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CONTAINING AN ELECTROLYTE

Lehigh University

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Perturbed-Hard-Sphere
Equation of State for
Solutions Containing an Electrolyte

by

Thomas Wesley Copeman

A Dissertation
Presented to the Graduate Committee
of Lehigh University
in Candidacy for the Degree of
Doctor of Philosophy
in
Chemical Engineering

Lehigh University
1986

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10 APRIL 1986
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Abstract

An equation of state was developed for mixtures containing polar components and a non-volatile electrolyte. The equation consists of hard-sphere, electrostatic, and attractive contributions to the Helmholtz free energy. An explicit mean spherical approximation (MSA) screening factor was derived for mixtures of electrolytes with unequal size ions using the asymptotic behavior of the ionic pair correlation function in the limit of small ion sizes. This development is based on the MSA theory for electrolytes, rather than on the more typical approach of extending the Debye Huckel theory. The explicit asymptotic MSA screening factor predictions were compared to the rigorous MSA screening factor predictions. To improve predictions for ion sizes comparable to that of water, an empirical correction was developed for the explicit MSA. This relation was used to obtain an expression for electrostatic internal energy and hence electrostatic Helmholtz free energy.

Mean ionic activity coefficients of twelve (non-volatile) salts in water were correlated using the equation of state. The salts chosen for the study are representative 1-1, 2-1 and 1-2 salts, exhibiting a wide range of nonideality in water. The binary interaction parameters obtained from regressing the data were shown to decrease qualitatively with increasing cation-anion average hard-sphere

diameter. For mixtures without electrolytes, the equation of state resembles a recent equation developed by Ludecke and Prausnitz and can describe phase equilibrium for a variety of non-ideal mixtures. Liquid-liquid equilibria of aniline-water mixtures with sodium chloride and with ammonium chloride were correlated with the equation of state. For both cases, the salting out of aniline from the aqueous phase was described with one (near unity) interaction parameter. In addition, vapor-liquid equilibria of methanol-water-sodium bromide mixtures were correlated with the equation of state.

Introduction

Engineering models used to describe phase equilibrium can be divided into two broad categories: equations of state and activity coefficient models. Equations of state have been successfully applied to mixtures of nonpolar and slightly polar compounds over a wide range of temperatures and pressures. These models have been used most extensively by the gas processing industry (for an example, see Chappelaar et al., 1977).

Conversely the mathematical flexibility of activity coefficient models has conventionally been considered necessary to describe mixtures which exhibit high nonideality in the liquid phase. These models have been used extensively by the chemical and polymer industries (for an example, see Miller and Geist, 1982). The activity coefficient approach is adequate only at low reduced temperatures where the liquid phase is incompressible, and the use of different models for the vapor and liquid phases precludes a correct description of mixture critical points.

The equation of state approach does not suffer inherently from these limitations and provides consistent phase-equilibrium, enthalpy, entropy and density predictions. The extension of equations of state to describe higher liquid-phase nonideality is an active area of research, (Copeman and Mathias, 1985).

The mixing rules proposed by Vidal (1978), Huron and Vidal (1979), Heyen (1981) and Won (1981) demonstrate that complex mixtures with polar components can be correlated with equations of state in the same empirical manner as activity coefficient models. However, these mixing rules do not predict a second virial coefficient with quadratic dependence on mole fraction. Consequently, density-dependent mixing rules have been proposed recently. The density-dependent mixing rules of Mathias and Copeman (1983) and Ludecke and Prausnitz (1985) have been used to correlate both vapor-liquid and liquid-liquid equilibrium of various polar systems.

Very little attention has been given to extending equations of state to mixtures containing polar components and electrolytes. With few exceptions, engineering models for electrolyte mixtures have been based on the activity coefficient approach, with the Debye Huckel (1923) theory for electrostatic interactions central to the development.

In this study, the equation-of-state approach will be applied to mixtures containing a non-volatile, fully dissociated electrolyte. The equation of state will consist of hard-sphere, electrostatic, and attractive contributions to the Helmholtz energy. The electrostatic contribution will be based on the mean spherical approximation theory (Blum, 1975) which takes sizes of the ions into account in a physically appealing manner, rather than on the usual Debye-Huckel theory.

