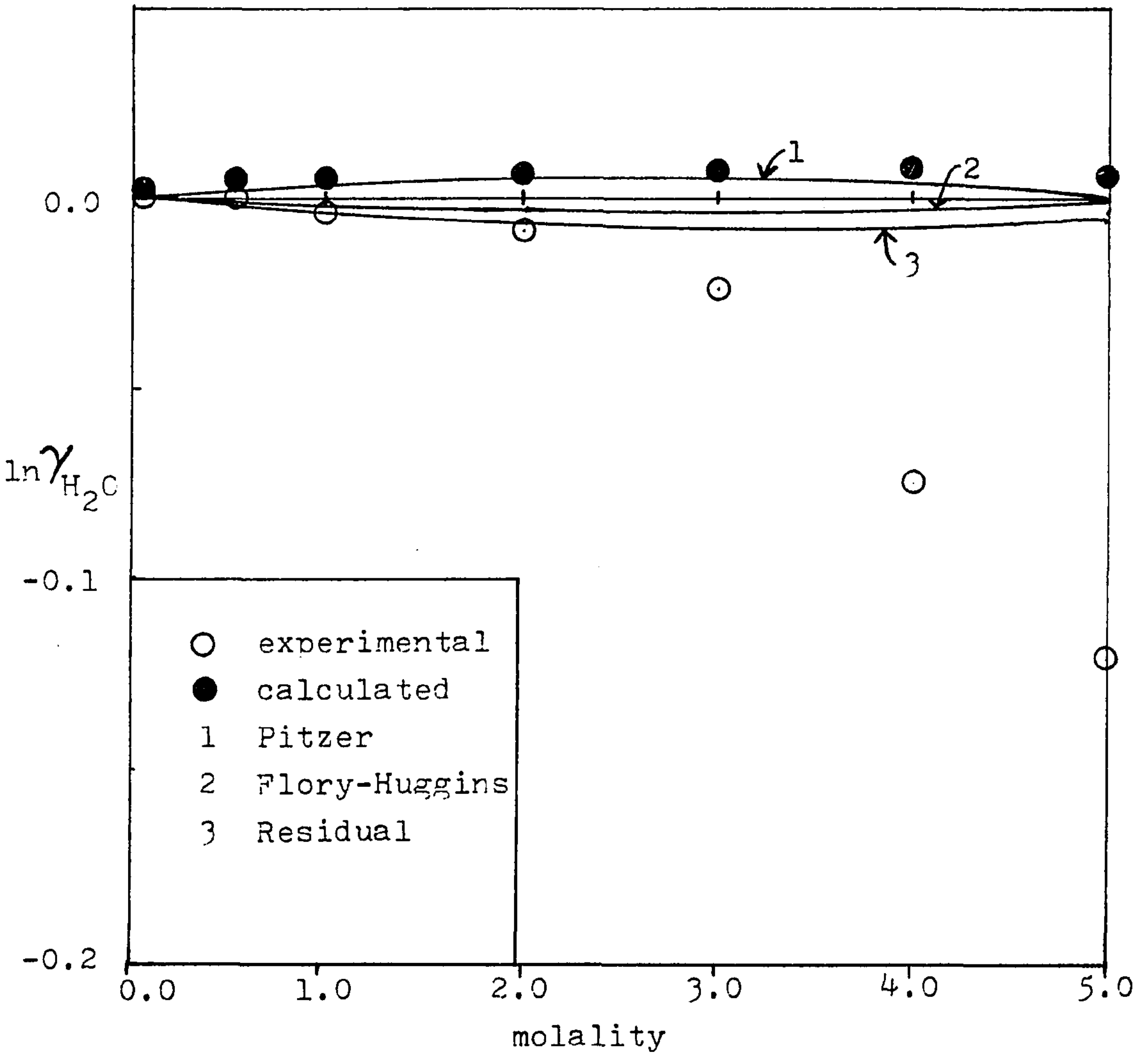
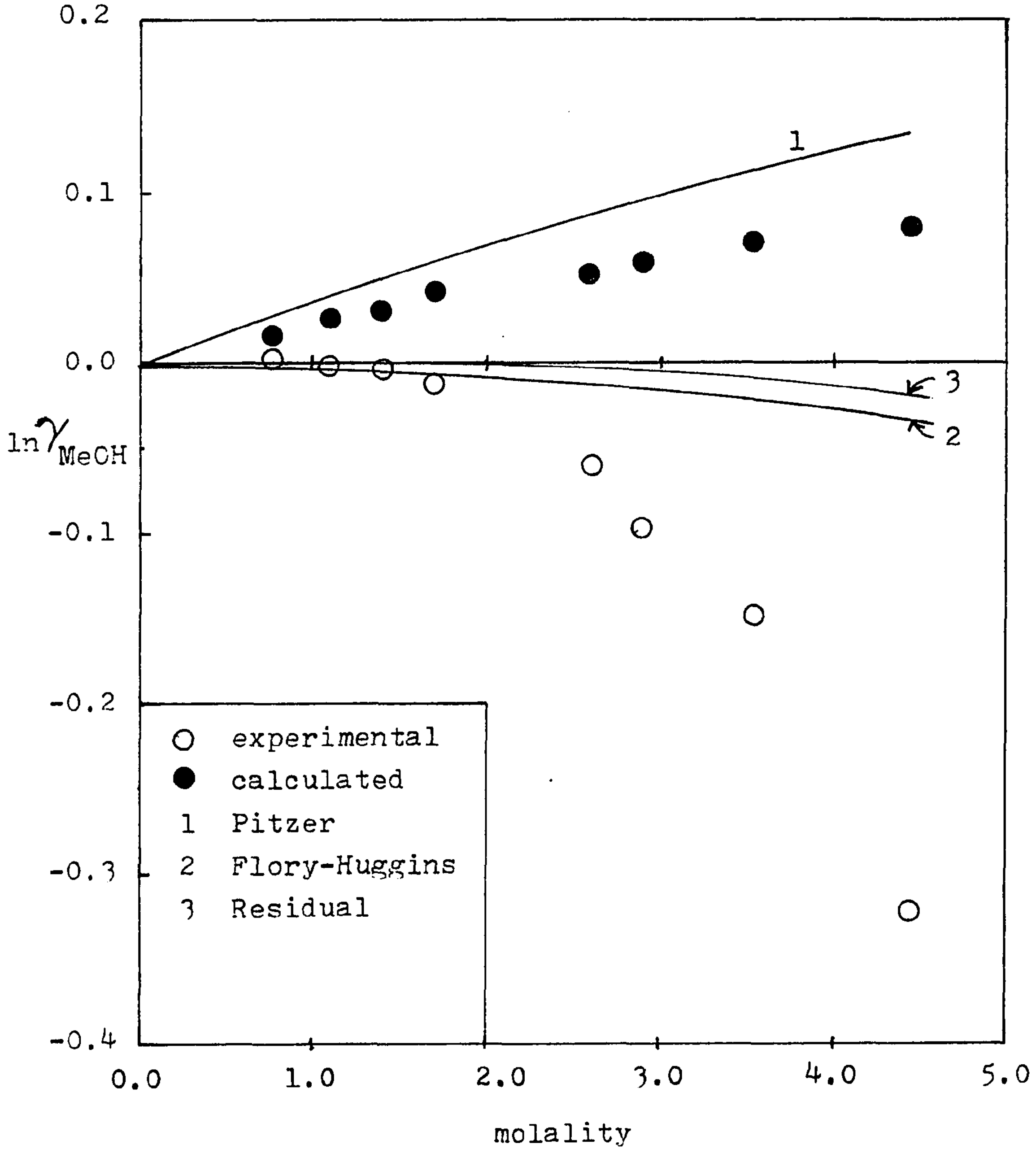


Figure 5.2 Case 1. The Contribution of the Pitzer, Flory-Huggins, and Residual Terms in the Calculation of $\ln\gamma_{MeOH}$ for the LiCl-Methanol System at 25°C.
(The parameter values are found in Table 5.6)



coefficients of water are negligible as the molality increases above 2m. The 1-1 chloride data were regressed again varying the starting values of A_{12}, A_{31}, and A_{32}, in equation (5-6) to check that the parameter values of Table 5.6 are the optimum ones. A± was set equal to zero. No changes in the parameter values or the value of the residual term were noted indicating no multiplicity of roots in the term.

Figure 5.2 shows that the contributions of the Flory-Huggins and the residual terms to the calculated solvent activity coefficients of methanol are negligible even at high molalities. The major contribution is due to the Pitzer term. However, this contribution is opposite in sign to that needed for the correlation of the experimental activity coefficients. Again, the residual term was checked for multiplicity of roots by varying the starting values of A_{12}, A_{31}, and A_{32} in equation (5-6). Again, A± was set equal to zero. No changes in the parameter values or the value of the residual term were noted.

In Case 2 (Table 5.7), the values of h_{o+j} and h_{o-j} were set equal to zero and a, A_{12}, A_{31}, and A_{32} were adjustable parameters. A± was found to be zero. The results for the LiCl-water and the LiCl-methanol systems at 25°C are plotted in Figures 5.3 and 5.4, respectively.

Figure 5.3 shows that the contributions of the Flory-Huggins and the residual terms to the calculated activity coefficients of water are negligible over the entire molality range. The major contribution to the calculated activity coefficients is due to the Pitzer term which decreases with increasing molality. This contrasts with Case 1 (Figure 5.1) in which the contribution of the Pitzer term is small.

Figure 5.4 indicates that the major contributions to the calculated

Figure 5.3 Case 2. The Contribution of the Pitzer, Flory-Huggins, and Residual Terms in the Calculation of $\ln \gamma_{H_2O}$ for the LiCl-Water System at 25°C.
(The parameter values are found in Table 5.7)

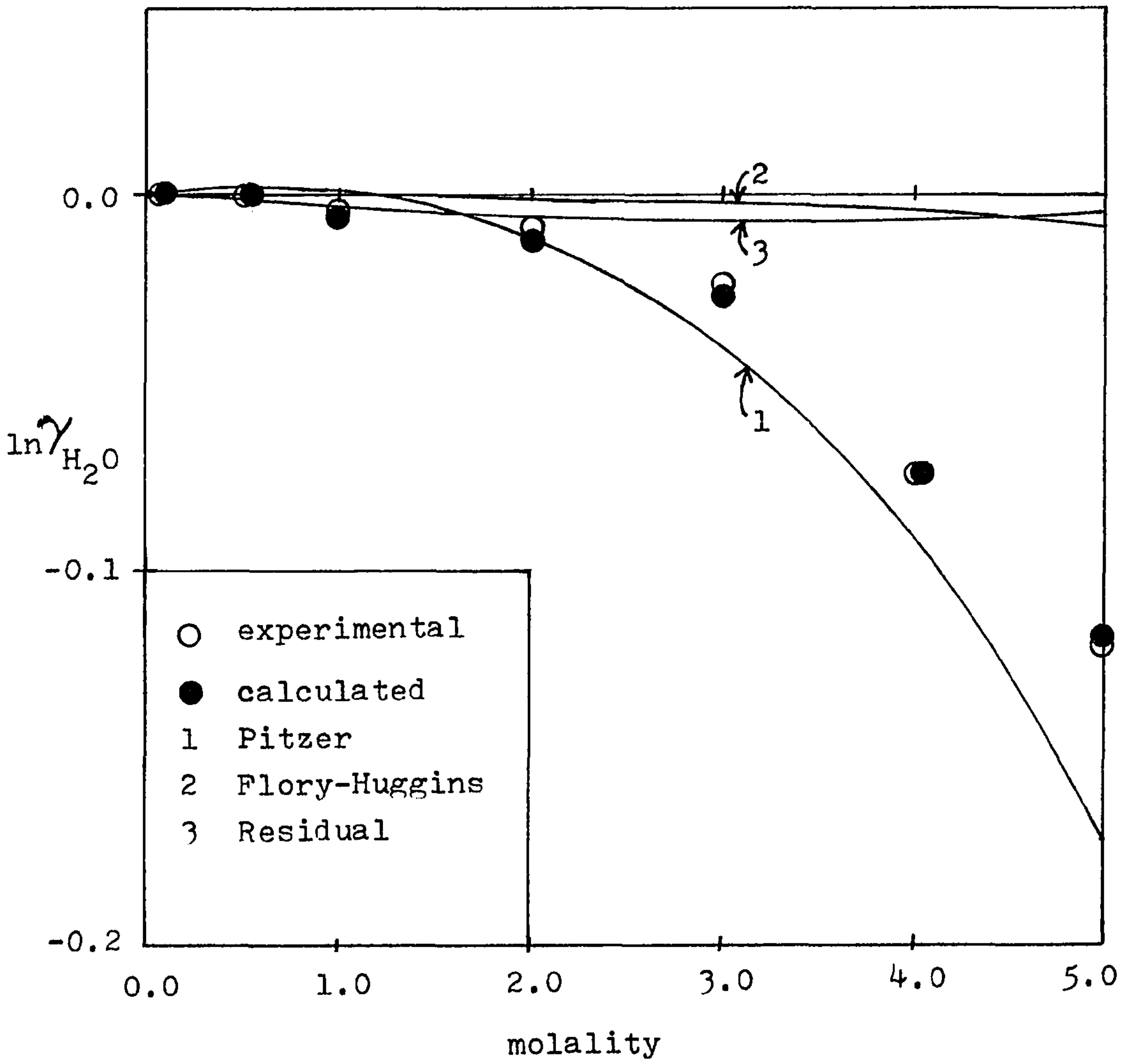
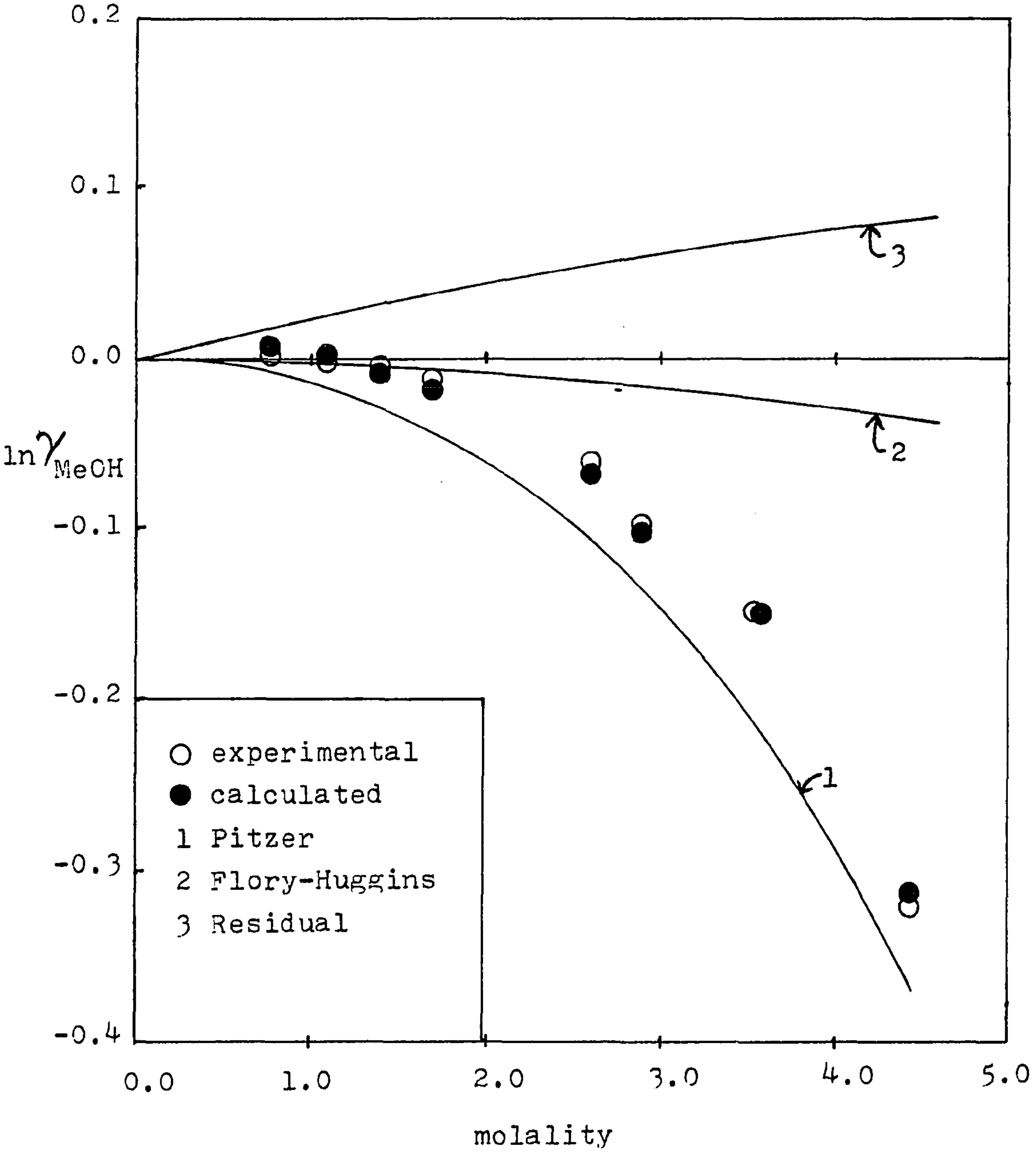


Figure 5.4 Case 2. The Contribution of the Pitzer, Flory-Huggins, and Residual Terms in the Calculation of ln γ_{MeOH} for the LiCl-MeOH System at 25°C.
(The parameter values are found in Table 5.7)



activity coefficients of methanol are due to the Pitzer and the residual terms. The Pitzer term decreases with increasing molality while the residual term increases with increasing molality. This is in contrast to Case 1 (Figure 5.2) where the Pitzer contribution is positive and the residual contribution negligible. The Flory-Huggins contribution in Cases 1 and 2 are identical.

Solvation of the positive ions was assumed in Case 3. a is the sum of the crystallographic radii for the aqueous systems and is an adjustable parameter for the methanol systems. (The case where a is the sum of the crystallographic radii and solvation is assumed for the methanol systems is not presented here since the methanol data are correlated as they are in Case 1 with this option.)

The results for the LiCl-water and the LiCl-methanol systems are plotted in Figures 5.5 and 5.6, respectively.

Figure 5.5 shows that the major contribution to the calculated solvent activity coefficients of water is due to the Flory-Huggins term. The Pitzer contribution is the same as it is in Case 1. The residual contribution is now positive where in Cases 1 and 2 it is negative.

The Flory-Huggins term is always negative. The magnitude of this term increases with increasing solvation number; i.e., the contribution of this term is greatest for the LiCl system which has the largest value of h_{o+j} and smallest for the CsCl system which has a value of h_{o+j} of zero

Figure 5.6 presents the results of Case 3 for the LiCl-methanol system at 25°C. The major contribution to the calculated solvent activity coefficients of methanol is due to the Pitzer term; however,

Figure 5.5 Case 3. The Contribution of the Pitzer, Flory-Huggins, and Residual Terms in the Calculation of $\ln\gamma_{H_2O}$ for the LiCl-Water System at 25°C.
(The parameter values are found in Table 5.9.)

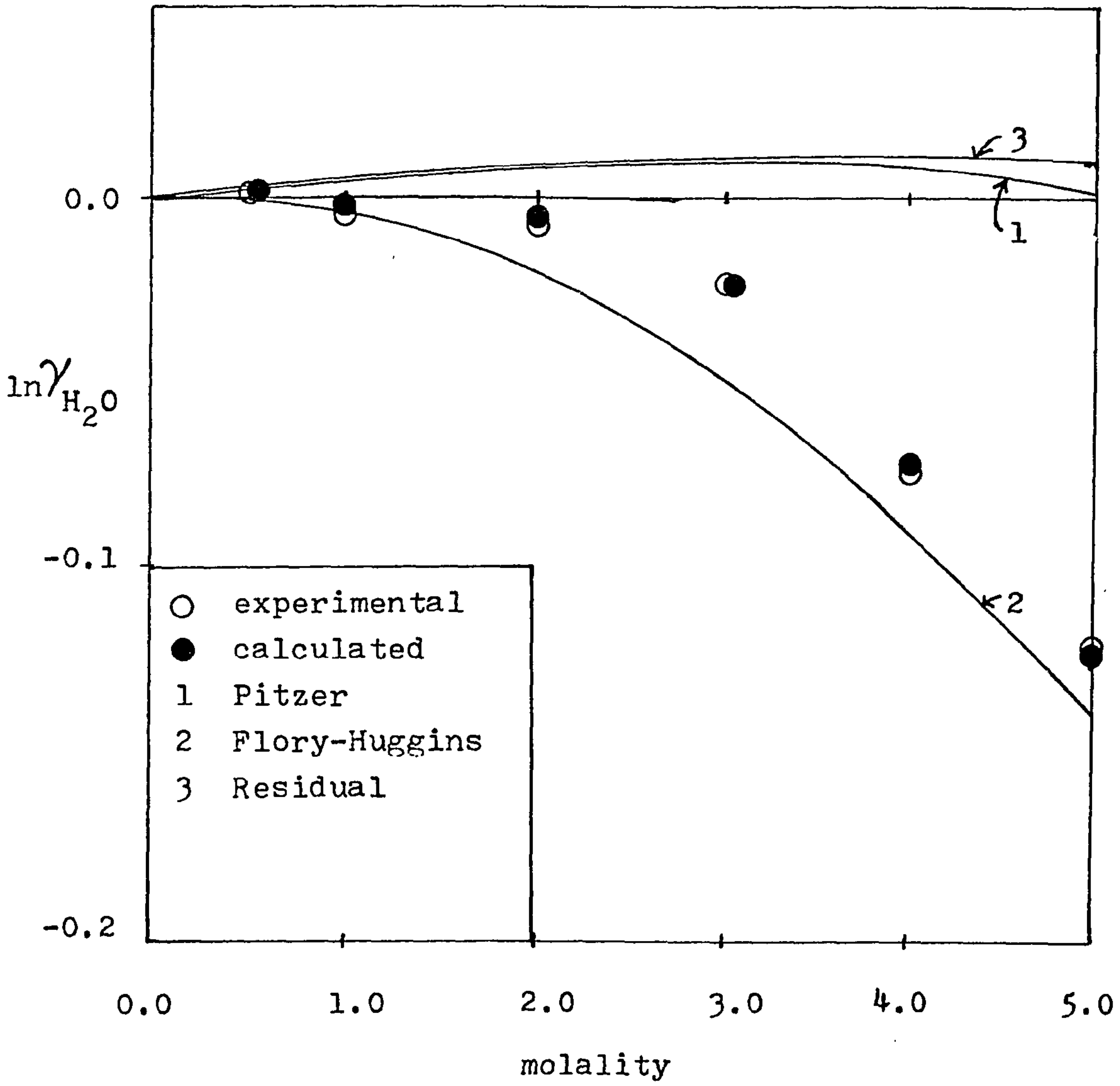
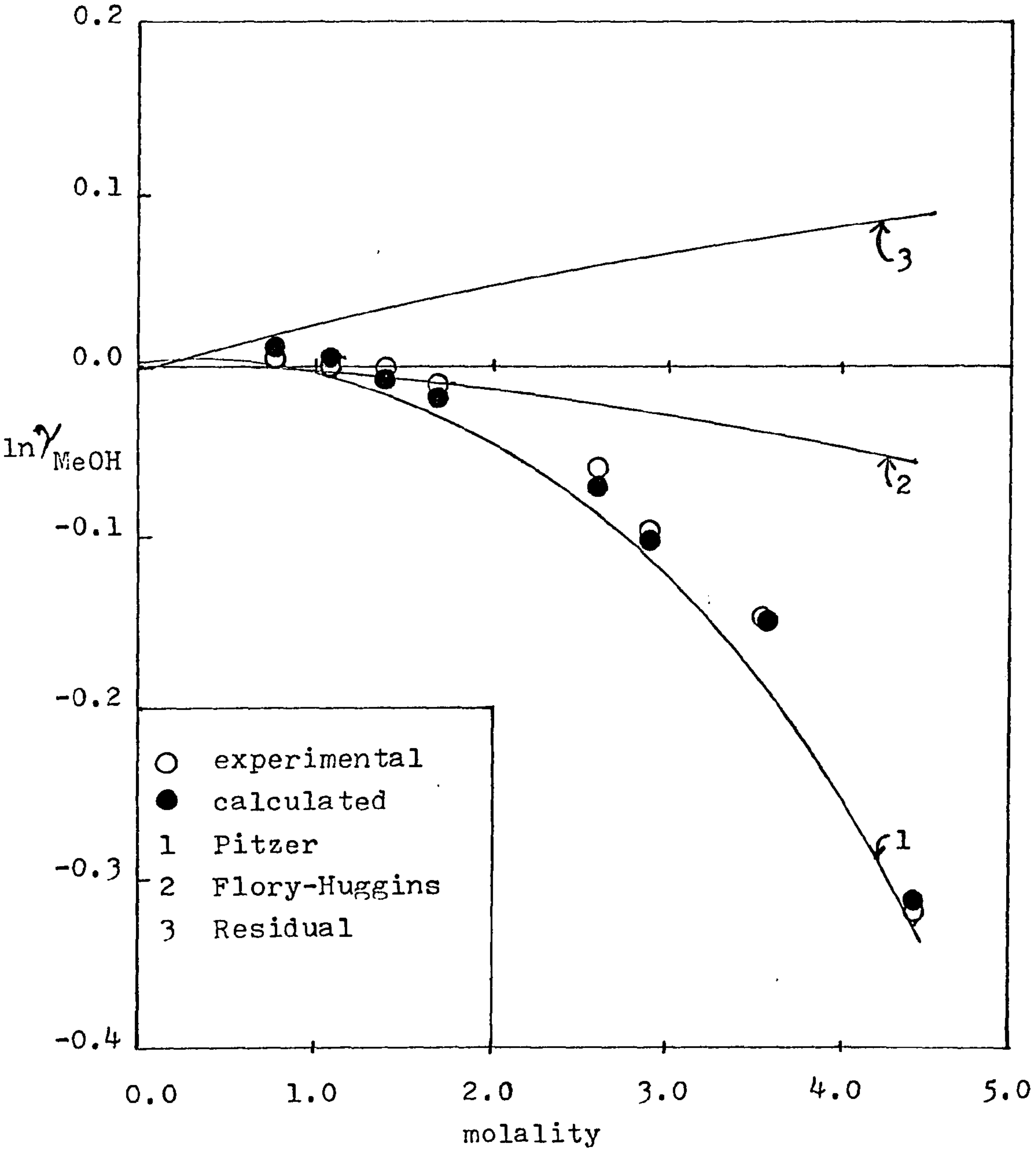


Figure 5.6 Case 3. The Contribution of the Pitzer, Flory-Huggins, and Residual Terms in the Calculation of $\ln\gamma_{MeOH}$ for the LiCl-Methanol System at 25°C.
(The parameter values are found in Table 5.9)



this contribution is not as great as it is in Case 2. The contribution of the Pitzer term is less in Case 3 than in Case 2 since the Flory-Huggins contribution is greater in Case 3 than in Case 2. The assumption of solvation decreases the value of this term. The residual contribution in Cases 2 and 3 is approximately the same.

Although the performance of the binary model is similar for Cases 2 and 3, it will be demonstrated in Chapter 6 that only the parameters of Case 3 allow the prediction of the properties of single salt-mixed solvent systems. It is for this reason that only the parameters determined using the assumption of Case 3 will be presented in the next section for the binary data base of Table 5.1.

5.3 Values of the Binary Ion-Solvent Interaction Parameters

The approach of Case 3 with a, the ion-size parameter of the Pitzer term set equal to the sum of the crystallographic radii, and h_{o+j} of the Flory-Huggins term set equal to the values of the third column of Table 5.8, is used to obtain the binary ion-solvent parameters of the residual term. The h_{o-j}, the solvation numbers of the negative ion, are set equal to zero. The calculation scheme used to obtain A_{12}, A_{31}, and A_{32} for the 1-1 chlorides has already been described in Section 5.2. $A\pm$ was found to be zero and is assumed to be zero for all salts in all solvents.

The parameters for the aqueous 1-1 chlorides at 25°C are shown in Table 5.10. The average percent error in Φ and the average percent error in the vapor pressure, P, is shown for each salt. The overall average percent errors Φ and P are also reported. Since no value of the crystallographic radii is available for the hydrogen ion, it was assumed that the radius of the hydrogen ion is zero. The value of h_{o+j} for the hydrogen ion was obtained by regression since no value is reported in the literature. The ammonium ion is assumed to have a solvation number of one since this ion is the same size as the rubidium ion which has a solvation number of one.

It is assumed that the value of A_{12} given in Table 5.10 is the same for all salts in water. The values of A_{31} from Table 5.10, the water-positive ion interaction parameters, and A_{12}, were used to determine A_{32}, the water-bromide ion interaction parameter and the water-iodide ion interaction parameter. Again, a is the sum of the crystallographic radii and the h_{o+j} are obtained from Table 5.8. The HBr, NaBr, KBr, RbBr and CsBr systems were regressed together to obtain A_{H_2O/Br^-} and

TABLE 5.10

Binary Interaction Parameters for the Aqueous 1-1 Chlorides at 25^{o}C

Salt	$a = \Sigma r_c$	ho_{+j}	$\underline{A}_{12}$	$\underline{A}_{31}$	$\underline{A}_{32}$	Avg. % Error, ϕ	Avg. % Error, P
HCl	1.81	6.0	-828.7	-365.5	-87.53	3.0	0.44
LiCl	2.41	5.0		-368.2		1.6	0.18
NaCl	2.76	3.0		-442.3		0.9	0.05
KCl	3.14	2.0		-13.7		1.7	0.12
RbCl	3.29	1.0		-142.0		1.4	0.10
NH_4Cl	3.29	1.0		-116.3		2.9	0.27
CsCl	3.47	0.0		-89.7		1.5	0.17
				Average % Errors =		1.9	0.19

the HI, NaI, KI, RbI, and CsI systems were regressed together to obtain A_{H_2O/I^-}. The LiBr and LiI systems were predicted from the resulting parameters.

The parameter values, the average percent error in Φ, and the average percent error in P, for the 1-1 bromides and 1-1 iodides are presented in Table 5.11. The average percent errors in Φ and P for these systems are also tabulated.

The average percent errors in Φ for the 1-1 bromide and iodide systems are 2.6 and 2.9, respectively, compared to the value of 1.9 obtained for the 1-1 chlorides. This is to be expected since only one parameter was used to correlate these systems versus the three parameters used to correlate a chloride system.

An attempt was made to correlate the 1-1 nitrates, perchlorates, acetates, and flourides, the 2-1 chlorides, bromides, and iodides, and the 1-2 sulfates of the binary data base of Table 5.1 using the parameters of Tables 5.10 and 5.11, the values of h_{o+j} given in Table 5.8, and the assumption that a is the sum of the crystallographic radii. In the case of the 1-1 and 1-2 salts, the data were regressed for A_{32} and in the case of the 2-1 salts, the data were regressed for A_{31}. While the results for the 1-1 flourides, perchlorates, and 2-1 chlorides are not as good as those of Table 5.10 and 5.11, poor correlation of the data was obtained for the 1-1 nitrates, acetates, and the 1-2 sulfates.

Typical results are shown in Table 5.12 for the 1-1 nitrates at 25°C. The data were regressed for A_{water/NO_3^-}, the water-nitrate ion interaction parameter. The average percent error in Φ is 8.5 and the average percent error in P is 0.55. These results are poor compared

TABLE 5.11

Binary Interaction Parameters for the Aqueous 1-1 Bromides and 1-1 Iodides at 25°C

$A_{12} = -828.7$

Salt	$a=\Sigma r_c$	ho_{+j}	A_{31}	A_{32}	Avg. % Error, ϕ	Avg. % Error, P
HBr	1.95	6.0	-365.5	-49.9	3.7	0.08
*LiBr	2.55	5.0	-368.2		3.5	0.70
NaBr	2.90	3.0	-442.3		2.1	0.13
KBr	3.28	2.0	-13.7		2.5	0.19
RbBr	3.43	1.0	-142.0		2.1	0.22
CsBr	3.61	0.0	-89.7		1.5	0.14
		Average % Errors =			2.6	0.24
HI	2.16	6.0	-365.5	-13.1	3.6	0.16
LiI	2.76	5.0	-368.2		3.2	0.16
NaI	3.11	3.0	-442.3		3.4	0.20
KI	3.49	2.0	-13.7		3.4	0.07
RbI	3.64	1.0	-142.0		2.6	0.31
CsI	3.82	0.0	-89.7		1.4	0.19
		Average % Errors =			2.9	0.18

*Predicted from the binary parameters

TABLE 5.12

Binary Interaction Parameters for the Aqueous 1-1 Nitrates at 25°C

$a = \Sigma r_c$ and $A_{12} = -828.7$

Salt	$a=\Sigma r_c$	ho_{+j}	$\underline{A}_{31}$	$\underline{A}_{32}$	Avg. % Error, ϕ	Avg. % Error, P
$LiNO_3$	2.49	5.0	-368.2	555.0	5.5	0.46
$NaNO_3$	2.85	3.0	-442.3		8.8	0.85
KNO_3	3.22	2.0	-13.7		7.8	0.29
$RbNO_3$	3.37	1.0	-142.0		11.9	0.55
		Average % Errors =			8.5	0.55

to the fit of the data obtained for the 1-1 chlorides, bromides, and iodides.

For these systems, the Flory-Huggins term may be regarded as fixed since it depends on literature values of the solvation number. Likewise, the residual term may be considered fixed since two out of three parameters, A_{12} and either A_{31} or A_{32}, have already been established. (Tables 5.10 and 5.11) The only other parameter that may be modified is a, which is assumed to be the sum of the crystallographic radii for the 1-1 chlorides, bromides, and iodides, and is adjustable for the methanol systems.

The 1-1 nitrates, perchlorates, acetates, and flourides, the 2-1 chlorides, bromides, and iodides, and the 1-2 sulfates, were regressed again, with a as an adjustable parameter, and for either A_{31} and A_{32}. The results are shown in Table 5.13.

The average percent error in Φ for the 1-1 nitrates is reduced to 3.1 with a an adjustable parameter compared to a value of 8.5 where a is assumed to be the sum of the crystallographic radii. The results for the other systems listed in Table 5.13 have also improved dramatically.

It should be noted that the values of h_{o+j} for the Ba^{++}, Co^{++}, and Sr^{++} ions, were obtained regarding h_{o+j} as an adjustable parameter since these values are not available in Bockris and Reddy (1977). Even though Bockris and Reddy indicate that the value of the hydration number of the Mg^{++} ion is between 13 and 16, it was found that a value of 10 gives better correlation results.

Robinson and Stokes (1959) indicate that the so called strong electrolytes, those which completely dissociate in solution, are

TABLE 5.13

Binary Interaction Parameters at 25°C

a is an adjustable parameter

$\underline{A}_{12} = -828.7$

Salt	$\underline{a}$	ho_{+j}	$\underline{A}_{31}$	$\underline{A}_{32}$	Avg. % Error, Φ	Avg. % Error, P
$LiNO_3$	1.79	5.0	-368.2	-13.3	4.1	0.42
$NaNO_3$	1.45	3.0	-442.3		3.9	0.24
KNO_3	1.69	2.0	-13.7		2.3	0.08
$RbNO_3$	1.98	1.0	-142.0		1.7	0.01
HNO_3	1.05	6.0	-365.5		3.6	0.16
		Average % Errors =			3.1	0.18
$LiClO_4$	2.72	5.0	-368.2	-33.8	1.4	0.08
$NaClO_4$	2.26	3.0	-442.3		2.3	0.15
$HClO_4$	1.42	6.0	-365.5		1.7	0.13
		Average % Errors =			1.8	0.12
LiAc	1.60	5.0	-368.2	-218.5	3.5	0.21
NaAc	3.28	3.0	-442.3		1.5	0.08
KAc	3.93	2.0	-13.7		1.5	0.08
RbAc	4.14	1.0	-142.0		1.2	0.07
CsAc	4.36	0.0	-87.7		1.6	0.10
		Average % Errors =			1.9	0.11
NaF	2.23	3.0	-442.3	-147.3	0.8	0.01
KF	3.27	2.0	-13.7		0.4	0.02
		Average % Errors =			0.6	0.015
Li_2SO_4	1.17	5.0	-368.2	147.6	14.4	0.85
Na_2SO_4	2.16	3.0	-442.3		0.8	0.01
K_2SO_4	3.32	2.0	-13.7		2.5	0.07
Rb_2SO_4	3.63	1.0	-142.0		3.0	0.10
Cs_2SO_4	4.18	0.0	-87.7		4.9	0.11
		Average % Errors =			5.1	0.23

Salt	$\underline{a}$	ho_{+j}	$\underline{A}_{31}$	$\underline{A}_{32}$	Avg. % Error, Φ	Avg. % Error, P
$CaCl_2$	2.93	9.0	-220.2	-87.5	2.8	0.67
$CaBr_2$	3.52			-45.9	2.8	1.14
CaI_2	3.72			-13.1	1.6	0.07
$BaCl_2$	3.19	7.0	-261.1	-87.5	3.3	0.14
$BaBr_2$	3.57			-45.9	2.3	0.11
BaI_2	4.21			-13.1	1.4	0.08
$CoCl_2$	2.89	9.0	-235.0	-87.5	4.9	0.69
$CoBr_2$	3.56			-45.9	2.3	0.65
CoI_2	3.98			-13.1	3.0	1.86
$SrCl_2$	3.19	8.0	-227.7	-87.5	2.2	0.13
$SrBr_2$	3.54			-45.9	1.7	0.07
SrI_2	3.94			-13.1	1.3	0.05
$MgCl_2$	2.82	10.0	-193.9	-87.5	2.8	0.50
$MgBr_2$	3.33			-45.9	1.6	0.23
MgI_2	3.70			-13.1	2.2	0.67
		Average % Errors =			2.4	0.47

comprised of the alkali halides, the alkaline-earth halides and perchlorates, and some transition-metal halides. The flouride, perchlorate, and the 2-1 salts of Table 5.13 are in this category. The nitrate, acetate, and sulfate salts are weak electrolytes since it is believed that association occurs between the oppositely charged ions as a result of electrostatic attraction.

The Pitzer term, if used alone in the correlation of 1-1 and 2-1 strong electrolytes in water, has been shown to be applicable up to a molality of 6 for the 1-1 salts and a molality of 2 for the 2-1 salts, when a is an adjustable parameter. (Tomasula, et.al., 1985) It does not correlate these systems if a is set equal to the sum of the crystallographic radii. The addition of the Flory-Huggins and the residual terms extends the molality range of the Pitzer term in the case of the 2-1 salts of this study since the data are correlated up to a molality of 6 when a is adjustable. If a is set equal to the sum of the crystallographic radii, the average percent errors in Φ for the $CaCl_2$, $CaBr_2$, and CaI_2 systems are 4.5, 7.1, and 7.9, respectively, up to a molality of 2. The addition of these terms allows the correlation of the 2-1 aqueous salt systems up to a molality of 6. The Bromley (1973) model which contains four fixed water specific parameters and one salt-specific parameter, correlates these systems up to a molality of 1. The Pitzer (1973) model, which contains two fixed water specific parameters and three salt-specific adjustable parameters, correlates the $MgCl_2$ system up to a molality of 4.5, the $SrCl_2$ system up to a molality of 4, and the other 2-1 salts of Table 5.13 up to a molality of 2.

The addition of the Flory-Huggins and the residual terms also allows the value of a to be set equal to the sum of the crystallographic radii for the 1-1 chlorides, bromides, and iodides. This is apparently coincidental since a must be an adjustable parameter for the strong electrolytes listed in Table 5.13.

For the ion-pairing electrolytes of Table 5.13 (1-1 nitrates and 1-2 sulfates), the value of a obtained through regression is generally less than the sum of the crystallographic radii. Even though equation (5-6) was derived assuming complete dissociation of the electrolyte, the model correlates the 1-1 nitrates with an average percent error in Φ of 3.1 and an average percent error in Φ for the 1-2 sulfates of 5.1. However, the Li_2SO_4 system is correlated with an average percent error in Φ of 14.4.

The binary interaction parameters for the salt-methanol systems listed in the binary data base of Table 5.1 are shown in Table 5.14. a is an adjustable parameter and h_{o+j} is calculated using equation (5-9). The LiCl and LiBr methanol systems at 25°C were regressed together to establish the individual values of a for LiCl and LiBr, A_{12}, A_{31}, and A_{32}. $A\pm$ was found to be equal to zero. The value of A_{12} obtained for these systems is assumed to be the value of A_{12} for all the other salts in methanol. The values of $A_{\text{methanol/Br}^-}$ and A_{12} were used to establish the value of a of the NaBr-methanol system and the $A_{\text{methanol/Na}^+}$ parameter. The $A_{\text{methanol/Na}^+}$ parameter and A_{12} allowed the determination of the values of a for the NaI and NaSCN systems as well as the values of $A_{\text{methanol/I}^-}$ and $A_{\text{methanol/SCN}^-}$. The parameters for the other salts listed in Table 5.14 are determined as above.

The overall average percent error in Φ for the systems listed

Table 5.14 Binary Interaction Parameters for Salt-Methanol Systems at 25°C. a is an Adjustable Parameter. $A_{12} = -253.1$

Salt	a	h_{o+j}	A_{31}	A_{32}	Avg. % Error, Φ	Avg. % Error, P
LiCl	5.35	2.00	620.8	782.3	2.3	0.50
LiBr	5.70	2.00	620.8	938.4	1.5	0.43
NaI	5.35	1.25	-281.6	219.8	0.8	0.20
KI	4.73	0.88	-302.1	219.8	2.0	0.03
NaBr	5.19	1.25	-281.6	938.4	2.0	0.14
NaSCN	4.73	1.25	-281.6	-42.6	2.4	0.35
KCH_3COO	4.00	0.88	-302.1	213.0	3.3	0.30
$CuCl_2$	3.65	4.17	-2362.8	782.3	8.0	0.93
$CaCl_2$	5.11	3.75	-118.2	782.3	2.7	0.42
NH_4SCN	3.93	0.42	-410.7	-42.6	7.9	0.99
AVG. =	4.77			AVG. =	3.3	

in Table 5.14 is 3.3. Most systems are correlated well with the exception of the $CuCl_2$-methanol system which has an average percent error in Φ of 8.0 and the NH_4SCN system which has an average percent error in Φ of 7.9.

The binary interaction parameters for the salt-ethanol systems listed in the binary data base of Table 5.1 are shown in Table 5.15. The LiCl and $CaCl_2$ systems were chosen as the base systems from which the other salt-ethanol interaction parameters are determined. The value of A_{12} was not regarded as an adjustable parameter for these systems but was calculated based on the values of A_{12} obtained for the water and methanol systems. This was done to decrease the number of parameters in the residual term which need to be established for solvent systems in which few salt-solvent data exist.

The values of A_{12} for the water and methanol systems were assumed to be linear functions of the dielectric constants of these solvents at 25°C. The relationship between A_{12} and the dielectric constant is

$$A_{12} = 156.8 - 12.57D_{25°C} \qquad (5\text{-}10)$$

The values of A_{12} and the values of h_{o+j} calculated using equation (5-9) were used to determine the value of A_{32}, the ethanol/Cl^- interaction parameter, and the values of A_{31}, the ethanol/Li^+ and ethanol/Ca^{+2} interaction parameters. The values of a of the Pitzer term for LiCl and $CaCl_2$ were also calculated.

The ethanol/Li^+ parameter allowed the calculation of the values of a and A_{32} for the LiBr-ethanol system. The parameters for the NaI-ethanol system, with the exception of A_{12}, were determined independently since no other salt-ethanol data are available which have ions in common with this system.

Table 5.15 Binary Interaction Parameters for Salt-Ethanol and Salt-Isopropanol Systems. a is an Adjustable Parameter. A_{12} ethanol = -147.9 A_{12} isopropanol = -68.8 (The parameters were established at the indicated temperatures.)

Ethanol Salt	T°C	a	A_{31}	A_{32}	Avg. % Error, Φ	Avg. % Error, P
LiCl	35.0	4.84	4634.1	926.9	3.3	1.33
LiBr	50.0	6.60	4634.1	1349.5	2.9	2.29
$CaCl_2$	50.0	5.27	90.3	926.9	3.7	0.50
NaI	50.0	6.08	-279.2	1098.3	1.6	0.34
		AVG. = 5.70			AVG. = 2.9	

Isopropanol Salt	T°C	a	A_{31}	A_{32}	Avg. % Error, Φ	Avg. % Error, P
LiCl	75.1	6.10	2398.9	9377.9	4.3	0.51
LiBr	75	6.50	2398.9	2160.0	3.2	0.80
		AVG. = 6.30			AVG. = 3.8	

The binary interaction parameters for the salt-isopropanol systems are presented in Table 5.15. A_{12} was calculated from equation (5-10) and the value of h_{o+j} for the Li^+ ion was calculated by equation (5-9). The LiCl and LiBr-isopropanol systems were regressed simultaneously to obtain the values of a for the two salts, $A_{isopropanol/Li^+}$, $A_{isopropanol/Cl^-}$ and $A_{isopropanol/Br^-}$. The values of a and $A_{isopropanol/Ca^{++}}$ for the $CaCl_2$-isopropanol system could not be established since this system could not be correlated by the binary model.

The parameters for the $CaCl_2$-propanol system are not presented, since this system could not be correlated by the binary model.

The possible reasons for the failure of the model to correlate the $CaCl_2$-isopropanol and the $CaCl_2$-propanol systems are discussed in Chapter 7.

5.4 Temperature Extrapolation of the Binary Parameters

It is important to examine the effect of temperature on the parameter values of the model since in the isobaric salt-mixed solvent systems, temperature varies with composition.

Table 5.16 presents the prediction results, based on the parameter values at 25°C, for some aqueous systems. These results can be considered good for the temperature range involved. The average percent error in Φ for all systems is 4.2. An average percent error in Φ surpassing 10% is observed only for the LiCl-water system at 150°C.

The parameters of the Bromley (1973) model and the Pitzer (1973, 1977) models, which were obtained at 25°C, were used to predict the osmotic coefficients and vapor pressures of some salts in water up to an ionic strength of 6m. (Tomasula, et.al., 1985) The Bromley model, termed B-1, contains four fixed water specific parameters and one adjustable parameter. The Pitzer (1973) model, termed P-3, has two fixed water specific parameters and three salt-specific adjustable parameters. The Pitzer (1977) model, termed P-1, is given by equation (5-1) and has one adjustable parameter.

The models are compared in Table 5.17. The binary model of this study allows the prediction of salt-water systems with temperature independent parameters as well as the B-1, P-1, and P-3 models.

Table 5.18 presents the prediction results, based on the parameter values at 25°C, for some methanol systems. The average percent error in Φ for all systems is 3.2 and it may be concluded that this model provides reliable extrapolations with respect to temperature using temperature independent parameters up to a molality

Table 5.16 Average % Error in Φ and in P in Prediction from Parameter Values at 25°C in Aqueous Systems

Salt	T°C	Avg. % Error, Φ	Avg. % Error, P	Maximum Molality	Reference
LiCl	50	3.8	0.35	3.2	Campbell and Bhatnagar (1979)
	75	5.7	0.57		
	100	4.4	0.43		
	125	6.7	0.65		
	150	10.2	0.93		
CsCl	110	2.5	0.43	6.0	Holmes and Mesmer (1981)
	140	3.4	0.56		
	170	4.3	0.67		
	200	5.4	0.77		
KCl	40	1.7	0.11	4.5	Snipes, et.al. (1975)
	50	1.6	0.08		
	60	1.5	0.09		
	70	1.5	0.09		
	80	1.5	0.09		
KI	100	8.5	2.68	10.0	Weast (1970)
LiI	100	3.1	1.28		
NaI	100	7.7	2.09		
KI	100	3.7	0.59	6.0	
LiI	100	2.3	0.85		
NaI	100	8.0	1.60		
LiBr	100	1.3	0.29	10.0	
NaBr	100	5.1	0.84	8.0	
LiBr	100	1.5	0.24	6.0	

Table 5.16 continued

Salt	T°C	Avg. % Error, Φ	Avg. % Error, P	Maximum Molality	References
NaBr	100	5.8	0.80	6.0	Weast (1970)

Table 5.17 A Comparison of the Average % Error in Φ in Prediction from Parameter Values at 25°C in Aqueous Systems for Four Models

		Avg. % Error, Φ				
Salt	T°C	B-1	P-1	P-3	This Study	Maximum Molality
LiCl	50	3.4	3.6	3.0	3.8	3.2
	75	6.2	6.4	5.1	5.7	
	100	4.9	4.8	3.5	4.4	
	125	7.6	7.3	5.7	6.7	
	150	11.6	10.9	9.1	10.2	
KCl	40	0.9	1.9	1.1	1.7	4.5
	50	1.4	2.4	1.7	1.6	
	60	1.8	2.8	2.2	1.5	
	70	2.0	3.1	2.6	1.5	
	80	2.3	3.4	2.9	1.5	
CsCl	110	4.9	6.5	7.0	2.5	6.0
	140	5.1	7.3	8.1	3.4	
	170	4.9	7.9	9.1	4.3	
	200	4.5	8.2	10.6	5.4	

Table 5.18 Average % Error in Φ and in P in Prediction from Parameter Values at 25°C in Methanol Systems

Salt	T°C	Avg. % Error, Φ	Avg. % Error, P	Maximum Molality	Reference
LiCl	35	1.9	0.46	4.6	Tomasula (1980)
	45	1.6	0.29		
	60	3.6	1.30	5.9	Hala (1969)
LiBr	35	1.9	0.44	4.3	
	45	2.6	0.46		
NaSCN	40	3.1	0.53	3.4	This Study
NH_4SCN	40	7.0	0.89	5.2	
KCH_3COO	40	4.2	0.40	2.5	
NaI	40	2.9	0.76	4.3	
Average % Error, Φ		3.2			

of 6.0 and up to 60°C.

The results of this study are compared to those of the B-1, P-1, and P-3 models in Table 5.19 and are comparable in all cases to those of the P-3 model.

The temperature dependency of the ethanol and isopropanol salt-solvent parameters could not be investigated since the data for these systems (Table 5.1) which are at temperatures other than 25°C, were used to establish the model parameters.

Table 5.19 A Comparison of the Average % Error in Φ in Prediction from Parameter Values at 25°C in Methanol Systems for Four Models

Average % Error in the Predicted Osmotic Coefficients

Salt	T°C	B-1	P-1	P-3	This Study
LiCl	35	2.4	4.1	1.1	1.9
	45	4.7	6.6	1.4	1.6
	60	5.4	8.5	3.5	3.6
LiBr	35	5.5	7.0	1.2	1.9
	45	4.6	7.0	2.0	2.6

5.5 Molality Range of the Binary Model

The binary parameters of Table 5.13 were used to predict the osmotic coefficients at 25°C of some 1-1 electrolytes in water at molalities greater than 6m. The results are shown in Table 5.20 and are reported as the relative percent error in Φ at each molality.

The results indicate that relative percent errors in Φ greater than 10% are to be expected if the parameters obtained from regression of the data up to a molality of 6 are used to extrapolate to molalities greater that 6. The only exception occurs with the LiCl-water system. Reliable predictions are obtained up to m = 13.

The dashed lines for some of the salts in Table 5.20 indicate the region in which the model breaks down entirely. This occurs when the model indicates there are no longer any solvent molecules with which to solvate the ions, or x_3', given by equation (3-32) becomes zero.

x_3', the mole-fraction of the free-solvent molecules in a binary electrolytic solution, is given by

$$x_3' = (x_3 - x_1 h_{o+1} x_3)/(1 - x_1 h_{o+1}) \qquad (5\text{-}11)$$

where h_{o+1} is the solvation number of the positive ion, x_3, is the apparent mole-fraction of the positive ion. x_1 and x_3 are given by equations (3-24) and (3-26), respectively. x_3' becomes zero when the numerator of equation (5-11) is zero, or when

$$x_1 = 1/h_{o+1} \qquad (5\text{-}12)$$

For the LiCl-water system in which the solvation number of the Li^+ ion is 5, x_3' from equation (5-11) is zero and x_1 from equation (5-12) is 0.2. This corresponds to a molality of 18.5. At molalities greater than 18.5, x_3' becomes negative.

Table 5.20 Prediction of the Osmotic Coefficents at 25°C of Some Aqueous Systems at High Molalities. The Data are from Robinson and Stokes (1959).

Salt	m	Rel. % Error, Φ	Salt	m	Rel. % Error, Φ
HCl	7.0	-10.8	$LiNO_3$	7.0	-12.6
	8.0	-14.8		8.0	-17.3
	9.0	-19.9		9.0	-22.6
	10.0	-27.8		10.0	-28.8
	11.0	-39.2		11.0	-36.1
	12.0	-56.5		12.0	-44.4
	13.0	-87.2		13.0	-54.5
	14.0	-186.2			
	15.0	----	LiBr	7.0	10.8
	16.0	----		8.0	12.2
				9.0	13.1
$HClO_4$	7.0	-10.8		10.0	14.2
	8.0	-10.6		11.0	14.8
	9.0	-11.3		12.0	13.6
	10.0	-13.7		13.0	12.3
	11.0	-18.3		14.0	9.4
	12.0	-27.1		15.0	3.7
	13.0	-44.9		16.0	-4.9
	14.0	-109.3		17.0	-19.5
	15.0	----		18.0	-54.3
	16.0	----		19.0	----

Table 5.20 continued

Salt	m	Rel. % Error,Φ	Salt	m	Rel. % Error,Φ
LiCl	7.0	3.7			
	8.0	4.3	CsCl	7.0	-10.6
	9.0	4.0		8.0	-15.0
	10.0	2.8		9.0	-20.6
	11.0	0.9		10.0	-27.1
	12.0	-2.3		11.0	-34.3
	13.0	-6.9			
	14.0	-13.3			
	15.0	-22.2			
	16.0	-35.3			
	17.0	-56.8			
	18.0	-105.9			
	19.0	-----			
	20.0	-----			

It is recommended, therefore, that the binary model parameters not be used to predict the thermodynamic properties of electrolytic solutions beyond a molality of 6 in water.

The molality range for the salt-nonaqueous systems could not be investigated since data greater than 6m are not available.

5.6 Values of the Binary Solvent (1) - Solvent (2) Interaction Parameters

The solvent activity coefficient of component i in a multicomponent nonelectrolytic solution is:

$$\ln\gamma_i = \ln\gamma_i\binom{\text{Flory-}}{\text{Huggins}} + \ln\gamma_i(\text{Residual}) \quad (5\text{-}13)$$

where

$$\ln\gamma_i\binom{\text{Flory-}}{\text{Huggins}} = \ln\Phi_i/x_i^\circ + 1 - \Phi_i/x_1^\circ \quad (5\text{-}14)$$

and $\ln\gamma_i$(Residual) is given by equation (3-19). The volume fraction, Φ_i, is defined

$$\Phi_i = r_i x_i^\circ/\Sigma_j r_j x_j^\circ \quad (5\text{-}15)$$

and the area fraction, Θ_i, is defined

$$\Theta_i = q_i x_i^\circ/\Sigma_j q_j x_j^\circ \quad (5\text{-}16)$$

where the x_j° are the mole-fractions of the solvents. The UNIQUAC volume (r_i) and surface area (q_i) parameters for the solvents in this study are found in Table 5.3.

The solvent activity coefficient of solvent 1(3), in a binary nonelectrolytic solution of 3 and solvent 2(4), is obtained from equations (5-13), (5-14), and (3-19).

$$\begin{aligned}\ln\gamma_3 &= \ln\Phi_3/x_3^\circ + 1 - \Phi_3/x_3^\circ \\ &+ q_3(1- \ln(\Theta_3 + \Theta_4\psi_{34}) - \Theta_3/(\Theta_3 + \Theta_4\psi_{34}) \\ &-\Theta_4\psi_{34}/(\Theta_3\psi_{34} + \Theta_4)) \quad (5\text{-}17)\end{aligned}$$

The solvent activity coefficient of 4 is given by

$$\begin{aligned}\ln\gamma_4 &= \ln\Phi_4/x_4^\circ + 1- \Phi_4/x_4^\circ \\ &+ q_4(1- \ln(\Theta_3\psi_{34} + \Theta_4) - \Theta_3\psi_{43}/(\Theta_3 + \Theta_4\psi_{43}) \\ &- \Theta_4/(\Theta_3\psi_{43} + \Theta_4)) \quad (5\text{-}18)\end{aligned}$$

The group interaction parameter, ψ_{mn}, is defined

$$\psi_{mn} = \exp - (A_{mn}/T) \qquad (5\text{-}19)$$

The binary nonelectrolyte solvent activity coefficient expressions contain two adjustable parameters, A_{34} and A_{43}.

The mixed solvent data of this study were correlated using the objective function

$$F = \sum_{s=1}^{NP}((P_{cal} - P_{exp})/P_{exp})_s^2 + \sum_{s=1}^{NP} ((Y_{3cal} - Y_{3exp})x10)^2_s \qquad (5\text{-}20)$$

where P_{exp} and Y_{3exp} are the experimental values of the total pressures of the mixed solvent system and the vapor-phase compositions of solvent 1. A weighing factor of 10 is used for the deviation in vapor-phase composition in order to make the magnitude of this term equal to that of the first term of equation (5-20).

For isothermal P-x-y data, P_{cal} is obtained from the value of the temperature, the values of the solvent mole-fractions, equations (5-17) and (5-18), and the relationships developed in Chapter 1.

$$P_{cal} = x_3 \gamma_3 \Phi_3{}^s P_3{}^s (\exp(P_{cal} - P_3{}^s) v_3/RT)/\hat{\Phi}_3$$

$$+ x_4 \gamma_4 \Phi_4{}^s P_4{}^s (\exp(P_{cal} - P_4{}^s) v_4/RT)\hat{\Phi}_4 \qquad (5\text{-}21)$$

$$Y_{3cal} = x_3 \gamma_3 \Phi_3{}^s P_3{}^s (\exp(P_{cal} - P_3{}^s) v_3/RT)\hat{\Phi}_3 P_{cal} \qquad (5\text{-}22)$$

The fugacity coefficients are calculated using the Hayden-O'Connell (1975) correlation which is presented in Appendix A. The Hankinson (1979) correlation is used to calculate the pure-component liquid volumes. This method is discussed in Appendix B.

Equations (5-21) and (5-22) are solved by using a bubble point calculation.

For isobaric T-x-y data, T_{cal} and Y_{3cal} are obtained from the value of the experimental total pressure of the system, the values of the solvent mole-fractions, equations (5-17) and (5-18), and the relationships of Chapter 1. P_{cal} is set equal to P_{exp} in equations (5-21) and (5-22). A bubble point calculation is used.

The regression results for the mixed-solvent systems of this study are presented in Table 5.21. The quality of the correlation of the data is shown by comparing the experimental and calculated quantities through the following expressions:

$$\Delta T = (1/NP)\sum^{NP} |T_{cal} - T_{exp}|\,^{\circ}K \qquad (5\text{-}23a)$$

$$\Delta P = (1/NP)\sum^{NP} |P_{cal} - P_{exp}|\,\text{mmHg} \qquad (5\text{-}23b)$$

$$\Delta y = (1/2NP)\sum^{NP} \sum^{2} |y_{cal} - y_{exp}| \qquad (5\text{-}23c)$$

In the case of the isothermal systems, ΔP and Δy are reported. ΔP, ΔT, and Δy are reported for the isobaric systems.

No Δy is reported for the H_2O-EtOH system at 30°C since experimental values of y_3 and y_4 were not available.

TABLE 5.21

Correlation of Binary Solvent Nonelectrolyte Data

Solvent 1(3)	Solvent 2(4)	T°C or Pmm Hg	A_{34}	A_{43}	ΔT°C	ΔPmmHg	Δy_3	Reference
H_2O	MeOH	25.0°C	168.1	-15.0	--	0.8	0.00395	Gmehling et al. (1977)
		39.9°C	226.2	-22.1	--	2.1	0.00145	
		60.0°C	137.1	64.3	--	5.9	0.00465	
		760mm	242.6	7.0	0.2	0.1	0.00231	
H_2O	EtOH	25.0°C	183.6	144.4	--	0.7	0.00694	
		30.0°C	200.0	132.0	--	0.5	--	
		50.0°C	235.1	153.7	--	6.4	0.00504	
		760mm	320.2	94.4	0.3	0.1	0.00969	
H_2O	IsoPrOH	75°C	359.6	166.1	--	3.0	0.00448	Sada et al. (1975)
		760mm	394.0	150.7	0.4	0.1	0.00587	
H_2O	n-PrOH	760mm	426.1	175.9	0.3	0.2	0.00634	Gmehling et al. (1977)
MeOH	EtOH	760mm	35.6	-22.0	0.1	0.1	0.00464	Kato (1971)
n-PrOH	IsoPrOH	760mm	-16.9	25.3	0.3	0.1	0.00409	Gmehling et al. (1977)
n-PrOH	EtOH	760mm	-79.5	98.9	0.5	0.2	0.00817	

CHAPTER 6

6.1 The Ternary Model for the Prediction of Salt-Mixed Solvent Data

Equations (3-8), (3-19), and (3-28) are used to obtain the solvent activity coefficients for a ternary electrolytic solution containing a single salt. (The subscripts 1,2,3, and 4 refer to the positive ion, the negative ion, solvent 1(3), and solvent 2(4), respectively, in the following discussion.)

The Coulombic contributions to the solvent activity coefficients are calculated directly from equation (3-8). The terms in equation (3-8) are defined by equations (3-9) - (3-18).

The residual contributions to the solvent activity coefficients are calculated from equation (3-19). The terms of equation (3-19) are defined by equations (3-19) - (3-27).

The Flory-Huggins contributions to the solvent activity coefficients are given by equation (3-28). The terms of equation (3-28) are defined by equations (3-29) - (3-38).

The solvent activity coefficient for component 3 in a salt-mixed solvent solution is therefore given by

$$
\begin{aligned}
\ln \gamma_3 = {} & \ln \gamma_3^{\text{Coulombic}}(\text{equation 3-8}) + \ln \Phi_3'/x_3' + 1 - \Phi_3'/x_3' \\
& + q_3(1 - \ln(\Theta_1 A^{\pm}/Q_1 + \Theta_3 + \Theta_4 \Psi_{43}) \\
& - \Theta_1 \Psi_{31}/(\Theta_1 + \Theta_2 \Psi_{21} + \Theta_3 \Psi_{31} + \Theta_4 \Psi_{41}) \\
& - \Theta_2 \Psi_{32}/(\Theta_1 \Psi_{12} + \Theta_2 + \Theta_3 \Psi_{32} + \Theta_4 \Psi_{42}) \\
& - \Theta_3/(\Theta_1 A^{\pm}/Q_1 + \Theta_3 + \Theta_4 \Psi_{43}) \\
& - \Theta_4 \Psi_{34}/(\Theta_1 B^{\pm}/Q_1 + \Theta_3 \Psi_{34} + \Theta_4)) \\
& + \ln x_3' - \ln x_3 \qquad (6\text{-}1)
\end{aligned}
$$

The solvent activity coefficient for component 4 in a salt-mixed solvent solution is given by

$$\begin{aligned}\ln \gamma_4 = {} & \ln \gamma_4^{\text{Coulombic}}(\text{equation 3-8}) + \ln\Phi_4'/x_4' + 1 - \Phi_4'/x_4' \\ & + q_4(1 - \ln(\Theta_1 B\pm/Q_1 + \Theta_3 \psi_{34} + \Theta_4) \\ & - \Theta_1 \psi_{41}/(\Theta_1 + \Theta_2 \psi_{21} + \Theta_3 \psi_{31} + \Theta_4 \psi_{41}) \\ & - \Theta_2 \psi_{42}/(\Theta_1 \psi_{12} + \Theta_2 + \Theta_3 \psi_{32} + \Theta_4 \psi_{42}) \\ & - \Theta_3 \psi_{43}/(\Theta_1 A\pm/Q_1 + \Theta_3 + \Theta_4 \psi_{43}) \\ & - \Theta_4/(\Theta_1 B\pm/Q_1 + \Theta_3 \psi_{34} + \Theta_4)) \\ & + \ln x_4' - \ln x_4 \qquad (6\text{-}2)\end{aligned}$$

A± is defined by equation (5-4b). B± is defined

$$B\pm = Q_1 \psi_{14} + (v_2/v_1) Q_2 \psi_{24} \qquad (6\text{-}2a)$$

(Note that the solvent was referred to as component 3 in Chapter 5 for both aqueous and nonaqueous electrolytic solutions. In this Chapter, component 3 is generally water and component 4 is the nonaqueous solvent.)

The values of A± and B± were found to be zero from the regression of binary aqueous and nonaqueous data.

It is also to be noted here that the solvation numbers of the negative ions are assumed to be zero.

For isothermal P-x-y data, the experimental values of the liquid-phase mole fractions for each component, the temperature of the system, and equations (6-1) and (6-2) allow the calculation of the pressure and vapor-phase mole fraction at each data point. From the relationships of Chapter 1,

$$P_{cal} = \overset{j}{\Sigma}_j\, x_j \gamma_j P_j^s \Phi_j^s (\exp(P_{cal} - P_j^s) v_j/RT)/\Phi_j \qquad (6\text{-}3)$$

$$y_{ical} = x_i \gamma_i P_i^s \Phi_i^s (\exp(P_{cal} - P_i^s) v_i/RT)/\Phi_i P_{cal} \qquad (6\text{-}4)$$

The vapor pressures, P_i^s, of the solvents are determined using the Antoine equation. The constants are given in Appendix A. The Hayden-O'Connell (1975) correlation is used to calculate the fugacity coefficients. The procedure is discussed in Appendix A. The Hankinson and Thomson (1979) correlation is used to calculate the pure-component liquid volumes, v_i. (See Appendix B) Equations (6-1) - (6-4) must be solved using a bubble point calculation.

For isobaric T-x-y data, the experimental values of the system pressure and the liquid-phase mole fractions for each component are used to generate the bubble-point temperatures and the vapor-phase mole-fractions. P_{cal} in equations (6-3) and (6-4) are replaced by P_{exp}, the experimental system pressure. A bubble point calculation is used to solve the equations.

The ternary model of equations (6-1) - (6-2) was used in the prediction of the vapor-phase compositions given by equations (6-3) and (6-4) considering the cases discussed below.

6.2 Case 1. Solvation Effects are Neglected in the Model

The binary solvent-ion parameters of Table 5.7 and the binary solvent-solvent parameters of Table 5.21 are utilized. The binary solvent-ion parameters of Table 5.7 were obtained with a, the ion-size parameter of the Coulombic (Pitzer) term, an adjustable parameter. The solvation numbers of the positive ion were set to zero. The prediction results for the corresponding data of the ternary data base (Table 5.2) are presented in Table 6.1. The quality of the prediction of the data is indicated by ΔP, ΔT, and Δy, defined by equations (5-23a), (5-23b), and (5-23c). The average percent errors in γ_3 and γ_4 given by

$$\text{Average \% error } \gamma_i = (1/NP) \sum_j^{j} |(\gamma_{j_{exp}} - \gamma_{j_{cal}} / \gamma_{j_{exp}})| \times 100 \qquad (6\text{-}5)$$

are also reported.

The average percent ratio is defined

$$\begin{array}{c}\text{Average \%}\\ \text{Ratio}\end{array} = \left(\frac{1}{NP}\right) \sum_j^{j} \left(\frac{y_{4_{jcal}} - y_{4_j}\ \text{salt-free}}{y_{4_{exp}} - y_{4_j}\ \text{salt-free}}\right) \times 100 \qquad (6\text{-}6)$$

and is a measure of how well the calculated values of y_4 agree with the experimental values of y_4. The calculation is based on y_4 since this component is enriched in the vapor-phase upon the addition of a salt to a mixed-solvent system. Component 4 is referred to as the salted-out component and component 3 is referred to as the salted-in component. This will be discussed in a later section.

Table 6.1 Case 1. Prediction of the Vapor Phase Compositions of Ternary Data Using the Binary Parameters of Tables 5.7 and 5.21. (All Solvation Numbers are Set Equal to Zero.)

Water (3)-MeOH(4)

Salt	T°C or Pmm Hg	Maximum Molality	Δy	ΔPmm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio
LiCl	25°C	1.0	0.022	1.5	--	13.7	4.7	31.0
	60°C	14.1	0.062	16.8	--	4.1	25.5	-17.0
	60°C	6.1	0.047	16.8	--	4.6	15.5	-17.0
	760mm	3.8	0.043	0.2	1.4	7.3	12.0	-17.8
NaBr	25°C	7.0	0.044	8.9	--	2.9	18.2	23.8
	40°C	6.2	0.025	17.0	--	5.8	13.1	24.4
	760mm	4.1	0.052	0.2	1.5	8.4	14.9	-11.9

A value of Average % Ratio equal to zero indicates that the predicted vapor-phase compositions of component 4 in the salt-mixed solvent solutions are the same as the vapor-phase compositions of component 4 in the salt-free mixed-solvent solutions of the same salt-free liquid phase composition. This indicates poor prediction. A value of Average % Ratio equal to 100 indicates that the predicted vapor-phase compositions of component 4 equal the experimental values, or perfect prediction. An Average % Ratio between 0 and 100 shows that the predicted vapor-phase compositions of component 4 lie between the experimental values of y_4 for the salt-mixed solvent solutions and the values of y_4 for the salt-free mixed solvent solutions.

Negative Average % Ratios indicate that the model predicts that component 3 is enriched in the vapor phase instead of component 4, a sign of very poor prediction. Average % Ratios greater than 100 mean that the model overpredicts the vapor phase composition of component 4 in the salt-mixed solvent system relative to the experimental values.

The results presented in Table 6.1 show that the Average % Ratios for the $LiCl-H_2O-MeOH$ system at 25°C and the $NaBr-H_2O-MeOH$ systems at 25°C and 40°C are between 0 and 100 indicating that the model predicts correctly the salting-out of methanol. The negative values of the Average % Ratios for the $LiCl-H_2O-MeOH$ systems at 60°C and 760mm Hg and for the $NaBr-H_2O-MeOH$ system at 760mm Hg indicate that the model predicts that water is salted-out instead of the methanol, clearly a failure of the model.

Figures 6.1 and 6.2 show the y-x diagrams for the LiCl-H_2O-MeOH systems at 25°C and 760 mm. Figure 6.1 shows that even though the Average % Ratio for the LiCl-H_2O-MeOH system is 31.0, the relative % ratios range from approximately unity at low mole-fractions of methanol x_4° = .152 to over 100 at high methanol mole-fractions x_4° = 0.958. This indicates that the model, where the solvation numbers of water and methanol are assumed to be zero, is only applicable at mole fractions of methanol greater that 0.95. The impact of molality can not be ascertained for this system since the data are available only at m = 1.

Figure 6.2 shows that the model, where the solvation numbers of water and methanol are assumed to be zero, predicts that methanol is salted-in at mole fractions of methanol less than 0.5. The data for this system are available at molalities ranging from 0.1 - 3.8. Molality has no impact on the prediction of the vapor-phase compositions of component 4.

Figure 6.3 compares the solvent activity coefficients for the H_2O-MeOH system at 25°C with and without LiCl. In the absence of the salt, the solvent activity coefficients of water and MeOH exhibit positive deviations from Raoult's law. The addition of LiCl increases the activity coefficient of MeOH, indicating that MeOH is salted-out, but causes the activity coefficient of H_2O to exhibit negative deviations from Raoult's law. Negative deviations from Raoult's law are indicative of solvation effects, in this case, between the salt and the water. (An example of solvation effects in nonelectrolytic solutions is observed for the chloroform-acetone system.)

Figure 6.1 Predicted y-x Diagram for the LiCl-H_2O-MeOH System at 25°C and m=1. (Solvation Effects are Neglected.)

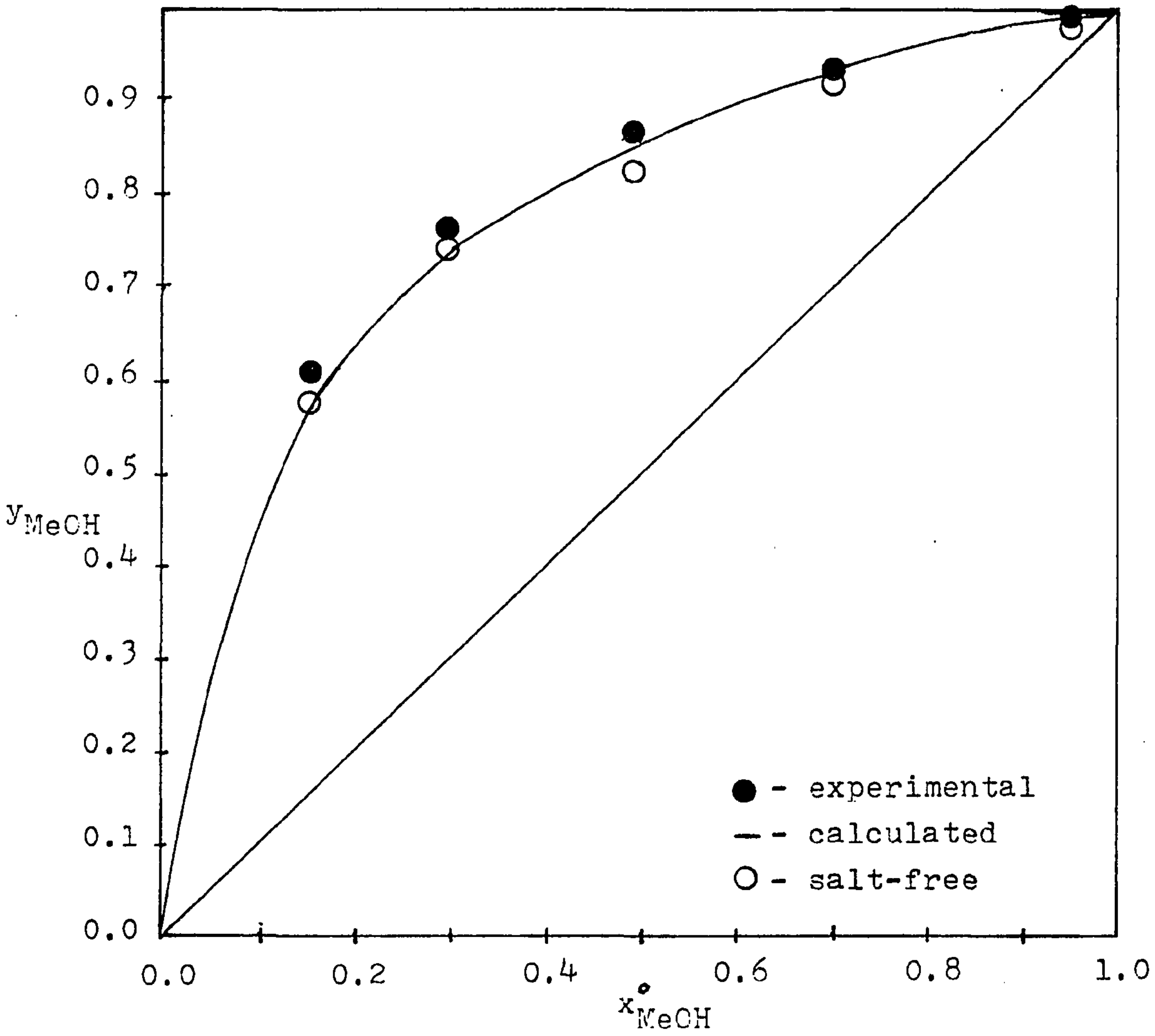


Figure 6.2 Predicted y-x Diagram for the LiCl-H_2O-MeOH System at 760mm Hg and Molality Range 0.1-3.8m. (Solvation Effects are Neglected.)

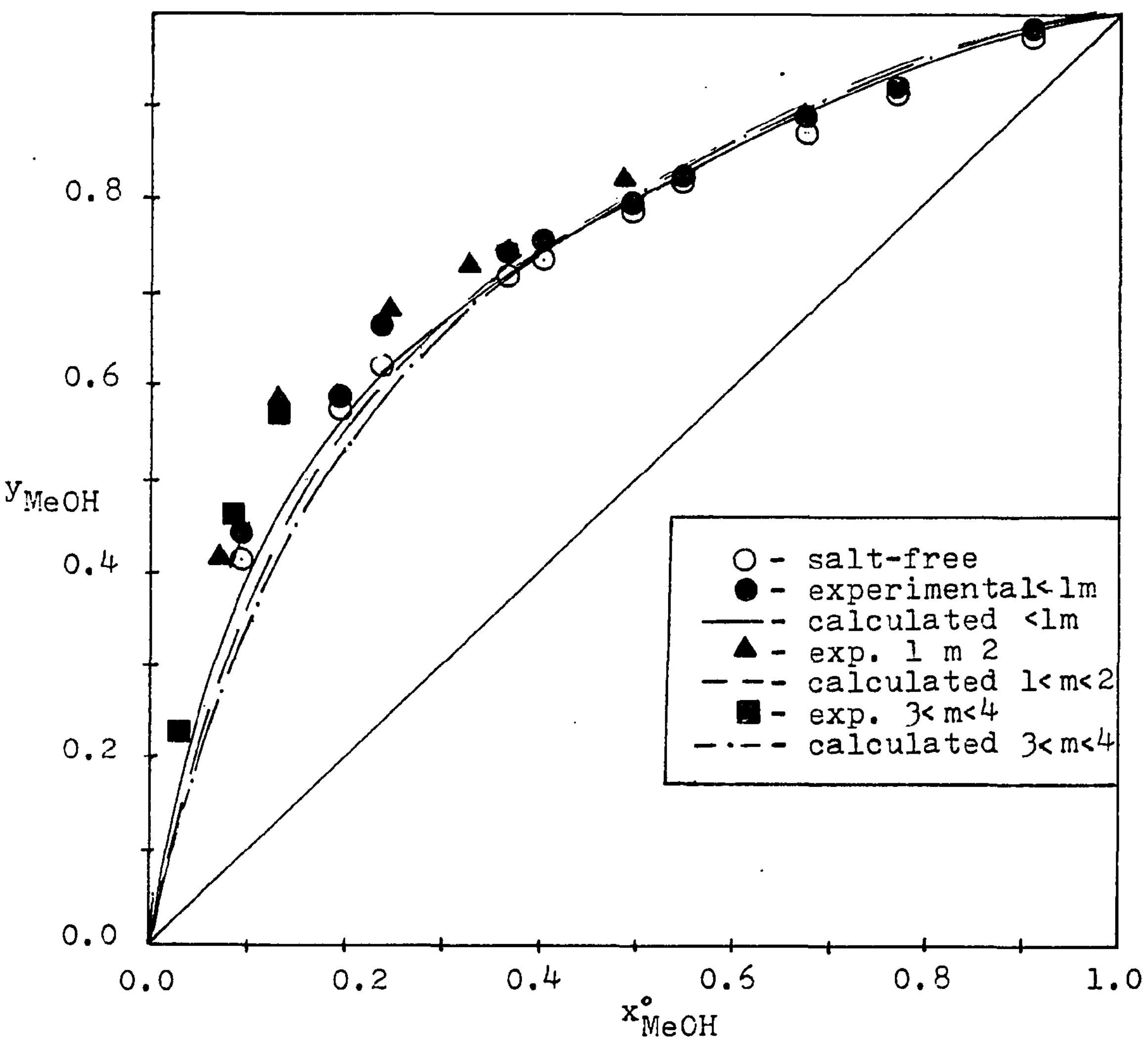


Figure 6.3 Comparison of the Activity Coefficients of the H_2O-MeOH System With and Without Added Salt. Salt System: LiCl-H_2O-MeOH at 25°C and m=1.

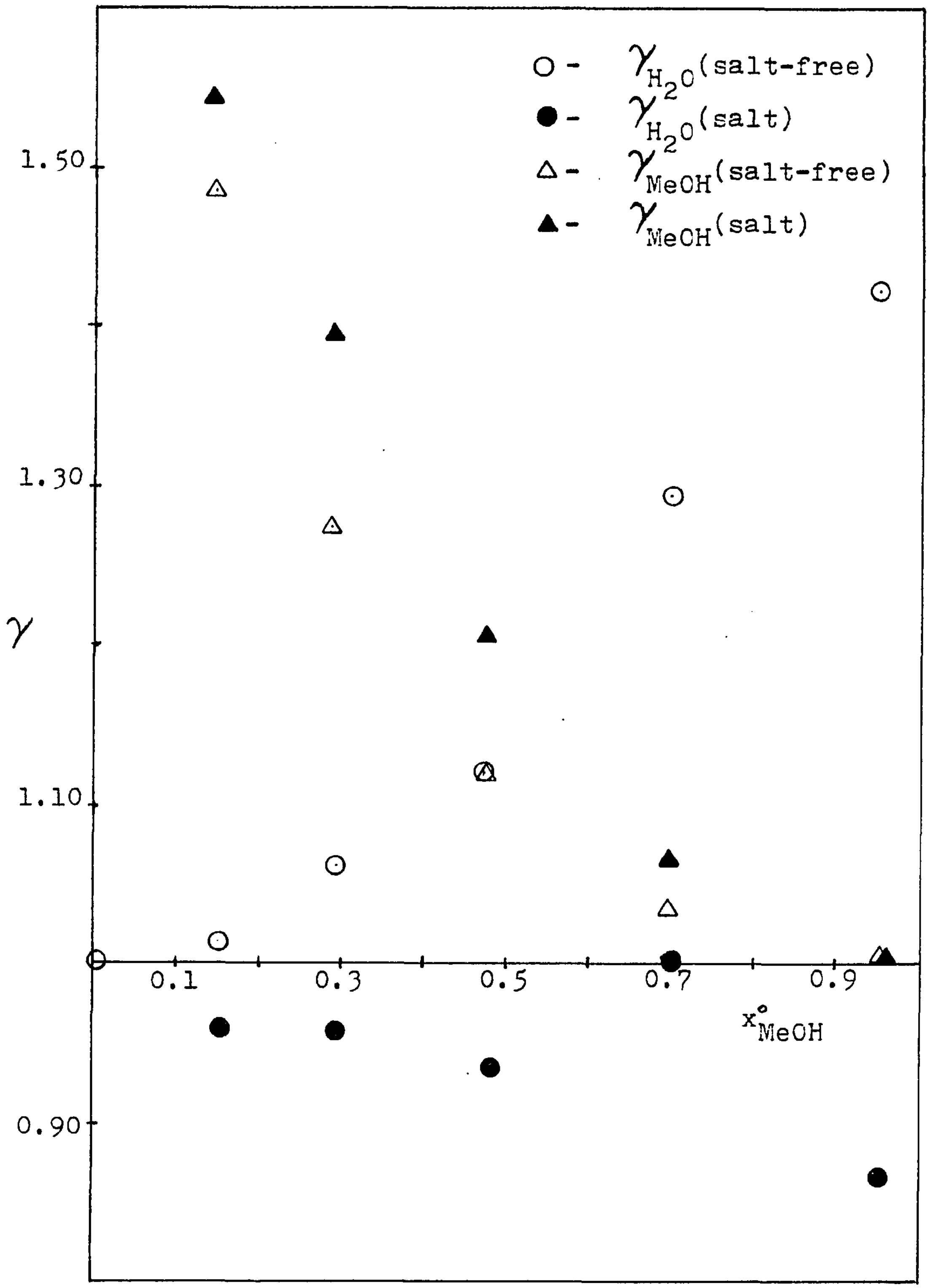


Figure 6.4 compares the solvent activity coefficients for the H_2O-MeOH system at 760mm with and without LiCl. The activity coefficients of H_2O in the presence of salt are less than their values in the salt-free solution, but negative deviations from Raoult's law are not always observed. Activity coefficients less than unity for this system are only observed at molalities greater than 1 and at salt-free mole fractions of water greater that 0.45. This is to be expected since the greater the molality, the greater the number of ions in the solution which can remove water from the bulk solvent to enter into solvation. At salt-free mole fractions of water less than 0.45 and any molality the activity coefficient of H_2O is less than it is in the salt-free mixture but is not negative. This indicates that there are not enough water molecules available to solvate the ions of the salt.

The addition of LiCl increases the activity coefficients of MeOH relative to those in the salt-free solution with one exception. At a salt-free mole fraction of water of 0.06, and $m = 0.1$ the activity coefficient of MeOH in the absence of salt is 1.00194 and that in the presence of salt is 0.99875. While it can be argued that the lowered activity coefficient is due to experimental error, it will be shown that negative deviations from Raoult's law are observed at low (around $x_3^{\circ} = .1$) mole-fractions of water indicating that methanol, as well as the other solvents of this study, is involved in the solvation of the ions of the salt. Unfortunately, this is observed only at one data point for this system.

Figure 6.5 shows the contributions of the Pitzer, Flory-Huggins, and the residual terms to the calculated activity coefficients of

Figure 6.4 Comparison of the Activity Coefficients of the H_2O-MeOH System With and Without Added Salt.
Salt System: LiCl-H_2O-MeOH at 760mm Hg and Molality Range 0.1-3.8m.

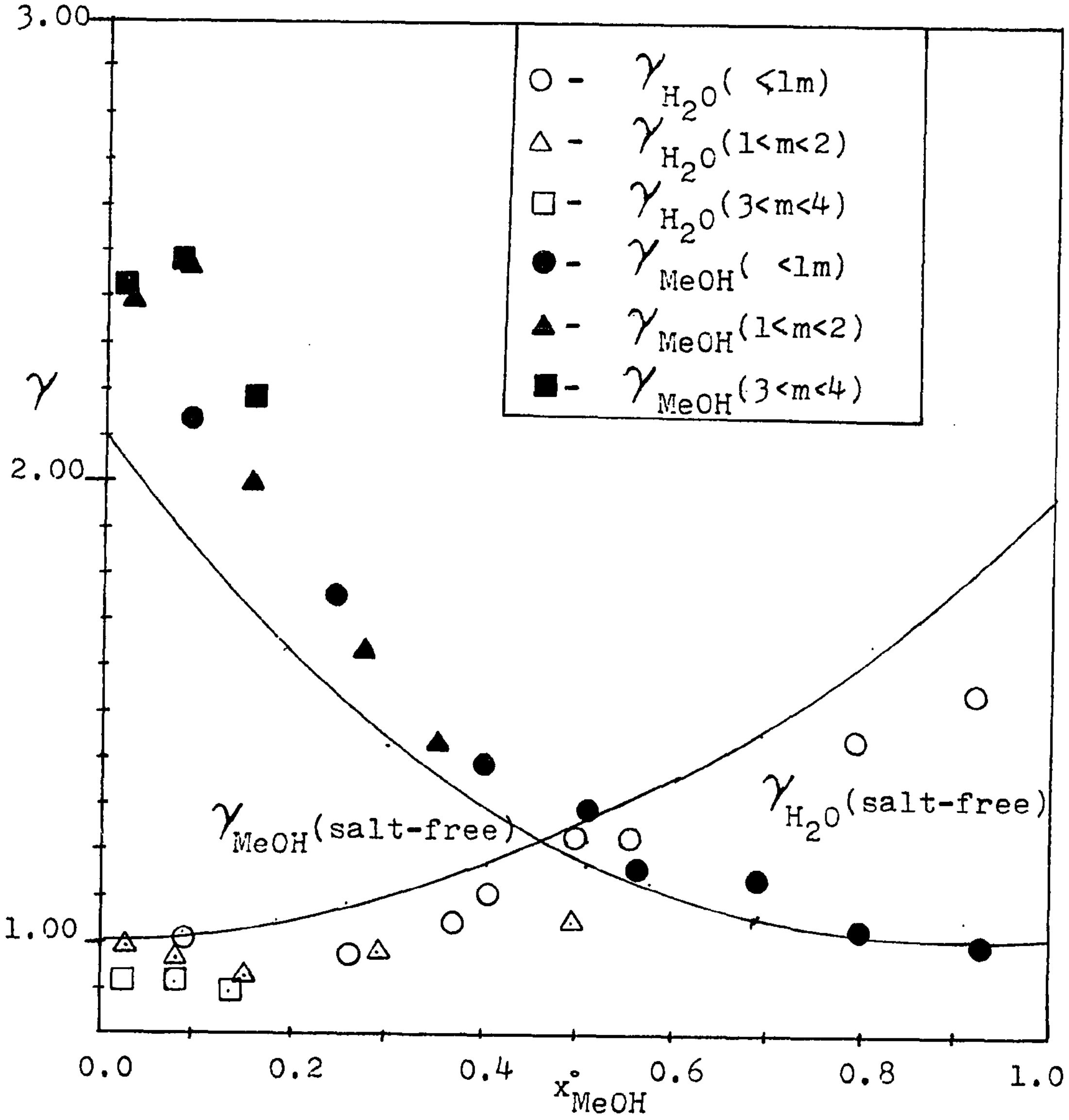
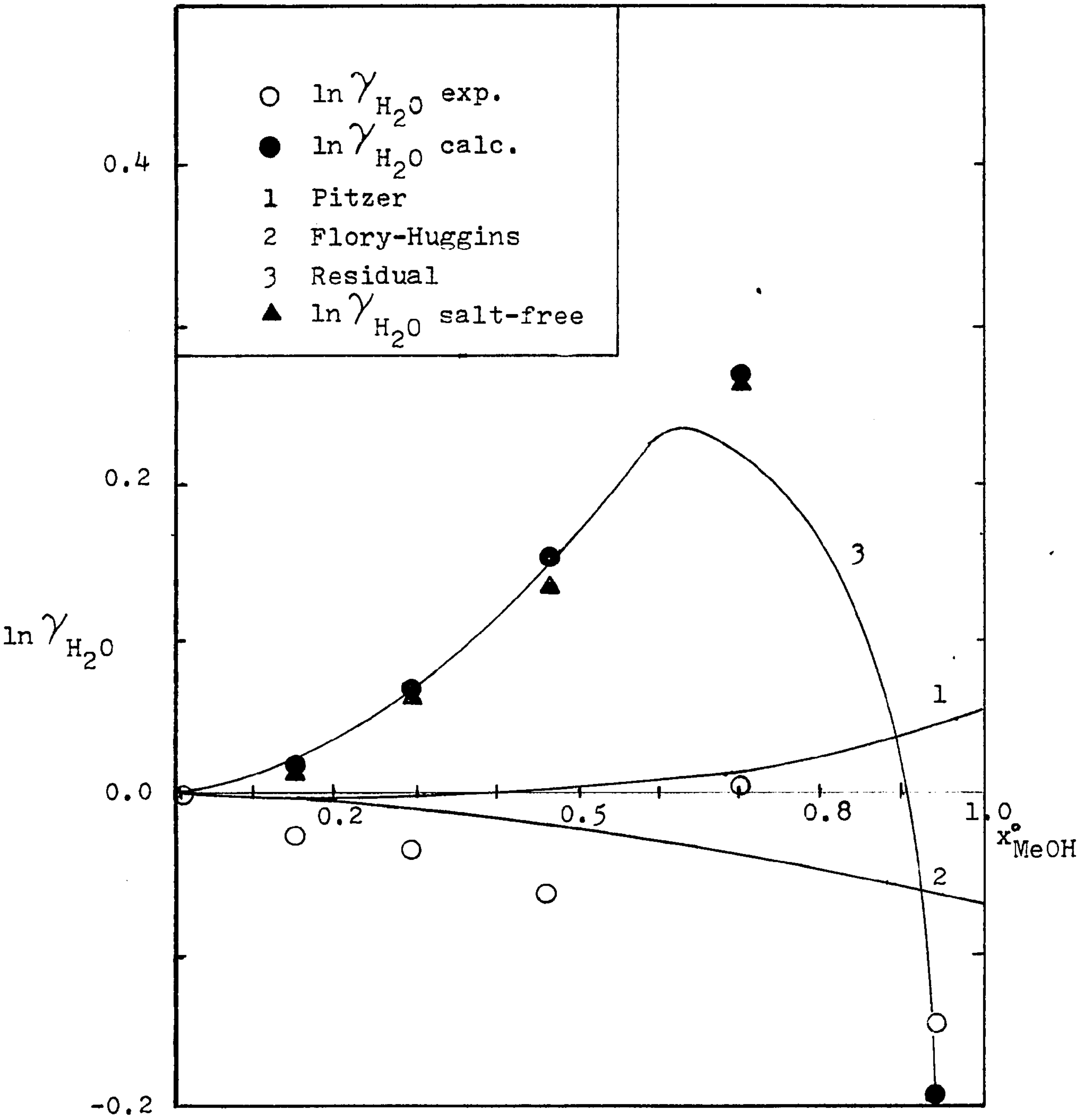


Figure 6.5 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to $\ln \gamma_{H_2O}$ for the LiCl-MeOH-H_2O System at 25°C and 1 molal.

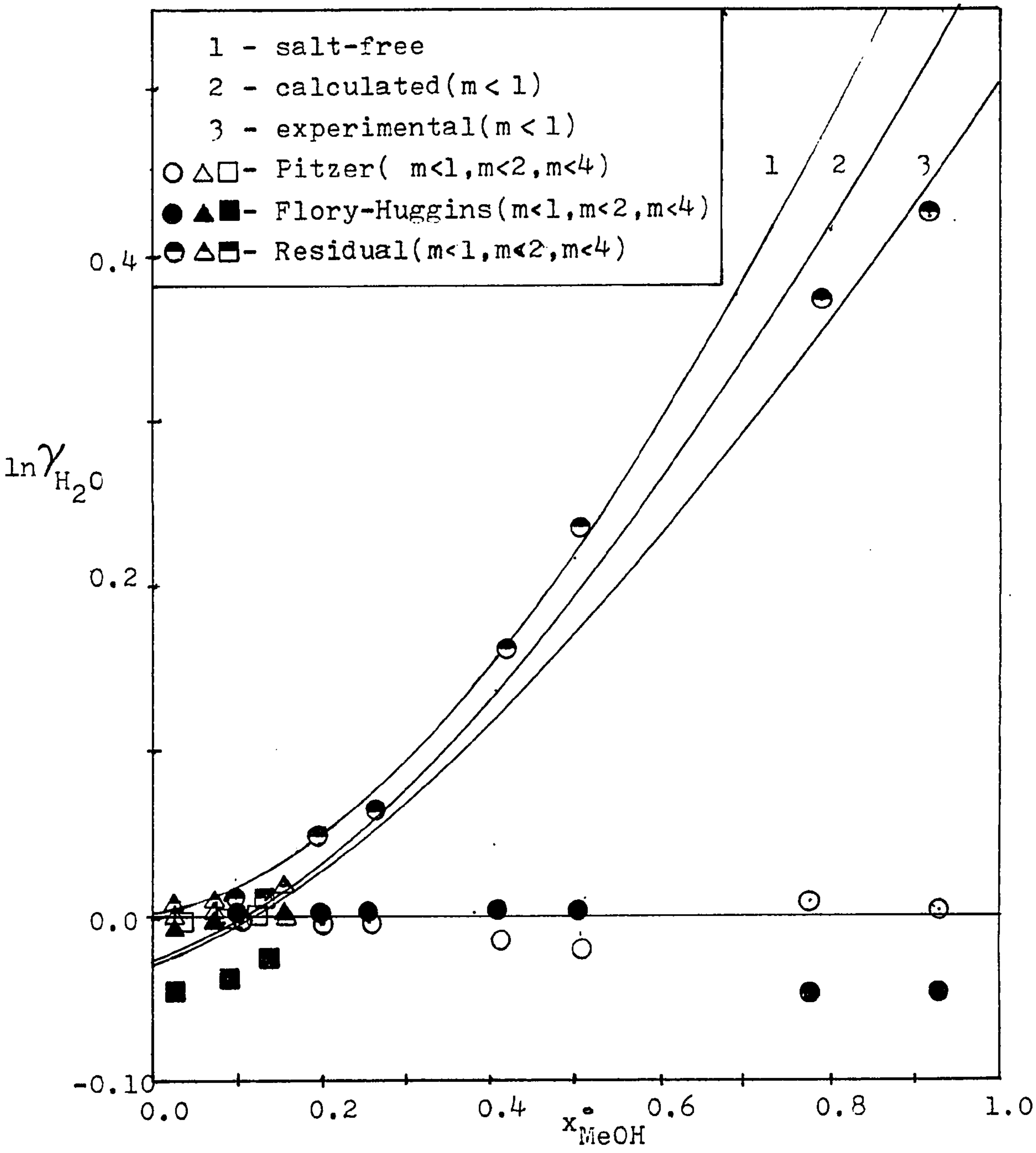


water for the LiCl-H_2O-MeOH system at 25°C. (Solvation is not considered.) It is seen that that contribution of the Pitzer term is positive while that of the Flory-Huggins term is negative. The sum of these terms gives a negligible contribution to the calculated activity coefficients. The major contribution to the calculated activity coefficients is due to the residual term which is positive and predicts water activity coefficients greater that unity up to a salt-free mole fraction of water of 0.3. The residual term is negative at a salt-free mole fraction of water of 0.042. Although not shown, the model predicts solvent activity coefficients of MeOH which are essentially the same as those in the salt-free solution. With the exception of the data point at $x_3^\circ = 0.042$, it is evident that solvation should be considered in the model. At $x_3^\circ = 0.042$, the solvation of the ions by water is negligible due to the low concentration of water.

Figure 6.6 shows the contributions of the Pitzer, Flory-Huggins, and the residual terms to the calculated activity coefficients of water for the LiCl-H_2O-MeOH system at 760 mm Hg. Again, solvation is not considered.

The contribution of the Pitzer term is negligible in most cases except at molalities greater than 3.0 and salt-free mole fractions of water greater than 0.75. The contribution of the Flory-Huggins term is negligible at all molalities and water compositions. The contribution of the residual term is negligible at molalities greater than 1 and salt-free mole-fractions of water greater than 0.8. The contribution is significant for the other compositions. In most cases, the calculated activity coefficients agree closely with those in the

Figure 6.6 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to ln γ_{H_2O} for the LiCl-H_2O-MeOH System at 760mm Hg and Molality Range 0.1-3.8m. (Solvation Effects are Neglected.)



salt-free solution indicating the failure of this model. The calculated activity coefficients of MeOH in the presence of the salt (not shown) also agree with those of the salt-free solution and not the experimental values.

The trends observed in Figures 6.1 - 6.6 for the LiCl-H_2O-MeOH systems at 25°C and 760 mm Hg are also observed for the LiCl-H_2O-MeOH system at 60°C and the NaBr-H_2O-MeOH systems at 25 and 40°C and at 760 mm Hg.

It is to be noted that the results for the LiCl-H_2O-MeOH at 60°C are reported for two molality ranges. While Hala (1969) reports the experimental ternary data up to a molality of 14.1, the binary interaction parameters used to predict the data were established from binary data that are available up to a molality of 6.0m. Also, as discussed in Section 5.5, the model should be used up to a molality of approximately 6.0 since all the binary interaction parameters were determined up to this molality.

Figures 6.3 and 6.4 indicate that solvation effects are important in salt-mixed solvent systems and must be considered in a model which predicts the properties of such solutions. (The trends observed in these figures also apply to the other systems of the ternary data base of Table 5.2.) In the next section, solvation effects will be considered.

6.3 Case 2. Solvation Effects are Considered

The binary solvent-ion parameters of Tables 5.10-5.15 and the binary solvent-solvent parameters of Table 5.21 are utilitized in equations (6-1) and (6-2). The binary solvent-ion parameters of Tables 5.10 and 5.11 for the aqueous 1-1 chlorides, bromides, and iodides were obtained with a, the ion-size parameter of the Pitzer term, set equal to the sum of the crystallographic radii of Table 5.4. a is an adjustable parameter for the other aqueous 1-1 electrolytes, the 2-1 aqueous electrolytes, and for all binary nonaqueous electrolytes. The solvation numbers of Table 5.8 for the solvation of the positive ion by water at infinite dilution were used. The solvation numbers at infinite dilution for the solvation of the positive ion by nonaqueous solvents are given by equation (5-9). The positive ion in a mixed solvent solution is assumed to be solvated by both solvents. The solvation numbers are assumed to vary linearly with the mole-fractions of the solvents. (See equation (3-33))

$$\begin{aligned} h_{+3} &= h_{o+3}x_3 \\ h_{+4} &= h_{o+4}x_4 \end{aligned} \qquad (6\text{-}8)$$

The prediction results for the corresponding data of the ternary data base of Table 5.2 are presented in Table 6.2. ΔP, ΔT, and Δy, which indicate the quality of the prediction, are defined by equations (5-23a), (5-23b), and (5-23c). The average percent errors in γ_3 and γ_4, defined by equation (6-5), and the average percent ratio, defined by equation (6-6) and discussed in Section 6.2, are also presented in the table.

The results for the LiCl-H_2O-MeOH and the NaBr-H_2O-MeOH systems are significantly improved. (See Table 6.1 for the case where

Table 6.2 Case 2. Prediction of the Vapor Phase Compositions of Ternary Data Using the Binary Parameters of Tables 5.8 - 5.15 and 5.21. (Solvation is Considered)

Water(3)-MeOH(4)

Salt	T°C or Pmm Hg	Maximum Molality	Δy	ΔPmm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio
LiCl	25.0°C	1.0	0.008	1.8	--	12.7	1.7	74.5
	60.0°C	14.1	0.032	18.2	--	4.8	24.8	162.0
	60.0°C	6.1	0.019	15.6	--	3.9	10.5	154.0
	760mm	3.8	0.016	0.2	0.5	5.4	3.8	81.8
NaBr	25.0°C	7.0	0.012	4.4	--	3.5	8.2	86.0
	40.0°C	6.2	0.003	7.4	--	6.2	7.4	103.0
	760mm	4.1	0.034	0.2	0.9	7.5	9.5	37.9
$CaCl_2$	760mm	1.8	0.010	0.2	0.8	4.0	4.0	96.7
Water(3)-EtOH(4)								
LiCl	25.0°C	4.0	0.007	2.4	--	7.8	9.1	130.0
NaI	700mm	4.9	0.005	0.2	1.2	11.0	4.0	104.0
$CaCl_2$	760mm	1.8	0.048	0.2	1.5	16.1	12.3	67.2
Water(3)-IsoprOH(4)								
LiCl	75.1°C	11.1	0.100	62.8	--	29.2	23.9	44.9

Table 6.2 Case 2. continued

Salt	T°C or Pmm Hg	Maximum Molality	Δy	ΔPmm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio
Water(3)-IsoprOH(4)								
LiCl	75.1°C	1.8	0.047	19.5	--	14.0	9.7	45.8
LiBr	75.0°C	8.1	0.042	22.2	--	19.9	9.7	73.8
		3.9	0.032	11.4	--	10.8	6.1	72.8
MeOH(3)-EtOH(4)								
$CaCl_2$	760mm	1.8	0.070	0.3	0.6	21.4	20.7	-49.6

solvation is not considered.) The salting-out of methanol is now observed in all cases. The LiCl-H_2O-MeOH system at 60°C is now overpredicted.

The results for some salts in the mixed solvents, water-ethanol, water-isopropanol, and ethanol-methanol are also presented. The results are good for the water-ethanol systems but are poor for the water-isopropanol systems. (The results for the water-isopropanol systems are shown for two molality ranges.) Salting-in is observed for the $CaCl_2$-MeOH-EtOH system.

Figure 6.7 shows the contributions of the Pitzer, Flory-Huggins, and residual terms to the calculated solvent activity coefficients of water for the LiCl-H_2O-MeOH system at 25°C and a molality of 1. A comparison of Figure 6.7 with 6.5 shows that with solvation of the positive ion by water and methanol, the magnitudes of the Pitzer and Flory-Huggins terms decrease. Where in Figure 6.5 the sum of these contributions is approximately zero, in Figure 6.7, there is a net negative, although small contribution to the calculated activity coefficients at high methanol concentrations. In addition, the residual contribution does not decrease as drastically above a mole fraction of methanol of 0.7 as it does when solvation effects are neglected.

Figure 6.8 shows the contributions of the Pitzer, Flory-Huggins, and residual terms to the calculated solvent activity coefficients of methanol for the $CaCl_2$-MeOH-EtOH system at 760 mm and 1.806m. Ethanol is the salted-out component for this system. At this molality, the activity coefficients of methanol show negative deviations from Raoult's law at salt-free mole fractions of ethanol from 0.1 to 0.9. Below a

Figure 6.7 Contribution of the Pitzer, Flory-Huggins, and Residual Terms of $\ln \gamma_{H_2O}$ for the LiCl-H_2O-MeOH System at 25°C and m=1. (Solvation of Li^+ by H_2O and MeOH is Assumed.)