1. Review of Electrolyte Phase Equilibrium Models

Activity coefficients, osmotic coefficients and the various partial molar properties of aqueous electrolytes at low concentrations have been modelled by numerous extensions of the Debye-Huckel (1923) theory. Debye-Huckel is an electrostatic theory, originally derived from the work (or free energy) required to charge fully dissociated ions in the solution to their full electrostatic potential. The derivation, e.g., presented in Moore (1972), begins by relating the electrostatic potential to the charge density or number of ions (each multiplied by its charge) per unit volume. The Poisson differential equation is written for a spherically symmetric distribution of charge.

$$\nabla^2 \phi_i(r) = \frac{4\pi}{D} \rho_c \quad (1.1)$$

where ∇^2 = the Laplacian operator

ρ_c = charge density

$\phi_i(r)$ = total potential energy about central ion i

D = dielectric constant of the solution

The charge density is related to the potential of mean force (McQuarrie, 1976) by

$$\rho_c = \sum_j x_j Z_j e \exp \left(- \frac{\phi_i(r) Z_j e}{kT} \right) \quad (1.2)$$

where Z_j = charge number of species j

x_j = mole fraction of species j

e = elementary charge

Equations (1.1) and (1.2) are combined, the Boltzmann factor is expanded and the quadratic and higher terms are neglected to give

$$\nabla^2 \Phi_i(r) = \frac{4\pi}{D} \left(\sum_j x_j Z_j e - \frac{1}{kT} \sum_j x_j Z_j^2 e^2 \Phi_i(r) \right) \quad (1.3)$$

The term $\sum x_j Z_j$ is zero by bulk electroneutrality. Equation (1.3) is then integrated and boundary conditions are evaluated at $r = a$ (ionic diameter, or distance of closest approach) and $r = \infty$. The resulting equation for the total potential around ion i is

$$\Phi_i = eZ_i \text{EXP}(-K(r-a))/(Dr(1+Ka)) \quad (1.4)$$

for $r > a$

$$\text{where } K = \left(\frac{4\pi e^2}{DkT} \sum_j x_j Z_j^2 \right)^{1/2}$$

Equation (1.4) can then be substituted into an expression for the work to charge an ion from zero charge to the full value in the ionic atmosphere. The resulting expression for the mean-ionic activity coefficient is

$$\ln \gamma^\pm = -|Z_+ Z_-| \frac{e^2}{2DkT} \left(\frac{K}{1+Ka} \right) \quad (1.5)$$

The assumptions used in deriving the Debye-Huckel model must be noted. First, the potential of mean force used to calculate the charge density is given only in terms of the electrostatic potential. Other forces, attractive and repulsive, are not considered. Also, all ions are assumed to have a fixed diameter a in

a dielectric medium with no free-volume effects on the macroscopic electrostatic properties. The exponential was expanded and linearized. As stated by McQuarrie (1976), the Debye-Huckel theory is strictly valid only at low concentrations and in the limit of $Ka \rightarrow 0$. Further, deviations between the Debye-Huckel model and experimental data are expected for ion concentrations greater than about 0.01 mole/liter, or about 0.0004 mole fraction of ions in solution. For non-negligible concentrations, the ion size (a) should be generally much smaller than $1 \text{ \AA}$ for Ka to be negligibly small. In practical application of the theory, the distance-of-closest-approach parameter, a , can be obtained empirically by correlating experimental data (Butler, 1964).

The most popular extensions of the Debye-Huckel theory are based on virial expansions (see Guggenheim, 1935, Bromley, 1972, and Pitzer, 1973). At first thought, a virial expansion for liquid electrolyte mixtures using the coulombic potential would appear to be impractical. The second virial coefficient is given by

$$B_{1,1} = - 4\pi \int_0^{\infty} (\exp - (Z_+ Z_- e^2 / (DrkT)) - 1) r^2 dr \quad (1.6)$$

This integral is infinite because the electrostatic potential is long range, however Mayer (1950) combined the infinite portions of the virial coefficients so that they would cancel. The Debye-Huckel expression was shown to arise from a combination of "cycle-graph" terms, Mayer (1950).

Pitzer (1973) developed the most popular model for electrolyte mixtures by postulating

$$G^E/RT = G_{DH}^E/RT + \sum_i \sum_j \lambda_{ij} (I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \quad (1.7)$$

where: m = molality

G^E = excess Gibbs free energy

The short-range interparticle effects are described by the virial coefficients λ_{ij} and μ_{ijk} and the long-range electrostatic effects are described by a type of Debye-Huckel contribution. Pitzer derived the Debye-Huckel contribution from the pressure equation of statistical mechanics and arrived at a form similar to the conventional charging procedure. The electrostatic contribution to the mean-ionic activity coefficients is

$$\ln \gamma_{\pm} = |Z_+ Z_-| A (I^{1/2}/(1 + b I^{1/2}) + 2/b \ln (1 + b I^{1/2})) \quad (1.8)$$

where: I = ionic strength = $(1/2) \sum m_i Z_i^2$

A = a Debye-Huckel constant

b = a Debye-Huckel constant

Pitzer claims that the electrostatic effects cause the virial coefficients to depend on ionic strength in addition to the temperature. Various applications of the virial expansion method were made without the allowance for ionic strength effects on the virial coefficients (i.e., Guggenheim (1935)). Pitzer developed

empirical ionic-strength functions for the second virial coefficient. Values of Pitzer's virial coefficients have been correlated for about 300 electrolytes at ambient temperature by Pitzer and Mayorga (1973). As stated by Maurer (1983), Pitzer's model is currently regarded as the most generally successful model for engineering calculations.