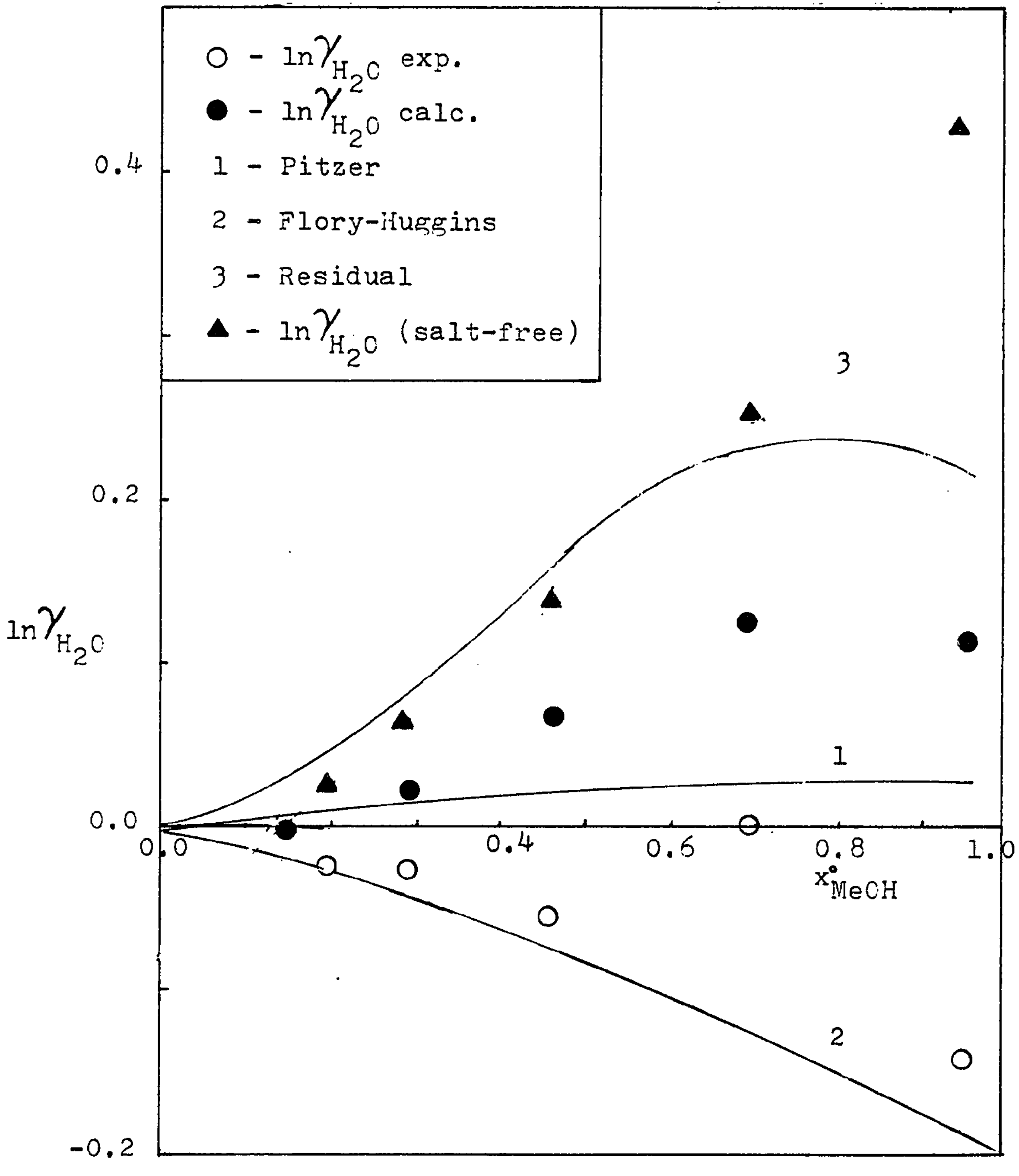
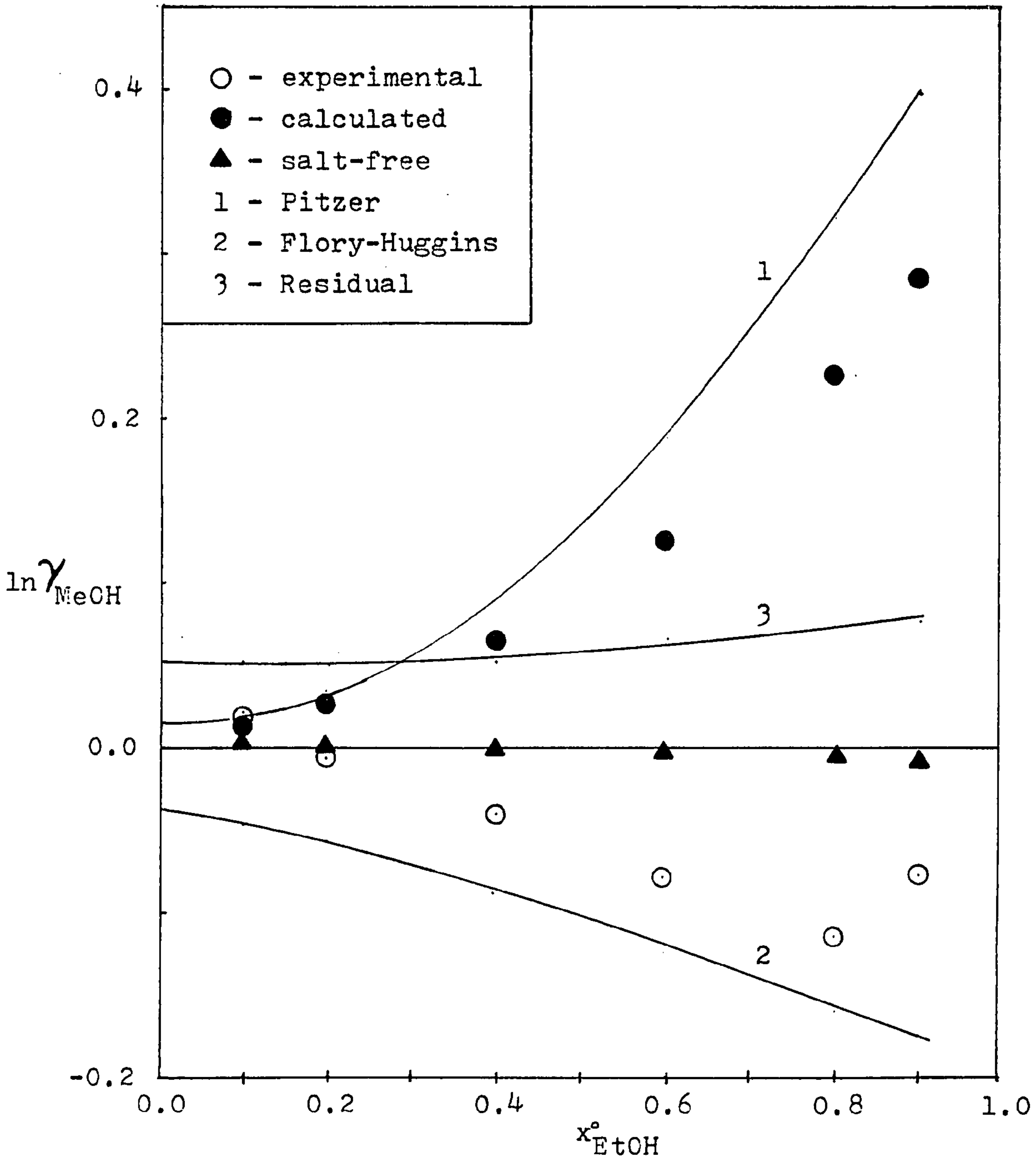


Figure 6.8 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to $\ln\gamma_{MeOH}$ for the $CaCl_2$-MeOH-EtOH System at 760 mm Hg and 1.806 molal. (The positive ion is solvated by MeOH and EtOH.)



mole-fraction of 0.1, positive deviations from Raoult's law are observed.

The Pitzer term is the major contribution to the calculated activity coefficients of MeOH at salt-free mole fractions of EtOH less than 0.4. The sum of the Flory-Huggins and residual contributions is approximately zero in the region. Above a mole-fraction of 0.4 the residual term becomes important.

The results indicate that salting-out is always predicted when the solvation number of the salted-in component is much greater than that of the salted-out component. For example, the solvation number of the Li^+ ion in water is 5 while that of the Li^+ ion in methanol is 2. However, in the case of the $CaCl_2$-MeOH-EtOH system, the solvation number of the Ca^{+2} ion in methanol is 3.8 while it is 2.8 for the Ca^{+2} ion in ethanol.

Since the model breaks down for the $CaCl_2$-MeOH-EtOH system, it is apparent that the solvation numbers calculated by equation (6-7) and (6-8) should be modified to give some recognition to the properties of the mixed solvent system. This will be done in the next section utilizing the concept of preferential solvation.

6.4 Case 3. The Preferential Solvation of the Positive Ions in Mixed-Solvent Systems is Considered.

Debye (1927), who introduced the concept of preferential solvation, showed that the solvent with the higher dielectric constant will preferentially solvate the ions in a mixed-solvent system. He assumed that the solvent activity coefficients are unity. (Ideal solution)

He developed an expression which relates the salt-free mole-fractions of the components of the bulk mixed-solvent system to the mole-fractions of the solvent species in the vicinity of an ion.

$$v_1 \ln x_2/x_2^\circ - v_2 \ln x_1/x_1^\circ = - v_2(z_i^2 e_i^2/8\pi kT)(1/D^2 r^4)\,\partial D/\partial n_1 \tag{6-9}$$

r is the average distance between the central positive ion and the nearest solvent molecules. x_1° and x_2° are the mole fractions of each of the solvents in the bulk solution when $r = \infty$. x_1 and x_2 are the mole-fractions of the solvents in the vicinity of the positive ion; i.e., the solvated compositions. v_1 and v_2 are the molar volumes of the solvents and D is the dielectric constant of the salt-free mixed-solvent.

Equation (6-9) cannot be used readily since the value of r is unknown. If it were to be used, an additional parameter would be added to the ternary model which could only be evaluated through regression of the ternary data.

While equation (6-9) cannot be adapted for use in equations (6-1) and (6-2), it does suggest which solvent properties and system conditions are important if one is to account for preferential solvation; namely, the change in the dielectric constants of the mixed-solvent systems with composition, the temperature of the system, and the molar volumes of the solvents. The effect of the molar volumes of the solvents was not considered since the solvents of this study have nearly identical molar volumes.

To maintain the predictive capability of the model, only the $CaCl_2$-MeOH-EtOH system at 760 mm and m = 1.806 was used to develop the expressions which account for preferential solvation. (If the other systems listed in Table 6.2 were used, the model would reduce to a correlation method.)

Several sets of expressions were developed and were tested using the $CaCl_2$-MeOH-EtOH system. The expressions for h_{+3} and h_{+4} given by equations (6-7) and (6-8) were replaced by the equations for preferential solvation. Only two of the sets of expressions caused equations (6-1) and (6-2) to predict the salting-out of EtOH and the salting-in of MeOH. The first set of expressions are given by

$$h_{+3} = h_{o+3}x_3 \exp(z_+z_-(D_m/D_{3T})x_4) \qquad (6\text{-}10a)$$

$$h_{+4} = h_{o+4}x_4 \exp(- z_+z_-(D_m/D_{4T})x_3) \qquad (6\text{-}10b)$$

The second set of expressions are given by

$$h_{+3} = h_{o+3}x_3 \exp(z_+z_-(D_m/D_{3T})x_4)(298.15/T) \qquad (6\text{-}11a)$$

$$h_{+4} = h_{o+4}x_4 \exp(-z_+z_-(D_m/D_{4T})x_3)(298.15/T) \qquad (6\text{-}11b)$$

and will be discussed in the next section. In equations (6-10) and (6-11), component 3 is the salted-in component and component 4 is the salted-out component.

Equations (6-10a) and (6-10b) recognize the temperature of the system indirectly through the dielectric constants of the mixed-solvents, D_m, and the pure solvents, D_{3T} and D_{4T}. D_m, D_{3T}, and D_{4T} are evaluated at the system temperature. Both equations reduce to equation (3-33), which gives h_{+3} and h_{+4} as functions of composition for the binary solutions, when the appropriate limits are taken.

The results for the $CaCl_2$-MeOH-EtOH system using equations (6-10a) and (6-10b) in equations (6-1) and (6-2) are shown in Table 6.3. The expressions were also used in the predictions of the other systems of Table 6.3.

The $CaCl_2$-MeOH-EtOH system now has an Average % Ratio of 152 compared to the value of -49.6, obtained when the concept of preferential solvation was not utilized. The average value of Δy is now 0.034, which is a significant improvement over the value of 0.070 obtained previously.

The contributions of the Pitzer, Flory-Huggins, and residual terms to the calculated activity coefficients of MeOH for the $CaCl_2$-MeOH-EtOH system are shown in Figure 6.9. The Pitzer and residual terms are the same as those in Figure 6.8 since the same binary interactions are utilized. However, the contribution of the Flory-Huggins term is now more negative than it is when preferential solvation is not considered. While the average percent error in γ_4 is approximately the same in both cases, the calculated activity coefficients with the assumption of preferential solvation correctly indicate negative deviations from Raoult's law.

The contributions of the Pitzer and residual terms to the calculated activity coefficients of EtOH for the $CaCl_2$-MeOH-EtOH systems are the same as the case when preferential solvation is not considered. The Flory-Huggins contribution is negative when preferential solvation is not taken into account and positive when it is. The Flory-Huggins term, when used in nonelectrolytic systems,

Table 6.3 Case 3. Prediction of the Vapor-Phase Compositions of Ternary Data Using the Bainary Parameters of Tables 5.8 - 5.15 and 5.21 (Preferential Solvation is Considered: No Temperature Correction.)

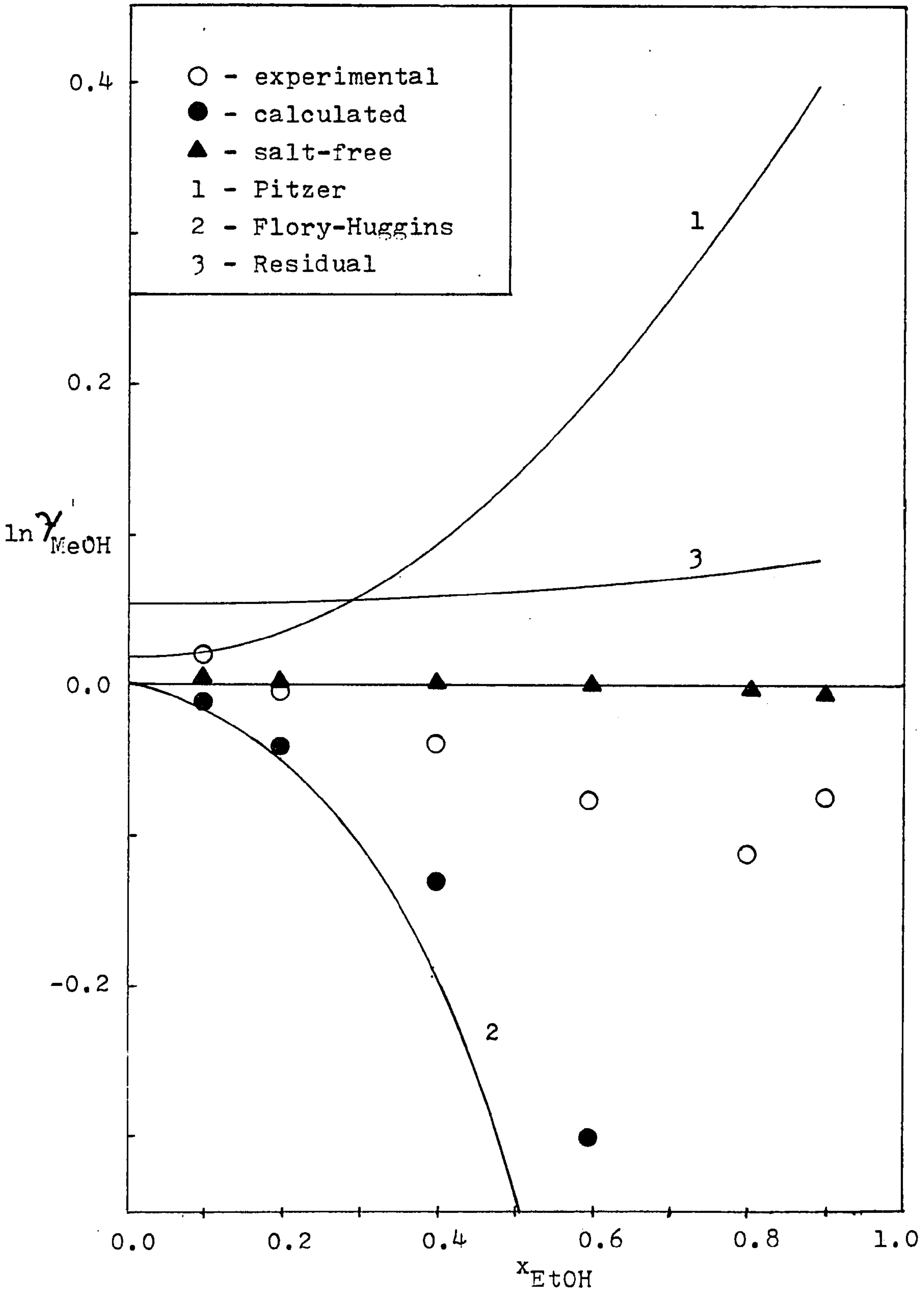
Salt	T°C or Pmm Hg	Maximum Molality	Δy	ΔPmm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio
Water(3)-MeOH(4)								
LiCl	25.0°C	1.0	0.005	3.2	--	7.7	4.5	105.3
	60.0°C	14.1	0.075	33.2	--	10.5	51.2	253.0
	60.0°C	6.1	0.054	31.5	--	8.2	24.7	240.1
	760mm	3.8	0.018	0.2	1.1	4.1	7.8	147.7
NaBr	25.0°C	7.0	0.009	2.4	--	6.7	3.7	118.8
	40.0°C	6.2	0.015	3.4	--	10.2	1.2	150.0
	760mm	4.1	0.022	0.3	0.8	6.4	6.2	67.9
$CaCl_2$	760mm	1.8	0.055	0.2	1.6	32.1	13.9	215.0
Water (3)-EtOH(4)								
LiCl	25.0°C	4.0	0.018	3.0	--	13.1	12.8	160.0
NaI	700mm	4.9	0.013	0.2	1.2	23.0	3.2	121.0
$CaCl_2$	760mm	1.8	0.030	0.3	0.6	22.7	5.3	126.0
Water(3)-IsoprOH(4)								
LiCl	75.1	11.1	0.062	61.6	--	27.5	17.6	85.9
		1.8	0.025	13.6	--	3.9	5.6	72.5

Table 6.3 Case 3. continued

Water(3)-IsoprOH(4)

Salt	T°C or Pmm Hg	Maximum Molality	Δy	ΔPmm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio
LiBr	75.0	8.1	0.023	27.3	--	9.5	11.3	109.0
		3.9	0.017	12.8	--	6.0	4.6	96.8
MeOH(3)-EtOH(4)								
$CaCl_2$	760mm	1.8	0.034	20.4	2.5	9.7	20.1	152.0

Figure 6.9 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to $\ln\gamma_{MeOH}$ for the $CaCl_2$-MeOH-EtOH System at 760 mm Hg and 1.806 molal. (Preferential Solvation assumed.)



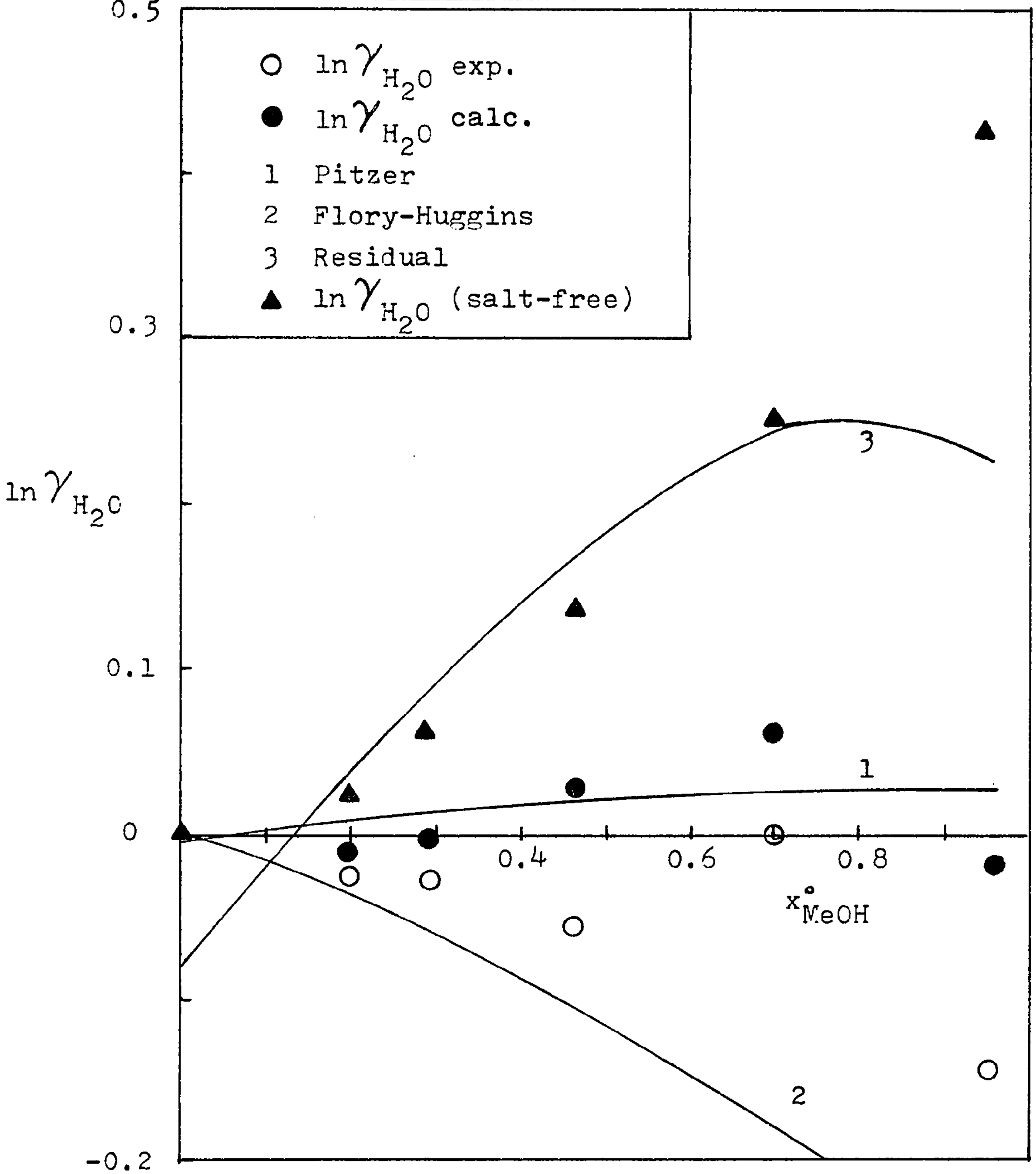
should never predict positive deviations from Raoult's law since its development is based on the assumption of an athermal solution. The Flory-Huggins solvent activity coefficient for EtOH on a solvated basis, $\ln \gamma'_{EtOH}$, is negative, which is correct since this term is identical to the Flory-Huggins equation for nonelectrolytic solutions. This contribution only becomes positive when the term $\ln x'_{EtOH}/x_{EtOH}$ is added to $\ln \gamma'_{EtOH}$. (See equation (3-6)) If $\ln \gamma'_{EtOH}$ were positive, the model would be incorrect.

The introduction of preferential solvation increases the magnitude of the Flory-Huggins term for the salted-in component; i.e., causes it to become more negative. The magnitude of the Flory-Huggins term for the salted-out component becomes more positive.

The contributions of the Pitzer, Flory-Huggins, and residual terms to $\ln \gamma_{H_2O}$ for the LiCl-H_2O-MeOH system at 25°C are shown in Figure 6.10. A comparison with Figure 6.7 shows the impact of preferential solvation. The Flory-Huggins contribution to the solvent activity coefficient has become more negative. Although not shown, the Flory-Huggins contribution to the coefficients of MeOH have become more positive. However, this term is negligible compared to the residual term.

The introduction of preferential solvation given by equations (6-10a) and (6-10b) in equations (6-1) and (6-2) worsened the results; i.e., the Average % Ratio, for many of the systems of Table 6.3. (Compare with Table 6.2, where preferential solvation is not taken into account). Poor results are indicated when the Average percent ratio is greater than 150% (overprediction) and Δy is greater than 0.03. A value of Δy of 0.03 was chosen since predictions of the

Figure 6.10 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to $\ln \gamma_{H_2O}$. (The positive ion is solvated by water and methanol. Preferential Solvation assumed)



vapor phase compositions by the UNIFAC model of nonelectrolytic solutions are usually considered poor if Δy is 0.03.

For example, when preferential solvation is not taken into account, the average error in Δy and the Average percent ratio for the $CaCl_2$-H_2O-MeOH system at 760mm Hg and m = 1.806, are 0.010 and 96.7, respectively. When preferential solvation is used, Δy is 0.055 and the Average % Ratio is 215.0.

The contributions of the Pitzer, Flory-Huggins, and residual terms are plotted in Figure 6.11 for the $CaCl_2$-H_2O-MeOH system. The results with and without preferential solvation are indicated. The Pitzer and residual contributions are the same in both cases. It is obvious that the Flory-Huggins term overcompensates for the preferential solvation of the Ca^{+2} ion by water. In this case, no preferential solvation term is needed.

The results of Table 6.3 for the LiCl-Isopropanol-H_2O and LiBr-Isopropanol-H_2O systems at 75°C improved with the introduction of the preferential solvation term. The results for the LiCl-Isopropanol-H_2O system up to a molality of 11 are poor since this system was predicted with binary interaction parameters obtained only up to a molality of 1.8.

The contributions of the Pitzer, Flory-Huggins, and residual terms are plotted in Figure 6.12 for the LiBr-Isopropanol-H_2O system at 75°C. The results with and without preferential solvation are indicated. Since the Pitzer and residual terms are the same, the improvement in the results is due solely to the Flory-Huggins term. Again, the Flory-Huggins term with preferential solvation is more negative that it is without preferential solvation. The results would be further improved

Figure 6.11 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to $\ln\gamma_{H_2O}$. Comparison of Preferential Solvation Assumption and Solvation.

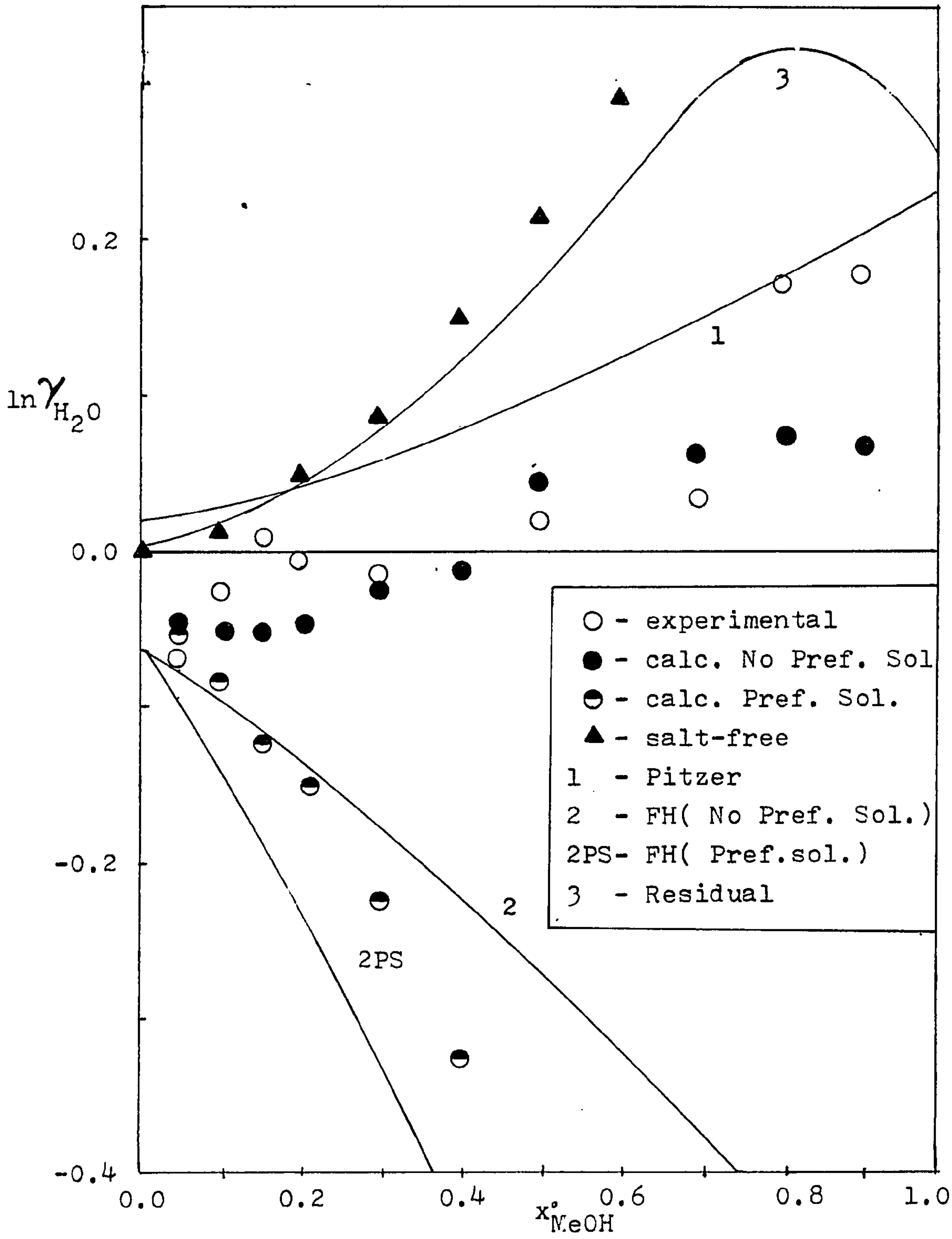
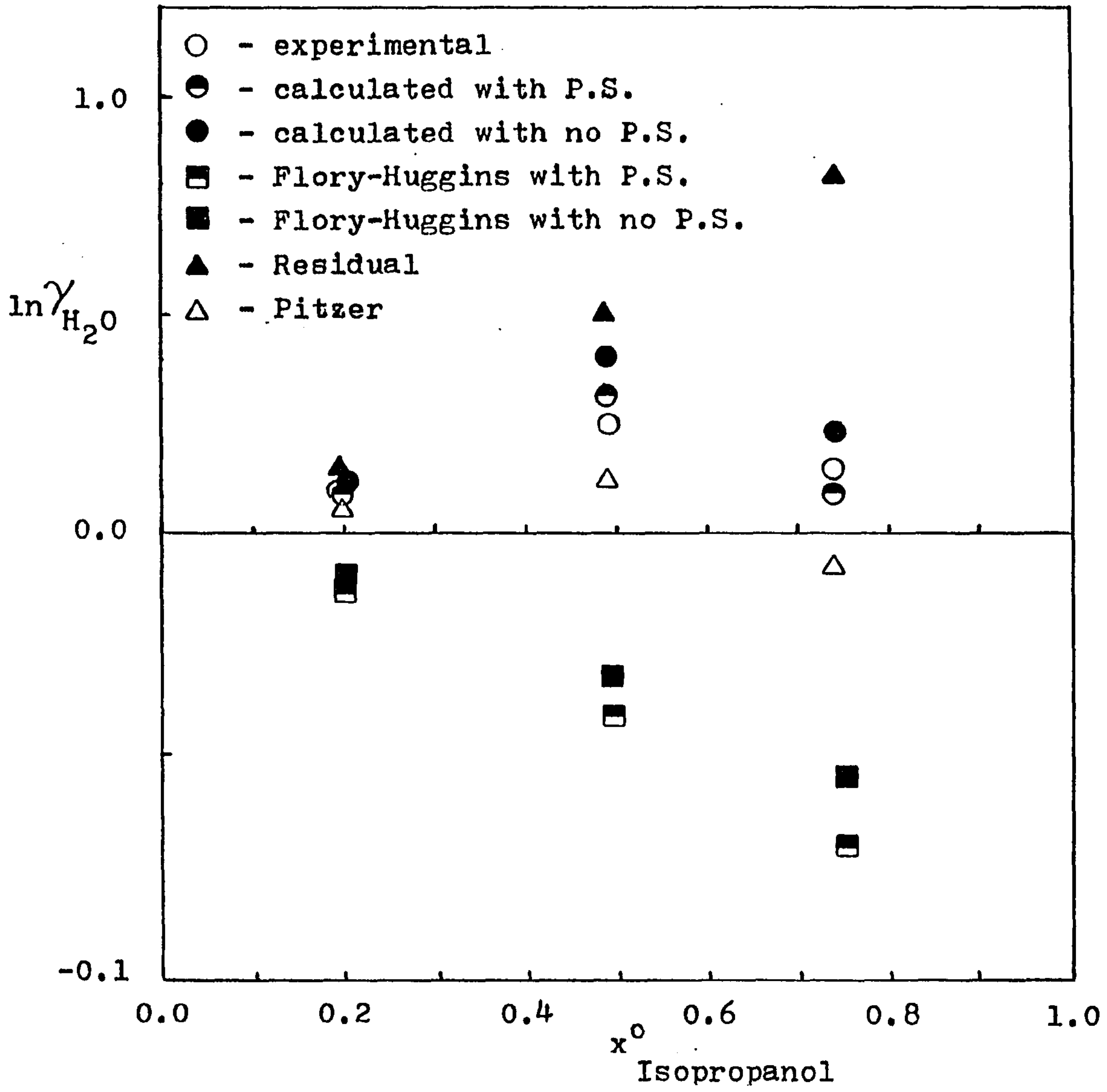


Figure 6.12 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to $\ln\gamma_{H_2O}$ for the LiBr-H_2O-Isopropanol System at 75°C and m = 1.4. (With and Without Preferential Solvation.)

P.S. = Preferential Solvation



if the Flory-Huggins term with preferential solvation was more negative at salt-free mole fractions of isopropanol of 0.48.

In the next section, the results using the preferential solvation results of equations (6-11a) and (6-11b) will be presented.

6.5 Case 4. The Preferential Solvation of the Positive Ions in Mixed-Solvent Systems. The Temperature Correction Term is Applied. (Equations (6-11a) and (6-11b) are Used.)

Equations (6-11a) and (6-11b) recognize the temperature of the system implicitly through the dielectric constants of the solvents, and explicitly, through the factor 298.15/T. These equations reduce to equation (3-33) for the binary systems when the appropriate limits are taken.and only if the temperature of the ternary system is 298.15°K. Their use is not strictly valid unless the solvation numbers in the binary are temperature dependent in the same manner; i.e., equation (3-33) is multiplied by the factor 298.15/T.

The temperature correction term serves to lower the values of h_{+3} and h_{+4} given by equations (6-10a) and (6-10b). This correction in turn decreases the impact of the Flory-Huggins term for the salted-in component; i.e., makes it less negative, depending on the values of h_{o+3} and h_{o+4}, and decreases the values of the Flory-Huggins terms for the salted-out component; i.e., makes them less positive.

The temperature correction term will not affect the results already shown in Table 6.3 for the systems at 25°C. The results utilizing equations (6-11a) and (6-11b) are shown in Table 6.4. As expected, the Δy and Average % Ratios for the systems which are overpredicted (See Table 6.3) have decreased.

While this is desirable for most of the systems of Table 6.3, it is not desirable for the Isopropanol-H_2O systems. (In Section 6.4, it was pointed out that the preferential solvation numbers calculated by equations (6-10a) and (6-10b), should be larger at salt-free mole-fractions of isopropanol of 0.47.) In addition, the Average % Ratio

Table 6.4 Case 4. Prediction of the Vapor-Phase Compositions of Ternary Data Using the Binary Parameters of Tables 5.8 - 5.15. (Preferential Solvation is Considered. Temperature Correction Term)

Salt	T°C or Pmm Hg	Maximum Molality	Δy	ΔPmm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio
Water(3)-MeOH(4)								
LiCl	25.0°C	1.0	0.005	3.2	--	7.7	4.5	105.3
	60.0°C	14.1	0.060	31.2	--	7.4	43.7	221.2
	60.0°C	6.1	0.029	28.3	--	6.4	20.8	224.0
	760mm Hg	3.8	0.013	0.2	0.9	4.5	5.6	122.4
NaBr	25.0°C	7.0	0.009	2.4	--	6.7	3.7	118.0
	40.0°C	6.2	0.014	3.7	--	9.5	1.4	144.0
	760mm Hg	4.1	0.027	0.3	0.9	6.8	7.4	56.7
$CaCl_2$	760mm Hg	1.8	0.040	0.2	1.0	23.2	9.9	177.0
Water(3)-EtOH(4)								
LiCl	25.0°C	4.0	0.018	3.0	--	13.1	12.8	160.0
NaI	700mm	4.9	0.008	0.2	1.1	15.5	3.5	113.4
$CaCl_2$	760mm	1.8	0.027	0.2	0.9	11.6	8.3	94.2
Water(3)-IsoprOH(4)								
LiCl	75.1°C	11.1	0.069	60.8	--	23.9	21.1	60.6

Table 6.4 Case 4. continued

Salt	T°C or Pmm Hg	Maximum Molality	Δy	ΔPmm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio
Water(3)-IsoprOH(4)								
		1.8	0.038	16.4	--	10.4	7.6	58.1
LiBr	75.0°C	8.1	0.027	21.6	--	15.0	8.9	89.4
		3.9	0.022	9.1	--	8.1	4.5	88.2
MeOH(3)-EtOH(4)								
$CaCl_2$	760mm	1.8	0.020	0.2	1.9	10.3	11.8	103.0

for the NaBr-H_2O-MeOH systems at 760mm Hg is lowered from 67.9 with no temperature correction term to 56.7 with the temperature correction term.

It is recommended that the temperature correction term be used to improve the results of systems that can only be predicted using preferential solvation. The $CaCl_2$-H_2O-EtOH system at 760mm Hg and the $CaCl_2$-MeOH-EtOH system at 760mm Hg are examples of systems that can be predicted well using preferential solvation.

6.6 The Use of Preferential Solvation

It is apparent from Tables 6.2 and 6.3 that the prediction results for some systems are improved when preferential solvation is used and worsened in other cases. The results of Table 6.3 indicate that the prediction results are improved for the NaBr-H_2O-MeOH system at 760mm, the $CaCl_2$-H_2O-EtOH system at 760mm, the Isopropanol-H_2O systems, and the $CaCl_2$-MeOH-EtOH system at 760mm. The prediction results for the LiCl-H_2O-MeOH at 60°C deviated considerably. The results for the other systems, which deteriorated with the introduction of preferential solvation, are acceptable and represent good prediction of the experimental data.

It is recommended that the preferential solvation equations, (6-10a) and (6-10b), be used for all nonaqueous mixed-solvent systems that have dielectric constants less than that of water. As shown in Table 6.2 and Figure 6.8 salting-in is predicted for the $CaCl_2$-MeOH-EtOH system if preferential solvation is not used.

It is also recommended that preferential solvation be used for all salts in H_2O-MeOH mixtures except for the lithium and calcium salts, and for all other salts in H_2O-nonaqueous solvent mixtures.

6.7 Comparison of the Prediction Results of this Study with the Correlation and Prediction Results of Other Models.

The prediction results of this study are compared to the correlation and prediction results of the Rastogi (1981), Hala (1983), Mock, et.al. (1984), and Sander, et.al. (1984) models. The comparisons are shown in Table 6.5.

The Rastogi model combines a modified Debye-Huckel equation and the NRTL (Renon and Prausnitz, 1968) equation. The interaction parameters are salt-solvent specific as opposed to the ion-solvent specific parameters used in this work. Prediction is only possible when the constituent binary data are available. The maximum molality at which data can be predicted is 2m.

The prediction results of this study are much better than those of the Rastogi model. In addition, the model allows the prediction of the data up to a higher molality range.

The Mock, et.al., model can only correlate electrolytic solution data. The model is based solely on the NRTL model and contains salt-solvent and solvent-solvent interaction parameters. The model, which contains 9 adjustable parameters, does not represent the long-range coulombic forces through an additional term. For a salt-water-alcohol system, three of the adjustable parameters represent the water-alcohol interactions, three represent the salt-water interactions, and the last three represent the salt-alcohol interactions. Salt-water data and water-alcohol data were correlated to obtain the needed interaction parameters for the ternary model. This reduces the number of parameters in the ternary model to three salt-alcohol parameters. These salt-alcohol parameters were determined through the regression

Table 6.5 Comparison of the Results of This Study with Those of Rastogi (1981), Hala (1983), Mock, et.al. (1984); and Sander, et.al. (1984).

H_2O-MeOH	T°C or Pmm Hg	maximum molality	Δy [This Study]	Δy (Rastogi)	Δy (Mock)	Δy [Hala or Sander]
Salt						
LiCl	25°C	1.0	0.008	0.032	0.019	----
	60°C	14.1	0.032	-----	-----	0.019 (Hala)
		6.1	0.019	-----	-----	0.024 (Hala)
	760mm Hg	3.8	0.016	-----	0.013	-----
NaBr	25°C	7.0	0.009	0.019 up to m=1.9	0.006	-----
	40°C	6.2	0.015	-----	0.006	-----
	760mm Hg	4.1	0.022	-----	0.013	-----
$CaCl_2$	760mm Hg	1.8	0.010	-----	0.015	-----
H_2O-EtOH						
LiCl	25°C	4.0	0.007	0.028 up to m=1	0.006	-----
$CaCl_2$	760mm Hg	1.8	0.0314	-----	0.024	-----
			0.027*	-----	-----	-----
MeOH-EtOH						
$CaCl_2$	760mm Hg	1.8	0.034	-----	-----	0.023 (Sander)
			0.020*	-----	-----	-----

Table 6.5 continued

H_2O-IsoprOH	T°C or Pmm Hg	maximum molality	Δy [This Study]	Δy (Rastogi)	Δy (Mock)	Δy [Hala or Sander]·
LiCl	75°C	11.0	0.062	-----	0.006	-----
		1.8	0.025	-----	-----	-----
LiBr	75°C	8.1	0.023	-----	0.010	-----
		3.9	0.017	-----	-----	-----

⁎ Temperature correction terms in equations (6-11a) and (6-11b) applied.

of the ternary salt-water alcohol data. The authors did not regress these systems with the available binary salt-alcohol data meaning that a unique set of salt-alcohol interaction parameters which correlate the ternary as well as the constituent binary data were not obtained. The authors obtained a different set of binary salt-alcohol interaction parameters through the regression of salt-alcohol systems. Substitution of these parameters, along with the 3 solvent-solvent and 3 salt-water parameters, do not allow the prediction of the ternary system.

The prediction results of this study compare remarkably well with the correlation results of Mock, et.al. The only exception noted is for the LiCl-H_2O-Isopropanol system up to a molality of 11. However, this system was predicted with ion-water parameters established from data available up to a molality of 6 and ion-isopropanol parameters established from data available up to a molality of 1.8.

The Hala model, which contains six adjustable parameters, combines a semi-empirical electrostatic term and the Wilson (1964) equation. The model was used only in the prediction of the LiCl-H_2O-MeOH system at 60°C. Two of the adjustable parameters, which represent the interactions between water and methanol, were established through the regression of water-methanol data at 60°C. Two of the parameters were established through the correlation of LiCl-water data at 60°C and the other two through correlation of LiCl-methanol data at 60°C.

The results of this study compare well with those of Hala. Apparently, the Hala model performs better at high molalities of salt. It should be pointed out that in this study, the LiCl-H_2O-MeOH system at 60°C was predicted from binary solvent-ion interaction parameters determined from data at 25°C and water-methanol parameters determined at 60°C. As shown in Section 5.4, the binary interaction parameters obtained at 25°C allow the prediction of Φ and P for binary data up to 200°C in the case of aqueous systems and up to 60°C in the case of methanol. (See Tables 5.16 and 5.18)

The Sander, et.al., model combines the Debye-Huckel and UNIQUAC (Abrams and Prausnitz, 1975) equations. The UNIQUAC parameters are functions of concentration and are ion-solvent specific. Parameters were established for salt-water-alcohol and salt-mixed alcohol systems through the simultaneous regression of the ternary data and the constituent binary data. Since the binary and ternary data bases were used to establish the parameters, (the data base of Sander, et.al. is similar to that given in Tables 5.1 and 5.2) few systems were left with which to test the predictive capabilities of the model.

The results of this study compare well with those of Sander, et. al., especially when the temperature correction term is applied. The results for the $CaCl_2$-MeOH-EtOH system of this study are not true prediction since this system was used to establish the preferential solvation equations. However, the ion-solvent parameters were obtained only from binary data at 25°C whereas the ion-solvent parameters of Sander, et.al., were determined from isothermal and isobaric binary and ternary data. It is unknown if the Sander model allows the prediction of ternary and higher-order systems from binary data alone, since the concentration dependency of the parameters can only be established in mixed solvent systems and not in single solvent systems. This would be a true test of the model.

The models presented here, with the exception of the Mock, et.al. model, were developed assuming that the excess free energy of solution is the sum of two terms. The first term is a Coulombic term, which represents the long range ion-ion interactions. The second term represents the short-range interactions between the various species in the solution. The Mock model neglects the Coulombic term.

The activity coefficients of the solvent in a binary electrolytic solution exhibit negative deviations from Raoult's law except for a region at low salt concentrations (typically, for 1-1 salts, at $m < 1$), where positive deviations from Raoult's law are observed. In this, study, these deviations are interpreted through a solvation model of the electrolytic solution.

If a solvation model is used to describe the properties of a binary electrolytic solution, it is assumed that the ions of the solution are solvated by the solvent. At extremely low concentrations of the electrolyte ($m < 0.001m$) where positive deviations from Raoult's law are observed, the long-range forces between the solvated ions predominate. These forces, which are inversely proportional to the distance between the species squared (r^2), are the most important since there are too few ions in the solution available to interact with each other at close distances, or to affect the properties of the bulk solvent. As the concentration of the electrolyte increases to approximately 1 molal, the short-range interactions between the ions become important and remain important over the entire concentration range. These short-range solute-solute interactions are of the charge-induced dipole type; i.e., the solvated ions induce dipole moments in the other ions. These forces are inversely proportional to r^6. In addition, there are dispersion (London) interactions which occur when two ions are attracted to each other. These dispersion forces are inversely proportional to r^7.

Increasing the salt concentration causes more and more solvent molecules to be removed from the bulk solution. At molalities above 1 molal, sufficient numbers of solvent molecules are removed from the bulk solution to cause a decrease in the solvent activity coefficient.

There are also short-range interactions between the solvated-ions and the solvent molecules of the bulk solution. These are of the same type as those which operate between the solvated-ions.

The solvent-solvent interactions are also short range in nature and have been described in Chapter 3.

The forces between molecules which operate in binary electrolytic solutions also operate in salt-mixed solvent solutions. However, in these systems, the ions of the salt are preferentially solvated by the solvent with the larger dielectric constant in most cases. The activity coefficents of the solvent which preferentially solvates the ions are lower than their values in the salt-free solution and most times exhibit negative deviations from Raoult's law. The activity coefficients of the salted-out solvent exhibit positive deviations from Raoult's law. This is in contrast to its behavior in the pure solvent.

The quality of the prediction of salt-mixed solvent systems from binary data alone indicates that the assumptions used to develop the model of this study are valid.

The model of this study differs from those previously mentioned in that solvation effects are explicitly accounted for. In addition, the short-range interactions between ions are accounted for in the Pitzer term. These interactions are neglected in the Rastogi and Sander models.

6.8 Use of the Ternary Model in Data Correlation

The ability of the ternary model, given by equations (6-1) and (6-2), to represent salt effects is important in the event that the experimental salt-mixed solvent data are already available.

The correlation capability of the model was tested using the LiCl-H_2O-MeOH systems at 25 and 60°C, and the LiCl-H_2O-Isopropanol systems at 75°C. In the examples to follow, it is assumed that the ion-nonaqueous solvent parameters are unknown.

The number of parameters in equation (6-1) and (6-2) are reduced to five immediately since data for the H_2O-nonaqueous solvent and LiCl-H_2O systems are readily available. These systems were regressed to obtain the binary interaction parameters given in Tables 5.10 and 5.21, respectively.

Two of the five parameters in equation (6-1) and (6-2) are the solvation number of the nonaqueous solvent and A_{12}. The solvation number is calculated from equation (5-9) and A_{12} may be estimated from equation (5-10). The parameters that need to be established are a_4, A_{41} and A_{42}.

The ternary data can now be regressed for a_4, A_{41}, and A_{42}. To show that meaningful parameters are obtained when the model is used in correlation, the ternary systems were regressed for a_4, A_{41}, and A_{42} along with the binary salt-nonaqueous data. This is not possible using the Mock, et.al., (1984) correlation. (See Section 6.7)

The LiCl-H_2O-MeOH and LiCl-MeOH systems at 25°C were regressed to obtain a_4, A_{41}, and A_{42}. These parameters were used to predict the LiCl-H_2O-MeOH systems at 760mm Hg. (The preferential solvation terms given by equations (6-10a) and (6-10b) were not utilized.)

The LiCl-H_2O and LiCl-MeOH systems at 60°C were regressed together and the resulting parameters were used to predict the LiCl-H_2O-MeOH systems at 25°C and 760 mm Hg.

Finally, the LiCl-H_2O-isopropanol and LiCl-Isopropanol systems at 75°C were regressed to obtain a_4, A_{41}, and A_{42}.

The results for all systems are shown in Table 6.6. The error in Δy obtained through regression of the ternary system and the average percent error in Φ for the binary data are indicated, as well as the Δy for the predicted systems.

The Δy obtained from the regression of the ternary systems agrees well with those of Table 6.2 and 6.3. This is to be expected since the data were correlated with the same binary data used to predict them. The only exception to this is for the LiCl-H_2O-MeOH system at 60°C which was correlated with the binary LiCl-MeOH data at 60°C. This would explain the difference in the values of the parameters obtained in Table 6.6 compared to the parameters of Table 5.14.

The results of Table 6.6 indicate that the model can be used in the correlation of ternary data. The parameters are meaningful since the same ternary systems at different temperatures or isobaric conditions can be predicted from the parameters. Also, the model parameters allow the prediction of the osmotic coefficient data of the LiCl-MeOH system at 25°C using the parameters obtained from the 60°C data and vice versa. This is not possible with the Mock model.

Table 6.6 Demonstration of the Correlation Capability of the Model

Regression of	maximum molality	T°C	a_4	A_{41}	A_{42}	Average % Error, Φ Reg	Δy(Reg)	Δy	Δy	Average % Error, Φ Pred
LiCl-H_2O-MeOH	1.0	25.0	5.08	452.5	387.0	-----	0.006	0.032(a)	0.016(b)	3.7(d)
and										
LiCl-MeOH	4.5	25.0				3.7				
LiCl-H_2O-MeOH	14.1	60.0	4.67	-905.8	-562.1		0.017	0.010(c)	0.017(b)	3.8(e)
and										
LiCl-MeOH	7.1	60.0				3.7				
LiCl-H_2O-IsoprOH	1.8	75.0°	6.18	3350.0	5040.0	7.5	0.024	-----	-----	---
and										
LiCl-IsoprOH	1.8									

a) prediction of the LiCl-H_2O-MeOH system at 60°C

b) prediction of the LiCl-H_2O-MeOH system at 760mm Hg

c) prediction of the LiCl-H_2O-MeOH system at 25°C

d) prediction of the LiCl-MeOH system at 60°C

e) prediction of the LiCl-MeOH system at 25°C

6.9 Use of the Model in the Prediction of Salt-Mixed Solvent Systems when a_4 or A_{mn} has not been Established.

For the NaCl and KCl-H_2O-MeOH systems and the NaCl-H_2O-EtOH systems of the ternary data base of Table 5.2, the values of a_4, the ion-size parameter of the Pitzer term in equations (6-1) and (6-2), have not been established since the constituent salt-alcohol data do not exist. (The data are not available since sodium chloride is generally soluble in alcohols up to a molality of approximately 1.0.) The values of A_{mn} have been established for these systems. (See Tables 5.14 and 5.15) In order to predict these systems, the average values of a_4 obtained from the regression of the halide salt-alcohol data are assumed to be the values of a_4 for these salt systems.

The prediction results (preferential solvation terms of equations (6-10a) and (6-10b) are used) are shown in Table 6.7. The average value of a_4 for the halide salt-methanol systems is 5.23. The average value of a_4 for the halide salt-ethanol systems is 5.70.

The prediction results for the H_2O-EtOH systems are reported up to two maximum molalities. Reducing the molality ranges improves Δy but does not improve the Average % Ratio significantly.

Examination of Table 6.7 for the H_2O-EtOH systems, indicates that at the upper molality limit reported for each system, the average percent error in γ_4 is generally large compared to that in γ_3. Reducing the molality range

Table 6.7 Prediction Results Using an Average Halide Value of a_4

$\bar{a}_{MeOH} = 5.23$ $\bar{a}_{EtOH} = 5.70$

Salt	T°C or P mm Hg	Maximum Molality	Δy	ΔP mm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio
H_2O-MeOH								
NaCl	762 mm	6.0	0.030	0.2	1.6	7.0	9.8	66.9
KCl	760 mm	1.9	0.037	0.2	0.8	9.4	13.2	12.2
H_2O-EtOH								
NaCl	30°C	4.1	0.042	3.9	--	6.4	12.6	52.5
		2.0	0.018	1.3	--	4.3	2.6	53.3
NaCl	755 mm	6.3	0.059	0.2	3.3	2.1	19.1	45.8
		1.5	0.010	0.2	0.7	1.7	3.4	53.3

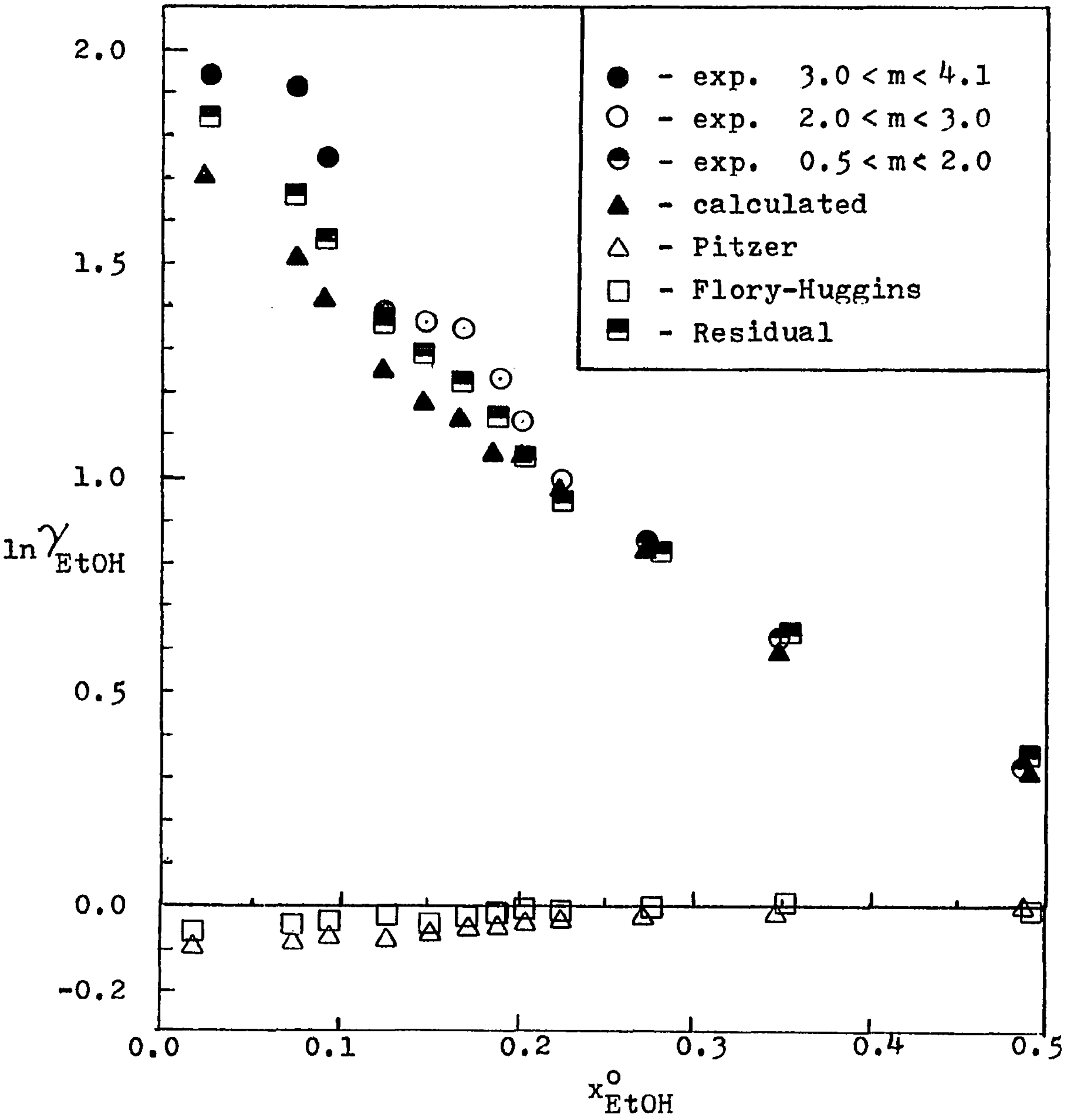
reduces the average percent error in γ_4 but has no affect on the average percent error in γ_3.

To see why this occurs, the contributions of the Pitzer, Flory-Huggins, and residual terms to the solvent activity coefficients of ethanol for the NaCl-H_2O-EtOH system at 30°C are plotted in Figure 6.13. At low ethanol concentrations and high salt molalities the residual term provides the major contribution to the calculated solvent activity coefficients. The data would be predicted well in this region if the Pitzer and Flory-Huggins terms were positive. However, the Flory-Huggins term is correct at this low concentration of ethanol, where solvation of the positive ion by ethanol is negligible. Therefore, it is the Pitzer term which is causing the poor results at high molalities.

The Pitzer term which accounts for the long-range ion-ion and short-range ion-ion interactions, incorrectly predicts the salting-in of ethanol instead of the salting-out of ethanol at high molalities and low ethanol concentrations. The reason for this is that the Pitzer equation assumes that the dielectric constant of the solvent is constant. It does not allow for changes in the dielectric constant with salt concentration.

The NaCl-H_2O-EtOH system at 30° C was regressed for a_4 to see if the assumption that a_4 is the average value of a_4 for the halide salts is a valid one. The regression results yielded a value of a_4 of 11.0, Δy of 0.014, and an

Figure 6.13 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to $\ln\gamma_{EtOH}$ for the $NaCl-H_2O-EtOH$ System at $30^\circ C$. Molality range: 0.56-4.10m.



Average % Ratio of 112. The average percent error in γ_3 is 6.2 and that in γ_4 is 3.8. When a_4 is 11.0, the Pitzer term is positive. However, this value of a_4 is unreasonable in light of the values of a_4 obtained for the ethanol systems of Table 5.15.

There is also the possibility that the experimental data are inexact, but this is unlikely since the trends observed for the NaCl-H_2O-EtOH system at 30°C are also observed for the other systems of Table 6.7.

There does appear to be a link between the solubility of the salt in ethanol and the molality range to which the ternary data can be predicted. The salts of Table 6.2 are soluble in the nonaqueous solvents over the entire molality range at which the ternary data are available. The prediction of the ternary data from the binary is also excellent. (See Tables 6.2 and 6.3.) Good predictions are obtained up to twice the saturated values for the NaCl-H_2O-EtOH systems. The results for the NaCl and KCl-H_2O-MeOH systems are not significantly improved by reducing the molality range.

The values of a_4 and A_{MeOH/F^-} for the NaF-H_2O-MeOH system, a_4 and A_{EtOH/F^-} for the NaF-H_2O-EtOH system, and a_4 and A_{EtOH/K^+} for the KI-H_2O-EtOH system have not been established since the constituent salt-alcohol data are not available. These salts are not very soluble in the nonaqueous solvents.

As in the case discussed above, a_4 is assumed to equal the average halide values of a_4 obtained from the regression of the salt-alcohol data. The average value of a_4 for methanol is 5.23. The average value of a_4 for the ethanol systems is 5.70.

The A_{MeOH/F^-} interaction parameter is assumed to have the same value as the A_{MeOH/Cl^-} interaction parameter. This was done since the Cl^- ion is the only negative ion which is close in size to the F^- ion. The crystallographic radii of the Cl^- ion is 1.81 Å while that of the F^- ion is 1.40 Å. The A_{EtOH/F^-} interaction parameter is assumed to have the same value as the A_{EtOH/Cl^-} interaction parameter.

It is further assumed that the A_{EtOH/K^+} interaction parameter may be calculated from a linear relationship between $A_{solvent/K^+}$ and the dielectric constant of the solvent at 25 °C. The A_{H_2O/K^+} and A_{MeOH/K^+} interaction parameters of Tables 5.10 and 5.14 are used to establish this linear relationship.

$$A_{solvent/K^+} = -507.5 + 6.3D_{25^oC} \qquad (6\text{-}12)$$

The value of A_{EtOH/K^+} calculated from equation (6-12) is -353.8.

The average halide values of a_4 and the estimated parameters were used to predict the vapor phase compositions for the systems of Table 6.8. All of the salts listed in the table are barely soluble in the nonaqueous

Table 6.8 Prediction Results Using Estimated Values of A_{mn} and a_4

Salt	T°C or Pmm Hg	Maximum Molality	Δy	ΔPmm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio
H_2O-MeOH								
NaF	760mm Hg	1.0	0.014	0.2	0.4	5.5	3.5	30.6
H_2O-EtOH								
NaF	700mm Hg	0.8	0.010	0.2	0.8	2.5	5.4	32.9
KI	700mm Hg	6.5	0.033	0.2	1.7	7.6	9.1	72.3
		2.2	0.007	0.2	0.5	5.0	2.4	90.3

solvent alone.

The results for the $KI-H_2O-EtOH$ system are improved when the maximum molality is reduced to 2.2. As in the $NaCl-H_2O-EtOH$ system, it is the Pitzer contribution to the solvent activity coefficient of ethanol which lowers the contribution of the residual term. The residual term predominates at high molalities and low ethanol concentrations.

The $NaF-H_2O$-alcohol systems are predicted with Δy values of 0.01 but low Average % Ratios. No conclusions can be drawn as to why the Average % Ratio of the $NaF-H_2O-EtOH$ system is low since there are too few data points for this system with which to analyze the data.

The contributions of the Pitzer and Flory-Huggins terms to the calculated activity coefficients of MeOH for the $NaF-H_2O-MeOH$ system are negligible compared to the contribution of the residual term. Although negative deviations from Raoult's law are observed for this system at salt-free mole-fractions of water of 0.8, the model predicts positive deviations from Raoult's law. Increasing the solvation number of the Na^+ ion in water would decrease the Flory-Huggins contribution and increase the Average % Ratio. However, this option is not possible since the solvation numbers are fixed in this study. The residual term can be readjusted through regression of the data to find an optimum value of A_{MeOH/F^-}.

6.10 Use of the Model in the Prediction of Salt-Mixed Solvent Systems When More Than one Value of a_4 or A_{mn} has not been Established.

In Section 6.9, the model was used to predict salt-mixed solvent systems in the case where a_4 or A_{mn} has not been established. The value of a_4 in the salt-mixed solvent system was assumed to equal the average halide value of a_4 obtained from the values of a_4 for the halide salt-nonaqueous systems already established. The value of A_{mn} was assumed to equal the value of the ion of the same charge and nearest in size if it is unavailable in a particular solvent. For example, the values of A_{MeOH/F^-} and A_{EtOH/F^-} were assumed to have the same values as A_{MeOH/Cl^-} and A_{EtOH/Cl^-}, respectively. If the value of A_{mn} was established in two of the solvents but unavailable in a third, a linear relationship between the values of A_{mn} and the dielectric constants was assumed. (See equation (6-12).) This relationship was used to obtain the value of A_{EtOH/K^+} from the values of A_{H_2O/K^+} and A_{MeOH/K^+}.

Since these methods of predicting the unknown parameters gave reasonably good prediction results, they are utilized in this section.

The values of $A_{solvent/ion}$ may be estimated using the equations shown in Table 6.9. All the equations, with the exception of that for the A_{s/K^+} parameter, were established using the values of the interaction parameters

Table 6.9 Equations for the Estimation of A_{mn}.

S = solvent D_s is equal to value at 25°C

Ion	Correlation	Correlation Coefficient
Cl^-	$A_{s/Cl^-} = 1385.0 - 18.769D_s$	1.0
Br^-	$A_{s/Br^-} = 1829.8 - 24.280D_s$	1.0
I^-	$A_{s/I^-} = 1128.8 - 15.320D_s$	0.5
Li^+	$A_{s/Li^+} = 4716.4 - 68.600D_s$	0.5
Na^+	$A_{s/Na^+} = -191.8 - 3.160D_s$	1.0
K^+	$A_{s/K^+} = -507.5 - 6.300D_s$	1.0
Ca^{+2}	$A_{s/Ca^{+2}} = 122.2 - 4.500D_s$	0.7

obtained for water, methanol, and ethanol. The equation correlates the $A_{s/ion}$ values with a correlation coefficient of 1.0 for three of the ions. Poor correlation is obtained for the iodide, lithium, and calcium ions. (Logarithmic and exponential equations were also tried, but similar results were obtained.)

It is recommended that the equations of Table 6.9 be used only when the values of $A_{s/ion}$ are not available.

The systems of Table 6.10 were predicted using the equations of Table 6.9 for the missing parameters. Preferential solvation is assumed. The values of a_4 were assumed to equal the average halide value of a_4 obtained from the values of a_4 for the halide salt-nonaqueous systems already established. Since no values of a_4 for salts in n-propanol are available at all, it was assumed that a_4 for LiCl in n-propanol has the same value as the average a_4 of the salt-isopropanol systems. (At 25°C, the dielectric constants of isopropanol and n-propanol are 18.0 and 20.2, respectively. This indicates that the Pitzer contribution is approximately the same for both systems.

It should be noted that the binary data for the $CaCl_2$-Isopropanol system could not be correlated by the binary model given by equation (5-6). The binary data were regressed for a_4 and $A_{isopropanol/Ca^{+2}}$. The value of $A_{isopropanol/Cl^-}$ was established from regression of the LiCl-Isopropanol system at 75.1°C. A_{12} was calcula-

Table 6.10 Prediction Results Using Estimated Values of a_n and A_{mn}

H_2O-IsoprOH

Salt	T°C or P mm Hg	Maximum Molality	Δy	ΔP mm Hg	ΔT°C	Average % Error, γ_3	Average % Error, γ_4	Average % Ratio	Ref.
$CaCl_2$	760 mm	0.40	0.016	0.2	0.4	6.1	3.5	76.0	Ohe (1976)
$CaCl_2$	75.1°C	6.00*	0.281	190.0	---	38.3	37.7	125.0	Sada (1975)
		0.44	0.012	7.3	---	1.7	3.2	79.0	
H_2O-PrOH									
LiCl	760 mm	2.60	0.021	0.2	0.5	2.2	7.8	118.0	Boone (1976)

* Molality range of the model exceeded. See Equation (5-12).
System splits into two-phases at a molality of approximately 1.0.

ted from equation (5-10). Since the data were correlated poorly using the approach above, the $CaCl_2$-Isopropanol system was then regressed for all the parameters of equation (5-6). The data were still correlated poorly. Since the LiCl and LiBr-Isopropanol systems were correlated well using the model, (see Table 5.15), it can only be concluded that the binary data for the $CaCl_2$-Isopropanol system are poor and that the poor results are not due to a failure of the model.

The data for the $CaCl_2$-H_2O-Isopropanol system at 75.1°C are available up to a molality of 6.0. The prediction results up to this molality indicate a value of Δy of 0.281, which is extremely poor. The reason for this is that the range of the model, given by equation (5-12), has been exceeded. This occurs when either x_3' or x_4', the mole-fractions of components 3 and 4, respectively, on a solvated basis, become zero. (For the $CaCl_2$-H_2O-Isopropanol system, x_{H_2O}' becomes zero when the molality is greater than 4.0) The values of Δy are also very poor at molalities greater than 0.44m and up to salt-free mole-fractions of isopropanol of 0.33, the maximum value reported by the workers. The value of Δy is 0.012 at a molality of 0.44.

Mock,et al.,(1984), correlated this system only at a molality of 0.44 and report a value of Δy of 0.013.

This system cannot be predicted beyond a molality of 0.44 since it splits into two liquid phases at a molality of approximately unity. No data are reported between a molality of 0.44 and 1.0.

The prediction results for the LiCl-H_2O-n-propanol system are good. This system was predicted with estimated values of a_4, $A_{n\text{-propanol}/Li^+}$, and $A_{n\text{-propanol}/Cl^-}$. Δy is 0.021.

6.11 Use of the Model in the Prediction of Salt-Multicomponent Solvent Systems.

In Sections 6.9 and 6.10, the model was used to predict salt-mixed solvent systems in the cases where a_4 or A_{mn} have not been established. The value of a_4 was assumed to equal the average halide value of a_4 obtained from the values of a_4 for the halide salt-nonaqueous systems already established. A_{mn} may be calculated from the equations of Table 6.9.

In this section, the LiCl-water(3)-methanol(4)-n-propanol(5) and the LiCl-water(3)-ethanol(4)-n-propanol(5) systems at 760 mm Hg are predicted using the methods described in Sections 6.9 and 6.10. The data are from Boone(1976).

The Pitzer term contains one parameter, a. a is calculated using equation (3-17). The values of a_3 and a_4 have been established. (See Tables 5.10, 5.14, and 5.15.) The value of a_5, the ion-size parameter of LiCl in n-propanol, must be estimated. As in Section 6.10, it is assumed that a_5 for LiCl has the same value as the average a_5 of the salt-isopropanol systems.

The values of the solvation numbers for the Li^+ ion in water, methanol or ethanol, and n-propanol for use in the Flory-Huggins terms are given by the following expressions: (Preferential solvation is assumed.)

$$h_{+_3} = h_{o+_3} x_3 \exp(z_+ z_- (D_M/D_{3T})(x_4 + x_5)) \qquad (6\text{-}12a)$$

$$h_{+_4} = h_{o+_4} x_4 \exp(-z_+ z_- (D_M/D_{4_T})(x_3 + x_5)) \quad (6\text{-}12b)$$

$$h_{+_5} = h_{o+_5} x_5 \exp(-z_+ z_- (D_M/D_{5_T})(x3 + x_4)) \quad (6\text{-}12c)$$

The exponents of equations (6-12b) - (6-12c) are negative since the alcohols are the salted-out components.

The values of A_{31}, A_{32}, A_{41}, and A_{42} of the residual term are found in Tables 5.10, 5.14, 5.15. The values of A_{34}, A_{43}, A_{35}, A_{53}, A_{45} and A_{54} are found in Table 5.21. The values of A_{51} and A_{52} are calculated from the equations of Table 6.9.

The prediction results for the two systems are shown in Table 6.11. The Δy are compared to those of Boone who used the Wilson and UNIQUAC equations and a pseudo-binary approach.

The results of this study compare well with those of Boone. They are surprisingly good considering that only binary parameters and estimated binary parameters were used to effect the multicomponent predictions. The Boone approach utilizes ternary data to effect multicomponent predictions.

Table 6.11 Prediction Results for Multicomponent Systems

Salt	P mm Hg	maximum molality	Δy	ΔP	$\Delta T\,^{o}C$	Average % Error, γ_3	Average % Error, γ_4	Average % Error, γ_5	Average % Ratio
$H_2O(3)$-MeOH(4)-n-PrOH(5)									
LiCl	760	3.1	0.030	0.3	0.8	11.4	5.0	20.0	62.2
			0.020(1)						
			0.028(2)						
$H_2O(3)$-EtOH(4)-n-PrOH(5)									
LiCl	760	3.4	0.036	0.3	2.0	8.0	18.4	18.7	40.3
			0.035(1)						
			0.034(2)						

(1) = pseudobinary approach of Boone (1976) using the Wilson equation.

(2) = pseudobinary approach of Boone using the UNIQUAC equation.

CHAPTER 7

DISCUSSION OF RESULTS

The objective of this study was to develop a model for the prediction of mixed solvent-single electrolyte mixtures from binary data alone. The following approach was taken: 1) Establish a phase equilibrium data base of systems containing mixed solvents with one electrolyte, 2) Develop the corresponding binary data base from the literature data, 3) Provide the missing data through experimental measurements of salt-methanol systems, 4) Develop a model containing binary parameters only, 5) Evaluate the model with binary data and determine the corresponding binary parameters, and 6) Test the model with multicomponent data.

The phase equilibrium data base for salt-mixed solvent systems is shown in Table 5.2 and contains data for 16 salt-water-alcohol systems and one salt-mixed alcohol solvent. These systems were chosen since the construction of a group contribution model for the prediction of salt-mixed solvent data from binary data alone requires that the ion-solvent interaction parameters evaluated from the constituent binary data be firmly established. This is only possible if the binary data are reliable; i.e., verified through a variety of measurements.

The only binary data meeting these requirements are those for the salt-water systems. The compilation of Robinson and Stokes (1959) reports osmotic coefficient and mean activity coefficient data for these systems. The aqueous data used in this study are listed in Table 5.1.

The data for the salt-nonaqueous systems (also shown in Table 5.1) comprising the ternary systems of Table 5.2, were obtained through vapor pressure measurements only. The methanol data base was extended in this study. (See Chapter 4 and Appendix E.) The data base is almost complete for the methanol systems; i.e., the values of a_4, the ion-size parameters of the Pitzer term, and the interaction parameters of the residual term can be obtained directly from the regression of the data in the binary model. The values of a_4 cannot be established for the NaCl, NaF, and KCl-water-methanol systems, nor can the value of A_{MeOH/F^-}. They were estimated in this study. The method is presented in Chapter 6 and will be discussed later in this section.

The values of a_4 for the NaCl, NaF, KCl, and KI-water-ethanol systems as well as the values of A_{EtOH/K^+} and A_{EtOH/F^-}, also had to be estimated since the data for these systems are not available. These salts, as well as those listed above for the methanol systems, are not very soluble in their respective solvents. This means that if the data were available, they would extend to a molality of no more than unity. Meaningful ion-solvent parameters are not obtained if data below this molality are regressed since each parameter is multiplied by a concentration term. If the concentration is below unity, the ion-solvent parameters of the residual term will assume any value. For example, consider one of the terms of the binary residual expression of equation (5-5) given below.

$$- \Theta_2\Psi_{32} / (\Theta_1\Psi_{12} + \Theta_2 + \Theta_3\Psi_{32})$$

If Θ_1 and Θ_2, the area fractions of the solvated positive and negative ions, respectively, are very small, then $\Theta_1\Psi_{12} + \Theta_2$ is negligible compared to $\Theta_3\Psi_{32}$. Even if Ψ_{12} assumes a large value in regression, it is minimized through multiplication by Θ_1. The term then reduces to

$$- \Theta_2\Psi_{32} / \Theta_3\Psi_{32}$$

and any value of Ψ_{32} will give the same value for this term.

The only way to obtain meaningful parameters for these systems is to regress them with a system that has a common ion and is soluble in the solvent up to a high molality. For example, the maximum molality of the KI-MeOH system is 0.8 meaning that this system cannot be regressed in the binary model to obtain a and the ion-solvent parameters. However, it can be regressed with either the KCH_3COO-MeOH system which has a maximum molality of 2.5 or the NaI system which has a maximum molality of 4.3.

The binary data base for the prediction of the salt-isopropanol-water and methanol-ethanol systems is complete.

The binary model presented in Section 5.1 (equation (5-6)) was developed assuming complete dissociation of the salt. Ion-association effects are neglected. The dissociation of a salt in a solvent depends on the charge densities of the ions comprising the salt, the dielectric constant of the solvent, and the temperature of the system. An increase in temperature results in a lowering of the dielectric constant.

Most of the salts in water at 25°C of this study are completely dissociated, with the exception of the 1-1 nitrates and 1-2 sulfates. The dielectric constant of water at this temperature is 78.38. In solvents other than water, incomplete dissociation of the salt usually occurs. Dissociation constant data are reported for some of the salts in this study including the NaSCN and KCl salts in methanol and the LiCl, NaCl, KCl, and KI salts in ethanol at 25°C. (Kratochvil and Yeager, 1972) It is reported that LiCl is completely dissociated in methanol. Waddington (1969) gives the rule of thumb that an electrolyte can be considered completely dissociated up to a moderate concentration range in a solvent with a dielectric constant greater than 30. The dielectric constant of methanol at 25°C is 32.6 and that of ethanol is 24.3. The incomplete dissociation of LiCl and LiBr in isopropanol can be assumed based on Waddington's rule and the fact that LiCl is incompletely dissociated in ethanol which has a higher dielectric constant.

The assumption of complete dissociation appears to be valid for the aqueous 1-1 and 2-1 halides, the 1-1 chlorates, and the 1-1 acetates of this study since the average percent error in Φ for these systems is 2.24. However, the average percent error in Φ for the 1-1 nitrates and 1-2 sulfates is 4.1 indicating a decline in the correlation ability of the model for these systems. In systems in which there is incomplete dissociation, the decrease in the solvent activity coefficient curves with increasing molality is not as great as it is for systems in which there is no ion-pairing. This effect can be explained in terms of the hydration model. As the concentration of the electrolyte is increased, the incidence of ion-pairing increases; i.e., since there are more ions in solution, the probability that they will come into contact increases. This contact is likely to reduce the ion-solvent interactions, so that the paired ions will have less complete solvation sheaths. (Robinson and Stokes, 1959) The net effect, then, is to return solvent molecules to the bulk solution which results in solvent activity coefficients which are higher than those noted for completely dissociated systems having the same positive ion or lowered osmotic coefficients. At a molality of 3.0, the LiCl-water system has an osmotic coefficient of 1.286, while the $LiNO_3$-water system has an osmotic coefficient of 1.181.

Two terms in the model can be modified to account for ion-pairing, the first being the Flory-Huggins contribution. For the LiCl-water system of Figure 5.5, the

Flory-Huggins term represents the largest contribution to the calculation of the activity coefficients of water. This contribution is approximately the same for the $LiNO_3$ system since the crystallographic radii of the nitrate ion is 1.89 Å while that of the chloride ion is 1.81 Å.

The values of h_+ in this study are assumed to be a linear function of the solvent mole fractions. (See equation (3-33).) For a particular negative ion, decreasing the value of h_{o+} decreases the contribution of the Flory-Huggins term, (making it less negative). The value of h_{o+} should not be adjusted to improve the results for the $LiNO_3$ system since at low molalities, the osmotic coefficients of $LiNO_3$ and LiCl are of nearly the same magnitude. At a molality of 0.1, the osmotic coefficient of LiCl is 0.939 while that of $LiNO_3$ is 0.938. This indicates that the "amount of solvent removal" by the Li^+ ion is about the same in both cases. The values of the osmotic coefficients diverge at a molality of 0.7. Since h_{o+} cannot be adjusted, the concentration dependence of the solvation number would have to be investigated for ion-pairing systems. A power law model, where x_3 is raised to the (n) power in equation (3-33), would decrease the value of h_+ and therefore increase the Flory-Huggins contribution, (making it less negative.) This would increase the calculated values of the activity coefficients of the $LiNO_3$ system compared to those of the LiCl system.

The Pitzer term could also be modified, but any modification would involve the addition of a parameter to the equation. This parameter would have to include an equilibrium constant to account for the fraction of ions removed from the solution.

The values of a obtained from regression of the nitrate and sulfate salts are less than the sum of the crystallographic radii of these salts. (See Table 5.13.) This indicates a "failure" of the Pitzer term since the minimum value a can have is the hard-core distance between the ions which is assumed to be the sum of the crystallographic radii.

In a sense, the model has already been modified since it has been found that a should be less than the sum of the crystallographic radii to improve the correlation of the nitrate systems. The average percent error in Φ, when a is set equal to the sum of the crystallographic radii is 8.5 and 3.1 when a is an adjustable parameter.

It is most likely that both of the modifications suggested above would have to be incorporated into the present binary model to improve the correlation of incompletely dissociated salts, as well as the physical reality of the model.

The data of Kratochvil and Yeager (1972) indicate that while LiCl completely dissociates in methanol, NaSCN and KCl do not. The value of a for the LiCl system is 5.7 while that of NaSCN is 4.73. The values of a for LiBr, NaI, NaBr, and $CaCl_2$ are also above 5.0. Since the value of a gives some indication of whether or not a salt undergoes ion-pairing, it can be deduced that KI, KCH_3COO, and $CaCl_2$ form ion-pairs since their values of a are less than 4.73. In addition, the fit of the $CuCl_2$ and NH_4SCN systems is poor compared to that of the other systems. With the exception of these systems, the model correlates the data well with an overall average percent error in Φ of 3.3.

Even though ion-pairing is observed for the LiCl-ethanol system (Kratochvil and Yeager, 1972), and most likely occurs in the other systems of Table 5.15, the fit of the data is quite good. The average percent error in Φ for the ethanol systems is 2.9. The average percent error in Φ for the isopropanol systems is 3.8.

It should be noted that the $CaCl_2$-Isopropanol and the $CaCl_2$-n-propanol systems of the binary data base could not be correlated by the model. The average percent errors in Φ for these systems were approximately 60. The LiCl and LiBr-Isopropanol systems were correlated well. It can only be concluded that the binary data for the $CaCl_2$-Isopropanol system are poor and that the poor results are not due to a failure of the model. Since no other salt-n-propanol data are available, it is difficult to conclude if the $CaCl_2$-n-propanol data are poor by comparison.

Even though the model neglects the effects of ion-pairing, it is evident that in the majority of cases the model gives a good representation of the experimental data. Since this representation is good, the assumption of complete dissociation of the salt is a valid one.

The Pitzer(1973) term accounts for the long and short-range ion interactions. It gives some recognition to ion-solvent interactions since it is a function of the dielectric constant. The contribution of this term is smallest in water systems and largest in the isopropanol systems. (greatest negative contribution)

$$\ln\gamma^{P}_{H_2O} < \ln\gamma^{P}_{MeOH} < \ln\gamma^{P}_{EtOH} < \ln\gamma^{P}_{Isoprop}$$

This is to be expected since the forces between ions are inversely proportional to the dielectric constant of the solvent. Decreasing the dielectric constant of the solvent, increases the magnitude of the forces between the ions.

The residual term accounts for short-range interactions between the species of the solution not defined in the model. The contribution of the residual term is negligible for the aqueous systems indicating that the model adequately accounts for the intermolecular forces operating in the solution.

It would be expected that the contribution of the residual term would be greatest for the ion-pairing systems. However, the method of parameter estimation in this study prevented this observation. The values of

A_{12} and A_{31} were established from data for the 1-1 chlorides, where the residual term gives a negligible contribution to the calculated solvent activity coefficients. These values of A_{12} and A_{31} were then used to estimate A_{32} for the nitrate and sulfate interaction parameters, respectively. However, since the contribution of the term is essentially "set" by A_{12} and A_{31}, the value of A_{32} affects the residual term by at most 5%. It can be argued that the 1-1 nitrates or the 1-1 sulfates should have been selected as the base system for parameter estimation. However, these aqueous ion-pairing systems are not included in the ternary data base of Table 5.2. All of the salts of the ternary data base are completely dissociated in water.

The Flory-Huggins term accounts for deviations from ideality due to the sizes of the molecules. (Entropic Effects) In other words, it is assumed that a solution of solvated ions would not show ideal behavior if the interionic forces were absent. In addition, the term accounts for the lowering of the solvent activity due to the removal of solvent molecules by the ions. (See equations (3-1)-(3-7)). This was done to simplify the model. The impact of h_{o+} and h_{+} on the Flory-Huggins term has already been discussed.

While literature values of h_{o+} are available for the aqueous systems, none were found for the nonaqueous systems. They were estimated from equation (5-9). This equation was chosen because it relates the values of h_{0+} of water to the best values of h_{0+} which fit the binary LiCl and LiBr-methanol data at 25°C.

The model for the prediction of the properties of single electrolyte-mixed solvent systems is presented in Section 6.1. The Pitzer term contains the parameter, a, which is the mole-fraction average of a_3 and a_4 obtained from the constituent binary data. The Flory-Huggins term contains the parameter, h_{0+j}, where the j refers to each of the solvent species. The residual term contains seven parameters. Ion-solvent interactions are represented through four of the parameters. Two of the parameters represent the interactions between the solvent molecules, and one represents the short-range interactions between the positive and negative ions. The ion-solvent, solvent-solvent, and positive ion-negative ion interaction parameters are obtained directly through regression of the constituent binary data. Since the ternary expression contains only one positive ion-negative ion interaction parameter, it is assumed that A_{12} is the mole-fraction average of the A_{12} obtained from the constituent binary data.

The performance of the model was first evaluated by neglecting the solvation effects; i.e., h_{0+3} and h_{0+4} were set equal to zero. The performance of the model is extremely poor as indicated by negative values of the Average % Ratio for some of the systems. (See Table 6.1.) The model predicts the salting-in of methanol instead of the salting-out of methanol.

The contributions of the Pitzer, Flory-Huggins, and residual terms to the calculated activity coefficients of water, are shown in Figure 6.5 for the LiCl-H_2O-MeOH system at 25°C. (Water is the salted-in component.) The Pitzer term in this case, predicts the salting-out of water (indicated by its positive contribution at high salt-free methanol mole-fractions) instead of the salting-in of water. The Flory-Huggins term is in the right direction but its magnitude is approximately equal to that of the Pitzer term canceling the effects of both terms. The residual contribution is positive at salt-free mole fractions of methanol less than 0.7, and becomes negative at salt-free mole-fractions of methanol of approximately 0.9. Since the Flory-Huggins term is in the right direction, it can only be concluded that the poor results are due to the Pitzer and residual terms.

Regression of the binary LiCl-water system at 25°C, where solvation effects are neglected and a is an adjustable parameter in the Pitzer term, shows that the major contribution to the calculated solvent activity coefficients of water is due to the Pitzer term. (See Figure 5.3.) Since the solvation effects are neglected, the Flory-

Huggins contribution only accounts for entropic effects and their effects are negligible. The residual contribution is also negligible. This indicates that the Pitzer term alone adequately describes the system. At a molality of unity, which corresponds to the molality of the LiCl-H_2O-MeOH system for which data are available, the Pitzer contribution is very small. In the ternary system, the Pitzer term initially decreases and then increases with increasing salt-free methanol mole-fraction. As the mole-fraction of methanol increases, the dielectric constant of the mixture changes from that of water to that of methanol. Apparently, the Pitzer contribution to the calculated solvent activity coefficients of water, behaves like the solvent activity coefficients of methanol in the LiCl-MeOH binary. (See Figure 5.4.) Although not shown, the Pitzer contribution to the calculated solvent activity coefficients of methanol is negative, where it should be positive. The Pitzer contribution to the activity coefficients of methanol is similar to the contribution for the LiCl-H_2O system.

The Pitzer (1977) term was derived through consideration of the long and short-range ionic interactions only. It does not account for interactions between different solvent molecules or explicitly for ion-solvent interactions.

The behavior of the residual term is dictated solely by the parameter values obtained from binary regression.

It corrects for any short-range interactions not accounted for by the Pitzer and Flory-Huggins terms. Figure 6.5 shows that at salt-free methanol mole-fractions less than 0.6, the residual term represents the salt-free activity coefficients of water in the water-methanol system. Above this concentration, the residual term gives the value of the infinite dilution activity coefficient of water.

Solvation effects were introduced into the model to correct for the inadequacies of the Pitzer, Flory-Huggins, and residual terms in predicting ternary electrolytic solutions. (See Section 6.2.)

Rastogi (1981), whose model is based on the Debye-Huckel and NRTL equations, noted that the Debye-Huckel equation calculates the salting-out of water in a salt-water-alcohol system, instead of the salting-in of water. He modified the Debye-Huckel term using a semi-empirical expression. The expression cannot be extended to systems consisting of more than two mixed solvents. Sander, et al.,(1984), developed a model based on the Debye-Huckel and the UNIQUAC equations. The UNIQUAC equation corrected for the deficiencies in the Debye-Huckel term through the introduction of concentration dependent parameters.

The results when solvation is introduced into the model are shown in Table 6.2. Salting-out of the correct component is predicted in every case with the exception of the $CaCl_2$-MeOH-EtOH system at 760 mm Hg.

The contribution of the Pitzer, Flory-Huggins, and residual terms for the LiCl-H_2O-MeOH system at 25°C to the calculated values of the activity coefficients of water when solvation of the lithium ion by water and methanol is assumed, is shown in Figure 6.7. The introduction of solvation increases the negative contribution of the Flory-Huggins term. The larger the value of h_{0+}, the larger the negative contribution. A comparison of Figures 6.5 and 6.7 indicates this. The Flory-Huggins term also corrects for the residual term. The residual term does not become negative at mole fractions of methanol greater than 0.9, but its contribution is approximately the same at mole fractions of methanol less than 0.7.

The contribution of the Pitzer, Flory-Huggins, and residual terms to the calculated activity coefficients of methanol for the $CaCl_2$-MeOH-EtOH system are shown in Figure 6.8. The effects of introducing solvation to the model are canceled by the magnitudes of the Pitzer and residual terms. The contribution of the Pitzer, Flory-Huggins, and residual terms to the calculated activity coefficients of ethanol are almost equal in magnitude but opposite in sign to those shown in Figure 6.8. The solvation number of the calcium ion by methanol is 3.7, while that of the calcium ion by ethanol is 2.7.

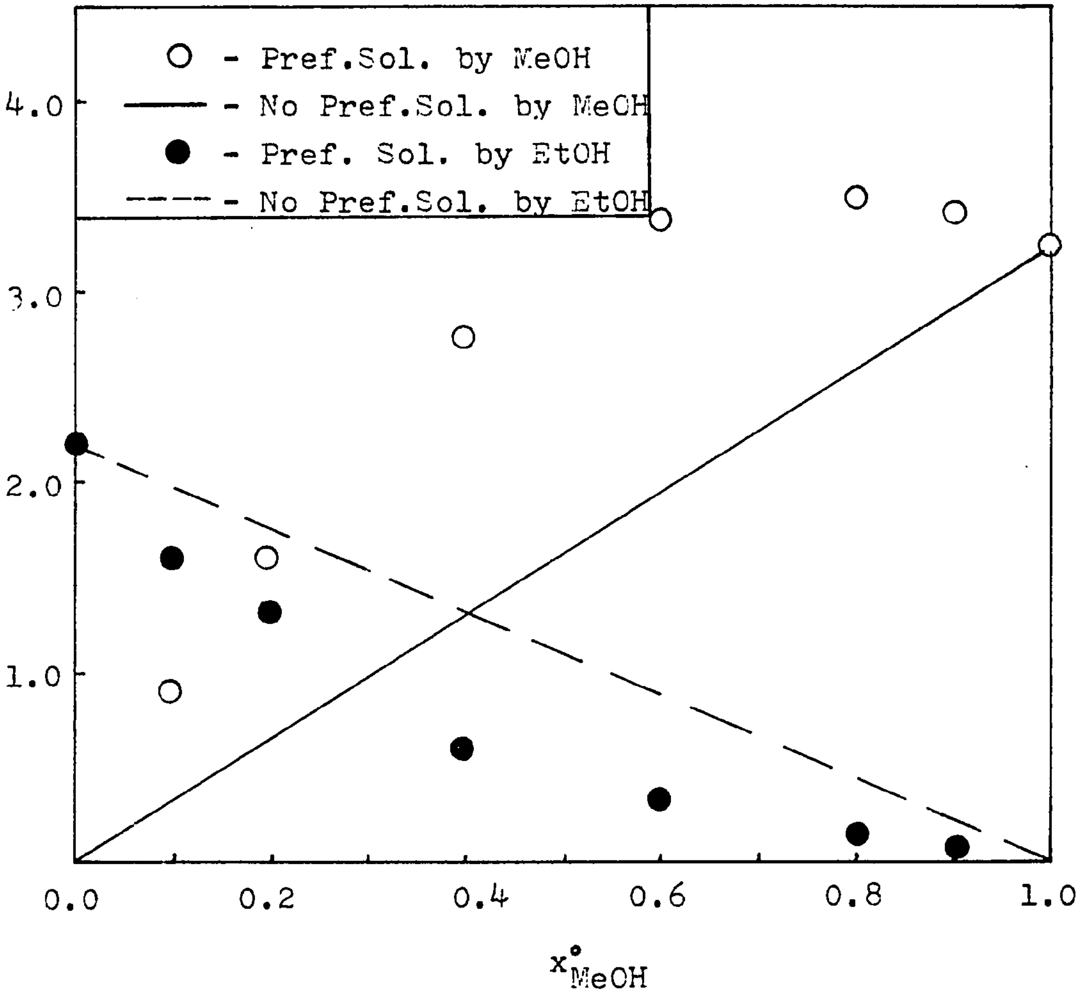
To improve the results of the $CaCl_2$-MeOH-EtOH system at 760 mm Hg, the concept of preferential solvation was introduced in Section 6.4. The contributions of the Pitzer, Flory-Huggins, and residual terms to the calculated activity coefficients of methanol are shown in Figure 6.9. h_{0+} for methanol and ethanol are calculated by equations (6-10a) and (6-10b).

The Flory-Huggins term cancels the effects of the Pitzer term; however, its effects are extreme. The Flory-Huggins term decreases rapidly with concentration as the salt-free mole fraction of ethanol increases.

Many expressions for h_{0+_3} and h_{0+_4} were tested for their effectiveness in causing the salting-in of methanol, but only those of equations (6-10a) and (6-10b) gave the desired results. According to Debye (1927), the expressions for h_{0+_3} and h_{0+_4} must be functions of the dielectric constant of the mixed solvent and the temperature of the system. The expressions were used in the prediction of the systems shown in Table 6.3. A comparison of these results with those of Table 6.2 indicates a worsening of the predicted Δy and Average % Ratio for many of the systems; i.e., they are overpredicted.

The preferential solvation term works to increase the solvation number of the salted-in component and to suppress the solvation number of the salted-out component. The solvation numbers of the calcium ion by methanol and ethanol, with and without preferential solvation are plotted in Figure 7.1. The use of preferential solvation

Figure 7.1 A Comparison of the Solvation Numbers of the Calcium Ion by Methanol and Ethanol With and Without Preferential Solvation.



enhances the solvation number of methanol over the entire concentration range while suppressing that of ethanol. As already indicated, the preferential solvation term overcalculates the solvation number of methanol.

The results of Table 6.3 suggest the possibility that equation (5-9), which was developed to relate the solvation number of the lithium ion in methanol to that of water, should be modified. (This relationship is assumed to be valid for all systems.) The form of this relationship can only be established using the systems of Table 6.2. This study would then reduce to a correlation scheme.

To reduce the impact of the preferential solvation term if the contribution of the Flory-Huggins term is too large; e.g., for the $CaCl_2$-MeOH-EtOH system, the preferential solvation term was multiplied by the factor 298.15/T. (See equations (6-11a) and (6-11b) and Table 6.4.) Even though this correction term is useful for some systems, it was found to be inapplicable for the $LiCl-H_2O$-Isopropanol system at 75.1°C which would be predicted better if the Flory-Huggins term were more negative; i.e. if the value of the solvation number of water were increased and that of isopropanol decreased. In addition, the introduction of this term prevents the ternary expression from reducing to the binary expression.

In Sections 6.9 and 6.10, the model was used in the prediction of salt-mixed solvent systems when a_4 or A_{mn} have not been established because the constituent binary salt-alcohol data do not exist. In order to predict these systems, the average halide values of a_4 obtained from the regression of halide salt-alcohol data are assumed to be the value of a_4 in the ternary system. If an ion-solvent interaction parameter is not available, it is assumed to have the same value as the ion nearest in size and of the same charge. For example, the A_{MeOH/F^-} interaction parameter, which is unavailable, is assumed to have the same value as the A_{MeOH/Cl^-} interaction parameter. The prediction results are shown in Tables 6.7 and 6.8.

The results indicate that good prediction of the ternary data are achieved for salts in H_2O-MeOH mixtures and for H_2O-EtOH mixtures up to approximately twice the solubility of the salt in the nonaqueous solvent. It is also important to note that the salts of Tables 6.7 and 6.8 are not completely dissociated in the nonaqueous solvents of the ternary systems. However, this does not seem to affect the quality of the predictions. If it did, the predictions would probably be valid only up to molalities of 0.5 where the properties of incompletely dissociated electrolytes diverge from those of completely dissociated solutions.

If $A_{s/ion}$ is available for at least two of the solvents, the value of $A_{s/ion}$ for another solvent may be estimated by assuming a linear relationship between the already established $A_{s/ion}$ and the dielectric constant of the solvent at 25°C. This method was used to develop the equations of Table 6.9 in Section 6.10. For example, the $A_{n\text{-propanol}/Li^+}$ parameter and the $A_{n\text{-propanol}/Cl^-}$ parameter were estimated from the equations for A_{s/Li^+} and A_{s/Cl^-} of Table 6.9. Even though the correlation coefficient of the equation for A_{s/Li^+} is 0.5, indicating a poor correlation of the $A_{s/Li+}$ with dielectric constant, the prediction results for the $LiCl-H_2O(3)-n-PrOH(4)$ system of Table 6.10 are quite good. The correlation coefficient for the A_{s/Cl^-} equation is 1.0. a_4 was also estimated.

It is not recommended that the estimated values of a_4 and A_{mn} or the equations of Table 6.9 be used to predict the osmotic coefficients or vapor pressures of binary nonaqueous electrolytic solutions. As shown in Chapter 5, the major contribution to the calculated solvent activity coefficients of the nonaqueous solvent is the Pitzer term. The wide range in the values of a_4 within each nonaqueous system shown in Tables 5.14 and 5.15, indicate that it would be coincidental if the average halide value of a_4 was able to predict the binary data.

It is possible to use an average halide value of

a_4 in the prediction of the ternary systems since in most cases, the Flory-Huggins and residual terms provide the largest contributions to the calculated solvent activity coefficients.

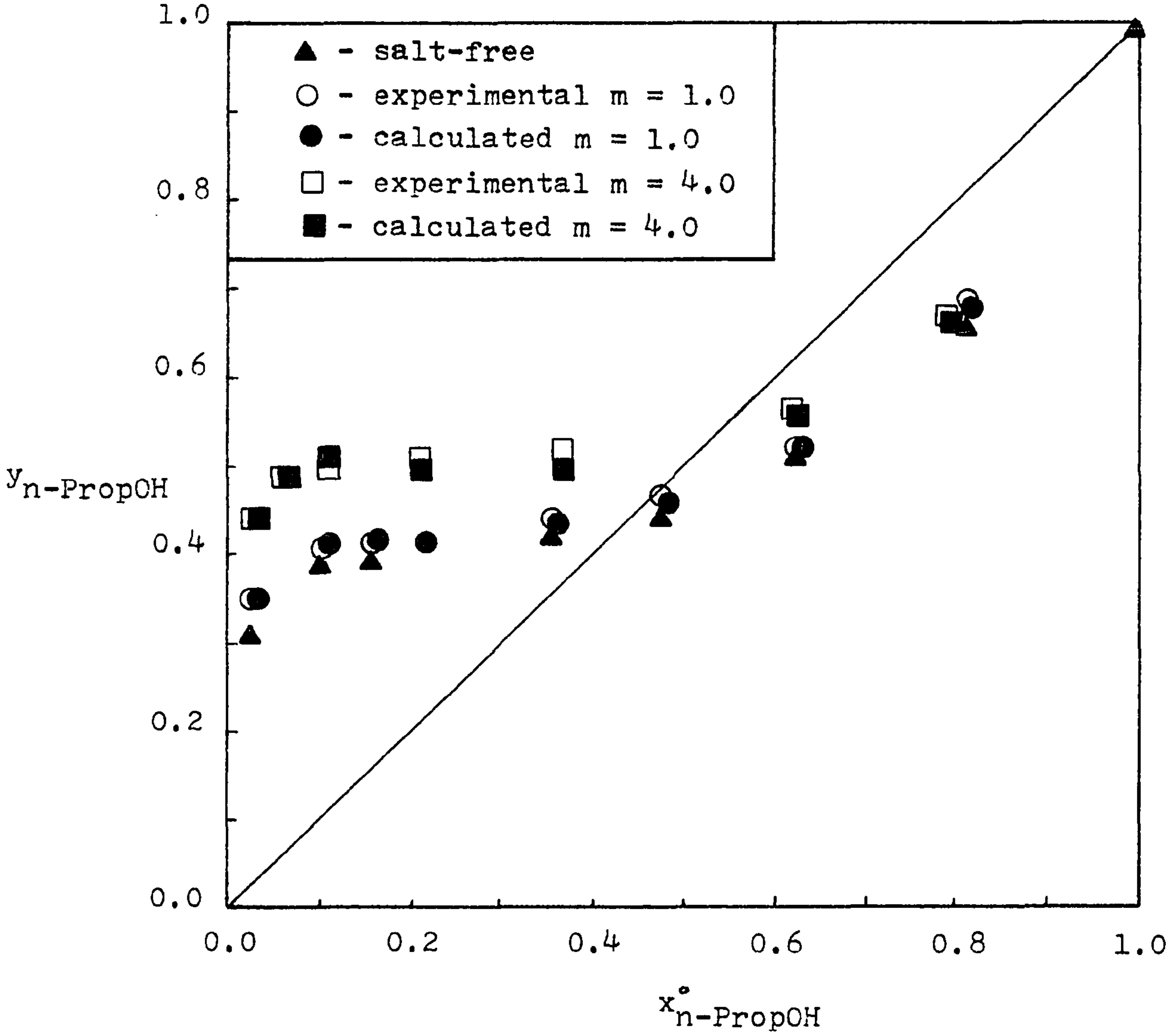
In Section 6.11, the model was used to predict the salt-effects on the vapor-liquid equilibrium of the LiCl-water(3)-methanol(4)-n-propanol(5) and the LiCl-water(3)-ethanol(4)-n-propanol(5) systems at 760 mm Hg. The data are from Boone (1976). The parameters of Tables 5.10, 5.14, and 5.15 and the estimation techniques of Sections 6.9 and 6.10 were used to effect the predictions.

The results are shown in Table 6.11 and compare well with the results of Boone who used a pseudobinary approach and ternary data to obtain the parameters for the multicomponent predictions.

The results of this study would of course be improved if binary data for the LiCl-n-propanol system were available. Even though the LiCl-H_2O-n-propanol system at 760 mm Hg of Table 6.10 was predicted with a Δy of 0.021, it should be noted that a plot of the predicted vapor phase compositions of n-propanol as a function of the salt-free mole-fractions of n-propanol indicates that the model possibly predicts an immiscible region around a mole-fraction of 0.2 for the molalities indicated. (See Figure 7.2. The results for a molality of 2.0 are not indicated. The molalities are on a propanol-free basis.)

To investigate this possibility, a plot of the exper-

Figure 7.2 Predicted y-x Diagram for the LiCl-H_2O-n-PropOH System at 760 mm Hg. (Indicated molalities are on a propanol-free basis.)



imental and predicted activities of n-propanol as a function of the salt-free mole fractions of n-propanol at molalities of 1.0, 2.0, and 4.0, respectively, was prepared. (See Figure 7.3.) The figure indicates that the experimental data exhibit a point of incipient instability at a mole-fraction of n-propanol of approximately 0.2 and a propanol-free molality of 4.0.

A point of incipient instability is indicated when

$$(\partial \ln a_4 / \partial x_4)_{T,P} = 0 \qquad (7\text{-}1)$$

$$(\partial^2 \ln a_4 / \partial x_4^2)_{T,P} = 0 \qquad (7\text{-}2)$$

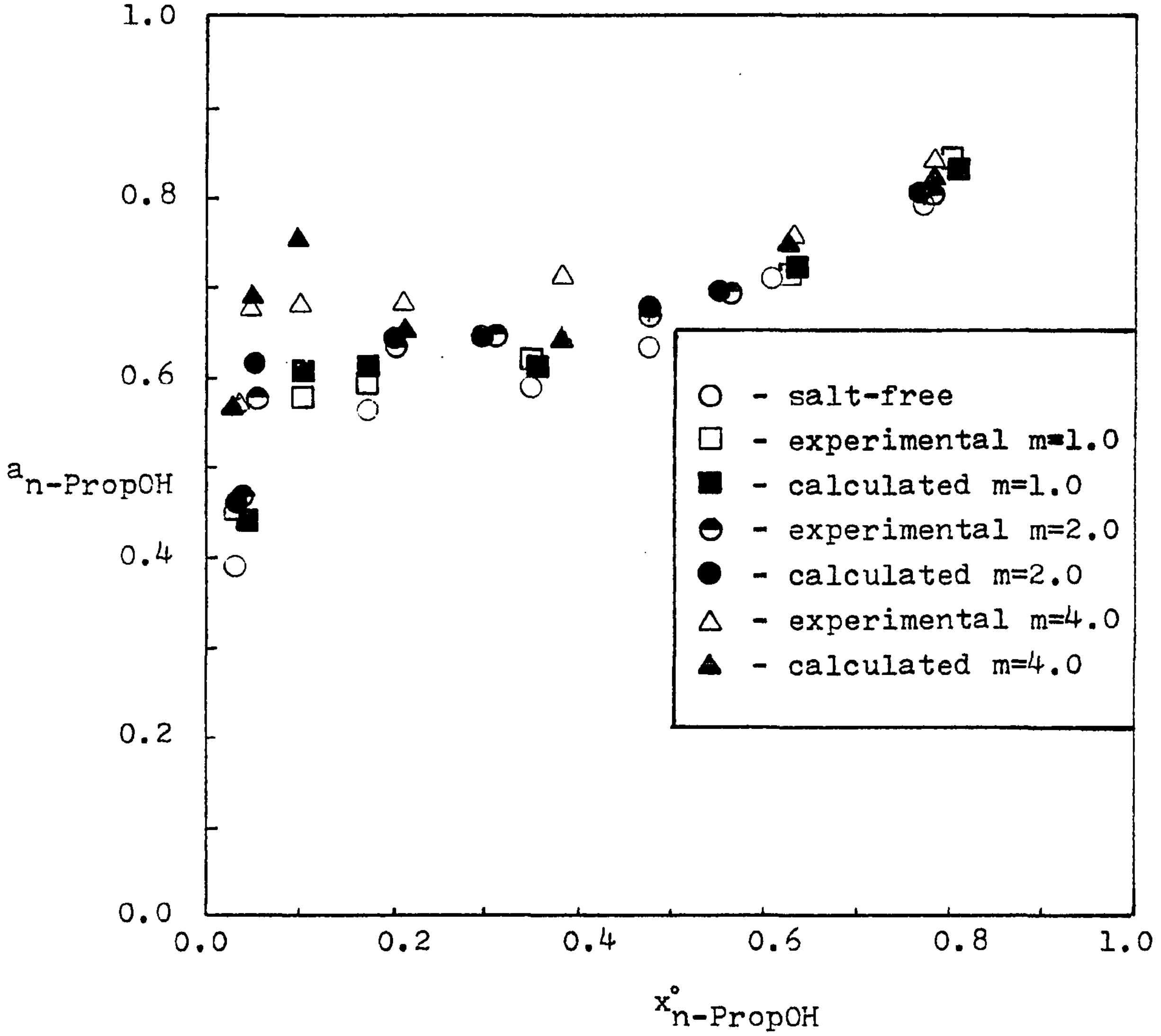
Graphically, a point of incipient instability is indicated by a horizontal inflection point.

An unstable system is indicated by a maximum on a plot of activity as a function of liquid-phase mole fraction.

Equations 7.1 and 7.2 require that isothermal data be available to evaluate the derivatives. However, as Boone (1976) indicates, the boiling point range for the $LiCl$-H_2O-n-propanol system is 14°C, but for the n-propanol composition range (0.03-0.8 mole-fraction propanol) for which data are available, the boiling point varies only 3°C. Therefore, the system can be assumed to be isothermal.

The prediction results of Figure 7.3 indicate that at

Figure 7.3 A Comparison of the Activities of n-propanol Calculated Using the Model With the Experimental Values. System: LiCl-H_2O-n-Propanol at 760 mm Hg. (Indicated molalities are on a propanol-free basis.)



a propanol-free molality of 2.0, a point of incipient instability exists at a mole-fraction of propanol of approximately 0.2. At the same mole-fraction and a molality of 4.0, the model predicts that the system is unstable. Boone's model gave similar results. Boone's experimental data indicate that the LiCl-H_2O-n-propanol system at 760 mm Hg splits into two liquid phases at a propanol-free molality of 4.4 and a mole fraction of propanol of 0.2.

Even though the model predicts a point of incipient instability at a molality of 2.0 and an unstable system at a molality of 4.0, it does predict correctly the mole fraction of n-propanol at which the point of incipient instability is observed for the experimental data.

Figures 7.4 and 7.5 show the contributions of the Pitzer, Flory-Huggins, and residual terms to the calculation of the solvent activity coefficients of n-propanol as a function of the salt-free mole fractions of propanol at molalities of 2.0 and 4.0, respectively. As Figure 7.4 shows, the agreement between the experimental and calculated activity coefficients of n-propanol is good. The figure gives no information as to why a point of incipient instability is predicted. The contribution of the Pitzer term is negligible over the entire concentration range of n-propanol. Of course, an adjustment in the value of the solvation number of the Li^+ ion in n-propanol to lower the contribution of the Flory-

Figure 7.4 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to $\ln\gamma_4$ for the LiCl-H_2O-n-PropOH System at 760 mm Hg. (m = 2 on a n-propanol-free basis.)

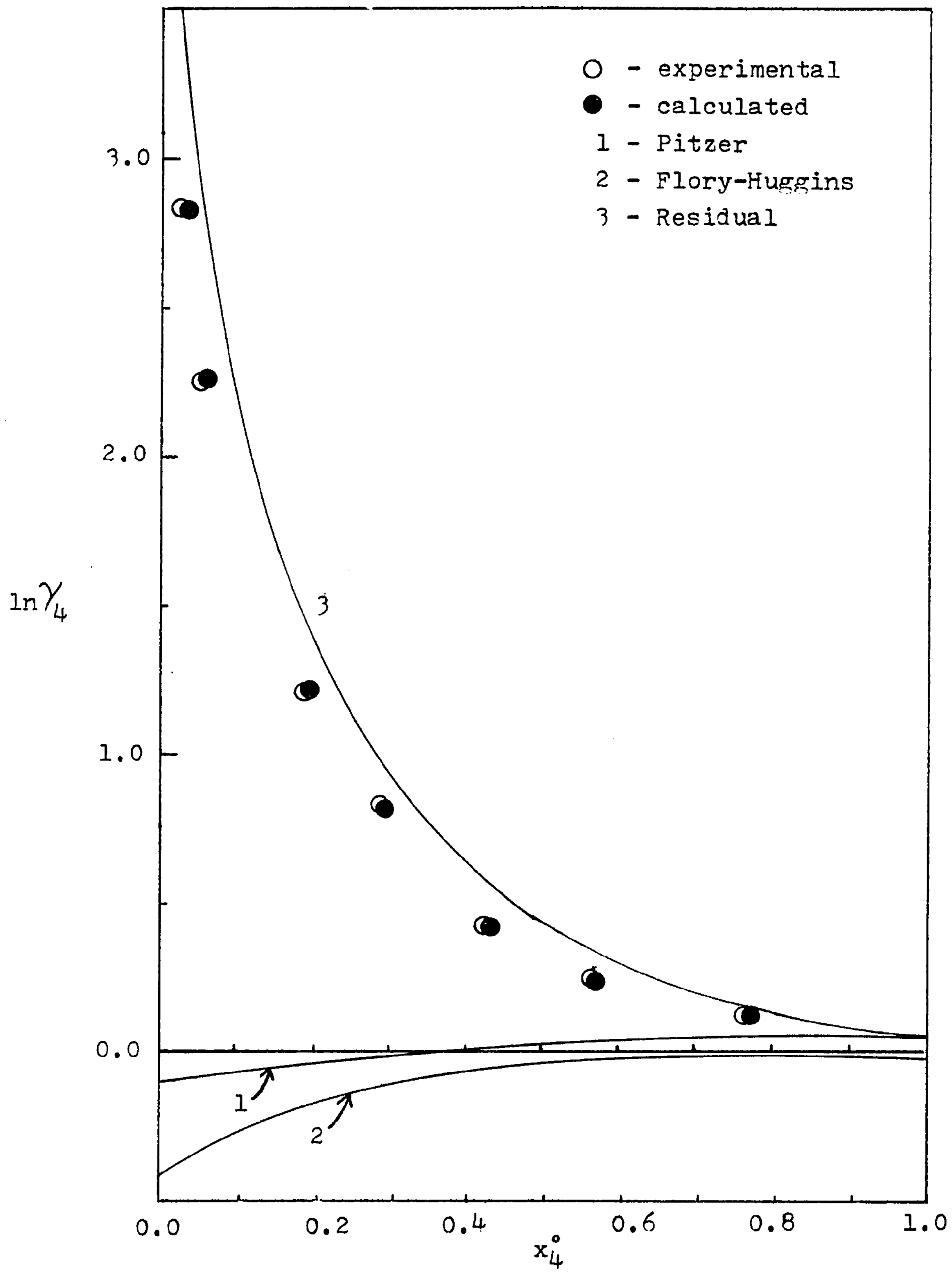
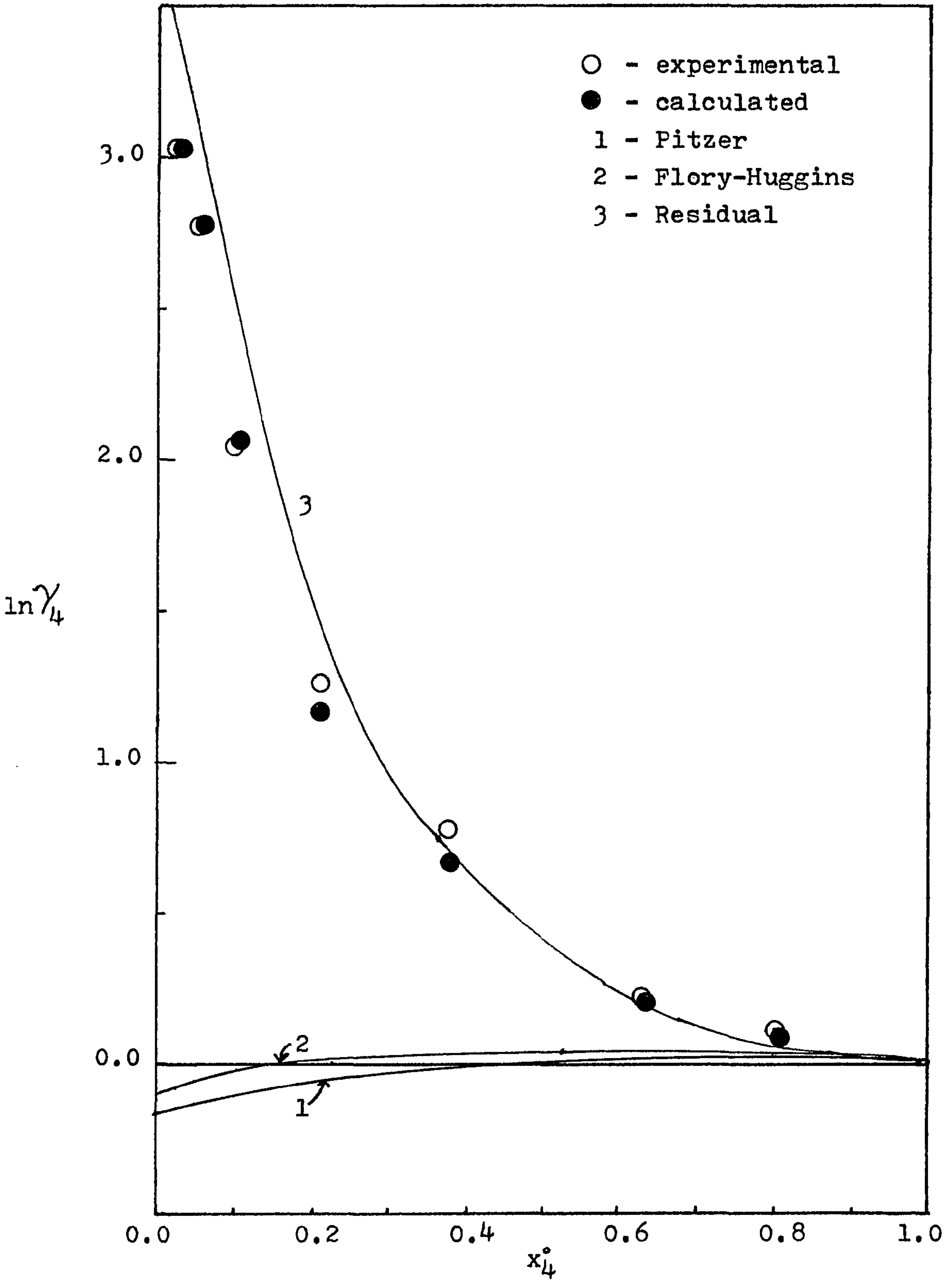


Figure 7.5 Contribution of the Pitzer, Flory-Huggins, and Residual Terms to $\ln\gamma_4$ for the LiCl-H_2O-n-PropOH System at 760 mm Hg. (m = 4 on a n-propanol-free basis.)



Huggins term (make it more negative), would decrease the contribution of the residual term and improve the results; i.e., a point of incipient instability would not be predicted. Adjustments in the values of $A_{n\text{-propanol}/Li^+}$ and $A_{n\text{-propanol}/Cl^-}$ could also be made but the binary data for the LiCl-n-propanol system are not available.

As shown in Figure 7.5 for a propanol-free molality of 4.0 where an unstable system is predicted at a mole-fraction of propanol of approximately 0.2, the agreement between the calculated and experimental activity coefficients of n-propanol is not good. The relative percent error in the activity coefficient at this point is -5.0. (At a mole fraction of propanol of 0.38, the relative percent error in the activity coefficients is -8.8) Apparently, at a mole fraction of 0.2, the contribution of the Pitzer term is too large. (negative contribution) The contribution of the Flory-Huggins term is negligible. However, at a mole fraction of 0.38, the contributions of the Pitzer and Flory-Huggins terms are negligible and the residual term is the predominate contribution. As in the case where the molality is 2.0, the results would be improved through an adjustment of the solvation number of the Li^+ ion in propanol. However, at a molality of 4.0, the Flory-Huggins term should be increased in a positive direction where for a molality of 2.0, this term must be more negative. In both cases, adjustments in the value of a_4 of the Pitzer term would also improve the results but of course, this would require the experimental data of the LiCl-n-propanol binary.

It is generally difficult to predict liquid-liquid equilibria using parameters obtained from vapor-liquid equilibrium data. In the case of the LiCl-H_2O-n-propanol system and the systems of Table 6.11, the value of a_4 or a_5 and the values of the ion-solvent interaction parameters for the constituent LiCl-n-propanol binary were estimated. Even though these parameters were estimated, the correct mole-fraction at which the point of incipient instability occurs for the experimental data of Boone is predicted although the molality at which this occurs is incorrect. The results of Table 6.11 can also be considered good.

CHAPTER 8

CONCLUSIONS

A group-contribution model for the prediction of salt-effects on the vapor-liquid equilibria of multicomponent electrolytic solutions containing a single electrolyte has been presented. The model uses only binary parameters obtained from the regression of binary salt-solvent osmotic coefficient and vapor-pressure depression data at 25°C and binary solvent VLE data.

Methods are presented for the estimation of the ion-solvent and ion-size parameters needed for multicomponent prediction when the constituent binary data are not available. However, these parameters should not be used in the prediction of binary electrolytic solutions.

The prediction of liquid phase activity coefficients and vapor phase compositions was demonstrated for 25 data sets of isothermal and isobaric salt-water-alcohol and salt-alcohol mixtures and gave an average absolute error in the vapor phase compositions of 0.019.

The ability of the ternary model to represent salt-effects was also shown. The results are superior to those of Mock, et.al., (1984).

The liquid phase immiscibility of the LiCl-water-n-propanol system was also predicted. Although the model predicted that phase separation occurs above a molality of 2.0, the correct mole-fraction of n-propanol at which phase separation occurs was predicted.

APPENDIX A

1. Vapor Pressures of Solvents Used in this Study

The Antoine equation

$$\log P_i^{sat} = A - \frac{B}{T^{o}C + C} \qquad \text{(A-1)}$$

where P_i^{sat} is the saturated vapor pressure in mmHg and T is the temperature of the system in °C, is used to calculate vapor pressures. This equation is not used in the following cases: 1) for binary aqueous systems at all temperatures, where the vapor pressures are given by Weast (1970); 2) in the calculation of osmotic coefficients from the vapor pressure depression data of salts in methanol measured in this study since the vapor pressures of methanol at m=0 are given; and 3) in the calculation of osmotic coefficients of salts in various solvents measured by other workers where the vapor pressure at m=0 is given.

The constants of equation (A-1) are given in Table (A-1).

TABLE A-1

Antoine Constants for Solvents Used in this Study

All Values are from Gmehling and Onken (1977)

Solvent	A	B	C	Temperature Range
Water	8.07131	1730.630	233.426	1-100°C
Methanol	7.76879	1408.360	223.600	25-56°C
Methanol	7.97010	1521.230	233.970	65-100°C
Ethanol	8.11220	1592.864	226.184	20-93°C
n-Propanol	7.61785	1374.890	193.00	1-100°C
Isopropanol	8.11676	1580.630	219.610	1-100°C

2. Calculation of the Fugacity Coefficients at Saturation and of the Vapor Phase Using the Hayden-O'Connell Correlation

The generalized method of Hayden and O'Connell (1975) for the prediction of pure component and cross second virial coefficients for simple and complex systems is used to calculate the fugacity coefficients at saturation and of the vapor phase. This method was chosen since it does not require experimental data to obtain parameters. The correlation requires only the critical temperatures and pressures, the dipole moments, the mean radii of gyration, and association and solvation parameters for the components of the mixture.

The fugacity coefficient of component i in the vapor is given by

$$\ln \phi_i = \frac{1}{RT} \int_0^P (\bar{V}_i - \frac{RT}{P})dP \qquad \text{(A-2)}$$

where T is the system temperature and $\bar{V}_i$ is the partial molar volume of i in the mixture.

The density-explicit virial equation which is valid at low pressures is

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT} \qquad \text{(A-3)}$$

where Z is the compressability factor and V is the molar volume of the mixture. B is the second virial coefficient for the mixture and is given by

$$B_{mix} = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij} \qquad \text{(A-4)}$$

for i, j = 1, 2, 3, ..., N components.

The B_{ii} and B_{jj} represent interactions between like components and are termed the pure-component second virial coefficients. B_{ij}, the cross second virial coefficient, represents interactions between unlike molecules i and j.

Combining equations (A-2)-(A-4) gives

$$\ln \phi_i = [2 \sum_{j=1}^{N} y_j B_{ij} - B_{mix}] \frac{P}{RT} \qquad \text{(A-5)}$$

Hayden and O'Connell assume that the B are the sums of various types of molecular interactions.

$$B = B_{free} + B_{metastable} + B_{bound} + B_{chem} \qquad \text{(A-6)}$$

B_{free} accounts for unbound pairs of molecules; $B_{metastable}$, for metastably bound pairs of molecules; B_{bound}, for physically bound pairs of molecules; and B_{chem}, for chemically bound pairs of molecules.

B_{free} in equation (A-6) is the difference between $B_{free\text{-}nonpolar}$ and $B_{free\text{-}polar}$. For interactions between like molecules, $B_{free\text{-}nonpolar}$ is given by

$$B_{free\text{-}nonpolar} = b_o(.94-1.47/T^{*\prime}-.85/T^{*\prime 2}+1.015/T^{*\prime 3} \qquad \text{(A-7)}$$

$T^{*\prime}$, the reduced temperature, is

$$\frac{1}{T^{*\prime}} = \varepsilon/T - 1.6\ w \qquad \text{(A-8)}$$

where w, the nonpolar acentric factor is a function of R', the mean radius of gyration.

$$w = .006\ R' + .02087\ R'^2 - .00136\ R'^3 \tag{A-9}$$

ε, the energy parameter for polar pairs of molecules is

$$\varepsilon = \varepsilon_1(1 - \zeta \bullet n + n(n+1)\ \frac{\zeta^2}{2}) \tag{A-10}$$

where

$$\varepsilon_1 = T_C(.748 + .91w - .4\eta/(2+20w)) \tag{A-11}$$

T_C is the critical temperature and η the association parameter.

$$n = (16 + 400w)/(10 + 400w) \tag{A-12}$$

$$\zeta = \mu^4/(C \bullet \varepsilon_1 \bullet \sigma^6 \bullet T_C \bullet 5.723x10^{-8}) \tag{A-13}$$

where μ is the dipole moment and

$$C = 2.882 - 1.882w/(0.03 + w) \tag{A-14}$$

$$\sigma = (2.44 - w)(T_C/P_C)^{1/3} \tag{A-15}$$

σ is the molecular-size parameter for non-polar pairs. b_O, the equivalent hard-sphere volume of molecules is given by

$$b_O = 1.2618\ \sigma' \tag{A-16}$$

where σ', the molecular-size parameter for pure polar and associating pairs is

$$\sigma'^3 = \sigma^3(1 + 3\zeta/(10 + 400w)) \tag{A-17}$$

$B_{free-polar}$, for interactions between like molecules, is given by equation (A-18).

$$B_{free-polar} = b_O\mu^{*'}(.75-3/T^{*'}+2.1/T^{*'2} + 2.1/T^{*'3}) \tag{A-18}$$

where b_o and $T^{*'}$ are given by equations (A-16) and (A-8), respectively. $\mu^{*'}$, the polar-reduced dipole moment is related to the reduced dipole moment by the following

$$\begin{aligned} \mu^{*'} &= \mu^* - .25 && \mu^* \geq .25 \\ &= 0 && .25 \geq \mu^* \geq .04 \\ &= \mu^* && .04 > \mu^* \geq 0 \end{aligned} \tag{A-19}$$

μ^* is given by

$$\mu^* = 7243.8\ \mu^2/\varepsilon\sigma' \tag{A-20}$$

ε and σ' are given by equations (A-10) and (A-17), respectively. The sum of $B_{metastable}$ and B_{bound} is given by

$$B_{metastable} + B_{bound} = b_o A \exp[\Delta H\varepsilon/T] \tag{A-21}$$

where

$$A = .3 - .05\ \mu^* \tag{A-22}$$

$$\Delta H = 1.99 + .2\ \mu^{*2} \tag{A-23}$$

μ^* is given by equation (A-20).

B_{chem} is given by

$$B_{chem} = b_o \exp(\eta(D-4.27))(1-\exp(1500\eta/T)) \tag{A-24}$$

where

$$D = 650/(\varepsilon + 300) \tag{A-25}$$

Values of T_C, P_C, η , R', and μ for the solvents used in this study are given in Table (A-2).

To evaluate B_{ij} for interactions between unlike polar molecules, the following mixing rules must be used in equations (A-6), (A-7), (A-18), (A-21), and (A-24):

TABLE A-2

Constants Used to Evaluate the Pure-Component Second Virial Coefficients B in Equation (A-6)

Ref: (Fredenslund, et al., 1977)

Solvent	T_C°K	P_C(atm)	R'(Å)	μ(D)	η
Water	647.3	218.3	0.615	1.83	1.70
Methanol	512.6	78.5	1.536	1.66	1.63
Ethanol	516.2	63.0	2.250	1.69	1.40
n-Propanol	536.7	51.0	2.736	1.68	1.40
Isopropanol	508.3	47.0	2.726	1.66	1.32

$$\varepsilon_{ij} = 0.7(\varepsilon_i\varepsilon_j)^{1/2} + .6(1/\varepsilon_i + 1/\varepsilon_j) \qquad \text{(A-26)}$$

$$\sigma'_{ij} = (\sigma'_i\sigma'_j)^{1/2} \qquad \text{(A-27)}$$

$$w_{ij} = .5(w_i + w_j) \qquad \text{(A-28)}$$

$$\mu_{ij}^* = 7243.8\ \mu_i\mu_j/(\varepsilon_{ij}\sigma'_{ij}) \qquad \text{(A-29)}$$

The ε_i, ε_j, σ_i, σ_j, w_i, and w_j, are calculated from equations (A-10), (A-17) and (A-9), respectively. η, in equation (A-24) is replaced by η_{ij}, the solvation parameter for unlike interactions. The values of η_{ij} are found in Table (A-3).

Once the pure-component and the cross second virial coefficients are evaluated from equation (A-6), they are substituted into equation (A-4) to obtain B_{mix}. The virial coefficients and B_{mix} are then substituted into equation (A-5) to obtain the vapor phase fugacity coefficients for each condensable component of the mixture.

The pure component virial coefficients calculated above are also used to evaluate the fugacity coefficients, ϕ_i^s, at saturation. ϕ_i^s is evaluated at the system temperature and saturated vapor pressure, P_i^{sat}, of component i and is given by

$$\ln \phi_i^s = \frac{B_{ii} \cdot P_i^{sat}}{RT} \qquad \text{(A-30)}$$

P_i^{sat} is given by equation (A-1).

TABLE A-3

Constants Used to Evaluate the Cross Second Virial Coefficients, B_{ij}, in Equation (A-6)

Ref: (Fredenslund, et al., 1977)

Solvent Mixture	η_{ij}
Water-Methanol	1.4
Water-Ethanol	1.7
Water-Isopropanol	1.55
Methanol-Ethanol	1.63
Isopropanol-n-Propanol	1.50
Water-n-Propanol	1.55

APPENDIX B

1. Densities of Pure Solvents Used in this Study

TABLE B-1

Solvent	Temperature Range	Reference
Water	0-100°C	Perry (1973)
Methanol	25-50°C	Mikhail & Kimel (1961)
Ethanol	0-40°C	Perry (1973)
n-Propanol	0-30°C	Perry (1973)
Isopropanol	0-30°C	Perry (1973)

2. Estimation of the Densities of Pure & Mixed Solvents

The correlation for the prediction of saturated densities of liquids and their mixtures developed by Hankinson and Thomson (1979) is used in this study. The correlation is a corresponding states equation which requires the reduced temperature, acentric factor, and a characteristic volume for each pure compound comprising the mixed solvent. Six combinations of mixing rules are presented to evaluate the pseudocritical constants of the mixture. The model is applicable over the reduced temperature range $0.25<T_R<0.98$.

For a pure or mixed solvent, the saturated liquid volume, V_S, is given by

$$V_S = V^* V_R^{(0)}[1-W_{SRK}V_R^{(\delta)}] \tag{B-1}$$

where

$$V_R^{(0)} = 1 + a(1-T_R)^{1/3} + b(1-T_R)^{2/3} + c(1-T_R) + d(1-T_R)^{4/3} \tag{B-2}$$

and

$$V_R^{(\delta)} = [e + f{\bullet}T_R + g{\bullet}T_R^2 + h{\bullet}T_R^3]/(T_R-1.00001) \tag{B-3}$$

The parameters for equations (B-2) and (B-3) are given in Table B-2.

V^*, the only adjustable parameter, is the characteristic volume specific for each pure compound and W_{SRK} is the acentric factor determined from the Soave equation of state.

TABLE B-2

Parameters for Equations (B-2) and (B-3)

a.	-1.52816
b.	1.43907
c.	-0.81446
d.	0.190454
e.	-0.296123
f.	0.386914
g.	-0.0427258
h.	-0.0480645

Table B-3 presents the values of W_{SRK}, V^*, and T_C for the solvents used in this study.

For the estimation of the densities of mixed solvents, V^* and W_{SRK} of equation (B-1) are replaced by V_m^*, the characteristic volume of the mixed solvent, and W_m, the acentric factor for the mixed solvent. Six combinations of mixing rules may be used to evaluate T_{cm}, the pseudocritical temperature of the mixed solvent, and W_m. V_m^* and the six combinations of mixing rules, Aa, Ab, Ba, Bb, Ca, and Cb, are given by the following equations:

$$V_m^* = \frac{1}{4}\left(\sum_i x_i V_i^* + 3\left(\sum_i x_i V_i^{*2/3}\right)\left(\sum_i x_i V_i^{*1/3}\right)\right) \tag{B-4}$$

A. $$T_{cm} = \sum_i\sum_j x_i x_j V_{ij}^* T_{cij} / V_m^* \tag{B-5}$$

$$V_{ij}^* T_{cij} = (V_i^* T_{ci} V^*_j T_{cj})^{1/2} \tag{B-6}$$

B. $$T_{cm} = \sum_i x_i V_i^* T_{ci} / \sum_i x_i V_i^* \tag{B-7}$$

C. $$T_{cm} = \left[\sum_i x_i V_i^* (T_{ci})^{1/2}\right]^2 / \left(\sum_i x_i V_i^*\right)^2 \tag{B-8}$$

a. $$W_m = \sum_i x_i W_{SRKi} \tag{B-9}$$

b. $$W_m = \sum_i x_i V_i^* W_{SRKi} / \sum_i x_i V_i^* \tag{B-10}$$

The six combinations of mixing rules were evaluated for the methanol-water system at 25 and 50°C, the ethanol-water system at 25°C, the n-propanol-water system at 30°C, and the isopropanol-water system at 30°C, using equations (B-1) to (B-10). The reduced temperature in equations (B-2) and (B-3) is given by

TABLE B-3

Values of W_{SRK}, V^*, and T_c

Solvent	W_{SRK}	$V^*(\frac{\text{liter}}{\text{mole}})$	T_c °K	Reference
Water	-0.65445	0.04357	647.3	Reid, et al. (1977)
Methanol	0.5536	0.1198	512.6	
Ethanol	0.6378	0.1752	516.2	
n-Propanol	0.6249	0.2305	536.7	
Isopropanol	0.6637	0.2313	508.3	

$$T_R = T/T_{cm} \tag{B-11}$$

The liquid volumes were converted to density, d, using the relationship

$$d = \Sigma_i x_i MW_i/(V_s \bullet 1000) \quad \text{grams/cc} \tag{B-12}$$

where MW_i is the pure component molecular weight. The results are shown in Tables B-4 and B-5.

Combination Aa is used in this study although combinations Ba and Ca give comparable results.

TABLE B-4

Results of the Evaluation of Mixing Rules for the Methanol-Water System at 25 and 50°C

(The data are from Mikhail and Kimel (1961))

Mixing Rule Combination	Average Percent Error in Density	
	25°C	50°C
Aa	2.16	2.50
Ab	2.48	1.59
Ba	2.23	2.58
Bb	2.40	1.50
Ca	2.28	2.64
Cb	2.33	1.43

TABLE B-5

Results of the Evaluation of Mixing Rules for the Ethanol-Water, n-Propanol-Water, and Isopropanol-Water Systems

(The data are from Perry (1973))

Mixing Rule Combination	Average Percent Error in Density		
	EtOH/H_2O, 25°C	n-Prop/H_2O, 30°C	iso-Prop/H_2O
Aa	1.77	1.12	1.24
Ab	5.15	6.93	6.61
Ba	1.72	0.729	1.034
Bb	5.27	7.45	6.92
Ca	1.76	0.763	1.093
Cb	5.21	7.40	6.84

3. Estimation of the Change in Density of Mixed Solvents with Composition

Differentiation of equation (B-12) with respect to the mole fraction of each component of the mixture gives the change in density of the mixed solvent system with composition. All derivatives presented here are with respect to component 1 for a k component system.

From equation (B-12)

$$\frac{\partial d}{\partial x_1} = \frac{1}{1000\ V_s}[MW_1 + \sum_{j\neq 1} MW_j \frac{\partial x_j}{\partial x_1} - d\ \frac{\partial V_s}{\partial x_1}] \qquad \text{(B-13)}$$

$\frac{\partial V_s}{\partial x_1}$ is obtained from equation (B-1)

$$\frac{\partial V_s}{\partial x_1} = V_m{}^*(1 - W_m V_R{}^{(\delta)})\frac{\partial V_R{}^{(0)}}{\partial x_1} + V_R{}^{(0)}(1 - W_m V_R{}^{(\delta)})\frac{\partial V_m{}^*}{\partial x_1}$$

$$- V_m{}^* V_R{}^{(0)}[W_m \frac{\partial V_R{}^{(\delta)}}{\partial x_1} + V_R{}^{(\delta)}\ \frac{\partial W_m}{\partial x_1}] \qquad \text{(B-14)}$$

$\frac{\partial V_R{}^{(0)}}{\partial x_1}$, $\frac{\partial V_R{}^{(\delta)}}{\partial x_1}$, $\frac{\partial V_m{}^*}{\partial x_1}$ and $\frac{\partial W_m}{\partial x_1}$ are obtained through differentiation of equations (B-2)-(B-4) and (B-10) with respect to x_1.

$$\frac{\partial V_R{}^{(0)}}{\partial x_1} = -[\frac{a}{3}(1-T_R)^{-2/3} + \frac{2b}{3}(1-T_R)^{-1/3} + c + \frac{4d}{3}(1-T_R)^{1/3}]\frac{\partial T_R}{\partial x_1} \qquad \text{(B-15)}$$

$$\frac{\partial V_R{}^{(\delta)}}{\partial x_1} = [f + 2gT_R + 3hT_R{}^2 - V_R{}^{(\delta)}](\frac{\partial T_R}{\partial x_1})/(T_R - 1.00001)$$

$$- V_R{}^{(\delta)}(\partial T_R/\partial x_1)/(T_R - 1.00001) \qquad \text{(B-16)}$$

$$\frac{\partial V_m^*}{\partial x_1} = \frac{1}{4}(V_1^* + \sum_{j\neq 1} V_j^*\frac{\partial x_j}{\partial x_1} + 3(V_1^{*2/3} + \sum_{j\neq 1} V_j^{*2/3}\frac{\partial x_j}{\partial x_1})(\Sigma_i x_i V_i^{*1/3})$$

$$+ 3(\Sigma_i x_i V_i^{*2/3})(V_1^{*1/3} + \sum_{j\neq 1} V_j^{*1/3}\frac{\partial x_j}{\partial x_1}) \qquad \text{(B-17)}$$

$$\frac{\partial W_m}{\partial x_1} = W_{SRK_1} + \sum_{j\neq 1} W_{SRK_j}\frac{\partial x_j}{\partial x_1} \qquad \text{(B-18)}$$

$\frac{\partial T_R}{\partial x_1}$ is determined from equations (B-8) and (B-11).

$$\frac{\partial T_R}{\partial x_1} = -\frac{T_R}{T_{cm}}\frac{\partial T_{cm}}{\partial x_1} \qquad \text{(B-19)}$$

$$\frac{\partial T_{cm}}{\partial x_1} = 1/V_m^*[2\sum_i\sum_j x_i V_{ij}^* T_{cij}\frac{\partial x_j}{\partial x_1} - T_{cm}\frac{\partial V_m^*}{\partial x_1}] \qquad \text{(B-20)}$$

The change in density with respect to the number of moles of component j in the mixed solvent is

$$\frac{\partial d}{\partial n_j} = \frac{\partial (d)}{\partial x_1}\frac{\partial x_1}{\partial n_j} \qquad \text{(B-21)}$$

where

$$\frac{\partial x_1}{\partial n_1} = \frac{1}{n_T}(1 - x_1) \qquad \text{(B-22a)}$$

and

$$\frac{\partial x_1}{\partial n_j} = -\frac{x_1}{n_T} \quad \text{for } j\neq 1 \qquad \text{(B-22b)}$$

APPENDIX C

1. Dielectric Constants of Pure and Mixed Solvents Used in this Study

TABLE C-1

Solvent	Temperature Range	Reference
Water	0-350°C	Bradley & Pitzer (1979)
Methanol/Water	5-55°C	Albright & Gosting (1946)
Ethanol/Water	20-80°C	Akerlof (1932)
n-Propanol/Water	20-80°C	
Isopropanol/Water	20-80°C	

2A. Correlation of Dielectric Constant Data for Binary Alcohol-Water Systems When Data are Available

The constants of the equation,

$$D = Ae^{Bt} \qquad \text{(C-1)}$$

where t is in ^{o}C, were determined from the data of Table C-1 at a fixed alcohol composition. The values of A and B thus obtained were fit to a fifth-order polynomial where

$$A = A(1) + A(2)x_4' + A(3)x_4'^2 + A(4)x_4'^3 + A(5)x_4'^4 + A(6)x_4'^5 \qquad \text{(C-2)}$$

and

$$B = B(1) + B(2)x_4' + B(3)x_4'^2 + B(4)x_4'^3 + B(5)x_4'^4 + B(6)x_4'^5 \qquad \text{(C-3)}$$

x_4' is the mole fraction of the alcohol on a salt-free basis.

The values of A(1) through A(6) and B(1) through B(6) are shown in Tables C-2 and C-3 for the alcohol-water systems of this study.

TABLE C-2

Values of A(1) through A(6) for Use in Equations (C-1) and (C-2)

System	A(1)	A(2)	A(3)	A(4)	A(5)	A(6)
Methanol/H_2O	88.125	-74.868	33.254	-30.567	56.733	-35.266
Ethanol/H_2O	88.287	-147.92	113.18	78.843	-198.89	94.818
n-Propanol/H_2O	88.359	-230.32	292.03	-36.066	-214.63	124.53
Isopropanol/H_2O	88.195	-254.26	473.89	-617.38	529.88	-198.57

TABLE C-3

Values of B(1) through B(6) for Use in Equations (C-1) and (C-3)

System	B(1)	B(2)	B(3)	B(4)	B(5)	B(6)
Methanol/H_2O	-0.00467	-0.00326	-0.00110	0.0142	-0.0221	0.01098
Ethanol/H_2O	-0.00468	-0.00591	0.0278	-0.0823	0.0986	-0.0397
n-Propanol/H_2O	-0.00472	-0.00540	0.00791	-0.0150	0.0210	-0.0106
Isopropanol/H_2O	-0.00471	-0.00187	-0.0148	0.0510	-0.0672	0.0301

2B. Calculation of the Change in Dielectric Constant with Composition of Binary Solvents When Data are Available

Differentiation of equation (C-1) with respect to the mole fraction of each component of the mixture gives the change in dielectric constant of the binary solvent system with respect to composition.

$$\frac{\partial D}{\partial x_4'} = e^{Bt}\left[\frac{\partial A}{\partial x_4'} + At\,\frac{\partial B}{\partial x_4'}\right] \qquad \text{(C-4)}$$

where from equation (C-2)

$$\frac{\partial A}{\partial x_4'} = A(2) + 2{\bullet}A(3)x_4' + 3{\bullet}A(4)x_4'^2 + 4{\bullet}A(5)x_4'^3 + 5{\bullet}A(6)x_4'^4 \qquad \text{(C-5)}$$

and from equation (C-3)

$$\frac{\partial B}{\partial x_4'} = B(2) + 2{\bullet}B(3)x_4' + 3{\bullet}B(4)x_4'^2 + 4{\bullet}B(5)x_4'^3 + 5{\bullet}B(6)x_4'^4 \qquad \text{(C-6)}$$

The change in dielectric constant with respect to the number of moles of alcohol or water is given by

$$\frac{\partial D}{\partial n_4'} = \frac{\partial D}{\partial x_4'}\,\frac{\partial x_4'}{\partial n_4'} \qquad \text{(C-7a)}$$

and

$$\frac{\partial D}{\partial n_3'} = \frac{\partial D}{\partial x_4'}\,\frac{\partial x_4'}{\partial n_3'} \qquad \text{(C-7b)}$$

where

$$\frac{\partial x_4'}{\partial n_4'} = x_3'/n_T' \qquad \text{(C-7c)}$$

$$\frac{\partial x_4'}{\partial n_3'} = - \frac{x_4'}{n_T'} \qquad \text{(C-7d)}$$

x_3' is the mole-fraction of water on a salt-free basis.

3A. Estimation of Dielectric Constant Data for Multicomponent Systems When Data as a Function of Composition are Unavailable

The mixture dielectric constant data for the methanol-ethanol and isopropanol-n-propanol systems were estimated assuming that the dielectric constant of the mixture is given by

$$D = D_3 x_3' + D_4 x_4' \tag{C-8}$$

D_3 and D_4 are the dielectric constant of the pure solvents at a fixed temperature.

D_3 and D_4 are calculated from equations (C-1), (C-2), and (C-3) with x_4' set equal to unity. The values of A(1) through A(6) and B(1) through B(6) are given in Tables (C-2) and (C-3).

The change in dielectric constant with composition is obtained through differentiation of equation (C-8) with respect to x_3' and x_4'.

$$\frac{\partial D}{\partial x_3'} = D_3 + D_4 \ \partial x_4'/\partial x_3' \tag{C-9a}$$

$$\frac{\partial D}{\partial x_4'} = D_3 \ \partial x_3'/\partial x_4' + D_4 \tag{C-9b}$$

where

$$\frac{dx_3'}{dx_4'} = -1 \tag{C-9c}$$

The change in the dielectric constant with respect to the number of moles of components 3 and 4 are given by equations (C-7a) through (C-7d).

APPENDIX D

Derivation of the Gibbs Free Energy Expression of the Pitzer (Coulombic) Term Used to Obtain the Activity Coefficients of the Salt and the Solvents

The coulombic contribution to the activity coefficient of the salt or of the solvent is evaluated using the equation for the osmotic coefficient developed by Pitzer (1977).

$$\phi - 1 = \frac{-wL\kappa}{6(1 + \kappa a)} + c(\frac{2\pi a^3}{3} + \frac{\pi a w^2 L^2}{3(1+\kappa a)^2} \qquad \text{(D-1)}$$

where

$$L = \frac{e^2}{DkT} \qquad \text{(D-2)}$$

$$w = \Sigma_i z_i^2 \; C_i/\nu c \qquad \text{(D-3)}$$

$$\kappa^2 = 4\pi L w \nu c \qquad \text{(D-4)}$$

a is the ion-size parameter; e, the electronic charge; D, the solvent dielectric constant; k, the Boltzmann constant; T, the temperature of the system; ν, the total number of ions; z_i, the ionic charge; e_i, the concentration of ion i; and c, the total ionic concentration. c is converted to molarity in this study since the units of c given by Pitzer are ions/cc.

$$c = \bar{c}N/1000 \qquad \text{(D-5)}$$

Expansion of equation (D-3) gives

$$w = \frac{z_+^2 \nu_+ + z_-^2 \nu_-}{v} \qquad \text{(D-6a)}$$

where ν_+ and ν_- are the number of positive and negative ions, respectively. From the principle of electroneutrality

$$|\nu_+ z_+| = |\nu_- z_-| \qquad \text{(D-6b)}$$

equation (D-6a) becomes

$$w = (|\nu_- z_-| z_+ + |\nu_+ z_+| z_-)/\nu$$

$$= \frac{|z_+ z_-|(\nu_+ + \nu_-)}{}$$

$$= |z_+ z_-| \nu \qquad \text{(D-6c)}$$

since $\nu_+ + \nu_- = \nu$.

The ionic strength on a molar basis is defined

$$I_c = \bar{c} w \nu / 2 \qquad \text{(D-7)}$$

Substitution of equations (D-5), (D-6c), and (D-7) into equations (D-4) and (D-1) gives the following expressions for κ^2 and ϕ.

$$\kappa^2 = 8\pi L \frac{N}{1000} I_c \qquad \text{(D-8)}$$

and

$$\phi - 1 = - \frac{|z_+ z_-|\kappa}{6(1+\kappa a)} + \frac{\nu \bar{c} N}{1000} \left(\frac{2\pi a^3}{3} + \frac{\pi a w^2 L^2}{3(1+\kappa a)^2}\right. \qquad \text{(D-9)}$$

Equation (D-9) must be converted to a molal basis since the experimental osmotic coefficient data are in terms of molality. With the assumption that concentration is proportional to molality

$$\bar{c} = m d_o \qquad \text{(D-10)}$$

where m is the molality and d_o the density of the pure solvent, equations (D-7), (D-8), and (D-9) become

$$I_m = I_c / d_o \qquad \text{(D-11)}$$

$$\kappa^2 = 8\pi L(Nd_o/1000)I_m \qquad \text{(D-12)}$$

and

$$\phi - 1 = -\frac{|z_+z_-|\kappa L}{6(1+\kappa a)} + \frac{\nu m d_o N}{1000}(2\pi a^3/3 + \frac{\pi a w^2 L^2}{3(1+\kappa a)^2} \qquad \text{(D-13)}$$

The coulombic contribution to the activity coefficient of the solvent for a binary salt-solvent system is easily obtained from the following relationship

$$\ln\gamma_s = -(\phi-1)\nu m(\text{M.W.})/1000 \qquad \text{(D-14)}$$

where (M.W.) is the molecular weight of the solvent.

$$\ln\gamma_s^{\text{Pitzer}} = (\text{M.W.}/1000)(\frac{\kappa I L}{3(1+\kappa a)} - \frac{\nu^2 m^2 d_o N}{1000}(\frac{2\pi a^3}{3} + \frac{\pi a w^2 L^2}{3(1+\kappa a)})) \qquad \text{(D-15)}$$

Pitzer gives the following expression for the excess Gibbs free energy of a binary electrolytic solution

$$(\frac{G^E}{ckT})^{\text{Coulombic}} = -\frac{Lw}{6}(\frac{\kappa}{1+\kappa a} + \frac{1}{a}\ln(1+\kappa a)) + 2\pi a^3 c/3 \qquad \text{(D-16)}$$

G^E has units of ergs/cc solution.

To convert G^E to calories, let

$$G^E = n_L g^E \qquad \text{(D-17a)}$$

where n_L has units of total number of moles of solution/cc solution and g^E of calories/total number of moles of solution.

The total number of moles of solution is given by

$$n_T = n_{\text{solvent}} + \nu n_{\text{salt}} \qquad \text{(D-17b)}$$

Multiplying equation (D-16) by cn_T/n_L gives

$$(\frac{G^E}{kT})^{\text{Coulombic}} = -\frac{Lwcn_T\,\kappa}{6n_L(1+\kappa a)} - \frac{Lwcn_T}{6an_L}\ln(1+\ a) + \frac{2\pi a^3 c^2 n_T}{3n_L} \qquad \text{(D-17c)}$$

Replacing k by R/N and letting

$$c = x_{salt} n_L \qquad \text{(D-17d)}$$

and

$$n_{salt} = x_{salt} n_T \qquad \text{(D-17e)}$$

equation (D-17c) becomes

$$\frac{G^E}{RT} = - \frac{wLn_{salt}}{6}\left(\frac{\kappa}{1+ka} + \frac{1}{a} \ln (1 + \kappa a)\right)$$

$$+ \nu^2 (2\pi a^3/3)\left(\frac{d_o N}{1000}\right) m n_{salt} \qquad \text{(D-17f)}$$

From the definition of molality

$$m = 1000\, n_{salt}/(M.W.) n_{solvent} \qquad \text{(D-17g)}$$

and equation (D-17f), the excess Gibbs free energy on a molality basis for binary electrolytic solutions is:

$$(G^E/RT)^{Coulombic} = -\left(\frac{(M.W.) n_{solvent}}{1000}\right)\left[\left(\frac{wL}{6}\right) m \left(\frac{\kappa}{1+\kappa a} + \frac{1}{a} \ln(1+\kappa a)\right)\right.$$

$$\left. + \nu^2 (2\pi a^3/3)\left(\frac{d_o N}{1000}\right) m^2\right] \qquad \text{(D-18)}$$

Equation (D-18) may be written in terms of the Debye-Huckel parameters, A_ϕ and b, given by equations (3-13) and (3-14).

$$\left(\frac{G^E}{RT}\right)^{Coulombic} = -2A_\phi \left(\frac{(M.W.) n_{solvent}}{1000}\right)\left[\frac{I^{3/2}}{1+bI^{1/2}} + \frac{I}{b} \ln(1+bI^{1/2})\right]$$

$$+ \nu^2 \left(\frac{2\pi a^3}{3}\right)\left(\frac{N}{1000^2}\right)\left(d_o (M.W.) n_{solvent} m^2\right) \qquad \text{(D-19)}$$

Equations (D-18) and (D-19) are easily extended to multicomponent solutions containing one salt by replacing (M.W.), the molecular weight of the solvent, by the molecular weight of the mixed solvent, given by equation (3-9). a, the ion-size parameter, is evaluated using equation (3-17). The density and dielectric constant are given by their values in the salt-free mixed solvent system. $n_{solvent}$ is replaced by the total number of moles of mixed solvent.

Differentiation of equation (D-18) or (D-19) with respect to the number of moles of solvent i gives the expression for the Coulombic contribution to the activity coefficient of the solvent (see equation 3-8).

The mean activity coefficient of the salt is obtained using the following relationship:

$$\nu \ln \gamma_{\pm} = \left(\frac{\partial G^E/RT}{\partial n_{salt}}\right) \tag{D-20}$$

Differentiation of equation (D-19) with respect to the number of moles of salt and substitution of this result into equation (D-20) gives

$$\nu \ln \gamma_{\pm} = -\nu|z_+z_-|A_\phi\left[\frac{2I^{1/2}}{1+bI^{1/2}} + \frac{1}{b}\ln(1 + bI^{1/2})\right]$$

$$+ (md_oN\nu^2/1000)\left(4\pi a^3/3 + \frac{\pi a w^2 L^2}{3(1+bI^{1/2})^2}\right) \tag{D-21}$$

Equation (D-21) is applicable to single and mixed-solvent systems containing one salt.

APPENDIX E

ERROR ANALYSIS

Determination of the Maximum Error in

The osmotic coefficient where

$$\phi = -\frac{1000 \ln P/P^s}{\nu m \, M.W.} \tag{E-1}$$

and

$$P = P^s - \Delta P \tag{E-2}$$

is a function of P^s, ΔP^s and m. M.W. and ν are constant. m is a function of the number of moles of salt, n_s, and the number of moles of solvent, n_3. m is defined by the following:

$$m = 1000\, n_s/(n_3 M.W.) \tag{E-3}$$

Differentiating equation (E-3) yields

$$dm = (\partial m/\partial n_s)dn_s + (\partial m/\partial n_3)dn_3 \tag{E-4}$$

or

$$\frac{dm}{m} = \frac{dw_s}{w_s} - \frac{dw_3}{w_3} \tag{E-5}$$

w_s is the weight of the salt and w_3 is the weight of the solvent. It is assumed that the errors in weighing the salt, dw_s, and the solvent, dw_3, are ±0.0001g.

Taking the absolute value of equation (E-5) gives

$$dm = m(0.0001)[\frac{1}{w_s} + \frac{1}{w_3}] \tag{E-6}$$

dm was calculated for each electrolytic solution in this study and was found to be ±0.0001m.

Differentiation of equation (E-1) gives

$$d\phi = (\frac{\partial\phi}{\partial m})dm + (\frac{\partial\phi}{\partial P^S})dP^S + (\frac{\partial\phi}{\partial P})dP \quad (E\text{-}7)$$

$$= (\frac{\partial\phi}{\partial m})dm + (\partial\phi/\partial a)da \quad (E\text{-}8)$$

where

$$a = P/P^S \quad (E\text{-}9)$$

Differentiation of (E-9) gives

$$da = a[\frac{dP}{P} - \frac{dP^S}{P^S}] \quad (E\text{-}10)$$

and taking the absolute value of (E-10) gives

$$da = a[\frac{\Delta P}{P} - \frac{\Delta P^S}{P^S}] \quad (E\text{-}11)$$

P is the error in the measurement of the vapor pressure of the electrolytic solution. ΔP^S is the error in the measurement of the pure solvent. ΔP^S is ±0.06 mmHg. ΔP is ±0.1 mmHg since it is calculated by subtracting ΔP from P^S.

Combination of equations (E-8) and (E-11) and taking the absolute value gives

$$\Delta\phi = \frac{\phi}{m}\Delta m + \frac{1000}{\nu m M.W.}[\frac{\Delta P^S}{P^S} + \frac{\Delta P}{P}] \quad (E\text{-}12)$$

For the methanol systems of this study

$$\Delta\phi = \frac{\phi}{m}(0.0001) + \frac{15.60452}{m}[\frac{0.06}{P^S} + \frac{0.1}{P}] \quad (E\text{-}13)$$

TABLE E-1

Experimental Values of ΔP, P, and ϕ for the NaI-MeOH System at 25 and 40°C

$m \pm 0.0001$	$\Delta P \pm 0.06$mmHg	$P \pm 0.1$mmHg	ϕ	$\pm d\phi$	$\Delta P \pm 0.06$mmHg	$P \pm 0.1$mmHg	ϕ	$\pm d\phi$
0.0	0.0	128.1	--	--	0.0	268.1	--	--
0.4963	3.56	124.5	0.89	0.03	7.27	260.8	0.87	0.01
0.7782	6.00	122.1	0.96	0.02	12.17	255.9	0.934	0.009
1.00978	8.28	119.8	1.03	0.02	16.66	251.4	0.993	0.007
1.2617	10.82	117.3	1.09	0.01	21.98	246.1	1.059	0.006
0.5965	14.42	113.4	1.17	0.01	29.17	238.9	1.127	0.005
2.03562	19.99	108.1	1.301	0.008	39.54	228.5	1.224	0.004
2.2485	22.76	105.3	1.357	0.007	45.42	222.7	1.289	0.003
2.5108	26.31	101.8	1.429	0.007	52.93	215.1	1.367	0.003
2.7632	30.05	98.1	1.510	0.006	59.86	208.2	1.427	0.003
3.0928	34.22	93.9	1.568	0.006	69.62	198.5	1.517	0.003
3.2513	36.80	91.3	1.625	0.005	74.75	198.3	1.569	0.003
3.5932	41.93	86.2	1.722	0.005	84.46	183.6	1.644	0.002
4.0088	47.84	80.3	1.820	0.005	96.22	171.9	1.731	0.002
4.3383	52.20	75.9	1.882	0.005	105.29	162.8	1.794	0.002

TABLE E-2

Experimental Values of ΔP, P, and ϕ for the KCH_3COO-MeOH System at 25 and 40°C

m±0.0001	ΔP±0.06mmHg	P±0.1mmHg	ϕ	±dϕ	ΔP±0.06mmHg	P±0.1mmHg	ϕ	±dϕ
0.0	0.00	128.1	--	--	0.0	268.1	--	--
0.7588	5.15	122.0	0.85	0.02	10.66	257.4	0.834	0.009
1.442	7.66	120.4	0.84	0.01	15.87	252.2	0.832	0.006
1.3916	9.38	118.7	0.85	0.01	19.09	249.0	0.828	0.005
1.6734	11.20	116.9	0.853	0.009	23.08	245.0	0.840	0.004
1.8929	12.79	115.3	0.867	0.008	26.17	241.9	0.845	0.004
2.10010	14.15	114.0	0.870	0.007	28.72	239.4	0.842	0.004
2.2376	15.09	113.0	0.874	0.007	30.56	237.5	0.844	0.003
2.2897	15.47	112.6	0.877	0.007	31.54	236.6	0.853	0.003
2.4825	16.80	111.3	0.884	0.006	33.68	234.4	0.844	0.003
2.4925	16.78	111.3	0.879	0.006	33.78	234.3	0.843	0.003
2.5110	16.91	111.2	0.880	0.006	34.68	233.4	0.861	0.003

TABLE E-3

Experimental Values of ΔP, P, and ϕ for the NH_4SCN-MeOH System at 25 and 40°C

m±0.0001	ΔP±0.06mmHg	P±0.1mmHg	ϕ	±d ϕ	ΔP±0.06mmHg	P±0.1mmHg	ϕ	±d ϕ
0.0	0.00	128.1	--	--	--	268.1	0.00	--
0.7551	0.09	123.0	0.83	0.02	0.803	257.9	10.19	0.009
0.7621	5.07	123.0	0.83	0.02	0.812	257.7	10.42	0.009
1.0076	6.88	121.2	0.86	0.02	0.8245	254.2	13.89	0.007
1.02661	7.22	120.9	0.88	0.02	0.816	254.1	14.01	0.007
1.2563	8.53	119.6	0.86	0.01	0.841	250.6	17.55	0.006
1.2601	8.65	119.5	0.87	0.01	0.846	250.4	17.71	0.006
1.5039	10.61	117.5	0.897	0.01	0.842	247.2	20.89	0.005
1.7716	12.36	115.7	0.894	0.009	0.882	242.6	25.54	0.004
2.0275	14.11	1141.0	0.898	0.008	0.878	239.2	28.90	0.004
2.2941	15.90	112.2	0.902	0.007	0.882	235.5	32.60	0.003
3.0447	20.94	107.2	0.915	0.005	0.904	224.7	43.37	0.003
3.2677	22.27	105.8	0.912	0.005	0.906	221.8	46.34	0.002
3.6949	25.30	102.8	0.929	0.004	0.913	216.0	52.11	0.002
5.1830	34.05	94.1	0.930	0.003	0.908	198.3	69.77	0.002

TABLE E-4

Experimental Values of ΔP, P, and ϕ for the NaSCN-MeOH System at 25 and 40°C

m±0.0001	ΔP±0.06mmHg	P±0.1mmHg	ϕ	±dϕ	ΔP±0.06mmHg	P±0.1mmHg	ϕ	±dϕ
0.0	--	128.1	--	--	0.00	268.1	--	--
0.4974	3.44	124.7	0.85	0.03	7.19	260.9	0.85	0.01
0.78187	5.85	122.3	0.93	0.02	12.15	255.0	0.926	0.009
1.06924	8.37	119.7	0.99	0.01	16.97	251.1	0.955	0.007
1.2543	10.02	118.1	1.02	0.01	20.44	247.7	0.987	0.006
1.5404	12.79	115.3	1.07	0.01	25.74	242.4	1.023	0.005
1.7873	15.25	112.9	1.103	0.009	30.54	237.6	1.055	0.004
2.2544	20.18	107.9	1.186	0.007	40.62	227.5	1.137	0.003
2.2544	20.18	107.9	1.186	0.007	40.62	227.5	1.137	0.003
2.9555	27.92	100.2	1.298	0.006	55.96	212.1	1.236	0.003
3.09445	29.36	98.7	1.313	0.005	59.36	208.7	1.262	0.003
3.36017	31.96	96.1	1.333	0.005	64.98	203.1	1.289	0.002

APPENDIX F

Calculation of the Mean Activity Coefficient of the Salt in Single and Mixed Solvents

Stokes and Robinson (1948) present the following relation between the observed molal mean activity coefficient, $\gamma_{\pm}$, and the rational (mole-fraction basis) activity coefficient, $f_{\pm}'$, of the solvated solute for binary electrolytic solutions. $\gamma_{\pm}$ and $f_{\pm}'$ observe the unsymmetric convention.

$$\ln \gamma_{\pm} = \ln f_{\pm}' - \int_0^m h_+/\nu \, d\ln a_3 - \ln(1-((M.W.)/1000)(h_+ - \nu)m) \qquad \text{(F-1)}$$

h_+ is the solvation number of the solvated positive ion and is discussed in Chapters 3 and 5. a_3 is the activity of the solvent.

$\ln f_{\pm}'$ is separated into three component terms:

$$\ln f_{\pm}' = \ln f_{\pm}'(\text{Coulombic}) + \ln f_{\pm}'(\text{FLORY-HUGGINS}) + \ln f_{\pm}'(\text{Residual}) \qquad \text{(F-2)}$$

The Coulombic contribution is evaluated using the equation for the mean molal activity coefficient presented by Pitzer (1977).

$$\begin{aligned}\ln \gamma_{\pm}' = &- |z_+ z_-| A_{\Phi}(2I^{\frac{1}{2}}/(1+bI^{\frac{1}{2}}) + I/b \ln(1+bI^{\frac{1}{2}})) \\ &+ (md_o N \nu/1000)(4\pi a^3/3 + \pi a w^2 L^2/3(1+bI^{\frac{1}{2}})^2)\end{aligned} \qquad \text{(D-21)}$$

Equation (D-21) is derived in Appendix D.

Since the value of a in equation (D-21) may have a value between the sum of the crystallographic radii and the sum of the solvated radii, it is assumed that equation (D-21) predicts the rational coefficient of the solvated ions or $f_{\pm}'$. This assumption was made by Stokes and Robinson where $\ln f_{\pm}'$ in equation (F-1) was replaced by the Debye-Huckel equation in the development of their hydration model.

$\ln f_{\pm}'(\substack{\text{FLORY-}\\ \text{HUGGINS}})$ is readily obtained from equation (3-28) and the following relationship:

$$\nu \ln f_{\pm}' = \nu_1 \ln f_1' + \nu_2 \ln f_2' \qquad \text{(F-3)}$$

where f_1' is the rational activity coefficient of the positive ion, (component 1), and f_2' is the rational activity coefficient of the negative ion, (component 2).

$$\nu \ln f_{\pm}'(\substack{\text{FLORY-}\\ \text{HUGGINS}}) = \nu_1(\ln \Phi_1'/x_1' + 1 - \Phi_1'/x_1')$$
$$+ \nu_2(\ln \Phi_2'/x_2' + 1 - \Phi_2'/x_2' \qquad \text{(F-4)}$$

Equation (F-4) is normalized to the unsymmetric convention by taking the limit of equation (F-4) as the mole fractions of the positive and negative ions approach zero (Equation (F-5)) and subtracting this result from equation (F-4). (Equation (F-6))

$$\lim_{\substack{x_1' \to 0\\ x_2' \to 0}} \nu \ln f_{\pm}'^{(\text{FLORY-HUGGINS})} = \nu_1(\ln r_1'^{\infty}/r_3 + 1 - r_1'^{\infty}/r_3)$$
$$+ \nu_2(\ln r_2'^{\infty}/r_3 + 1 - r_2'^{\infty}/r_3)$$
$$\text{(F-5)}$$

$$\nu \ln f_{\pm}'(\substack{\text{FLORY-HUGGINS}\\ \text{UNSYMMETRIC}}) = \nu_1(\ln \Phi_1'/x_1' + 1 - \Phi_1'/x_1')$$
$$+ \nu_2(\ln \Phi_2'/x_2' + 1 - \Phi_2'/x_2') - \nu_1(\ln r_1'^{\infty}/r_3 + 1 - r_1'^{\infty}/r_3)$$
$$- \nu_2(\ln r_2'^{\infty}/r_3 + 1 - r_2'^{\infty}/r_3)$$
$$\text{(F-6)}$$

$r_1'^{\infty}$ is given by

$$r_1'^{\infty} = r_1 + h_{o+}R_3 \qquad \text{(F-6a)}$$

and

$$r_2'^{\infty} = r_2 \qquad \text{(F-6b)}$$

since the negative ion is not solvated.

The residual contribution to equation (F-2) is obtained from equation (3-19) and the relationship of equation (F-3).

$$\nu \ln f\pm(\text{Residual}) = \nu_1 Q_1(1 - \ln(\Theta_1 + \Theta_2\Psi_{21} + \Theta_3\Psi_{31})$$

$$- \Theta_1/(\Theta_1 + \Theta_2\Psi_{21} + \Theta_3\Psi_{31}) - \Theta_2\Psi_{12}/(\Theta_1\Psi_{12} + \Theta_2 + \Theta_3\Psi_{32}) -$$

$$\Theta_3\Psi_{13}/(\Theta_1 A\pm/Q_1 + \Theta_3)) + \nu_2 Q_2(1 - \ln(\Theta_1\Psi_{12} + \Theta_2 + \Theta_3\Psi_{32}) -$$

$$\Theta_1\Psi_{21}/(\Theta_1 + \Theta_2\Psi_{21} + \Theta_3\Psi_{31}) - \Theta_2/(\Theta_1\Psi_{12} + \Theta_2 + \Theta_3\Psi_{32}) -$$

$$\Theta_3\Psi_{23}/(\Theta_1 A\pm/Q_1 + \Theta_3) \qquad \text{(F-7)}$$

A± is defined by equation (5-4b) and is set equal to zero. The fifth and tenth terms of equation (F-7) may be combined using equation (5-4b). Equation (F-7) then reduces to the following:

$$\nu \ln f\pm(\text{Residual}) = \nu_1 Q_1(1 - \ln(\Theta_1 + \Theta_2\Psi_{21} + \Theta_3\Psi_{31})$$

$$- \Theta_1/(\Theta_1 + \Theta_2\Psi_{21} + \Theta_3\Psi_{31}) - \Theta_2\Psi_{12}/(\Theta_1\Psi_{12} + \Theta_2 + \Theta_3\Psi_{32}))$$

$$+ \nu_2 Q_2(1 - \ln(\Theta_1\Psi_{12} + \Theta_2 + \Theta_3\Psi_{32})$$

$$- \Theta_1\Psi_{21}/(\Theta_1 + \Theta_2\Psi_{21} + \Theta_3\Psi_{31}) - \Theta_2/(\Theta_1\Psi_{12} + \Theta_2 + \Theta_3\Psi_{32}))$$

(F-8)

Equation (F-8) is normalized to the unsymmetric convention by taking the limit of equation (F-8) as the mole fractions of the positive and negative ions approach zero (equation (F-9)) and subtracting this result from equation (F-8). (Equation (F-10))

$$\lim_{\substack{x_1' \to 0 \\ x_2' \to 0}} \nu \ln f\pm(\text{Residual}) = \nu_1 Q_1(1 - \ln\Psi_{31}) + \nu_2 Q_2(1 - \ln\Psi_{32}) \qquad \text{(F-9)}$$

$$\nu \ln f\pm\left(^{\text{Residual}}_{\text{Unsymmetric}}\right) = \text{equation (F-8)} - \text{equation (F-9)} \qquad \text{(F-10)}$$

Substitution of equations (D-21), (F-6), and (F-10) into equation (F-2) allows the calculation of lnf±' in equation (F-1). lnf±' is therefore given by:

$$\ln f\pm' = \text{equation (D-21)} + (1/\nu)(\text{equation (F-6)}) + (1/\nu)(\text{equation (F-10)}) \qquad \text{(F-11)}$$

Substitution of equation (F-11) into (F-1) allows the calculation of $\ln\gamma\pm$.

The mean activity coefficient of the salt in a single solvent can be calculated in two ways from equation (F-1). In both methods, f±' is given by equation (F-11).

The first method, (method 1), utilizes the experimental values of the solvent activities, a_3, and the parameter values obtained through the regression of the osmotic coefficient data shown in Tables 5.10, 5.11, 5.13, 5.14, and 5.15.

To evaluate the integral of equation (F-1), the values of h_+, the solvation number of the positive ion given by equation (3-33), are plotted against $\ln a_3$. The area under the curve up to a molality of m is then determined. For computational purposes, h_+ may be fit to a polynomial in $\ln a_3$.

$$h_+ = A(1) + A(2)\ln a_3 + A(3)\ln a_3^2 + A(4)\ln a_3^3 + A(5)\ln a^4$$
$$A(6)\ln a_3^5 + A(7)\ln a_3^6 \qquad \text{(F-12)}$$

Once the constants are determined, equation (F-12) may be integrated to give:

$$\int_0^m h_+ d\ln a_3 = A(1)\ln a_3 + A(2)\ln a_3^2/2 + A(3)\ln a_3^3/3 + A(4)\ln a_3^4/4 +$$

$$A(5)\ln a_3{}^5/5 + A(6)\ln a_3{}^6/6 + A(7)\ln a_3{}^7/7 \qquad \text{(F-13)}$$

This method was used to calculate the mean activity coefficients of the LiCl-water and the NaCl-water systems at 25°C. The parameter values given in Table 5.10 were used to evaluate $\ln f\pm'$. The solvent activities were calculated from the osmotic coefficients of these systems (Robinson and Stokes, 1959) using equation (4-2). The results are presented in Table F-1 and are compared to the values of the mean activity coefficients given by Robinson and Stokes.

In method 2, the values of a_3 in equation (F-1) are calculated from equations (2-1) and(5-6), or

$$\ln a_3 = \text{equation (5-6)} + \ln x_3 \qquad \text{(F-14)}$$

where x_3 is the mole-fraction of the solvent given by equation (3-26). $f\pm'$ is evaluated as in Method 1. Method 2 represents true prediction since only the parameters obtained through regression of the osmotic coefficient data are used to predict the mean activity coefficients of the salt.

To evaluate the integral of equation (F-1), h_+ is fit to a polynomial in $\ln a_3$, given by equation (F-14). The polynomial expression of equation (F-12) is used. The constants thus obtained are then used in equation (F-13).

The results for this method are shown in Table F-2 and are comparable to those of Method 1.

Equations (F-1) and (F-12) through (F-14) can also be used to obtain the model parameters if mean activity coefficient data only are available. This was done for the HCl-MeOH and HCl-EtOH systems at 25°C. No osmotic coefficient or vapor pressure data are available for these

TABLE F-1

Method 1. Average Percent Errors in $\gamma\pm$ in Prediction from Parameter Values at 25°C and Experimental Solvent Activities for Aqueous Systems

Salt	Average % Error, $\gamma\pm$	Maximum Relative % Error, $\gamma\pm$
LiCl	5.0	-13.1 at 6m
NaCl	4.1	-11.3 at 6m

TABLE F-2

Method 2. Average Percent Errors in $\gamma\pm$ in Prediction Only from Parameter Values at 25°C for Aqueous Systems

Salt	Average % Error, $\gamma\pm$	Maximum Relative % Error, $\gamma\pm$
LiCl	4.8	-10.4 at 6m
NaCl	4.2	-11.2 at 6m

systems.

The values of a_{HCl} for HCl in methanol and HCl in ethanol as well as the values of A_{MeOH/H^+} and A_{EtOH/H^+} were determined. For the HCl-MeOH system, the values of A_{12} and the methanol-chloride ion interaction parameter, A_{32}, from Table 5.14 were used since they have already been established from the methanol data base. The values of A_{12} and the ethanol-chloride ion interaction parameter, A_{32}, from Table 5.15 are used for the HCl-EtOH system.

The results are shown in Table F-3. The values of A_{31} obtained through the regression of these systems are meaningless since the maximum molality range for the HCl-MeOH system is 0.56m and that for the HCl-EtOH system is 0.10m. The Flory-Huggins and residual contributions are negligible at such low molalities. Any value of A_{31} would give the results of Table F-3. The values of A_{31} obtained here should be used with caution in extrapolation to higher molalities. In addition, the poor performance of the model in the correlation of these systems at such low molalities suggests that extrapolation is not possible.

The expression which relates the rational activity coefficient, f±', of the solvated solute for a salt in two solvents to the observed molal mean activity coefficient, $\gamma_\pm$, is developed below.

If solvation is not considered, the activity of the salt, a_s, is related to the activities of solvent 1 (a_3) and solvent 2(a_4) by

$$n_s d\ln a_s = - n_3 d\ln a_3 - n_4 d\ln a_4 \qquad \text{(F-15)}$$

where n_s, n_3, and n_4 are the numbers of moles of the salt, solvent 1, and solvent 2, respectively.

If solvation is considered, the activity of the solvated salt,

TABLE F-3

Binary Interaction Parameters for the HCl-MeOH and HCl-EtOH Systems Obtained Through Regression of $\gamma\pm$ Data at 25°C

(Reference: Harned and Owen (1958))

System	a	Molality Range	A_{12}	A_{31}	A_{32}	Avg. % Error, $\gamma\pm$	Max. Rel. % Error, $\gamma\pm$
HCl-MeOH	4.03	0.56	-253.1	0.0	782.3	3.9	7.4 at .56m
HCl-EtOH	1.27	0.10	-147.9	0.0	926.9	10.7	-15.7 at .01m

a_s', is related to the activities of solvent 1 and solvent 2 by

$$n_s d\ln a_s' = - n_3' d\ln a_3 - n_4' d\ln a_4 \qquad \text{(F-16)}$$

where n_3' and n_4' are the numbers of moles of solvent 1 and solvent 2 not involved in solvation of the salt. n_3' and n_4' are related to n_3 and n_4 by the following:

$$n_3' = n_3 - h_+\nu_1 n_s \qquad \text{(F-17a)}$$

$$n_4' = n_4 - d_+\nu_2 n_s \qquad \text{(F-17b)}$$

In equations (F-17a) and (F-17b) solvation of the positive ions alone is assumed. h_+ represents the number of solvent 1 molecules involved in solvation and d_+ the number of solvent 2 molecules involved in solvation. h_+ and d_+ are given by equation (3-33).

Substitution of equations (F-15), (F-17a) and (F-17b) into (F-16) gives

$$d\ln a_s' = d\ln a_s + h_+\nu_1 d\ln a_3 + d_+\nu_1 d\ln a_4 \qquad \text{(F-18)}$$

By definition

$$a_s = a\pm^{\nu} = (f\pm x_s)^{\nu} \qquad \text{(F-18a)}$$

and

$$a_s' = a'\pm^{\nu} = (f\pm' x_s')^{\nu} \qquad \text{(F-18b)}$$

where x_s and x_s' are the mole-fractions of the salt on the two bases.

Substitution of equations (F-18a) and (F-18b) into equation (F-18) yields

$$d\ln f\pm' = d\ln f\pm + h_+(\nu_1/\nu)d\ln a_3 + d_+(\nu_1/\nu)d\ln a_4 + d\ln(x_s/x_s') \qquad \text{(F-19)}$$

$d\ln(x_s/x_s')$ may be written in the following manner.

$$d\ln(x_s/x_s') = d\ln(1+ (\nu - h_+ - d_+)(m(M.W.)/1000)) - d\ln(1+\nu m(M.W.)/1000) \qquad \text{(F-19a)}$$

where M.W. is the molecular weight of the mixed solvent.

If solvation is not assumed, the observed mean activity coefficient is related to the rational activity coefficent by the following expression

$$d\ln f\pm = d\ln\gamma\pm + d\ln(1+\nu m(M.W.)/1000) \qquad \text{(F-19b)}$$

Substitution of equations (F-19a) and (F-19b) into equation (F-19) gives

$$\int_0^m d\ln\gamma\pm = \int_0^m d\ln f\pm' - (\nu_1/\nu)\int_0^m h_+ d\ln a_3 - (\nu_1/\nu)\int_0^m d_+ d\ln a_4$$
$$- \int_0^m d\ln(1+(\nu - h_+ - d_+)(m(M.W.)/1000)) \qquad \text{(F-20)}$$

Integration of equation (F-20) gives the following expression which allows the calculation of the observed mean activity coefficient of a salt in a mixed solvent.

$$\ln\gamma\pm = \ln f\pm' - (\nu_1/\nu)\int_0^m h_+ d\ln a_3 - (\nu_1/\nu)\int_0^m d_+ d\ln a_4$$
$$- \ln(1+(\nu - h_+ - d_+)(m(M.W.)/1000)) \qquad \text{(F-21)}$$

Equation (F-2) is used to evaluate f±'. Equation (D-21) is used to evaluate the Coulombic contribution to equation (F-2). However, the density and dielectric constant of the pure solvent are replaced by the densities and dielectric constants of the mixed solvent. The molecular weight of the pure solvent is replaced by that of the mixed solvent. The value of a in equation (D-21) is replaced by equation (3-17).

$f\pm'\left(\begin{smallmatrix}\text{FLORY-HUGGINS}\\ \text{UNSYMMETRIC}\end{smallmatrix}\right)$ is given by equation (F-6). Φ_1' and Φ_2' must be replaced by their values in the ternary solution. $r_1'^{\infty}$ is given by

$$r_1'^{\infty} = r_1 + h_{o+}R_3 + d_{o+}R_4 \qquad \text{(F-21a)}$$

and $r_2'^{\infty}$ is given by equation (F-6b).

The residual contribution to equation (F-2) is obtained from equation (3-19) and the relationship of equation (F-3).

$$
\begin{aligned}
\nu \ln f_{\pm}(\text{Residual}) = {} & \nu_1 Q_1 (1- \ln(\Theta_1 + \Theta_2\psi_{21} + \Theta_3\psi_{31} + \Theta_4\psi_{41}) - \\
& - \Theta_1/(\Theta_1 + \Theta_2\psi_{21} + \Theta_3\psi_{31} + \Theta_4\psi_{41}) \\
& - \Theta_2\psi_{12}/(\Theta_1\psi_{12} + \Theta_2 + \Theta_3\psi_{32} + \Theta_4\psi_{42}) \\
& - \Theta_3\psi_{13}/(\Theta_1 A\pm/Q_1 + \Theta_3 + \Theta_4\psi_{43}) \\
& - \Theta_4\psi_{14}/(\Theta_1 B\pm/Q_1 + \Theta_3\psi_{34} + \Theta_4)) \\
& + \nu_2 Q_2 (1- \ln(\Theta_1\psi_{12} + \Theta_2 + \Theta_3\psi_{32} + \Theta_4\psi_{42}) \\
& - \Theta_1\psi_{21}/(\Theta_1 + \Theta_2\psi_{21} + \Theta_3\psi_{31} + \Theta_4\psi_{41}) \\
& - \Theta_2/(\Theta_1\psi_{12} + \Theta_2 + \Theta_3\psi_{32} + \Theta_4\psi_{42}) \\
& - \Theta_3\psi_{23}/(\Theta_1 A\pm/Q_1 + \Theta_3 + \Theta_4\psi_{43}) \\
& - \Theta_4\psi_{24}/(\Theta_1 B\pm/Q_1 + \Theta_3\psi_{34} + \Theta_4)) \qquad \text{(F-22)}
\end{aligned}
$$

A± and B± are equal to zero in this study. The sum of the fifth, sixth, eleventh, and twelfth terms of equation (F-22) are equal to zero from the definitions of A± and B±. Equation (F-22) then reduces to

$$
\begin{aligned}
\nu \ln f_{\pm}(\text{Residual}) = {} & \nu_1 Q_1 (1-(\Theta_1 + \Theta_2\psi_{21} + \Theta_3\psi_{31} + \Theta_4\psi_{41}) \\
& - \Theta_1/(\Theta_1 + \Theta_2\psi_{21} + \Theta_3\psi_{31} + \Theta_4\psi_{41}) \\
& - \Theta_2\psi_{12}/(\Theta_1\psi_{12} + \Theta_2 + \Theta_3\psi_{32} + \Theta_4\psi_{42})) \\
& + \nu_2 Q_2 (1- \ln(\Theta_1\psi_{12} + \Theta_2 + \Theta_3\psi_{32} + \Theta_4\psi_{42}) \\
& - \Theta_1\psi_{21}/(\Theta_1 + \Theta_2\psi_{21} + \Theta_3\psi_{31} + \Theta_4\psi_{41}) \\
& - \Theta_2/(\Theta_1\psi_{12} + \Theta_2 + \Theta_3\psi_{32} + \Theta_4\psi_{42})) \qquad \text{(F-23)}
\end{aligned}
$$

The limit of equation (F-23) as the mole-fractions of the positive and negative ions approach zero is given by

$$
\lim_{\substack{x_1' \to 0 \\ x_2' \to 0}} \nu \ln f_{\pm}'(\text{Residual}) = \nu_1 Q_1 (1- \ln(\Theta_3^{\infty}\psi_{31} + \Theta_4^{\infty}\psi_{41})
$$

$$+ \nu_2 Q_2 (1 - \ln(\Theta_3^{\infty} \psi_{32} + \Theta_4 \psi_{42})) \qquad \text{(F-24)}$$

$$\Theta_3^{\infty} = Q_3 x_3^{\infty} / (Q_3 x_3^{\infty} + Q_4 x_4^{\infty}) \qquad \text{(F-24a)}$$

$$\Theta_4^{\infty} = Q_4 x_4^{\infty} / (Q_3 x_3^{\infty} + Q_4 x_4^{\infty}) \qquad \text{(F-24b)}$$

x_3 and x_4 are the mole-fractions of solvent 1 and solvent 2 on a salt-free basis.

Subtracting equations (F-24) from equations (F-23) gives the unsymmetric residual contribution to equation (F-2).

$$\nu \ln f\pm'\left(\begin{smallmatrix}\text{Residual}\\ \text{Unsymmetric}\end{smallmatrix}\right) = \text{equation (F-32)} - \text{equation (F-24)} \qquad \text{(F-25)}$$

Substitution of the ternary forms of equation (D-21), (F-6) and equation (F-25) into equation (F-2) allows the calculation of f±' in equation (F-21). lnf±' is given by the following:

$$\ln f\pm' = \text{equation (D-21)} + (1/\nu)\ \text{equation (F-6)} + (1/\nu)\ \text{equation (F-25)} \qquad \text{(F-26)}$$

Equation (F-21) was used to calculate the mean activity coefficients of HCl for the HCl-MeOH-H_2O and HCl-EtOH-H_2O systems at 25°C. The solvent-ion parameters of Tables 5.10 and F-3 and the solvent-solvent interaction parameters of Table 5.21 were used in the prediction of the mean activity coefficients.

The results are presented in Table F-4. The maximum molalities and the salt-free mole fractions of the nonaqueous solvents at which the data were available are also indicated.

For the HCl-MeOH-H_2O system, the average percent errors in $\gamma\pm$ increase with increasing methanol mole fraction. The calculation of $\gamma\pm$ does not appear to be affected by changes in molality.

For the HCl-EtOH-H_2O systems, increasing the salt-free mole fraction of ethanol from 0.0427 to 0.0891 does not affect the

TABLE F-4

Prediction of the Mean Activity Coefficients of HCl in MeOH-H_2O and EtOH-H_2O Mixtures at 25°C

(Reference: Harned and Owen (1958))

System	X_4'	Maximum Molality	Average % Error, $\gamma\pm$	Maximum % Error, $\gamma\pm$
HCl-MeOH-H_2O	0.0588	2.0	3.6	-4.7 at m=0.001
	0.1233	2.0	20.2	-24.9 at m=2.0
	0.0588+0.1233	2.0	11.9	16.6 at m=2.0
HCl-EtOH-H_2O	0.0417	2.0	8.4	16.6 at m=2.0
	0.0891	2.1	6.0	11.2 at m=2.1
	0.50	2.5	464.0	
	0.0417	2.1	7.2	11.2 at m=2.1

calculated values of the average percent errors in $\gamma_\pm$. The calculation of $\gamma_\pm$ is affected by molality. The relative percent errors in $\gamma_\pm$ increase with increasing molality and are greatest at $m = 2.0$.

The model fails to predict the mean activity coefficients for the HCl-EtOH-H_2O at a salt-free mole fraction of 0.5 and over the available molalilty range. This is to be expected since the binary model, which was used to obtain the ethanol interaction parameters, poorly correlated the HCl-EtOH data.

It is recommended that the methanol-H^+ and ethanol-H^+ interaction parameters be used to predict ternary systems only at low mole-fractions of methanol or ethanol.

APPENDIX G

This appendix contains the following programs:

G.1 Binary Program for Salt-Solvent Systems

This program allows the correlation or prediction of binary electrolytic solution data. This program calls subroutine LSQ2 which in turn calls subroutine FN. The data may be in the form of osmotic coefficient or vapor pressure depression data as a function of molality.

G.2 Binary Salt-Free Program

This program allows the correlation or prediction of mixed-solvent binary data. Subroutines LSQ2, HANK, and PHIB are called. The salted-in component is termed solvent (1).

G.3 Ternary Program for Salt-Binary Mixed-Solvent Systems.

This program allows the prediction of ternary electrolytic solutions containing a single salt using the binary parameters obtained from programs G.1 and G.2. The values of A_{12} for the two solvents must be supplied to the program.

Subroutines HANK, PHIB, and HANKI are called by the program. The parameters AB(1)-AB(14) were determined from a fit of the mixed solvent dielectric constant data to a polynomial using FITIT. (See Appendix C for the constants.)

The salted-in component is Solvent (1) and is referred to by subscript 3.

G.4 Subroutine LSQ2

This subroutine uses a search technique to find the optimum values of the variables which minimize the objective function. Subroutine FN of the binary programs is called.

G.5 Subroutine HANK

This subroutine calculates the pure-component liquid molar volumes using the Hankinson and Thomson (1979) correlation. (See Appendix B.)

G.6 Subroutine PHIB

This subroutine calculates the fugacity coefficients at saturation and of the vapor phase using the Hayden-O-Connell correlation (1975). Subroutine SVIR is called for the prediction of the pure component and cross second virial coefficients. (See Appendix A.)

G.7 Subroutine HANKI

This subroutine calculates the densities of the salt-free mixed solvents and the changes in density with respect to composition. (See Appendix B.)

G.8 Program FITIT

This program calls subroutine POLIFI which makes a least-squares fit of the data. POLIFI calls subroutine DETERM which performs the error analysis for POLIFI. A polynomial of order 6 can be described by FITIT.

G.1 Binary Program for Salt-Solvent Systems

```
 COMMON APHIP(8,40),APHI(8,40),ACT(8,40),DPC(8,40),APHIP1(8,40)
C,XMOL(8,40)),PCAL(8,40),HON,XH1(8,40),XH2(8,40)),NOPT(8,3),
CR1P(8),R(8,40),Q(8,40),X30(8,40),XS(8,40),GEXP(8,40),YD
 COMMON   XP(8,40)),XN(8,40)),NIND,NSYS,R1(8),R2P(8),HOP(10)
 COMMON NPP,NP(8),FZP(8),FZN(8),FNP(8),FNM(8),FK(8),T(8),TA(8),
CDIELEC(8),DU(8),AMW(8),PSM(8),II,AAA(8),GBB(8,40)),APM
C,RP(8),RN(8),Q3(8),R3(8),  R2(8),Q1(8),Q2(8),A12(8),A31(8),A32(8)
 DIMENSION AMS(8),EPHI(8,40)),ERROG(8,40)),ERROP(8,40)),EDP(8,40))
 DIMENSION  DX(12),Y(12),X(9,15),XT(12),DPE(8,40),P(8,40)
C,GSEXP(8,40))
 REAL *8 NAME1,NAME2,NAME3
 *********************************************************
          BINARY PROGRAM

 THE BINARY DATA ARE:
    1)  REGRESSED FOR THE BINARY PARAMETERS WITH NIND = 1
    2) PREDICTED USING THE BINARY PARAMETERS WITH NIND = 2
 *********************************************************
 INTEGER FZP,FZN
 NOPT=1 FOR MOLALITY VS. DELTA P
 NOPT=2 WHEN DATA ARE MOLALITY VS. PEHI
 NDATA IS NO. OF DATA SET TO BE USED
 FZP IS THE CHARGE ON THE POSITIVE ION
 FZN IS THE CHARGE ON THE NEGATIVE ION(ABS. VALUE)
 FK IS THE SUM OF THE POSITIVE AND NEGATIVE IONS AND
    FK=FNP+FNM
 FNP IS THE SUM OF THE NUMBER OF POSITIVE IONS
 FNM IS THE SUM OF THE NEGATIVE IONS
 T IS THE TEMPERATURE OF THE SYSTEM
 AMW IS THE MOLECULAR WEIGHT OF THE SOLVENT
 PSM IS THE PURE SOLVENT VAPOR PRESSURE
 INDP=1 DATA ARE MOLALITY VS.DEPRESSION IN VAPOR PRESSURE
 INDP=2 DATA ARE MOLALITY VS.VAPOR PRESSURE
 XMOL IS THE MOLALITY OF THE SALT SOLUTION
 XMOL1 IS THE MOLALITY OF THE SOLUTION ACCOUNTING FOR
   SOLVATION
 XS IS THE MOLE FRACTION OF THE SOLVENT ASSUMING
    COMPLETE DISSOCIATION OF THE SALT
 XP IS THE MOLE FRACTION OF THE POSITIVE ION ASSUMING
    COMPLETE DISSOCIATION OF THE SALT
 XN IS THE MOLE FRACTION OF THE NEGATIVE ION ASSUMING
    COMPLETE DISSOCIATION OF THE SALT
 XH1 IS THE MOLE FRACTION OF THE SOLVATED POSITIVE ION
 XH2 IS THE MOLE FRACTION OF THE SOLVATED NEGATIVE  ION
 X30 IS THE MOLE FRACTION OF THE SOLVENT ON A SOLVATED BASIS
 APHI IS THE EXPERIMENTAL OSMOTIC COEFFICIENT
 APHIP1 IS THE CALCULATED OSMOTOC COEFFICIENT
 P IS THE EXPERIMENTAL VAPOR PRESSURE
 PCAL IS THE CALCULATED VAPOR PRESSURE
 GSEXP IS THE EXPERIMENTAL SOLVENT ACTIVITY COEFFICIENT
 GBB IS THE CALCULATED SOLVENT ACTIVITY COEFFICIENT
```

```
406    FORMAT(4I5)
410    FORMAT('-',5X,'THE TEMPERATURE OF THE SYSTEM=',F10.5)
100    FORMAT(4F10.5)
22     FORMAT(F10.6,F10.5)
40     FORMAT(F10.5,F10.3)
99     FORMAT('-')
1999   FORMAT(2I5)
1111   FORMAT(I5,3F5.1)
965    FORMAT(2I10)
2000   FORMAT(1X,3A8)
404    FORMAT(3F10.5)
2      FORMAT(2F10.5)
405    FORMAT('-','THE PURE COMPONENT VAPOR PRESSURE IS=',F10.5/'THE
      CSOLVENT MOLECULAR WEIGHT IS=',F10.5)
       READ 406,NSYS,IND,INDP,NIND
       DO 415 JJ=1,NSYS
       READ 1999,(NOPT(JJ,I),I=2,3)
       NOPT(JJ,1)=0
       READ 2,T(JJ),HOP(JJ)
       READ 2000,NAME1,NAME2,NAME3
       READ 1111,NP(JJ),FK(JJ),FNP(JJ),FNN(JJ)
       READ 965,FZP(JJ),FZN(JJ)
       READ 404,PSN(JJ),AMW(JJ),AMWS
       READ 100,RP(JJ),RN(JJ),R3(JJ),Q3(JJ)
       IF(NIND.EQ.2)GO TO 1
       IF(NIND.EQ.1)GO TO 3
3      READ 22,DUMMY,DUMMY1
       GO TO 97
1      READ 2,A31(JJ),A32(JJ)
       TA(JJ)=T(JJ)+273.15
97     READ 999,DUMMY3
       READ 22,DO(JJ),DIELEC(JJ)
999    FORMAT(F10.5)
       ANS(JJ)=1000./AMW(JJ)
       TA(JJ)=T(JJ)+273.15
       V1=(4./3.)*3.14*(1.*10**(-24.))*((RP(JJ) )**3.)*6.023*10**23.
       V2=(4./3.)*3.14*(1.*10**(-24.))*(RN(JJ)**3.)*6.023*10**23.
       A1=4.*3.14*(1.*10**(-16.))*(RP(JJ) )**2.*6.023*10**23.
       A2=4.*3.14*(1.*10**(-16.))*RN(JJ)**2.*6.023*10**23.
       R1(JJ)=V1/15.17
       R2(JJ)=V2/15.17
       Q2(JJ)=A2/(2.5*10**9.)
       Q1(JJ)=A1/(2.5*10**9.)
       PRINT99
       PRINT  410,T(JJ)
       PRINT 405,PSN(JJ),AMW(JJ)
       PRINT 2000,NAME1,NAME2,NAME3
       NPP=NP(JJ)
       DO 5000 IJ=2,3
       IF(NOPT(JJ,IJ).EQ.1)GO TO 901
       IF(NOPT(JJ,IJ).EQ.2)GO TO 903
```

```
      IF(NOPT(JJ,IJ).EQ.0)GO TO 5000
901   DO 1391 I=1,NPP
      READ 40,XMOL(JJ,I),DPE(JJ,I)
1391  CONTINUE
      DO 403 I=1,NPP
414   IF(INDP.EQ.1) P(JJ,I)=PSM(JJ) -DPE(JJ,I)
403   CONTINUE
      GO TO 910
903   DO 1392 I=1,NPP
      READ 2,XMOL(JJ,I),APHI(JJ,I)
1392  CONTINUE
911   DO 952 I=1,NPP
      ACT(JJ,I)=EXP(-FK(JJ)*XMOL(JJ,I)*AMW(JJ)*APHI(JJ,I)/1000.)
      P(JJ,I)=PSM(JJ)*ACT(JJ,I)
      DPE(JJ,I)=PSM(JJ)-P(JJ,I)
952   CONTINUE
910   DO 4000 I=1,NPP
      AP=FNP(JJ)*XMOL(JJ,I)
      AN=FNM(JJ)*XMOL(JJ,I)
      XS(JJ,I)=ANS(JJ)/(ANS(JJ)+AP+AN)
      XP(JJ,I)=AP/(ANS(JJ)+AP+AN)
      XN(JJ,I)=AN/(ANS(JJ)+AP+AN)
      IF(NOPT(JJ,IJ).EQ.3)GO TO 4000
      GSEXP(JJ,I)=P(JJ,I)/(XS(JJ,I)*PSM(JJ))
      IF(NOPT(JJ,IJ).EQ.2)GO TO 4000
      APHI(JJ,I)=-1000.*ALOG(P(JJ,I)/PSM(JJ))/(FK(JJ)*XMOL(JJ,I)
     C*AMW(JJ))
4000  CONTINUE
5000  CONTINUE
415   CONTINUE
      IT=2
      IF(NIND.EQ.2)GO TO 163
      IF(NIND.EQ.1)GO TO 601
163   CALL FR(YY,XT)
      IF(NIND.EQ.2)GO TO 523
601   M=7
      M1=M+1
      M3=M+3
      DO 21 J=1,M
      DO 21 K=1,M3
      X(J,K)=0.0
21    CONTINUE
      DO 507 JI=1,M
      XT(JI)=-300.
      DX(JI)=30.
507   CONTINUE
      L=900
      E=0.0001
      PRINT 4,E
4     FORMAT(///,10X,'E=',F10.8)
```

```
302    FORMAT(///,5X,'INITIAL VALUES FOR XT(',I2,')=',F15.5)
       CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
       PRINT 5,(I,XT(I),I=1,M)
5      FORMAT(///,SX,'FINAL VALUES FOR XT(',I2,')=',F15.5)
       PRINT 401,(I,Y(I),I=1,M1)
401    FORMAT('-',10X,'Y(',I2,')=',F10.5)
       PRINT 31,YD
31     FORMAT('-','MEAN=',F10.5)
523    CONTINUE
       PRINT 522
522    FORMAT('-')
       DO 715 KJ=1,NSYS
       NPP=RP(KJ)
       IF(NIND.EQ.2)II=2
       IF(NIND.EQ.1.AND.NOPT(KJ,II).EQ.2)PRINT 146
       IF(NIND.EQ.1.AND.NOPT(KJ,II).EQ.1)PRINT 148
146    FORMAT('-','OSMOTIC REG')
148    FORMAT('-','DELTA P REG')
       PRINT 5030,AAA(KJ)
5030   FORMAT('-','AAA(KJ)=',F10.5)
       PRINT 5899
5899   FORMAT(//,1X,2HRP,10X,2HRN,10X,2HR3)
       PRINT 5890,RP(KJ),RN(KJ),R3(KJ)
5890   FORMAT(/,3F10.5)
       PRINT 5891
5891   FORMAT(//,1X,2HR1,10X,2HR2,10X,2HQ1,10X,2HQ2,10X,2HQ3)
       PRINT 5892,R1(KJ),R2(KJ),Q1(KJ),Q2(KJ),Q3(KJ)
5892   FORMAT(/,5F10.5)
       PRINT 350
350    FORMAT(//,1X,3HA12,9X,3HHOP,9X,3HAPM,9X,3HA31,9X,3HHON,
      C9X,3HA32)
       PRINT 351,A12(KJ),HOP(KJ),APM,A31(KJ),HON,A32(KJ)
351    FORMAT(/,6F10.2)
5003   CONTINUE
       IF(NIND.EQ.2)GO TO 20
5022   FORMAT(7F10.5)
       IF(NOPT(KJ,II).LE.2)GO TO 224
20      DO 49 KK=1,NPP
       IF(II.EQ.3.AND.NOPT(KJ,II).EQ.3)GO TO 50
       IF(NOPT(KJ,II+1).EQ.0.AND.NOPT(KJ,II).EQ.3)P(KJ,KK)=0.0
       IF(NOPT(KJ,II+1).EQ.0.AND.NOPT(KJ,II).EQ.3)APHI(KJ,KK)=0.0
       IF(NOPT(KJ,II+1).EQ.0.ANO.NOPT(KJ,II).EQ.3)GO TO 49
50     EPHI(KJ,KK)=((APHI(KJ,KK)-APHIP1(KJ,KK))/APHI(KJ,KK))*100.
       ERROP(KJ,KK)=((P(KJ,KK)-PCAL(KJ,KK))/P(KJ,KK))*100.
       EDP(KJ,KK)=(DPE(KJ,KK)-DPC(KJ,KK))
       DIG=GSEXP(KJ,KK)-GBB(KJ,KK)
       ERROG(KJ,KK)=(DIG/GSEXP(KJ,KK))*100.
49     CONTINUE
224    PRINT 122
122    FORMAT('-','     XM            POBS            PCAL          ERROR')
       PRINT 100,(XMOL(KJ,I),P(KJ,I),PCAL(KJ,I),ERROP(KJ,I),I=1,NPP)
```

```
      IF(II.EQ.3.AND.NOPT(KJ,II).EQ.3)GO TO 51
      IF(NOPT(KJ,II+1),EQ,0,AND,NOPT(KJ,II),EQ,3)GO TO 192
51    SUM2=0.0
      DO 28 I=1,NPP
      DED=(ABS((PCAL(KJ,I)-P(KJ,I))/P(KJ,I)))**2.
28    SUM2=SUM2+ABS(ERROP(KJ,I))
      AVRGE2=SUM2/NPP
      PRINT 4025,AVRGE2
4025  FORMAT('-',10X,         'AVRGE2=',E15.8)
      PRINT 5073
5073  FORMAT('-','    XM          DPE          DPC        ERRDP ')
      PRINT 100,(XMOL(KJ,I),DPE(KJ,I),DPC(KJ,I),EDP(KJ,I),I=1,NPP)
      SUM12=0.00
      DO 5074 I=1,NPP
      DP=ABS(DPE(KJ,I)-DPC(KJ,I))
5074  SUM12=SUM12+DP
      AVDP=SUM12/NPP
      PRINT 5075,AVDP
5075  FORMAT('-',10X,       'AVDP=',E15.8)
192   CONTINUE
      PRINT 132
132   FORMAT('-','    XM       PHIEXP         PHICAL      ERROR')
      PRINT 100,(XMOL(KJ,I),APHI(KJ,I),APHIP1(KJ,I),EPHI(KJ,I),I=1,NPP)
      IF(II.EQ.3.AND.NOPT(KJ,II).EQ.3)GO TO 52
      IF(NOPT(KJ,II+1),EQ,0,AND,NOPT(KJ,II),EQ,3)GO TO 209
52    SUM=0.0
      DO 56 I=1,NPP
      DEE=(ABS(APHIP1(KJ,I)-APHI(KJ,I)))
      DEP=DEE**2.
56    SUM=SUM+ABS(EPHI(KJ,I))
      AVRGE=SUM/NPP   .
      PRINT 4020,AVRGE
4020  FORMAT('-',10X,    'AVRGE RELZERROR='E15.8)
209   CONTINUE
      IF(NOPT(KJ,II+1).EQ.0.)GO TO 5033
5033  CONTINUE
      PRINT 5008
5008  FORMAT('-','    XFAC       GSEXP        GSOLVCAL     ERROR')
5007  FORMAT('-',10X,     'AVRGE RELZERROR='E15,8)
      PRINT 100,(XS(KJ,I),GSEXP(KJ,I),GBB(KJ,I),ERROG(KJ,I),I=1,NPP)
      IF(II,EQ,3,AND,NOPT(KJ,II),EQ,3)GO TO 291
      IF(NOPT(KJ,II+1).EQ.0.AND.NOPT(KJ,II).EQ.3)GO TO 5020
291   SUMG=0,0
      DO 5010 I=1,NPP
5010  SUMG=SUMG+ABS(ERROG(KJ,I))
      AVG=SUMG/NPP
      PRINT 5011,AVG
5011  FORMAT('-',10X,    'AVG RELZ ERROR='E15.8)
5020  CONTINUE
      PRINT 5005
5005  FORMAT('-','    XH1      XH2       XH3   ')
```

```
       PRINT 404,(XH1(KJ,I),XH2(KJ,I),X30(KJ,I),I=1,NPP)
715    CONTINUE
       STOP
       END
       SUBROUTINE FR(YY,XT)
       COMMON APHIP(8,40),APHI(8,40),ACT(8,40),DPC(8,40),APHIP1(8,40)
      C,XMOL(8,40),PCAL(8,40),HON,XH1(8,40),XH2(8,40),NOPT(8,3),
      CR1P(8),R(8,40),Q(8,40),X30(8,40),XS(8,40),GEXP(8,40),YD
       COMMON   XP(8,40),XN(8,40),NIND,NSYS,R1(8),R2P(8),HOP(10)
       COMMON NPP,NP(8),FZP(8),FZN(8),FNP(8),FNN(8),FK(8),T(8),TA(8),
      CDIELEC(8),DO(8),AMW(8),PSM(8),II,AAA(8),GBB(8,40),APM
      C,RP(8),RN(8),Q3(8),R3(8), R2(8),Q1(8),Q2(8),A12(8),A31(8),A32(8)
       DIMENSION X(8),XT(12),SAI31(50),SAI32(50),SAI12(50),SAI21(50)
       DIMENSION  THET1(8,40),THET2(8,40),THET3(8,40),PH3(8,40)
      C,SUMM(8,40),SUMM3(8,40),SUMM4(8,40),TAU3(8,40),GB(8,40)
      C,GU1(8,40),GU2(8,40),XMOL1(8,40),HP(8,40),HN(8,40),AI(8,40)
      C,GU(8,40),GDHS1(8,40),GRES(8,40)
        INTEGER FZP,FZN
       YS=0.0
124    DO 125 I=1,NSYS
       NPP=NP(I)
       DO 1 KK=1,NPP
       IF(NIND.EQ.2)GO TO 126
       A12(I)=XT(1)
       A32(I)=XT(2)
       A31(1)=XT(3)
       A31(2)=XT(4)
       A31(3)=XT(5)
       A31(4)=XT(6)
       A31(5)=XT(7)
126    APM=0.
       AAA(I)=RP(I)+RN(I)
       A12(I)=-828.7
       TA(I)=T(I)+273.15
       HON=0.
       HP(I,KK)=HOP(I)*XS(I,KK)
       HN(I,KK)=HON*(XS(I,KK))
       ELEC=4.80223E-10
       AVOG=6.0238E23
       BOLTZ=1.380257E-16
       PI=3.14
       AK1=((8*PI*AVOG*ELEC**2.)/(1000.*DIELEC(I)*BOLTZ*TA(I)))**.5
       AL=(ELEC**2.)/(DIELEC(I)*BOLTZ*TA(I))
       APH=(1./3.)*((2.*PI*AVOG/1000.)**.5)*(AL**1.5)
       XH1(I,KK)=XP(I,KK)/(1.-XP(I,KK)*HP(I,KK)-XN(I,KK)*HN(I,KK))
       XH2(I,KK)=XN(I,KK)/(1.-XP(I,KK)*HP(I,KK)-XN(I,KK)*HN(I,KK))
       X30(I,KK)=(XS(I,KK)-XP(I,KK)*HP(I,KK)-XN(I,KK)*HN(I,KK))/
      C(1.-HP(I,KK)*XP(I,KK)-HN(I,KK)*XN(I,KK))
777    R1P(I)=R1(I)+HP(I,KK)*R3(I)
       R2P(I)=R2(I)+HN(I,KK)*R3(I)
       R(I,KK)=R1P(I)*XH1(I,KK)+R2P(I)*XH2(I,KK)+R3(I)*X30(I,KK)
       Q(I,KK)=XP(I,KK)*Q1(I)+XN(I,KK)*Q2(I)+XS(I,KK)*Q3(I)
```

```
      THET1(I,KK)=Q1(I)*XP(I,KK)/Q(I,KK)
      THET2(I,KK)=Q2(I)*XN(I,KK)/Q(I,KK)
      THET3(I,KK)=Q3(I)*XS(I,KK)/Q(I,KK)
      SAI31(I)=EXP(-A31(I)/TA(I))
      SAI32(I)=EXP(-A32(I)/TA(I))
      SAI12(I)=EXP(-A12(I)/TA(I))
      SAI21(I)=SAI12(I)
      SUMM(I,KK)=THET3(I,KK)
      SUMM3(I,KK)=THET1(I,KK)+THET2(I,KK)*SAI21(I)+THET3(I,KK)*SAI31(I)
      SUMM4(I,KK)=THET1(I,KK)*SAI12(I)+THET2(I,KK)+THET3(I,KK)*SAI32(I)
      PH3(I,KK)=R3(I)*X30(I,KK)/R(I,KK)
24    FF=ABS(AAA(I))*1.E-8
      W=(FNP(I)*FZP(I)**2.+FNM(I)*FZN(I)**2.)/FK(I)
      TERM4=((2.*PI*FF**(3.))/3.)
      BB=ABS(AAA(I))*AK1*1.E-8
      XMOL1(I,KK)=XMOL(I,KK)/(1.-.001*AMW(I)*XMOL(I,KK)*(HP(I,KK)
     C*FNP(I)+HN(I,KK)*FNM(I)))
      AI(I,KK)=XMOL(I,KK)*DO(I)*(FNP(I)*FZP(I)**2.+FNM(I)*FZN(I)**2.)
     C/2.
      TERM5=(PI*FF*((AL)**2.)*(W**2.))/(3.*(1.+BB*AI(I,KK)
     C**.5)**2.)
      D=(XMOL(I,KK)*DO(I)*FK(I)*6.023E23)/1000.
      T4=D*TERM4
      T5=D*TERM5
      C=-W*AL/6.
      TERM1=C*((AK1*AI(I,KK)**.5)/(1.+BB*AI(I,KK)**.5))
      APHIP(I,KK)=TERM1+T4+T5+1.
      GDHS1(I,KK)=-(APHIP(I,KK)-1.)*AMW(I)*FK(I)*XMOL(I,KK)/1000.
      GU(I,KK)=ALOG(PH3(I,KK)/X30(I,KK))+1.-PH3(I,KK)/X30(I,KK)
      TAU3(I,KK)=Q3(I)*(1.-ALOG(SUMM(I,KK))-THET1(I,KK)*SAI31(I)/SUMM3
     C(I,KK)-THET2(I,KK)*SAI32(I)/SUMM4(I,KK)-THET3(I,KK)/SUMM(I,KK))
      GRES(I,KK)=TAU3(I,KK)
      GU1(I,KK)=EXP(GU(I,KK))
      ACT2=GU1(I,KK)*X30(I,KK)
      GU2(I,KK)=ACT2/XS(I,KK)
      IF(X30(I,KK).LT.0)GO TO 1
      GB(I,KK)= GU(I,KK)+GDHS1(I,KK)   +ALOG(X30(I,KK))-ALOG(XS(I,KK))
      GBB(I,KK)=EXP(GB(I,KK)+GRES(I,KK))
      ACT(I,KK)=GBB(I,KK)*XS(I,KK)
      APHIP1(I,KK)=-1000.*ALOG(ACT(I,KK))/(AMW(I)*FK(I)*XMOL(I,KK))
      PCAL(I,KK)=ACT(I,KK)*PSM(I)
      DPC(I,KK)=PSM(I)-PCAL(I,KK)
7003  DIF=(ABS(APHIP1(I,KK)-APHI(I,KK)))
      IF(NOPT(I,II).EQ.1)Y=(DIF/APHI(I,KK))**2.
      IF(NOPT(I,II).EQ.2)Y=(DIF/APHI(I,KK))**2.
7000  YS=Y+YS
1     CONTINUE
125   CONTINUE
      YY=YS
      YO=YY
      RETURN
      END
```

G.2 Binary Salt-Free Program

```
       COMMON ANT1,ANT2,ANT3,T(50),TA(50),ANT4,ANT5,ANT6,
     CG3E(50),NCHOIC,TCAL(40),ERROR3(40),X4(40),A34,A43,DNU(40)
       COMMON  PT,BMIX,P(50),X3(40),G4E(40),ERROR4(40),ERRORP(40)
       COMMON   YF3(50),NCOMP,BF(40),YF4(40),YF3CP(40),YF4CP(40)
       COMMON RD(50),TX(50),DEVP(50) ,TC(50),PC(50),YD,YS,NNC(10),NOPT
       COMMON NP,N,VS(5),WSRK(4), TEMP,PP,ANW(4),V(40),BB(40),FUG(40)
       COMMON  R3,R4,Q3,Q4,NACID,ETA(40),PCALP(40),G3T1P(40),G4T1P(40)
       DIMENSION XT(12),DX(12),Y(8),X(7,10)
       DIMENSION NC(10),PSME(3,50),DEVT(50),DEVY3(50),DEVY4(50),
     1  ETM(10,10)
       REAL *8 NAME1,NAME2,NAME3
C      ***********************************************************
C
C                     BINARY SALT-FREE PROGRAM
C        THIS PROGRAM ALLOWS THE DETERMINATION OF THE INTERACTION
C      PARAMETERS BETWEEN TWO SOLVENTS.  (A34 AND A43)  THE
C      VLE OF A SYSTEM MAY ALSO BE CALCULATED GIVEN A34 AND
C       A43
C      IF NOPT=1 DATA ARE REGRESSED
C      IF NOPT=2 DATA ARE CALCULATED
C
C
C      ***********************************************************
       NSYS=1
C      T IS THE TEMPERATURE OF THE SYSTEM
C      ANW IS THE MOLECULAR WEIGHT OF THE SOLVENT
C      PSME IS THE PURE SOLVENT VAPOR PRESSURE
C      PSMC IS THE CALCULATED VAPOR PRESSURE
C      G3E AND G4E ARE THE EXPERIMENTAL ACTIVITY COEFFICIENTS
C      G3T1P AND G4T1P ARE THE CALCULATED ACT.COEFFICIENTS
C      X3 AND X4 ARE THE MOLE-FRACTIONS
C      YF3 AND YF4 ARE THE EXP. VAPOR PHASE COMPOSITIONS
C      YF3CP AND YF4CP ARE THE CALCULATED VAP PHASE COMPOSITIONS
C      P IS THE EXPERIMENTAL VAPOR PRESSURE
C      PCALP IS THE CALCULATED VAPOR PRESSURE
C      PT IS THE TOTAL PRESSURE FOR ISOBARIC SYSTEMS
7      FORMAT(4I5)
410    FORMAT('-',5X,'THE TEMPERATURE OF THE SYSTEM=',F10.5)
99     FORMAT('-')
2000   FORMAT(1X,3A8)
1      FORMAT(5F10.5)
3      FORMAT(3F10.5)
2      FORMAT(2F10.5)
405    FORMAT(' ','THE PURE COMPONENT VAPOR PRESSURE IS=',F10.5/'THE
     CSOLVENT MOLECULAR WEIGHT IS=',F10.5/'THE SALT MOLECULAR WEIGHT
     CIS='F10.5)
       DO 5000 IJ=1,NSYS
C      IF NCHOIC=1,DATA ARE ISOTHERMAL
C      IF NCHOIC=2,DATA ARE ISOBARIC
C      IF NCHOIC=3,DATA ARE ISOTHERMAL ANND IN FORM OF P VS X4
```

```
      READ 7,NP,NOPT,NCHOIC,NCOMP
      READ 2000,NAME1,NAME2,NAME3
      PRINT 2000,NAME1,NAME2,NAME3
      READ 76,ANT1,ANT2,ANT3,ANT4,ANT5,ANT6
571   READ 44,R3,Q3,R4,Q4
C            NNC = NUMBER OF COMPONENT
C            PPC = CRITICAL PRESSURE IN ATMOSPHERES
C            TTC = CRITICAL TEMPERATURE IN K
C            RD = MEAN RADIUS OF GYRATION IN A
C            DDMU = DIPOLE MOMENT IN DEBYE
C            EETA = ASSOCIATION PARAMETER FOR COMPONENT NNC
C          ETM = SOLVATION PARAMETERS. EACH CARD CONTAINS
C          THE SOLVATION PARAMETERS BETWEEN A
C          GIVEN I = 1,NCOMP-1 AND ALL J = I+1,NCOMP
C    5: 1 CARD, T(8F10.3)
C          T    = TEMPERATURES IN K, THE CARD CONTAINS NT TEMPERATURES
C
      DO 17 I = 1,NCOMP
17    READ 23,NNC(I),TC(I),PC(I),RD(I),DMU(I),ETA(I),ZZC
      DO 18 I=1,NCOMP
18    READ 2,WSRK(I),V(I)
23    FORMAT(I2,6F10.3)
      PRINT 24
 24   FORMAT(1H0,' COMPONENT PC IN ATM  RD IN A   DMU IN DEB.    ETA    TC
     1 IN K')
      PRINT 25,(NNC(I),PC(I),RD(I),DMU(I),ETA(I),TC(I),I=1,NCOMP)
25    FORMAT(5X,I2,3X,5F10.3)
      IN = NCOMP-1
      DO 30 I = 1,IN
      II = I+1
30     READ 26,(ETM(I,J),J=II,NCOMP)
      ETA(3)=ETM(1,2)
 26   FORMAT(8F10.3)
      WRITE(6,27)
 27   FORMAT(/1H0,'  SOLVATION PARAMETERS')
      IN = NCOMP-1
      DO 11 I = 1,IN
      II = I+1
      DO 11 J = II,NCOMP
 11   ETM(J,I) = ETM(I,J)
      DO 12 I = 1,NCOMP
 12   ETM(I,I) = ETA(I)
      PRINT 28,(NNC(I),I=1,NCOMP)
 28   FORMAT(10X,I2,9(8X,I2))
      DO 13 I = 1,NCOMP
13    PRINT 29,NNC(I),(ETM(I,J),J=1,NCOMP)
556   READ 3,AMW(1),AMW(2),PT
      IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)T(1)=PT
557   DO 8 I=1,NP
      READ 3,P(I),X4(I),YF4(I)
      IF(NCHOIC.EQ.2)T(I)=P(I)
      IF(NCHOIC.EQ.2)P(I)=PT
```

```
      IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)T(I)=T(1)
      IF(NCHOIC.EQ.2)TA(I)=T(I)+273.15
      PSME(1,I)=EXP(2.303*(ANT1-ANT2/(T(I)+ANT3)))
      PSME(2,I)=EXP(2.303*(ANT4-ANT5/(T(I)+ANT6)))
      TEMP=T(1)+273.15
      RG = 82.06
570   X3(I)=1.-X4(I)
      YF3(I)=1.-YF4(I)
      N=2
      NACID=0
           IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)PT=P(I)
      IF(NCHOIC.EQ.3)GO TO 8
      PP=PT/760.
      YX(1)=YF3(I)
      YX(2)=YF4(I)
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      FUG3=FUG(1)
      FUG4=FUG(2)
      PP=PSME(1,I)/760.
      YX(1)=1.
      YX(2)=1.E-24
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PHIR3=FUG(1)
      YX(1)=1.E-24
      YX(2)=1.
      PP=PSME(2,I)/760.
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PHIR4=FUG(2)
      CALL HANKI(TEMP,NCOMP,TC,VS,V,WSRK)
      FUG30=PSME(1,I)*PHIR3*EXP(VS(1)*(PT-PSME(1,I))/
     C(RG*760.*TEMP))
      FUG40=PSME(2,I)*PHIR4*EXP(VS(2)*(PT-PSME(2,I))/(
     CRG*760.*TEMP))
      IF(X3(I).EQ.0)GO   TO 4001
      G3E(I)=YF3(I)*FUG3*P(I)/(X3(I)*FUG30)
      IF(X4(I).EQ.0)GO TO 8
4001  G4E(I)=YF4(I)*P(I)*FUG4/(X4(I)*FUG40)
8     CONTINUE
 29   FORMAT(2X,I2,10F10.4)
      IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.2)TA(1)=T(1)+273.15
10    CONTINUE
      PRINT99
      IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)PRINT 410,T(1)
      IF(NOPT.EQ.2)GO TO 210
501   DO 21 J=1,7
      DO 21 K=1,10
      X(J,K)=0.0
21    CONTINUE
      M=2
      XT(1)=300.
      XT(2)=300.
      DO 507 I=1,M
```

```
      DX(I)=30.
507   CONTINUE
      M1=M+1
      M3=M+3
      L=900
      E=0.0001
      PRINT 4,E
4     FORMAT(///,10X,'E=',F10.8)
      PRINT 302,(I,XT(I),I=1,M)
302   FORMAT(///,5X,'INITIAL VALUES FOR XT(',I2,')=',F15.5)
210   DO 184 I=1,NP
      YF3CP(I)=YF3(I)
      YF4CP(I)=YF4(I)
184   CONTINUF
      IF(NOPT.EQ.2)CALL FN(YY,XT)
      IF(NOPT.EQ.2)GO TO 334
601   CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
      PRINT 5,(I,XT(I),I=1,M)
5     FORMAT(///,5X,'FINAL VALUES FOR XT(',I2,')=',F15.5)
      PRINT 401,(I,Y(I),I=1,M1)
401   FORMAT('-',10X,'Y(',I2,')=',F10.5)
      PRINT 31,YD
31    FORMAT('-','MEAN=',F10.5)
334   CONTINUE
163   PRINT 522
522   FORMAT('-')
5022  FORMAT(7F10.5)
      PRINT 5891
5891  FORMAT(//,1X,2HR3,10X,2HR4,10X,3HA34,10X,3HA43,10X,2HQ3,10X,
     C2HQ4)
      PRINT 5892,R3,R4,A34,A43,Q3,Q4
5892  FORMAT(/,6F10.5)
      DO 42 I=1,NP
      DEVY3(I)=YF3(I)-YF3CP(I)
      DEVY4(I)=YF4(I)-YF4CP(I)
      DEVT(I)=T(I)-TCAL(I)
      IF(NCHOIC.EQ.2)P(I)=PT
      IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)DEVP(I)=P(I)-PCALP(I)
      IF(NCHOIC.EQ.2)DEVP(I)=PT-PCALP(I)
42    CONTINUF
76    FORMAT(6F10.5)
      PRINT 5809
5809  FORMAT('-','  X3          Y3EX         Y3CAL              DY3              Y4EXP
     C Y4CAL        DY4')
      PRINT 5022,(X3(I),YF3(I),YF3CP(I),DEVY3(I),YF4(I),YF4CP(I),
     CDEVY4(I),I=1,NP)
      SUM1=0.0
      SUM2=0.0
      DO 80 I=1,NP
      SUM1=SUM1+ABS(DEVY3(I))
80    SUM2=SUM2+ABS(DEVY4(I))
      AVY3=SUM1/(NP)
```

```
      AVY4=SUM2/(NP)
      PRINT 81,AVY3
81    FORMAT('-',10X,'AVY3=',E15.8)
      PRINT 82,AVY4
82    FORMAT('-',10X,'AVY4=',E15.8)
44    FORMAT(4F10.5)
      PRINT 77
77    FORMAT('-','        X3     PEXP      PCAL       DELP ')
      PRINT 44,( X3(I),P(I),PCALP(I),DEVP(I),I=1,NP)
      SUM=0.0
      SUMM=0.
      DO 86 I=1,NP
      SUMM=SUMM+ABS(ERRORP(I))
86    SUM=SUM+ABS(DEVP(I))
      AVDP=SUM/(NP)
      AVVDP=SUMM/(NP)
      PRINT 87,AVDP
87    FORMAT('-',10X,'AVDP=',E15.8)
      PRINT 34,AVVDP
34    FORMAT('-',10X,'AVVDP=',E15.8)
            PRINT 5903
5903        FORMAT('-','  X3         G3E        G3T1    ERROR3')
            PRINT 44,(X3(I),G3E(I),G3T1P(I),ERROR3(I),I=1,NP)
      SUM=).0
      DO 72 I=1,NP
      SUM=SUM+ABS(ERROR3(I))
72    CONTINUE
      AVG3=SUM/(NP)
      PRINT 73,AVG3
73    FORMAT('-',10X,'AVG REL %ERROR=',E15.8)
      PRINT 5904
5904  FORMAT('-','  X4         G4E        G4CAL      ERROR4')
      PRINT 44,(X4(I),G4E(I),G4T1P(I),ERROR4(I),I=1,NP)
      SUM=0.0
      DO 79 I=1,NP
      SUM=SUM+ABS(ERROR4(I))
79    CONTINUE
      AVG4=SUM/(NP)
      PRINT 74,AVG4
74    FORMAT('-',10X,'AVG REL%ERROR=',E15.8)
      PRINT 46
46    FORMAT('-','    X3       TEXP      TCAL      ERRORT ')
      PRINT 44,(X3(I),T(I),TCAL(I),DEVT(I),I=1,NP)
      SUM1=0.0
      DO 93 I=1,NP
93    SUM1=SUM1+ABS(DEVT(I))
      AVT=SUM1/(NP)
      PRINT 92,AVT
92    FORMAT('-',10X,'AVT=',E15.8)
5000   CONTINUE
      STOP
      END
```

```
       SUBROUTINE FN(YY,XT)
       COMMON ANT1,ANT2,ANT3,T(50),TA(50),ANT4,ANT5,ANT6,
      CG3E(50),NCHOIC,TCAL(40),ERROR3(40),X4(40),A34,A43,DMU(40)
       COMMON   PT,BMIX,P(50),X3(40),G4E(40),ERROR4(40),ERRORP(40)
       COMMON    YF3(50),NCOMP,BF(40),YF4(40),YF3CP(40),YF4CP(40)
       COMMON RD(50),YX(50),DEVP(50)  ,TC(50),PC(50),ZD,ZS,NNC(10),NOPT
       COMMON NP,N,VS(5),WSRK(4), TEMP,PP,AMW(4),V(40),BB(40),FUG(40)
       COMMON  R3,R4,Q3,Q4,NACID,ETA(40),PCALP(40),G3T1P(40),G4T1P(40)
       DIMENSION X(5),P3(50),P4(50),PSM(3,50), Q(50),R(50)
       DIMENSION P4P(40),P3P(40),THET3P(40),THET4P(40),PGUESS(40)
      C,TGUESS(40)
       DIMENSION  XT(12)
       KOUNT=0
       IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)PGUESS(1)=P(1)
       TGUESS(1)=90.
       YS=0.0
       RG = 82.06
344    DO 343 KK=1,NP
       IF(NOPT.EQ.2)GO TO 342
       A34=    (XT(1))
       A43=  (XT(2))
342    Z=10.
       IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)TCAL(KK)=T(1)
549    QP=Q3*X3(KK)+Q4*X4(KK)
       RPP=R3*X3(KK)+R4*X4(KK)
       THET3P(KK)=Q3*X3(KK)/QP
       THET4P(KK)=Q4*X4(KK)/QP
       P3P(KK)=R3/RPP
       P4P(KK)=R4/RPP
             G3CP=ALOG(P3P(KK))+1.-P3P(KK)
             G4CP=ALOG(P4P(KK))+1.-P4P(KK)
       IF(KOUNT.EQ.0.AND.NCHOIC.EQ.2)TCAL(KK)=TGUESS(KK)
       IF(KOUNT.EQ.0.AND.NCHOIC.EQ.1.OR.NCHOIC.EQ.3)PCALP(KK)=PGUESS(KK)
       N=2
       NACID=0
20     TEMP=TCAL(KK)+273.15
       SAI43=EXP(-A43/(TCAL(KK)+273.15))
       SAI34=EXP(-A34/(TCAL(KK)+273.15))
       DEDP=THET3P(KK)+THET4P(KK)*SAI43
       DEEP=THET3P(KK)*SAI34+THET4P(KK)
       G3RP=Q3*(1.-ALOG(DEDP)-THET3P(KK)/DEDP-(THET4P(KK)*
      CSAI34)/DEEP)
       G4RP=Q4*(1.-ALOG(DEEP)-(THET3P(KK)*SAI43/DEDP)-
      CTHET4P(KK)/DEEP)
       G3T1P(KK)=EXP(G3CP+G3RP)
       G4T1P(KK)=EXP(G4CP+G4RP)
       PSM(1,KK)=EXP(2.303*(ANT1-ANT2/(TCAL(KK)+ANT3)))
       PSM(2,KK)=EXP(2.303*(ANT4-ANT5/(TCAL(KK)+ANT6)))
56     IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)PT=PCALP(KK)
       PP=PT/760.
       YX(1)=YF3CP(KK)
       YX(2)=YF4CP(KK)
```

```
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      FUG3=FUG(1)
      FUG4=FUG(2)
      PP=PSM(1,KK)/760.
      YX(1)=1.
      YX(2)=1.E-24
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PHIR3=FUG(1)
      YX(1)=1.E-24
      YX(2)=1.
      PP=PSM(2,KK)/760.
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PHIR4=FUG(2)
      CALL HANKI(TEMP,NCOMP,TC,VS,V,WSRK)
      FUG30=PSM(1,KK)*PHIR3*EXP(VS(1)*(PT-PSM(1,KK))/
     C(RG*760.*TEMP))
      FUG40=PSM(2,KK)*PHIR4*EXP(VS(2)*(PT-PSM(2,KK))/(
     CRG*760.*TEMP))
      PCALP(KK)=X3(KK)*G3T1P(KK)*FUG30/FUG3+X4(KK)*G4T1P(KK)*
     CFUG40/FUG4
55    YF3CP(KK)=G3T1P(KK)*X3(KK)*FUG30/(PT*FUG3)
      YF4CP(KK)=G4T1P(KK)*X4(KK)*FUG40/(PT*FUG4)
      SUMY=YF3CP(KK)+YF4CP(KK)
      TEST=SUMY-1.
      TEST1=ABS(1.-SUMY)
      IF(NCHOIC.EQ.2.AND.KOUNT.EQ.0)TGUESS(KK+1)=TCAL(KK)
      IF(NCHOIC.EQ.1.AND.KOUNT.EQ.0)PGUESS(KK+1)=PCALP(KK)
      IF(NCHOIC.EQ.3.AND.KOUNT.EQ.0)PGUESS(KK+1)=PCALP(KK)
      IF(KOUNT.EQ.0)YF4CP(KK+1)=YF4CP(KK)
      IF(KOUNT.EQ.0)YF3CP(KK+1)=YF3CP(KK)
      IF(TEST1.LT..0005)GO TO 13
      IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)GO TO 57
      IF(TEST)14,13,21
14    TCAL(KK)=TCAL(KK)*1.02
      GO TO 20
21    TCAL(KK)=TCAL(KK)*.98
      GO TO 20
57    IF(TEST.LT.1)GO TO 58
      IF(TEST.GT.1)GO TO 59
58    PCALP(KK)=PCALP(KK)*.98
      PT=PCALP(KK)
      GO TO 60
59    PCALP(KK)=PCALP(KK)*1.02
      PT=PCALP(KK)
      GO TO 60
60    YF3CP(KK)=G3T1P(KK)*X3(KK)*FUG30/(PT*FUG3)
      YF4CP(KK)=G4T1P(KK)*X4(KK)*FUG40/(PT*FUG4)
      SUMY1=YF3CP(KK)+YF4CP(KK)
      TEST2=SUMY1-1.
      TEST3=ABS(1.-SUMY1)
      IF(TEST3.LT..0005)GO TO 56
      IF(TEST2)58,56,59
```

```
13      CONTINUE
        IF(KOUNT.EQ.0.AND.NCHOIC.EQ.2)TGUESS(KK)=TCAL(KK)
        IF(KOUNT.EQ.0.AND.NCHOIC.EQ.1)PGUESS(KK)=PCALP(KK)
        IF(KOUNT.EQ.0.AND.NCHOIC.EQ.3)PGUESS(KK)=PCALP(KK)
        IF(NCHOIC.EQ.1)GO TO 511
        IF(NCHOIC.EQ.3)GO TO 512
12      DIF7=ABS(PCALP(KK)-PT)
511     DIF1=G3T1P(KK)-G3E(KK)
        DIF2=G4T1P(KK)-G4E(KK)
        DIF3=YF3CP(KK)-YF3(KK)
        DIF4=YF4CP(KK)-YF4(KK)
512     DIF5=PCALP(KK)-P(KK)
        IF(NCHOIC.EQ.3)GO TO 017
        IF(NCHOIC.EQ.2)DIF6=PCALP(KK)-PT
016     ERROR3(KK)=(DIF1/G3E(KK))*100.
015     ERROR4(KK)=(DIF2/G4E(KK))*100.
017     IF(NCHOIC.EQ.1.OR.NCHOIC.EQ.3)ERRORP(KK)=(DIF5/P(KK))*100.
        IF(NCHOIC.EQ.2)ERRORP(KK)=(DIF6/PT)*100.
        IF(NCHOIC.EQ.2)GO TO 11
        GO TO 10
10       Y=(ABS(DIF5/P(KK)))**2.+(ABS(DIF3*10.))**2.
        GO TO 7000
11      Y=(ABS(DIF6/PT))**2.+(ABS(DIF3*10.))**2.
7000    YS=Y+YS
343     CONTINUE
        KOUNT=KOUNT+1
        YY=YS
        YD=YY
        RETURN
        END
```

G.3 Ternary Program for Salt-Binary Mixed Solvent Systems.

```
      COMMON G3E(45), XF4(45),NCHOIC,TC(10),AM,AH,NACID,BMIX,BF(45)
      COMMON XMOL(45), PCAL(45),P(45),PP,NP,KK,G3C(45),G4C(3,45)
      COMMON X3(45),G4E(45), G3T(45),G4T(45),DOP,DON,TCAL(45)
      COMMON YF3C(45),YF4C(45),YF3(45),DDENX4(45),NOPT,HOP,HON,
     CAAA(45),PC(5),DMU(5),ETA(5),ERROR4(45),R1,R2,XF3(45),V(45)
      COMMON AI(45),WSRK(5),YF4(45),ERRORP(45),NCOMP, TEMP,VS(45)
      COMMON   ERROR3(45),XP(45),XN(45),X4(45),A3,A4,B3,B4
      COMMON N,FZP,FZN,FNP,FNM,FK,T(45)  ,DO(45),AMW(4),A32,A42
      COMMON RP,RN,R3,R4,Q1,Q2,Q3,Q4,ANT1,ANT2,ANT3,AB(20)
      COMMON APM,A31,BPM,A41,A34,A43,ANT4,ANT5,ANT6,PT,RD(6)
      COMMON G3T1P(45),G4T1P(45),PCALP(45),YF3CP(45),YF4CP(45),
     CFUC(45),BB(6),YX(6)
      DIMENSION DEVE(45), DEVT(45),DEVC(45),RAT(45),ETM(6,6)
     C ,DEVY3(45),DEVY4(45), X1(45),PSME(3,45),NNC(6),DEVP(45)
      REAL *8 NAME1,NAME2,NAME3
C     **************************************************
C
C             TERNARY SALT PROGRAM
C      THIS PROGRAM CALCULATES THE PHASE EQUILIBRIUM OF TERNARY
C      SYSTEMS CONSISTING OF A SALT AND TWO SOLVENTS
C      THE VALUES OF A12 FROM THE BINARY REGRESSION MUST BE
C      SUBSTITUTED INTO LINE 523
C
C
C     *****************************************************
      INTEGER FZP,FZN
      NSYS=1
C     1 = POSITIVE ION
C     2 = NEGATIVE ION
C     3 = SOLVENT 1
C     4 = SOLVENT 2
C     A31 = INTER. BETWEEN SOLVENT 1 AND POS. ION
C     A32 = INTER. BETWEEN SOLVENT 1 AND NEG. ION
C     A41 = INTER. BETWEEN SOLVENT 2 AND POS ION
C     A42 = INTER. BETWEEN SOLVENT 2 AND NEG ION
C     A34 = INTER. BETWEEN SOLVENTS 1 AND 2
C     A43 = INTER BETWEEN SOLVENTS 2 AND 1
C     AH IS THE ION-SIZE PARAMETER OF A SALT IN SALTED-IN
C          COMPONENT
C     AM IS THE ION-SIZE PARAMETER OF THE SALT IN SALTED-OUT COMP
C     HOP IS THE SOLVATION NUMBER OF THE POS. ION IN SALTED-IN
C        COMPONENT
C     DOP IS THE SOLVATION NUMBER OF THE NEG. ION IN SALTED-OUT
C         COMPONENT
C     DON IS THE SOLVATION NUMBER OF THE NEG. ION IN THE
C        SALTED-OUT SOLVENT = 0
C     TC IS THE CRITICAL TEMPERATURE
C     PCAL IS THE CALCULATED TOTAL PRESSURE
C     PT IS THE TOTAL PRESSURE FOR ISOBARIC SYSTEMS
C     P IS THE VAPOR PRESSURE FOR ISOTHERMAL SYSTEMS
C     G3C IS THE  FLORY-HUGGINS CONTRIBUTION FOR COMP. 3
```

```
C       G4C IS THE FLORY-HUGGINS CONTRIBUTION FOR COMP. 4
C       G3R IS THE  RES CONTRIB. OF COMP. 3
C       G4R IS THE RES. CONTRIB. OF COMP.4
C       FZP IS THE CHARGE ON THE POSITIVE ION
C       FZN IS THE CHARGE ON THE NEGATIVE ION(ABS. VALUE)
C       FK IS THE SUM OF THE POSITIVE AND NEGATIVE IONS AND
C          FK=FNP+FNM
C       FNP IS THE SUM OF THE NUMBER OF POSITIVE IONS
C       FNM IS THE NUMBER OF THE NEGATIVE IONS
C       T IS THE TEMPERATURE OF THE SYSTEM
C       AMW IS THE MOLECULAR WEIGHT OF THE SOLVENT
C       PSM IS THE PURE SOLVENT VAPOR PRESSURE
C       XMOL IS THE MOLALITY OF THE SALT SOLUTION
C       G3E IS THE EXPERIMENTAL ACTIVITY COEFF. OF SOLVENT 1
C           IN THE PRESENCE OF SALT
C       G4E IS THE CALCULATED ACTIVITY COEFF. OF SOLVENT 2
C           IN THE PRESENCE OF SALT
C       G3T IS THE CALC. ACT. COEFF. OF SOLV 1 WITH SALT
C       G4T IS THE CALC. ACT. COEFF. OF SOLVENT 2 WITH SALT
C       YF3 IS THE EXP. VAP. COMP. OF SOLV.1 WITH SALT
C       YF4 IS THE EXP. VAP. COMP. OF SOLV.2 WITH SALT
C       AAA IS MOLE FRAC. AVERAGE OF ION-SIZE PARAM.
C       PC IS CRIT. PRESSURE
C       AI IS THE IONIC STRENGTH
C       DO IS THE MIXED SOLVENT DENSITY
C       DIELEC IS THE DIELECTRIC CONSTANT OF THE SALT-FREE
C         MIXED SOLVENT
C       G3T1F IS THE ACT. COEFF. OF SOLV 1 IN SALT-FREE SYSTEM
C       G4T1F IS THE ACT COEFF OF SOLV  2 IN SALT-FREE SYSTEM
C       PCALF IS THE CALCULATED  TOTAL PRESSURE OF THE SALT-FREE SYSTEM
C       YF3CF IS THE CALC. VAP. COMP. OF SOLV1 IN SALT-FREE SYS
C       YF4CF IS THE CALC. VAP. COMP. OF SOLV2 IN SALT-FREE SYS
C       XF3 IS THE SALT-FREE MOLE FRAC. OF SOLVENT 1
C       XF4 IS THE SALT-FREE MOLE FRAC. OF SOLVENT 2
C       XP IS THE MOLE FRAC. OF THE POS. ION
C       XN IS THE MOLE FRAC. OF THE NEG. ION
C       X3 IS THE MOLE FRAC. OF SOLVENT 1
C       X4 IS THE MOLE FRAC. OF SOLVENT 2
C       XH1 IS MOLE FRAC. OF POS. ION ON SOLVATED BASIS
C       XH2 IS MOLE FRAC. OF NEG. ION ON SOLVATED BASIS
C       XH3 IS MOLE FRAC. OF SOLVENT 1 ON SOLVATED BASIS
C       XH4 IS MOLE FRAC. OF SOLVENT 2 ON SOLVATED BASIS
C       NP IS THE NUMBER OF DATA POINTS
C       NOPT = 2
C       NCOMP IS THE NUMBER OF SOLVENTS AND IS EQUAL TO 2
7       FORMAT(4I5)
410     FORMAT('-',5X,'THE TEMPERATURE OF THE SYSTEM=',F10.5)
100     FORMAT(6F10.5)
144     FORMAT(F10.5)
99      FORMAT('-')
965     FORMAT(2I10)
```

```
2000  FORMAT(1X,3A8)
1     FORMAT(5F10.5)
3     FORMAT(3F5.1)
2     FORMAT(2F10.5)
23    FORMAT(I2,6F10.3)
29    FORMAT(2X,I2,10F10.3)
31    FORMAT(3F10.5)
405   FORMAT('-','THE PURE COMPONENT VAPOR PRESSURE IS=',F10.5/'THE
     CSOLVENT MOLECULAR WEIGHT IS=',F10.5/'THE SALT MOLECULAR WEIGHT
     CIS='F10.5)
      DO 145 I=1,14
      READ 144,AB(I)
145   CONTINUE
      DO 5000 IJ=1,NSYS
      READ 7,NP,NOPT,NCHOIC,NCOMP
C     NCHOIC=1 IF THE DATA ARE ISOTHERMAL
C     NCHOIC=2 IF THE DATA ARE ISOBARIC
C     NCHOIC=3 IF THE DATA ARE ISOBARIC
C     NCHOIC=4 IF THE DATA ARE ISOBARIC
      READ 2000,NAME1,NAME2,NAME3
      PRINT 2000,NAME1,NAME2,NAME3
      READ 100,ANT1,ANT2,ANT3,ANT4,ANT5,ANT6
      READ 3,FK,FNP,FNM
      READ 965,F2P,F2N
      READ 100,RP,RN,R3,Q3,R4,Q4
      READ 100,AH,AN,HOP,HON,DOP,DON
      READ 101,A31,A32,A41,A42,A34,A43
      DO 17 I=1,NCOMP
17    READ 23,NNC(I),TC(I),PC(I),RD(I),DMU(I),ETA(I),ZZC
      DO 18 I=1,NCOMP
18    READ 2,WSRK(I),V(I)
      PRINT 24
 24   FORMAT(1H0,' COMPONENT PC IN ATM  RD IN A   DMU IN DEB.   ETA   TC
     1 IN K')
      PRINT 25,(NNC(I),PC(I),RD(I),DMU(I),ETA(I),TC(I),I=1,NCOMP)
25    FORMAT(5X,I2,3X,5F10.3)
      IN=NCOMP-1
      DO 30 I=1,IN
      II=I+1
30    READ 26,(ETM(I,J),J=II,NCOMP)
      ETA(3)=ETM(1,2)
 26   FORMAT(8F9.5)
      WRITE(6,27)
 27   FORMAT(/1H0,'  SOLVATION PARAMETERS')
      IN = NCOMP-1
      DO 11 I = 1,IN
      II = I+1
      DO 11 J = II,NCOMP
 11   ETM(J,I) = ETM(I,J)
      DO 12 I = 1,NCOMP
 12   ETM(I,I) = ETA(I)
```

```
      PRINT 28,(NNC(I),I=1,NCOMP)
 28   FORMAT(10X,I2,9(8X,I2))
      DO 13 I = 1,NCOMP
13    PRINT 29,NNC(I),(ETM(I,J),J=1,NCOMP)
      DO 8 I=1,NP
      IF(NCHOIC.EQ.1)GO TO 556
      IF(NCHOIC.EQ.2)GO TO 557
      IF(NCHOIC.EQ.3)GO TO  559
      IF(NCHOIC.EQ.4)GO TO 564
      IF(NCHOIC.EQ.5)GO TO 565
      IF(NCHOIC.EQ.6)GO TO 566
556   READ 1,XP4(I),X1(I),XMOL(I),YF4(I),P(I)
      GO TO 558
557   READ 1,XP4(I),XMOL(I),T(I),YF4(I),X1(I)
      P(I)=T(I)
      GO TO 558
559   READ 44,XP4(I),X1(I),T(I),YF4(I)
      P(I)=T(I)
      GO TO 558
564   READ 1,XP4(I),XMOL(I),T(I),YF4(I),X1(I)
      P(I)=T(I)
      GO TO 558
565   READ 1,XP4(I),X1(I),XMOL(I),YF4(I),T(I)
      P(I)=T(I)
      GO TO 558
566   READ 44,XP4(I),X1(I),YF4(I),T(I)
      P(I)=T(I)
558   XP3(I)=1.-XP4(I)
8     CONTINUE
      READ 31,AMW(1),AMW(2),PT
      IF(NCHOIC.EQ.4)READ 44,A3,B3,A4,B4
      IF(NCHOIC.EQ.1)T(1)=PT
      PRINT 41,(XP4(I),X1(I),XMOL(I),YF4(I),P(I),I=1,NP)
101   FORMAT(6F10.3)
      PRINT99
      IF(NCHOIC.EQ.1)PRINT 410,T(1)
      DO 4000 I=1,NP
       IF(NCHOIC.EQ.1)T(I)=T(1)
      PSME(2,I)=EXP(2.303*(ANT1-ANT2/(T(I)+ANT3)))
      PSME(1,I)=EXP(2.303*(ANT4-ANT5/(T(I)+ANT6)))
      IF(NCHOIC.EQ.2)GO TO 560
      IF(NCHOIC.EQ.3.OR.NCHOIC.EQ.6)GO TO 562
      AMWT=XP4(I)*AMW(2)+(1.-XP4(I))*AMW(1)
      XRAT=FK*X1(I)/(1.-X1(I))
      XSOLV=1.-XRAT/(1.+XRAT)
      X3(I)=XP3(I)*XSOLV
      X4(I)=XP4(I)*XSOLV
      XSALT=1.-X3(I)-X4(I)
      XP(I)=FNP*(XSALT/FK)
      XN(I)=FNN*(XSALT/FK)
      IF(NCHOIC.EQ.4.OR.NCHOIC.EQ.5)P(I)=PT
```

```
      GO TO 561
560   XP3(I)=1.-XP4(I)-X1(I)
      AN3=XP3(I)*100.
      AN4=XP4(I)*100.
      ANNS=X1(I)*100.
      XP3(I)=AN3/(AN3+AN4)
      XP4(I)=1.-XP3(I)
      X3(I)=AN3/(AN3+AN4+FK*ANNS)
      X4(I)=AN4/(AN3+AN4+FK*ANNS)
      XP(I)=FNP*ANNS/(AN3+AN4+FK*ANNS)
      XN(I)=FNM*ANNS/(AN3+AN4+FK*ANNS)
      XSALT=XP(I)+XN(I)
      AMWT=AMW(1)*XP3(I)+AMW(2)*XP4(I)
      XMOL(I)=1000.*ANNS/(AMWT*(AN3+AN4))
      P(I)=PT
      GO TO 561
562   AMWT=AMW(1)*XP3(I)+AMW(2)*XP4(I)
      P(I)=PT
      AN3=XP3(I)*100.
      AN4=XP4(I)*100.
      ANS=X1(I)*100./(1.-X1(I))
      X3(I)=AN3/(100.+FK*ANS)
      X4(I)=AN4/(100.+FK*ANS)
      XP(I)=FNP*ANS/(100.+FK*ANS)
      XN(I)=FNM*ANS/(100.+FK*ANS)
      XMOL(I)=1000.*ANS/(AMWT*100.)
      XSALT=XP(I)+XN(I)
561   YP3(I)=1.-YP4(I)
      TEMP=T(I)+273.15
      RG = 82.06
      N=2
      NACID=0
          IF(NCHOIC.EQ.1)PT=P(I)
      PP=PT/760.
      YX(1)=YP3(I)
      YX(2)=YP4(I)
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      FUG3=FUG(1)
      FUG4=FUG(2)
      PP=PSME(1,I)/760.
      YX(1)=1.
      YX(2)=1.E-24
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PHIR3=FUG(1)
      YX(1)=1.E-24
      YX(2)=1.
      PP=PSME(2,I)/760.
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PHIR4=FUG(2)
      CALL HANK(TEMP,NCOMP,TC,VS,V,WSRK)
      FUG30=PSME(1,I)*PHIR3*EXP(VS(1)*(PT-PSME(1,I))/
     C(RG*760.*TEMP))
```

```
       FUG40=PSME(2,I)*PHIR4*EXP(VS(2)*(PT-PSME(2,I))/(
      CRG*760.*TEMP))
       IF(X3(I).EQ.0)GO  TO 4001
       G3E(I)=YF3(I)*FUG3*P(I)/(X3(I)*FUG30)
       IF(X4(I).EQ.0)GO TO 4000
4001   G4E(I)=YF4(I)*P(I)*FUG4/(X4(I)*FUG40)
4000      CONTINUE
       DO 184 I=1,NP
       YF3C(I)=YF3(I)
       YF4C(I)=YF4(I)
       YF3CP(I)=YF3(I)
       YF4CP(I)=YF4(I)
184    CONTINUE
       CALL FN (YY,XT)
163    PRINT 522
522    FORMAT('-')
       PRINT 5899
5899   FORMAT(//,1X,2HRP,10X,2HRN,10X,2HR3,10X,2HR4)
       PRINT 5890,RP,RN,R3,R4
5890   FORMAT(/,4F10.5)
       PRINT 6899
6899   FORMAT(//,1X,3HA31,10X,3HA32,10X,3HA41,10X,3HA42,10X,
      C3HA34,10X,3HA43)
       PRINT 100,A31,A32,A41,A42,A34,A43
       PRINT 5891
5891   FORMAT(//,1X,2HR1,10X,2HR2,10X,2HQ1,10X,2HQ2,10X,2HQ3,10X,
      C2HQ4)
       PRINT 5892,R1,R2,Q1,Q2,Q3,Q4
5892   FORMAT(/,6F10.5)
       PRINT 5893
5893   FORMAT(//,1X,3HAPM,10X,3HBPM,10X,3HHOP,10X,3HDOP)
       PRINT 44,APM,BPM,HOP,DOP
       DO 42 I=1,NP
       DEVY3(I)=YF3(I)-YF3C(I)
       DEVY4(I)=YF4(I)-YF4C(I)
       DEVP(I)=P(I)-PCAL(I)
       DEVE(I)=YF4(I)-YF4CP(I)
       DEVC(I)=YF4C(I)-YF4CP(I)
       RAT(I)=(DEVC(I)/DEVE(I))*100.
       TCAL(I)=TCAL(I)-273.15
       DEVT(I)=T(I)-TCAL(I)
42     CONTINUE
       PRINT 20
20     FORMAT('-','     XSALT      XMOL        XIONSTR      AAA      X44 ')
       PRINT 44,(X1(I), AI(I),AAA(I),X4(I),I=1,NP)
41     FORMAT(5F10.5)
       PRINT 75
75     FORMAT('-','       Y3       Y3CAL       DELY       Y4       Y4CAL       DY4')
       PRINT 26,(XP4(I),XMOL(I),YF3(I),YF3C(I),DEVY3(I),YF4(I),YF4C(
      CI),DEVY4(I),I=1,NP)
       SUM1=0.0
       SUM2=0.0
```

```
      DO 80 I=1,NP
      SUM1=SUM1+ABS(DEVY3(I))
80    SUM2=SUM2+ABS(DEVY4(I))
      AVY3=SUM1/NP
      AVY4=SUM2/NP
      PRINT 81,AVY3
81    FORMAT('-',10X,'AVY3=',E15.8)
      PRINT 82,AVY4
82    FORMAT('-',10X,'AVY4=',E15.8)
      PRINT 309
309   FORMAT('-','  XP3        XMOL       DFEU        DFCU      RAT')
      PRINT 1,(XP3(I),XMOL(I),DEVE(I),DEVC(I),RAT(I),I=1,NP)
      SUM2=0.0
      DO 88 I=1,NP
88    SUM2=SUM2+ABS(RAT(I))
      AVR=SUM2/NP
      PRINT 98,AVR
98    FORMAT('-',10X,'AVR=',E15.8)
      PRINT 308
308   FORMAT('-','  XP3      G3T      G4T      PCALP      Y3P      Y4P ')
      PRINT 100,(XP3(I),G3T1P(I),G4T1P(I),PCALP(I),YF3CP(I),
     CYF4CP(I),I=1,NP)
      PRINT 84
84    FORMAT('-','        X3        GGEXP3       GCALT       ERROR3 ')
      PRINT41,(X3(I),XMOL(I),G3E(I),G3T(I),ERROR3(I), I=1,NP)
      SUM=0.0
      DO 72 I=1,NP
      IF(X3(I).EQ.0.)GO TO 72
      SUM=SUM+ABS(ERROR3(I))
72    CONTINUE
      AVG3=SUM/(NP)
      PRINT 73,AVG3
73    FORMAT('-',10X,'AVG REL %ERROR=',E15.8)
44    FORMAT(4F10.5)
      PRINT 85
85    FORMAT('-','        X4        GEXP4       GCAL4       ERROR4')
      PRINT 41,(X4(I),XMOL(I),G4E(I),G4T(I),ERROR4(I), I=1,NP)
      SUM=0.0
      DO 79 I=1,NP
      IF(X4(I).EQ.0.)GO TO 79
      SUM=SUM+ABS(ERROR4(I))
79    CONTINUE
      AVG4=SUM/(NP)
      PRINT 74,AVG4
74    FORMAT('-',10X,'AVG REL%ERROR=',E15.8)
      PRINT 77
77    FORMAT('-','    XMOL      X3       PEXP         PCAL          DELP ')
      PRINT 1,(XMOL(I),X3(I),P(I),PCAL(I),DEVP(I),I=1,NP)
      SUM=0.0
      DO 86 I=1,NP
86    SUM=SUM+ABS(DEVP(I))
      AVDP=SUM/NP
```

```
      PRINT 87,AVDP
87    FORMAT('-',10X,'AVDP=',E15.8)
      PRINT 5895
5895  FORMAT('-','  X3      T       TCAL      DEVT      DADX4 ')
      PRINT 44,(X3(I),T(I),TCAL(I),DEVT(I), I=1,NP)
      SUM2=0.0
      DO 90 I=1,NP
90    SUM2=SUM2+ABS(DEVT(I))
      AVT=SUM2/NP
      PRINT 91,AVT
91    FORMAT('-',10X,'AVT=',E15.8)
5000   CONTINUE
      STOP
      END
      SUBROUTINE FN(YY,XT)
      COMMON G3E(45), XP4(45),NCHOIC,TC(10),AM,AH,NACID,BMIX,BF(45)
      COMMON XMOL(45), PCAL(45),P(45),PP,NP,KK,G3C(45),G4C(3,45)
      COMMON X3(45),G4E(45), G3T(45),G4T(45),DOP,DON,TCAL(45)
      COMMON YF3C(45),YF4C(45),YF3(45),DDENX4(45),NOPT,HOP,HON,
     CAAA(45),PC(5),OMU(5),ETA(5),ERROR4(45),R1,R2,XP3(45),V(45)
      COMMON AI(45),WSRK(5),YF4(45),ERRORP(45),NCOMP, TEMP,VS(45)
      COMMON    ERROR3(45),XP(45),XN(45),X4(45),A3,A4,B3,B4
      COMMON N,FZP,FZN,FNP,FNM,FK,T(45) ,D0(45),ANW(4),A32,A42
      COMMON RP,RN,R3,R4,Q1,Q2,Q3,Q4,ANT1,ANT2,ANT3,AB(20)
      COMMON APM,A31,BPM,A41,A34,A43,ANT4,ANT5,ANT6,PT,RD(6)
      COMMON G31P(45),G41P(45),PCALP(45),YF3CP(45),YF4CP(45),
     CFUG(45),BB(6),YX(6)
      DIMENSION X(5),   R(45),TE(45),PSMC(3,45),PGUESS(45),TE1(45)
       DIMENSION THET3(45),THET4(45),THET1(45),THET2(45),TGUESS(45),
     CTHET3P(45),THET4P(45),P3P(45),HP(35),DP(35),XH1(35),XH2(35),
     CXH3(35),XH4(35),P4P(35),GUH(2,45),TAU3(45),TAU4(45)
      DIMENSION    TA(45),PSC(3,45),PGUES1(45),TGUES1(45),TCAL1(45)
       INTEGER FZP,FZN
      YS=0.0
      TGUESS(1)=T(1)+273.15
      TGUES1(1)=370.
      TCAL(1)=TGUESS(1)
      TCAL1(1)=TGUES1(1)
      IF(NCHOIC.EQ.1)PGUESS(1)=P(1)
      IF(NCHOIC.EQ.1)PGUES1(1)=P(1)
      NACID=0
      RG=82.06
      DO 343 KK=1,NP
      IF(NOPT.EQ.2)DAAX3=(AH-AM)*(1.E-8)
      DAAX4=-DAAX3
      DAAX3=DAAY3*XP4(KK)
      DAAX4= DAAX4*XP3(KK)
342   V1=(4./3.)*3.14*(1.*10.**(-24.))*RP**3.*6.023*10**23.
      V2=(4./3.)*3.14*(1.*10.**(-24.))*RN**3.*6.023*10**23.
      R2=V2/15.17
      A2=4.*3.14*(1.*10**(-16.))*RN**2.*6.023*10**23.
      R1=V1/15.17
```

```
        A1=4,*3,14*(1,*10**(-16,))*RP**2,*6,023*10**23,
        Q1=A1/(2,5*10**9,)
        Q2=A2/(2,5*10**9,)
        ELEC=4,80223E-10
        AVOG=6,0238E23
        BOLTZ=1,380257E-16
        PI=3,14
        IF(NCHOIC,EQ,1)GO TO 189
        TCAL(KK)=TGUESS(KK)
        TCAL1(KK)=TGUES1(KK)
189     IF(NCHOIC,EQ,1)TA(KK)=T(1)+273,15
        IF(NCHOIC,EQ,1)TCAL(KK)=TA(1)
        IF(NCHOIC,EQ,1)TCAL1(KK)=TA(1)
        IF(NCHOIC,EQ,1)PCAL(KK)=PGUESS(KK)
        IF(NCHOIC,EQ,1)PCALP(KK)=PGUES1(KK)
20      DO 1 I=1,2
        TE(KK)=TCAL(KK)-273,15
        IF(NCHOIC,EQ,4)GO TO 69
        A11=AB(1)+AB(2)*XP4(KK)+AB(3)*XP4(KK)**2,+AB(4)*XP4(KK)**3.
       C+AB(5)*XP4(KK)**4,+AB(6)*XP4(KK)**5,+AB(7)*XP4(KK)**6.
        B11=AB(8)+AB(9)*XP4(KK)+AB(10)*XP4(KK)**2,+AB(11)*XP4(KK)**3.
       C+AB(12)*XP4(KK)**4,+AB(13)*XP4(KK)**5,+AB(14)*XP4(KK)**6.
        DA11=AB(2)+2,*AB(3)*XP4(KK)+3,*AB(4)*XP4(KK)**2,+
       C4,*AB(5)*XP4(KK)**3,+5,*AB(6)*XP4(KK)**4,+6,*AB(7)*XP4(KK)**5.
        DB11=AB(9)+2,*AB(10)*XP4(KK)+3,*AB(11)*XP4(KK)**2,+
       C4,*AB(12)*XP4(KK)**3,+5,*AB(13)*XP4(KK)**4,+6,*AB(14)*XP4(KK)**5.
        DIELEC=A11*EXP(B11*TE(KK))
        D25H=AB(1)*EXP(AB(8)*TE(KK))
        AB1=AB(1)+AB(2)+AB(3)+AB(4)+AB(5)+AB(6)+AB(7)
        AB2=AB(8)+AB(9)+AB(10)+AB(11)+AB(12)+AB(13)+AB(14)
        D25M=AB1*EXP(AB2*TE(KK))
        DIELX4=DA11*EXP(B11*TE(KK))+A11*TE(KK)*DB11*EXP(B11*TE(KK))
        GO TO 70
69      D3=A3*EXP(B3*TE(KK))
        D4=A4*EXP(B4*TE(KK))
        D25H=D3
        D25M=D4
        DIELEC=D3*XP3(KK)+D4*XP4(KK)
        DIELX4=D4-D3
70      TEMP=TCAL(KK)
        CALL HANKI
        DDENDT=DDENX4(KK)*XP3(KK)
        DDENX3=-DDENX4(KK)*XP4(KK)
        DIELDT=DIELX4*XP3(KK)
        DIELX3=-DIELX4*XP4(KK)
        HN=HON*X3(KK)
        HP(KK)=(HOP*X3(KK)*EXP(FZP*(DIELEC/D25H)*X4(KK)))
        DN=DON*X4(KK)
        DP(KK)=(DOP*X4(KK)*EXP(-FZP*(DIELEC/D25M)*X3(KK)))
        AK1=((8*PI*AVOG*ELEC**2,)/(1000,*DIELEC*BOLTZ*TCAL(KK)))**,5
        AL=(ELEC**2,)/(DIELEC*BOLTZ*TCAL(KK))
        APH=(1,/3,)*((2,*PI*AVOG*D0(KK)/1000,)**,5)*(AL**1,5)
```

```
      XXX=1.-XP(KK)*(HP(KK)+DP(KK))-XN(KK)*(HN+DN)
      XH1(KK)=XP(KK)/XXX
      XH2(KK)=XN(KK)/XXX
      XH3(KK)=(X3(KK)-HP(KK)*XP(KK)-HN*XN(KK))/XXX
      XH4(KK)=(X4(KK)-DP(KK)*XP(KK)-DN*XN(KK))/XXX
835   XSH=XP(KK)+XN(KK)
      XRATH=XSH/(1.-XSH)
      IF(NOPT.EQ.2)AAA(KK)=AH*XP3(KK)+AM*XP4(KK)
           AMWT=XP4(KK)*AMW(2)+(1.-XP4(KK))*AMW(1)
           R1P=R1+HP(KK)*R3+DP(KK)*R4
           R2P=R2+HN*R3+DN*R4
      AI(KK)=XMOL(KK)*  (FNP*FZP**2.+FNM*FZN**2.)/2.
      DD=AMWT/1000.
      FF=ABS(AAA(KK))*1.E -8
      B=FF*(8.*PI*AL*AVOG*DO(KK)/1000.)**.5
      GG=1.+B*(AI(KK)**.5)
      DAX4=(1./2.)*APH*(1./DO(KK))*DDENDT-(3./2.)*APH*
     C(1./DIELEC)*DIELDT
      DAX3=(1./2.)*APH*(1./DO(KK))*DDENX3-(3./2.)*APH*
     C(1./DIELEC)*DIELX3
      DBX4=-(1./2.)*B*(1./DIELEC)*DIELDT+(B/2.)*(1./
     CDO(KK))*DDENDT+(B/FF)*DAAX4
      DBX3=-(1./2.)*B*(1./DIELEC)*DIELX3+(B/2.)*(1./
     CDO(KK))*DDENX3+(B/FF)*DAAX3
      IF(I.EQ.1)DADN=DAX3
      IF(I.EQ.2)DADN=DAX4
      IF(I.EQ.1)DBDN=DBX3
      IF(I.EQ.2)DBDN=DBX4
      TERM1=2.*APH*(AMW(I)/1000.)*(AI(KK)**1.5)/GG
      TERM2=-APH*(AMW(I)/1000.)*B*(AI(KK)**2.)/(GG**2.)
      TERM3=-2.*DD*((AI(KK)**1.5)/GG)*DADN
      TERM4=2.*APH*DD*((AI(KK)**2.)/(GG**2.))*DBDN
      TERM5=-2.*APH*DD*((AI(KK)**1.5)/B)*(1./GG)*DBDN
      TERM6=  (2.*DD*APH)*(AI(KK)/(B**2.))*ALOG(GG)*DBDN
      TERM66=-(2.*AI(KK)/B)*DD*ALOG(GG)*DADN
      IF(I.EQ.1)A0=DDENX3
      IF(I.EQ.2)A0=DDENDT
      IF(I.EQ.1)A0K=DAAX3
      IF(I.EQ.2)A0K=DAAX4
      TERM7=(FF**2.)*(2.*PI*(FF**3.)/3.)*(AVOG/(1000.**2.)
     C)*((XMOL(KK)**2.)*AMWT*A0-(XMOL(KK)**2.)*DO(KK)*AMW(I)
     C+(3./FF)*DO(KK)*(XMOL(KK)**2.)*AMWT*A0K)
22    GDH(I,KK)=TERM1+TERM2+TERM3+TERM4+
     CTERM5+TERM6+TERM66+TERM7
      Q=Q1*XP(KK)+Q2*XN(KK)+Q3*X3(KK)+Q4*X4(KK)
      QP=Q3*XP3(KK)+Q4*XP4(KK)
      RPP=R3*XP3(KK)+R4*XP4(KK)
      R(KK)=XH1(KK)*R1P+XH2(KK)*R2P+XH3(KK)*R3+XH4(KK)*R4
      THET1(KK)=Q1*XP(KK)/Q
      THET2(KK)=Q2*XN(KK)/Q
      THET3(KK)=Q3*X3(KK)/Q
      THET4(KK)=Q4*X4(KK)/Q
```

```
      THET3P(KK)=Q3*XP3(KK)/QP
      THET4P(KK)=Q4*XP4(KK)/QP
      SAI43=EXP(-A43/TCAL(KK))
      SAI34=EXP(-A34/TCAL(KK))
      SAI11=1.
      SAI22=1.
       A12=XP3(KK)*(-828.7)+XP4(KK)*(-253.1)
      SAI12=EXP(-A12/TCAL(KK))
      SAI21=SAI12
      SAI31=EXP(-A31/TCAL(KK))
      SAI41=EXP(-A41/TCAL(KK))
      SAI32=EXP(-A32/TCAL(KK))
      SAI42=EXP(-A42/TCAL(KK))
      P3P(KK)=R3/RPP
      P4P(KK)=R4/RPP
      P3=R3/R(KK)
      P4=R4/R(KK)
      G3C(KK)=ALOG(P3)+1.-P3
      G4C(I,KK)=ALOG(P4)+1.-P4
      APM=0.
      BPM=0.
      DED=THET1(KK)*APM/Q1+THET3(KK)+THET4(KK)*SAI43
      DEE=THET1(KK)*BPM/Q1+THET3(KK)*SAI34+THET4(KK)
      DAE=THET1(KK)*SAI12+THET2(KK)*SAI22+THET3(KK)*SAI32+
     CTHET4(KK)*SAI42
      DEA=THET1(KK)*SAI11+THET2(KK)*SAI21+THET3(KK)*SAI31+THET4(KK)*
     CSAI41
      TAU3(KK)=Q3*(1.-ALOG(DED)-THET1(KK)*SAI31/DEA
     C-THET2(KK)*SAI32/DAE-THET3(KK)/DED
     C-THET4(KK)*SAI34/DEE)
      TAU4(KK)=Q4*(1.-ALOG(DEE)-THET1(KK)*SAI41/DEA
     C-THET2(KK)*SAI42/DAE-THET3(KK)*
     CSAI43/DED-THET4(KK)/DEE)
1     CONTINUE
      G3R=TAU3(KK)
      G4R=TAU4(KK)
      G3T1=EXP(GDH(1,KK)+ G3C(KK)    )
      G4T1=EXP(GDH(2,KK)+G4C(2,KK)    )
      G3RE=EXP(G3R)
      G3T(KK)=G3RE*G3T1*XH3(KK)/X3(KK)
      G4RE=EXP(    G4R)
      G4T(KK)=  G4RE*G4T1*XH4(KK)/X4(KK)
      PSMC(2,KK)=EXP(2.303*(ANT1-ANT2/(TE(KK)+ANT3)))
      PSMC(1,KK)=EXP(2.303*(ANT4-ANT5/(TE(KK)+ANT6)))
56    IF(NCHOIC.EQ.1)PT=PCAL(KK)
      PP=PT/760.
      YX(1)=YF3C(KK)
      YX(2)=YF4C(KK)
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      FUG3=FUG(1)
      FUG4=FUG(2)
      PP=PSMC(1,KK)/760.
```

```
      YX(1)=1.
      YX(2)=1.E-24
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PHIR3=FUG(1)
      YX(1)=1.E-24
      YX(2)=1.
      PP=PSMC(2,KK)/760.
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PHIR4=FUG(2)
      CALL HANK(TEMP,NCOMP,TC,VS,V,WSRK)
      FUG30=PSMC(1,KK)*PHIR3*EXP(VS(1)*(PT-PSMC(1,KK))/
     C(RG*760.*TEMP))
      FUG40=PSMC(2,KK)*PHIR4*EXP(VS(2)*(PT-PSMC(2,KK))/
     C(RG*760.*TEMP))
203   PCAL(KK)=X3(KK)*G3T(KK)*FUG30/FUG3+X4(KK)*G4T(KK)
     C*FUG40/FUG4
506   YF3C(KK)=G3T(KK)*X3(KK)*FUG30/(PT*FUG3)
      YF4C(KK)=G4T(KK)*X4(KK)*FUG40/(PT*FUG4)
      SUMY=YF3C(KK)+YF4C(KK)
      TEST=SUMY-1.
      TEST1=ABS(TEST)
      IF(NCHOIC.EQ.2.OR.NCHOIC.EQ.3.OR.NCHOIC.EQ.6)TGUESS(KK+1)
     C=TCAL(KK)
      IF(NCHOIC.EQ.4.OR.NCHOIC.EQ.5)TGUESS(KK+1)=TCAL(KK)
      IF(NCHOIC.EQ.1)PGUESS(KK+1)=PCAL(KK)
      YF3C(KK+1)=YF3C(KK)
      YF4C(KK+1)=YF4C(KK)
      IF(TEST1.LT..0005)GO TO 13
      IF(NCHOIC.EQ.1)GO TO 57
      IF(TEST)49,13,21
49    TCAL(KK)=TCAL(KK)*1.02
      GO TO 20
21    TCAL(KK)=TCAL(KK)*.98
      GO TO 20
      IF(NCHOIC.EQ.2)GO TO 507
57    IF(TEST.LT.1)GO TO 58
      IF(TEST.GT.1)GO TO 59
58    PCAL(KK)=PCAL(KK)*0.98
      PT=PCAL(KK)
      GO TO 60
59    PCAL(KK)=PCAL(KK)*1.02
      PT=PCAL(KK)
60    YF3C(KK)=G3T(KK)*X3(KK)*FUG30/(PT*FUG3)
      YF4C(KK)=G4T(KK)*X4(KK)*FUG40/(PT*FUG4)
      SUMY1=YF3C(KK)+YF4C(KK)
      TEST2=SUMY1-1.
      TEST3=ABS(1.-SUMY1)
      IF(TEST3.LT..0005)GO TO 56
      IF(TEST2)58,56,59
13    CONTINUE
      IF(NCHOIC.EQ.1)PGUESS(KK)=PCAL(KK)
507   IF(NCHOIC.EQ.2.OR.NCHOIC.EQ.3.OR.NCHOIC.EQ.6)TGUESS(KK+1)
```

```
507   IF(NCHOIC.EQ.2.OR.NCHOIC.EQ.3.OR.NCHOIC.EQ.6)TGUESS(KK+1)
     C=T(KK)+273.15-5.
      IF(NCHOIC.EQ.4.OR.NCHOIC.EQ.5)TGUESS(KK+1)=T(KK)+273.15-5.
45    G3CP=ALOG(P3P(KK))+1.-P3P(KK)
      G4CP=ALOG(P4P(KK))+1.-P4P(KK)
      IF(NCHOIC.EQ.1)TCAL1(KK)=TA(KK)
      TE1(KK)=TCAL1(KK)-273.15
      TEMP=TCAL1(KK)
      SAI34=EXP(-A34/TCAL1(KK))
      SAI43=EXP(-A43/TCAL1(KK))
      DEDP=THET3P(KK)+THET4P(KK)*SAI43
      DEEP=THET3P(KK)*SAI34+THET4P(KK)
      G3RP=Q3*(1.-ALOG(DEDP)-THET3P(KK)/DEDP-(THET4P(KK)*
     CSAI34)/DEEP)
      G4RP=Q4*(1.-ALOG(DEEP)-(THET3P(KK)*SAI43/DEDP)-
     CTHET4P(KK)/DEEP)
      G3T1P(KK)=EXP(G3CP+G3RP)
      G4T1P(KK)=EXP(G4CP+G4RP)
      PSC(2,KK)=EXP(2.303*(ANT1-ANT2/(TE1(KK)+ANT3)))
      PSC(1,KK)=EXP(2.303*(ANT4-ANT5/(TE1(KK)+ANT6)))
      IF(NCHOIC.EQ.1)PT=PCALP(KK)
      YX(1)=YF3CP(KK)
      YX(2)=YF4CP(KK)
      PP=PT/760.
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PH33=FUG(1)
      PH44=FUG(2)
      PP=PSC(1,KK)/760.
      YX(1)=1.
      YX(2)=1.E-24
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PH30=FUG(1)
      PP=PSC(2,KK)/760.
      YX(1)=1.E-24
      YX(2)=1.
      CALL PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      PH40=FUG(2)
      CALL HANKI
      FU3=PSC(1,KK)*PH30*EXP(VS(1)*(PT-PSC(1,KK))/
     C(RG*760.*TEMP))
      FU4=PSC(2,KK)*PH40*EXP(VS(2)*(PT-PSC(2,KK))/
     C(RG*760.*TEMP))
      PCALP(KK)=G3T1P(KK)*XP3(KK)*FU3/PH33+XP4(KK)*G4T1P(KK)
     C*FU4/PH44
606   YF3CP(KK)=G3T1P(KK)*XP3(KK)*FU3/(PT*PH33)
      YF4CP(KK)=G4T1P(KK)*XP4(KK)*FU4/(PT*PH44)
      SUMYY=YF3CP(KK)+YF4CP(KK)
      TEST=SUMYY-1.
      TEST1=ABS(1.-SUMYY)
      IF(NCHOIC.EQ.1)PGUES1(KK+1)=PCALP(KK)
      IF(NCHOIC.EQ.2)TGUES1(KK+1)=TCAL(KK)
      IF(NCHOIC.EQ.3.OR.NCHOIC.EQ.6)TGUES1(KK+1)=TCAL(KK)
```

```
      IF(NCHOIC.EQ.4.OR.NCHOIC.EQ.5)TGUES1(KK+1)=TCAL(KK)
      YF4CP(KK+1)=YF4CP(KK)
      YF3CP(KK+1)=YF3CP(KK)
      IF(TEST1.LT..0005)GO TO 29
      IF(NCHOIC.EQ.1)GO TO 61
      IF(TEST)39,29,44
39    TCAL1(KK)=TCAL1(KK)*1.02
      GO TO 45
44    TCAL1(KK)=TCAL1(KK)*.98
      GO TO 45
61    IF(TEST.LT.1)GO TO 62
      IF(TEST.GT.1)GO TO 63
62    PCALP(KK)=PCALP(KK)*0.98
      PT=PCALP(KK)
      GO TO 64
63    PCALP(KK)=PCALP(KK)*1.02
      PT=PCALP(KK)
64    YF3CP(KK)=G3TIP(KK)*XP3(KK)*FU3/(PT*PH33)
      YF4CP(KK)=G4TIP(KK)*XP4(KK)*FU4/(PT*PH44)
      SUMY1=YF3CP(KK)+YF4CP(KK)
      TEST2=SUMY1-1.
      TEST3=ABS(1.-SUMY1)
      IF(TEST3.LT..0005)GO TO 45
      IF(TEST2)62,45,63
29    CONTINUE
      IF(NCHOIC.EQ.1)GO TO 511
508   TGUES1(KK+1)=TCAL1(KK)
      GO TO 511
511   DIF1=G3T(KK)-G3E(KK)
      DIF2=G4T(KK)-G4E(KK)
      DIF3=YF3C(KK)-YF3(KK)
      DIF5=PCAL(KK)-P(KK)
      IF(X3(KK).EQ.0.)GO TO 015
      IF(X4(KK).EQ.0.)GO TO  016
016   ERROR3(KK)=(DIF1/G3E(KK))*100.
      IF(X4(KK).EQ.0.)GO TO 017
015   ERROR4(KK)=(DIF2/G4E(KK))*100.
017     ERRORP(KK)=(DIF5/P(KK))*100.
343   CONTINUE
3     CONTINUE
      RETURN
      END
```

G.4 Subroutine LSQ2

```
         SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M2,L,E)
         DIMENSION XT(M),DX(M),X(M,M3),Y(M1),JJ(3),A(3,3)
         IL=0
         IH=0
         LIC=0
         IF(L.LE.0) GO TO 50
         IHC=M1+1
         EN=M
         EN=EN*1.5
         L1=L
         L =-L
         L2=(3*M)/2+5
         K3=2
           IF(M.GE.3)K3=3
         K4=K3-1
         G=K3*2
         G=1.0/G
         DO 100 I=1,M
100      X(I,1)=XT(I)
         CALL FN(Y(1),XT)
         DO 106 J=2,M1
         XT(J-1)=XT(J-1)+DX(J-1)
         DO 104 I=1,M
104      X(I,J)=XT(I)
         CALL FN(Y(J),XT)
         XT(J-1)=X(J-1,1)
106        CONTINUE
         L2C=0
         FLG=1.0
         GO TO 50
108      LIC=LIC+1
         IF(LIC.GE.L1)GO TO 400
50       YL=1.0E38
         YH=-YL
         Y2=YH
         Y3=YL
         DO 110 J=1,M1
         IF(Y(J).LT.YH)GO TO 1091
         Y2=YH
         I2=IH
         YH=Y(J)
         IH=J
         GO TO 109
1091       IF(Y(J).LT.Y2)GO TO 109
         Y2=Y(J)
         I2=J
109      IF(Y(J).GT.YL)GO TO 1101
         Y3=YL
         I3=IL
         IL=J
```

```
      YL=Y(J)
      GO TO 110
1101   IF(Y(J).GT.Y3)GO TO 110
      Y3=Y(J)
      I3=J
110    CONTINUE
      L2C=L2C+1
      IF(L2C.LT.L2)GO TO 111
      L2C=0
      JJ(1)=I1
      JJ(2)=I2
       JJ(3)=I3
      DO 60 K1=1,K3
      J1=JJ(K1)
      DO 60 K2=K1,K3
      J2=JJ(K2)
      S=0.0
      DO 55 I=1,M
55    S=S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
60     A(K1,K2)=S
      D=A(1,1)*A(2,2)-A(1,2)**2
      GO TO (62,61),K4
61     D1=A(1,1)*A(2,3)-A(1,2)*A(1,3)
      IF(A(1,1).EQ.0.0)A(1,1)=1.0E-5
      D=((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
62     IF(D.EQ.0.0)GO TO 65
      IF(D.LE.0.0)D=ABS(D)
      D=(D/4.0)**G
      IF(D.LT.E)GO TO 65
      FLG=1.0
      GO TO 111
65     IF(FLG.LT.0.0)GO TO 400
      FLG=-1.0
111    DO 115 I=1,M
      XT(I)=0.0
      DO 112 J=1,M1
      IF(J.NE.IH)XT(I)=XT(I)+X(I,J)
112   CONTINUE
115     XT(I)=(3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
121    CALL FN(YT,XT)
      IF(YT.GE.Y2)GO TO 167
      IHC=M1+1
      IF(YT.GE.YL)GO TO 140
      YTT=YT
      DO 135 I=1,M
135    XT(I)=1.5*XT(I)-0.5*X(I,IH)
      CALL FN(YT,XT)
      IF(YT.LE.YL)GO TO 140
      DO 138 I=1,M
138    X(I,IH)=(2.0*XT(I)+X(I,IH))/3.0
      Y(IH)=YTT
```

```
      GO TO 108
140    DO 142 I=1,M
142    X(I,IH)=XT(I)
      Y(IH)=YT
      GO TO 108
167    IHC=IHC-1
      IF(IHC.EQ.0)GO TO 300
      IF(YT.GE.YH)GO TO 173
       DO 168 I=1,M
      XS=XT(I)
      XT(I)=X(I,IH)
168    X(I,IH)=XS
173    DO 174 I=1,M
174    XT(I)=0.75*X(I,IH)+0.25*XT(I)
       CALL FN(YT,XT)
      IF(YT.GT.YH)GO TO 180
      Y(IH)=YT
      DO 175 I=1,M
175   X(I,IH)=XT(I)
      GO TO 108
180   DO 185 J=1,M1
      IF(J.EQ.IL)GO TO 185
      DO 182 I=1,M
      XT(I)=(X(I,J)+X(I,IL))/2.0
182   X(I,J)=XT(I)
      CALL FN(Y(J),XT)
185   CONTINUE
      GO TO 108
300   IHC=2*M1
      IF(M.GE.3)GO TO 350
      S=0.0
      DO 302 I=1,M
      X(I,M+2)=X(I,IH)-X(I,IL)
      X(I,M+3)=X(I,IH)-X(I,I3)
302   S=S+X(I,M+2)**2
303   S=SQRT(S)
      IF(S.EQ.0.0)S=1.0E-5
304   U=-X(2,M+2)/S
      X(2,M+2)=X(1,M+2)/S
      X(1,M+2)=U
      S=X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
      DO 305 I=1,M
305   X(I,M+2)=X(I,M+2)*S
306   DO 307 I=1,M
307   XT(I)=X(I,IH)+X(I,M+2)
      CALL FN(YT,XT)
      DO 309 I=1,M
309   XT(I)=X(I,IH)-X(I,M+2)
      CALL FN(YTT,XT)
      IF(YTT.LE.YT)GO TO 320
      DO 311 I=1,M
```

```
311   XT(I)=X(I,IH)+X(I,M+2)
      YTT=YT
320   Y(IH)=YTT
      DO 321 I=1,M
321   X(I,IH)=XT(I)
      GO TO 108
350   DO 352 I=1,M
      XT(I)=X(I,IH)-X(I,IL)
      X(I,M+2)=X(I,IH)-X(I,I2)
352   X(I,M+3)=X(I,IH)-X(I,I3)
      S=0.0
      S1=0.0
      DO 355 I=1,M
      S=S+XT(I)**2
355   S1=S1+X(I,M+3)**2
      S=SQRT(S)
      S1=SQRT(S1)
      S2=0.0
      DO 357 I=1,M
      IF(S.EQ.0.0)S=1.0E-5
      XT(I)=XT(I)/S
      S2=S2+XT(I)*X(I,M+2)
      IF(S1.EQ.0.0)S1=1.0E-5
357   X(I,M+3)=X(I,M+3)/S1
      DO 360 I=1,M
360   X(I,M+2)=X(I,M+2)-XT(I)*S2
      S1=0.0
      DO 362 I=1,M
362   S1=S1+X(I,M+2)**2
      S1=SQRT(S1)
      DO 365 I=1,M
      IF(S1.EQ.0.0)S1=1.0E-5
365   X(I,M+2)=X(I,M+2)/S1
      S1=0.0
      S2=0.0
      DO 367 I=1,M
      S1=S1+XT(I)*X(I,M+3)
367   S2=S2+X(I,M+2)*X(I,M+3)
      DO 370 I=1,M
370   X(I,M+2)=S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
      GO TO 306
400   S=Y(1)
      Y(1)=Y(IL)
      Y(IL)=S
      DO 402 I=1,M
      XT(I)=X(I,IL)
      X(I,IL)=X(I,1)
402   X(I,1)=XT(I)
      PRINT 772,LIC
772   FORMAT('-','LIC=',I5)
      RETURN
      END
```

G.5 Subroutine HANK

```
      SUBROUTINE HANK(TEMP,NCOMP,TC,VS,V,WSRK)
      DIMENSION VRO(50),VRD(50),TC(5),TR(5),VS(41),V(40),WSRK(10)
      A=-1.52816
      B=1.43907
      C=-.81446
      D=.190454
      E=-.296123
      F=.386914
      G=-.0427258
      H=-.0480645
      DO 12 JJ=1,NCOMP
      TR(JJ)=(TEMP)/TC(JJ)
      VRO(JJ)=1.+A*((1.-TR(JJ))**(1./3.))+B*((1.-TR(JJ))**(2./3.))+
     CC*(1.-TR(JJ))+D*(1.-TR(JJ))**(4./3.)
      VRD(JJ)=(E+F*TR(JJ)+G*TR(JJ)**2.+H*TR(JJ)**3.)/(TR(JJ)-1.00001)
12    VS(JJ)=1000.*V(JJ)*VRO(JJ)*(1.-WSRK(JJ)*VRD(JJ))
       RETURN
      END
```

G.6 Subroutine PHIB

```
C CALCULATION OF FUGACITY COEFFICIENTS FOR PURE SUBSTANCES AND
C BINARY MIXTURES WITH COMPOSITION GIVEN BY THE MOLE FRACTIONS
C Y AT PRESSURE P( IN ATM) AND TEMPERATURE TEMP ( IN DEG K)
C
C N = # OF COMPONENTS (U OR 2)
C PROGRAM CALL SUBROUTINE SVIR WHERE THE CONTENTS OF VIRDAT
C IS EXPLAINED
C NACID REPRESENTS THE NUMBER OF CARBON ATOMS IN
C AN ORGANIC ACID, FOR ACETIC ACID NACID IS 2.
C
C THE SUBROUTINE WILL VALUES OF FUGACITY COEFFICIENTS FUG
C**********************************************
      SUBROUTINE PHIB(PP,YX,FUG,TEMP,ETA,BB,BMIX,NACID,BF,N)
      DIMENSION A(4),B(4),YX(4),FUG(5),ETA(5),BB(5),BF(10)
C
      RG = 82.06
      PR = PP/(RG*TEMP)
C
C PURE COMPONENT OR BINARY MIXTURE
C NO ACIDS INVOLVED
C EQ'S (2.6) AND (2.7)
C
100   CALL SVIR
      DO 101 I = 1,N
      IF(ETA(I).EQ.4.5) GOTO 102
 101  CONTINUE
      IF(N.EQ.2) GOTO 103
      FUG(1) = PR*BB(1)
      FUG(1) = EXP(FUG(1))
      RETURN
 103  BMIX = YX(1)**2*BB(1)+YX(2)**2*BB(2)+2.*YX(1)*YX(2)*BB(3)
      FUG(1) = PR*(2.*YX(1)*BB(1)+2.*YX(2)*BB(3)-BMIX)
      FUG(2) = PR*(2.*YX(1)*BB(3)+2.*YX(2)*BB(2)-BMIX)
      DO 104 I = 1,2
 104  FUG(I) = EXP(FUG(I))
      RETURN
C
C PURE COMPONENT OR BINARY MIXTURE
C ONE COMPONENT IS AN ORGANIC ACID
C EQ'S (2.14),(2.15) AND (2.18)
C
102   IF(I.EQ.1) GOTO 106
      NA = 2
      NB = 1
      GOTO 107
 106  NA = 1
      NB = 2
 107  IF(NACID.GT.4) GOTO 105
C
C EXPERIMENTAL VALUE OF K
C
      AKA = A(NACID)-B(NACID)/TEMP
```

```
      AKA = EXP(-AKA*2.30259)*760
      GOTO 108
C
C K PREDICTED FROM SECOND VIRIAL COEFFICIENTS
C EQ (2.7)
C
 105  AKA =-(BB(NA)-BF(NA))/(RG*TEMP)
 108  AKT = AKA*PP*EXP(BF(NA)*PR)
      SQ = SQRT(1.+4.*AKT*YX(NA)*(2.-YX(NA)))
      ZA = (SQ-1.)/(2.*AKT*(2.-YX(NA)))
      FUG(NA) = (ZA/YX(NA))*EXP(BF(NA)*PR)
      IF(N.EQ.1) GOTO 109
      ZB = YX(NB)*(1.+4.*AKT*(2.-YX(NA))-SQ)
      ZB = ZB/(2.*AKT*(2.-YX(NA))**2)
      FUG(NB) = (ZB/YX(NB))*EXP(BF(NB)*PR)
 109  CONTINUE
      RETURN
      END
```

Subroutine SVIR

```
C*************************************************
C CALCULATION OF PURE COMPONENT AND CROSS VIRIAL COEFFICIENTS
C FOR TWO COMPONENTS AT TEMPERATURE TEMP
C FROM HAYDEN AND O'CONNELL
C IEC PROC.DES.DEV.14(3)209(1975)(
C N = NUMBER OF COMPONENTS (1 OR 2)
C BF = BFREE
C BB = BTOTAL
C          NC = # OF COMPONENTS
C          PC = CRITICAL PRESSURE, ATM
C          RD = MEAN RADIUS OF GYRATION, A
C          DMU = DIPOLE MOMENT IN DEBYE
C          ETA(1) AND ETA(2) = ASSOCIATION PARAMETERS (PURE COMPONENTS)
C          ETA(3) = SOLVATION PARAMETER (CROSS INTERACTION)
C          TC = CRITICAL TEMPERATURE , DEG K
C          ZC = CRITICAL COMPRESSIBILITY FACTOR
C FOR GIVEN COMMON VALUES OF VIRDAT THE SUBROUTIEE WILL
C RETURN VALUES OF BFREE AND BTOTAL
C*************************************************
      SUBROUTINE SVIR
      COMMON G3E(45), XP4(45),NCHOIC,TC(10),AM,AH,NACID,BMIX,BF(45)
      COMMON XMOL(45), PCAL(45),P(45),PP,NP,KK,G3C(45),G4C(3,45)
      COMMON X3(45),G4E(45), G3T(45),G4T(45),DOP,DON,TCAL(45)
      COMMON YF3C(45),YF4C(45),YF3(45),DDENX4(45),NOPT,HOP,HON,
     CAAA(45),PC(5),DMU(5),ETA(5),ERROR4(45),R1,R2,XP3(45),V(45)
      COMMON AI(45),WSRK(5),YF4(45),ERRORP(45),NCOMP, TEMP,VS(45)
      COMMON   ERROR3(45),XP(45),XN(45),X4(45),A3,A4,B3,B4
      COMMON N,FZP,FZN,FNP,FNM,FK,T(45) ,D0(45),AMW(4),A32,A42
      COMMON RP,RN,R3,R4,Q1,Q2,Q3,Q4,ANT1,ANT2,ANT3,AB(20)
      COMMON APM,A31,BPM,A41,A34,A43,ANT4,ANT5,ANT6,PT,RD(6)
      COMMON G3T1P(45),G4T1P(45),PCALP(45),YF3CP(45),YF4CP(45),
     CFUG(45),BB(6),YX(6)
C
      DIMENSION  W(3),EPSI(3),SIGM3(3),RDMU(3),RDMM(3),A(3),
     1DELH(3),D(3),B0(3)
C
C          CALCULATION OF COMPONENT PARAMETERS
C          EQ'S 15,30,17,24,25,23,21,22,10
C
      DO 101 I = 1,N
      W(I) = (0,006*RD(I)+0.02087*RD(I)**2-0.00136*RD(I)**3
      EPSI(I) = TC(I)*(0,748+0,91*W(I)-0,4*ETA(I)/(2,+20,*W(I)))
      SIGM3(I) = (2.44-W(I))**3*(TC(I)/PC(I))
      IF(DMU(I)-1,45) 101,101,103
  103 FN = 16,+400,*W(I)
      C = 2,882-1,882*W(I)/(0,03+W(I))
      XI = DMU(I)**4/(C*EPSI(I)*(SIGM3(I)**2)*TC(I)*5,723E-8)
      FFN = FN/(FN-6,)
      EPSI(I) = EPSI(I)*(1,-XI*FFN+FFN*(FFN+1,)*(XI**2)/2,)
      SIGM3(I) = SIGM3(I)*(1,+3,*XI/(FN-6,))
  101 RDMU(I) = (DMU(I)**2)*7243,8/(EPSI(I)*SIGM3(I))
      IF(N-1)300,300,400
```

```
 300  J = 1
      GOTO 301
 400  J = 3
      GOTO 401
C
C         NONPOLAR-NONPOLAR, EQ' , 32,33,34
C         PARAMETERS FOR MIXTURE CALCULATION
C
 401  EPSI(3) =0.7*SQRT(EPSI(1)*EPSI(2))+0.60/(1./EPSI(1)+1./EPSI(2))
      SIGM3 (3) = SQRT(SIGM3(1)*SIGM3(2))
      W(3) = 0.5*(W(1)+W(2))
      IF(DMU(1)*DMU(2))500,501,500
C
C         POLAR-NONPOLAR, EQ'S 38,24,36,37
C
 501  IF(DMU(1)+DMU(2)-2.)500,500,19
 19   XI38 = (DMU(1)**2*(EPSI(2)**2*SIGM3(2))**(1./3.)*SIGM3(2)+DMU(2)*
     1*2*(EPSI(1)**2*SIGM3(1))**(1./3.)*SIGM3(1))/(EPSI(3)*SIGM3(3)**2)
      PN = 16.+400*W(3)
      EPSI(3) = EPSI(3)*(1.+XI38*PN/(PN-6.))
      SIGM3(3) = SIGM3(3)*(1.-3.*XI38/(PN-6.))
C
C         POLAR-POLAR,EQ'S 35,37
C
 500  RDMU(3) = 7243.8*DMU(1)*DMU(2)/(EPSI(3)*SIGM3(3))
 301  DO 600 I = 1,J
      IF(RDMU(I)-0.04)14,15,15
 14   RDMM(I) = RDMU(I)
      GOTO 600
 15   IF(RDMU(I)-0.025)16,17,17
 16   RDMM(I) = 0.
      GOTO 600
 17   RDMM(I) = RDMU(I)-0.25
 600  CONTINUE
C
C         LAST PARAMETERS, EQ'S 7,8,9,29
C
      DO 609 I = 1,J
      BO(I) = 1.2618*SIGM3(I)
      A(I) =-0.3-0.05*RDMU(I)
      DELH(I) = 1.99+0.2*RDMU(I)**2
      IF(ETA(I)-4.)604,604,605
 604  D(I) = 650./(EPSI(I)+300.)
      GOTO 609
 605  D(I) = 42800./(EPSI(I)+22400.)
 609  CONTINUE
C
C         CALCULATION OF VIRIAL COEFFICIENTS,EQ'S 14,13,26,6,29
C
      DO 651 I = 1,J
      TSTR = EPSI(I)/TEMP-1.6*W(I)
      BFN = 0.94-1.47*TSTR-0.85*TSTR**2+1.015*TSTR**3
```

```
      BFF = (0.75-3.*TSTR+2.1*TSTR**2+2.1*TSTR**3)*RDMM(I)
      BF(I) = (BFN-BFF)*B0(I)
      BB(I) = BF(I)+B0(I)*A(I)*EXP(DELH(I)*EPSI(I)/TEMP)
      IF(ETA(I))651,651,653
653   BCHEM = B0(I)*EXP(ETA(I)*(D(I)-4.27))*(1.-EXP(1500.*ETA(I)/TEMP))
      BB(I) = BB(I)+BCHEM
651   CONTINUE
      RETURN
      END
```

G.7 Subroutine HANKI

```
      SUBROUTINE HANKI
      COMMON G3E(45), XP4(45),NCHOIC,TC(10),AM,AH,NACID,BMIX,BF(45)
      COMMON XMOL(45), PCAL(45),P(45),PP,NP,KK,G3C(45),G4C(3,45)
      COMMON X3(45),G4E(45), G3T(45),G4T(45),DOP,DON,TCAL(45)
      COMMON YF3C(45),YF4C(45),YF3(45),DDENX4(45),NOPT,HOP,HON,
     CAAA(45),PC(5),DMU(5),ETA(5),ERROR4(45),R1,R2,XP3(45),V(45)
      COMMON AI(45),WSRK(5),YF4(45),ERRORP(45),NCOMP, TEMP,VS(45)
      COMMON    ERROR3(45),XP(45),XN(45),X4(45),A3,A4,B3,B4
      COMMON N,FZP,FZN,FNP,FNM,FK,T(45) ,D0(45),AMW(4),A32,A42
      COMMON RP,RN,R3,R4,Q1,Q2,Q3,Q4,ANT1,ANT2,ANT3,AB(20)
      COMMON APM,A31,BPM,A41,A34,A43,ANT4,ANT5,ANT6,PT,RD(6)
      COMMON G3T1P(45),G4T1P(45),PCALP(45),YF3CP(45),YF4CP(45),
     CFUG(45),BB(6),YX(6)
      DIMENSION TCM(45),VMS(45),VRO(45),WM(45),VSS(45)
      DIMENSION TR(45),VRD(45),BM(45),DWM1(45),DVMS1(45),DTCM1(45)
      DIMENSION DTR1(45),DVROR(45),DVR1(45),DVRD(45),DVS(45)
C     COMP1 IS ALCOHOL
C     COMB.AA NSELEC=1
      A=-1.52816
      B=1.43907
      C=-.81446
      D=.190454
      E=-.296123
      F=.386914
      G=-.0422258
      H=-.0480645
      KI=KK
10    WM(KI)=XP4(KI)*WSRK(2)+XP3(KI)*WSRK(1)
      DWM1(KI)=WSRK(2)-WSRK(1)
11    AA=(V(2)*TC(2)*V(2)*TC(2))**.5
      HH=(V(1)*TC(1)*V(1)*TC(1))**.5
      GB=(V(2)*TC(2)*V(1)*TC(1))**.5
      BA=(V(1)*TC(1)*V(2)*TC(2))**.5
      VMS(KI)=(1./4.)*(XP4(KI)*V(2)+XP3(KI)*V(1)+3.*(XP4(KI)
     C*V(2)**(2./3.
     C)+XP3(KI)*V(1)**(2./3.))*(XP4(KI)*V(2)**(1./3.)+XP3(KI)
     C*V(1)**(1./3.)))
      DVMS1(KI)=(1./4.)*(V(2)-V(1)+3.*(V(2)**(2./3.)-V(1)**(2./3.
     C))*(XP4(KI)*V(2)**(1./3.)+XP3(KI)*V(1)**(1./3.))
     C+3.*(XP4(KI)*V(2)**(
     C2./3.)+XP3(KI)*V(1)**(2./3.))*(V(2)**(1./3.)-V(1)**(1./3.)))
      TCM(KI)=((XP4(KI)**2.)*AA+XP4(KI)*XP3(KI)*GB
     C+XP3(KI)*XP4(KI)*BA+(XP3(KI)**2.)*HH)/VMS(KI)
      DTCM1(KI)=(2.*XP4(KI)*AA+2.*XP3(KI)*GB-2.*XP4(KI)*GB-2.*XP3(KI)
     C*HH)/VMS(KI)-TCM(KI)*DVMS1(KI)/VMS(KI)
12    TR(KI)=(TCAL(KI))/TCM(KI)
      DTR1(KI)=-((TCAL(KI))/(TCM(KI)**2.))*DTCM1(KI)
      VRO(KI)=1.+A*((1.-TR(KI))**(1./3.))+B*((1.-TR(KI))**(2./3.))+
     CC*(1.-TR(KI))+D*(1.-TR(KI))**(4./3.)
      DVROR(KI)=-(1./3.)*A*(1.-TR(KI))**(-2./3.)-(2./3.)*B*(1.-
     CTR(KI))**(-1./3.)-C-(4./3.)*D*(1.-TR(KI))**(1./3.)
      DVR1(KI)=DVROR(KI)*DTR1(KI)
```

```
 VRD(KI)=(E+F*TR(KI)+G*TR(KI)**2.+H*TR(KI)**3.)/(TR(KI)-1.00001)
 GAA=TR(KI)**2.
 GAB=    (TR(KI)-1.00001)
 DVRD(KI)=DTR1(KI)*(F+2.*TR(KI)*G+3.*(GAA)*H)/(GAB
C   )-DTR1(KI)*VRD(KI)/(TR(KI)-1.00001)
 VSS(KI)=VMS(KI)*VRO(KI)*(1.-WM(KI)*VRD(KI))
 DVS(KI)=VMS(KI)*DVR1(KI)+VRO(KI)*DVMS1(KI)-VMS(KI)*VRO(KI)*WM(KI)
C*DVRD(KI)-VMS(KI)*VRD(KI)*VRO(KI)*DWM1(KI)-VMS(KI)*WM(KI)*VRD(KI)
C*DVR1(KI)-VRO(KI)*WM(KI)*VRD(KI)*DVMS1(KI)
 AMWT=XP4(KI)*AMW(2)+XP3(KI)*AMW(1)
 DO(KI)=AMWT/(VSS(KI)*1000.)
 DMW=AMW(2)-AMW(1)
 DDENX4(KI)=(1./1000.)*(DMW/VSS(KI)-(AMWT*DVS(KI)/(VSS(KI)**2.)))
  RETURN
 END
```

G.8 Program FITIT

```
      DIMENSION Y(50),X(50)
C      X - INDEPENDENT VARIABLE
C      Y - DEPENDENT VARAIABLE
C     NP - # OF POINTS
      READ(1,*)NP,T
      WRITE(2,*)NP,T
      DO 10 I=1,NP
      READ 999,X(I),Y(I)
999   FORMAT(2F10,6)
10    CONTINUE
      CALL FITIT(NP,X,Y)
20    CONTINUE
       STOP
       END
      SUBROUTINE FITIT(NPOINT,X1,AGAMA)
C
C      TIHS PROGRAM FITS A POLYNOMIAL OF ORDER 6
C
       DIMENSION SIGMAY(50),X1(50),AGAMA(50),A(50),DELTAY(50),YCAL(50)
       IF(NPOINT,LE,3) GO TO 99
C
       DO 2 I=1,NPOINT
       SIGMAY(I)=0,
2      CONTINUE
       NCODE=0
       MAXORD=NPOINT/2
       IF(NPOINT.LE.4) MAXORD=2
       IF(MAXORD,GT,6) MAXORD=6
       NNK=MAXORD
       DO 3 K=1,NNK
       K1=K+1
C
       CALL POLIFI(X1,AGAMA,SIGMAY,NPOINT,K1,0,A,CHISQR)
      WRITE(2,600)K
600   FORMAT(///,2X,'POLYNOMIAL FITTED IS OF THE DEGREE =',I3)
      WRITE(2,100)
100   FORMAT(///,8X,'YEXP',8X,'YCAL',13X,'DY')
C
       ERROR=0,0
       DO 4 J=1,NPOINT
       SUM=A(1)
       DO 5 I=2,K1
       SUM=SUM+A(I)*X1(J)**(I-1)
5      CONTINUE
       YCAL(J)=SUM
      DELTAY(J)=((YCAL(J)-AGAMA(J))/AGAMA(J))*100.
      WRITE(2,200)AGAMA(J),YCAL(J),DELTAY(J)
200   FORMAT(/,5X,3G12.5)
4      ERROR=ERROR+DELTAY(J)**2
       ERROR=ERROR/NPOINT
```

```
      WRITE(2,500)
500   FORMAT(///,5X,'POLYNOMIAL CONSTANTS')
      DO 20 I=1,K1
      WRITE(2,250)I,A(I)
250   FORMAT(//,5X,'A(',I2,')=',G12.5)
20    CONTINUE
      WRITE(2,300)ERROR
300   FORMAT(///,5X,'SUM OF DEELTAY SQUARED DIVIDED BY THE'
     %' # OF POINTS =',G12.5)
C
3       CONTINUE
C
99      RETURN
        END
        SUBROUTINE POLIFI(X,Y,SIGMAY,NPTS,NTERMS,MODE,A,CHISQR)
C
C       EXTRACTED FROM! BEVINGTON,P. R., 'DATA REDUCTION AND
C       ERROR ANALYSIS FOR THE PHYSICAL SCIENCES', MCGRAW HILL,1969
C
C       SUBROUTINE POLIFIT PURPOSE
C
C       MAKE A LEAST-SQUARES FIT TO DATA WITH A POLYNOMIAL CURVE
C       Y = A(1) + A(2)*X + A(3)*X**2 + A(4)*X**3 + ...
C
C       DESCRIPTION OF PARAMETERS
C       X    -ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLE
C       Y    -ARRAY OF DATA POINTS FOR DEPENDENT VARIABLE
C       SIGMAY - ARRAY OF STANDARD DEVIATIONS FOR Y DATA POINTS
C       NPTS    -NUMBER OF PAIRS OF DATA POINTS
C       NTERMS -NUMBER OF COEFFICIENTS(DEGREE OF POLYNOMIAL + 1)
C       MODE  -DETERMINANTS METHOD OF WEIGHTING LEAST-SQUARES FIT
C                +1 (INSTRUMENTAL) WEIGHT(I)=1./SIGMAY(I)**2
C                 0 (NO WEIGHTING) WEIGHT =1.
C               -1 (STATISTICAL) WEIGHT(I) = 1./Y(I)
C       A   - ARRAY OF COEFFICIENTS OF POLYNOMIAL
C       CHISQR - REDUCED CHI SQUARE FOR FIT
C
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C         DELTERM (ARRAY,NORDER)
C         EVALUATES THE DETERMINANTS OF A SYMMETRIC TWO-DIMENSIONAL
C         MATRIX OF NORDER
C
        DOUBLE PRECISION SUMX,SUMY,XTERM,YTERM,ARRAY,CHISQ
        DIMENSION X(50), Y(50), SIGMAY(50), A(50)
        DIMENSION SUMX(50),SUMY(50),ARRAY(8,8)
C
C       ACCUMULATE WEIGHTING SUMS
C
11      NMAX = 2*NTERMS - 1
        DO 13 N=1, NMAX
13      SUMX(N) = 0.
        DO 15 J=1, NTERMS
```

```
15      SUMY(J)= 0.
        CHISQ =0.
21      DO 50 I=1, NPTS
        XI=X(I)
        YI= Y(I)
31      IF (MODE) 32,37,39
32      IF(YI) 35,37,33
33      WEIGHT = 1./YI
        GO TO 41
35      WEIGHT = 1,/(-YI)
        GO TO 41
37      WEIGHT = 1.
        GO TO 41
39      WEIGHT = 1. / SIGMAY(I)**2
41      XTERM=WEIGHT
        DO 44 N=1,NMAX
        SUMX(N) = SUMX(N) + XTERM
44      XTERM = XTERM * XI
45      YTERM = WEIGHT*YI
        DO 48 N=1, NTERMS
        SUMY(N)=SUMY(N) + YTERM
48      YTERM = YTERM *XI
49      CHISQ = CHISQ + WEIGHT*YI**2
50      CONTINUE
C
C       CONSTRUCT MATRICES AND CALCULATE COEFFICIENTS
C
51      DO 54 J=1, NTERMS
        DO 54 K=1, NTERMS
        N = J + K - 1
54      ARRAY(J,K) = SUMX(N)
        DELTA = DETERM (ARRAY,NTERMS)
        IF(DELTA) 61,57,61
57      CHISQR = 0.
        DO 59 J=1, NTERMS
59      A(J) = 0.
        GO TO 80
61      DO 70 L=1, NTERMS
62      DO 66 J=1, NTERMS
        DO 65 K=1,NTERMS
        N = J+K-1
65      ARRAY(J,K)=SUMX(N)
66      ARRAY(J,L)=SUMY(J)     .
70      A(L)=DETERM(ARRAY,NTERMS)/DELTA
C
C       CALCULATES CHI SQUARE
C
71      DO 75 J=1, NTERMS
        CHISQ = CHISQ - 2,*A(J)*SUMY(J)
        DO 75 K=1, NTERMS
        N=J+K-1
75      CHISQ=CHISQ+A(J)*A(K)*SUMX(N)
```

```
76      FREE=NPTS-NTERMS
77      CHISQR=CHISQ/FREE
       WRITE(2,100)CHISQR
100    FORMAT(///,5X,'CHISQR =',G12.5/////)
80      RETURN
        END
        FUNCTION DETERM(ARRAY,NORDER)
C
C       EXTRACTED FROM: BEVINGTON,P. R., 'DATA REDUCTION AND
C       ERROR ANALYSIS FOR THE PHYSICAL SCIEINCES',MCGRAW HILL,1969
C
C       FUNCTION DETERM
C
C       PURPOSE
C       CALCULATES THE DETERMINANT OF A SQUARE MATRIX
C
C       USAGE
C       DET = DETERM(ARRAY,NORDER)
C
C       DESCRIPTION OF PARAMETERS
C         ARRAY  -MATRIX
C         NORDER -ORDER OF DETERMINANT (DEGREE OF MATRIX)
C
C       SUBROUTINE AND FUNCTION SUBPROGRAMS REQUIRED
C       NONE
C
C       COMMENTS
C       THIS SUBPROGRAM DESTROYS THE INPUT MATRIX ARRAY
C
        DOUBLE PRECISION ARRAY,SAVE
        DIMENSION ARRAY(8,8)
10      DETERM =1.
11      DO 50 K=1, NORDER
C
C        INTERCHANGE COLUMNS IF DIAGROL ELEMENT IS ZERO
C
        IF(ARRAY(K,K)) 41,21,41
21      DO 23 J=K, NORDER
        IF(ARRAY(K,J)) 31,23,31
23      CONTINUE
        DETERM = 0.
        GO TO 60
31      DO 34 I=K, NRODER
        SAVE = ARRAY(I,J)
        ARRAY(I,J)=ARRAY(I,K)
34      ARRAY(I,K)=SAVE
        DETERM = -DETERM
C
C       SUBTRACT ROW K FROM LOWER ROWS TO GET DIAGONAL MATRIX
C
41      DETERM = DETERM*ARRAY(K,K)
```

```
       IF(K - NORDER) 43,50,50
43     K1=K+1
       DO 46 I=K1, NORDER
       DO 46 J=K1,NORDER
46     ARRAY(I,J)=ARRAY(I,J)-ARRAY(I,K)*ARRAY(K,J)/ARRAY(K,K)
50     CONTINUE
60     RETURN
       END
```

NOMENCLATURE

A = Antoine constant. equation (A-1)
A_{mn} = UNIQUAC binary interaction parameter. equation (3-27)
A_{wk} = van der Waals group surface area
$A\pm$ = parameter of equations (5-5) and (6-1).
A = see equation (3-13)
a = ion-size parameter of equation (3-8). calculated using equation (3-17) for mixed solvents.
a_i = solvent activity. equation (2-1)
B = virial coefficient. See Appendix A.
B = Antoine constant. equation (A-1)
b = see equation (3-14)
b_o = equivalent hard-sphere volume of molecules.
C = Antoine constant. equation (A-1)
c = total ionic concentration. (ions/cc). equation (D-1)
$\bar{c}$ = molar concentration. (g - mol/liter)
D = dielectric constant of pure or mixed solvent on a salt-free basis.
d = density of mixed solvent on a salt-free basis.
d_o = density of pure solvent
e = electronic charge, 4.8029×10^{-10} esu
F = minimization function given by equations (5-7) and (5-20)
f = fugacity
$f\pm$ = rational activity coefficient
G^E = excess Gibbs free energy
g^E = excess Gibbs free energy per mole
$\bar{g}_i^E$ = partial molar excess Gibbs free energy
ΔH = see equation (A-23)
h_{o+K} = solvation number at infinite dilution of the positive ion in a single solvent. See Table 5.8
h_{o-K} = solvation number at infinite dilution of the negative ion in a single solvent. See Table 5.8
h_{+k} = solvation number of the positive ion as a function of solvent mole-fraction. (See equation (3-33)) for binary electrolytic solutions and equations (6-8) and (6-11a) and (6-11b) for ternary electrolytic solutions.
h_{-k} = solvation number of the negative ion as a function of solvent mole-fraction. Set equal to zero for binary and ternary electrolytic solutions.

I = ionic strength. equation (3-12)

k = Boltzmann constant, 1.38045 x 10^{-16} erg/deg

L = see equation (D-2)

M.W. = molecular weight of mixed solvent on a salt-free basis. equation (3-9)

m = molality (g - mol/kg solvent)

N = Avogadro's number, 6.0232 x 10^{23} mole^{-1}

n = number of moles

P = total vapor pressure, mm Hg

P_i^s = pure-component vapor pressure

Q_k = group area parameter. equation (3-20)

q = pure-component area parameter

R = gas constant, 1.98726 cal/deg mole or 82.0597 cc atm/deg mole

R_k = group volume parameter, equation (3-36)

R' = mean radius of gyration

r = pure-component volume parameter, equation (3-35)

r_c, r° = crystallographic radii. Table 5.4

r = intermolecular distance

T = temperature, °K or °C

T_R = reduced temperature

u_{mn} = UNIQUAC binary interaction parameter, equation (3-27)

V = molar volume of the salt-free mixed solvent equation (A-3)

V_s = saturated liquid volume. equation (B-1)

V_{wk} = van der Waals group surface volume. equation (3-39)

$\bar{V}_i$ = partial molar volume of component i

V^* = characteristic volume. equation (B-1)

v = molar volume of pure solvent

$v_k^{(i)}$ = number of groups of type k in molecule i.

w = weight of salt or solvent in equation (E-1)

w = nonpolar acentric factor

w = parameter in equation (D-1)

w_{SRK} = acentric factor determined from the Soave equation of state.

x = liquid-phase mole fraction equations (3-24) - (3-26)

x° = liquid-phase mole fraction on a salt-free basis. equation (3-10)

x' = liquid-phase mole fraction on a solvated basis. equations (3-30) - (3-32)

y = vapor-phase mole fraction

Z = compressability factor. equation (A-3)

z = ionic charge

GREEK LETTERS

γ_i = solvent activity coefficient

$\gamma_\pm$ = mean activity coefficient of the salt

Δ = indicates difference between an experimental and a calculated value

ϵ = energy parameter for polar pairs of molecules. equation (A-10)

η = association parameter. Table (A-2)

Θ_k = area fraction of group k. equation (3-23)

κ = parameter in equation (D-1)

μ = dipole moment. Table (A-2)

μ_i° = chemical potential of the standard state of component i

ν = number of ions

π = 3.14159

σ = molecular-size parameter for non-polar pairs. equation (A-15)

σ' = molecular-size parameter for pure polar and associating pairs. equation (A-17)

Φ = osmotic coefficient. equation (4-2)

Φ_i' = segment fraction of component i. equation (3-29)

$\hat{\Phi}_i$ = fugacity coefficient of component i. equation (A-2)

ψ_{mn} = UNIQUAC binary interaction parameter. equation (3-27)

SUBSCRIPTS

1 = positive ion

2 = negative ion

3 = solvent 1

4 = solvent 2

$+$ = positive ion

$-$ = negative ion

c = critical property

c = molar basis

cal = calculated value

cm = indicates pseudocritical mixing rule used.

E = excess property indicated

exp = experimental value
i = component i
ij = interaction between molecules i and j
j = component j
k = component k or group k
m = molal basis
m = group m
mix = mixture
n = group n
s = salt
T = total

SUPERSCRIPTS

$^{\circ}$ = pure component or standard state
$'$ = solvated basis
$*'$ = reduced property
∞ = infinite dilution
L = liquid phase
s = saturated
v = vapor phase

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