Phase equilibrium correlations were developed by Edwards et al., (1978) and Buetier and Renon (1978) for weak and volatile electrolytes using the Pitzer model for ionic activity coefficients. Phase equilibrium correlations were developed by Deshmukh and Mather (1981) and Copeman and Stein (1983) for an aqueous monoethanolamine - acid gas system using the Guggenheim (1935) model for ionic activity coefficients.

The virial expansion method does unfortunately have a major limitation (like vapor phase virial expansions). The ionic-liquid virial expansion is difficult to apply at conditions where higher-body interactions dominate the phase behavior. The Pitzer model is applicable to electrolyte mixtures up to ionic strengths of about six molal.

Cruz and Renon (1978) and Chen et al. (1982) replaced the virial expansion terms with local-composition activity-coefficient models. Two advantages of this approach are claimed: 1) no restrictions on

the maximum ionic strength and 2) flexibility of the local-composition model to describe liquid mixtures when the electrolytes are absent. These models can be summarized as

$$\frac{E}{G} = \frac{E}{G_{\text{long-range}}} + \frac{E}{G_{\text{local-composition}}} \quad (1.9)$$

The "long-range" electrostatic contribution is described by the Debye-Huckel-Pitzer expression in the Chen (1982) model and by the Debye-Huckel-Pitzer-Born expression in the Cruz (1978) model.

Another, less publicized, model of this type was proposed by Hala (1969) who separated long-range and short-range forces similar to equation (1.9). Hala (1969) assumed the long-range forces are given by an empirical expression resembling a Debye-Huckel term and the short-range forces are given by a Margules type of term.

A major deficiency of Debye-Huckel models is the neglect of excluded volume effects (Blum, 1980). Waisman and Lebowitz (1970, 1972) first derived a "Mean Spherical Approximation" (MSA) model which accounts for excluded volume effects and simplifies to the Debye-Huckel model under appropriate conditions. The Waisman and Lebowitz model assumes all species have the same diameter. Blum (1975) extended their derivations to mixtures of species with different sizes. There are various forms of the MSA model with varying degrees of complexity (Blum, 1980).

Planche and Renon (1981) developed a mean-spherical electrolyte model based on Blum's mathematical approach. In Planche and Renon's work, spherical species, of different sizes, are considered to interact by coulombic long-range forces and attractive short-range (Dirac function) forces. This model is highly complex and requires a large number of parameters. Ball, et al. (1985) have simplified the Planche and Renon model by neglecting several small terms. Osmotic pressure of several aqueous salt systems has been correlated up to approximately 6 molal.

To correlate the effect of electrolytes on vapor-liquid equilibrium, Furter (1975), Rousseau and Boone (1978), and Schmidt and Vogelpohl (1982) use "pseudo-binary" approaches. Ternary liquid mixtures were reduced to psuedo-binary mixtures, for example, using a salt-free basis. These approaches lack a realistic physical basis and are ambiguous in application to multicomponent non-electrolyte and electrolyte mixtures in general.

Shoor and Gubbins (1969) developed a model for prediction of non-polar gas solubilities in aqueous electrolyte mixtures based on scaled-particle theory. The model can predict gas solubilities well, however the solubility is extremely sensitive to the molecular diameter. Also, the model is not applicable to partial molar properties of the electrolytes and water.

The chemical theory of solutions provides a useful method for description of highly non-ideal systems. A general formulation of chemical theory, Copeman and Stein (1982), was applied to the aqueous monoethanolamine-acid gas system by Copeman and Stein (1983). The effect of the partially-dissociating acid-gas and monoethanolamine chemical equilibria on apparent unsymmetrical activity coefficients was illustrated.

If the electrostatic interactions in aqueous solutions were to be postulated as chemical equilibria, the shape of the "apparent" activity coefficient curves could not be accurately described with a simple one-reaction model. The model could be extended to include more reactions with different stoichiometric coefficients, however the complexity increases dramatically (see Huemer and Moser, 1981). The behavior of strong electrolytes is too complex to be described easily by a simple chemical-theory model, and the predictive capabilities of chemical-theory models for the nonidealities of strong electrolytes are very limited. Chemical theory is best applied to the chemical equilibrium of partially dissociated species in solution.

2. Perturbation Theory (General)

Perturbation theories have contributed significantly to the understanding and modelling of fluid-phase behavior, Gubbins (1973). These theories enable the properties of real systems to be predicted from the known properties of a chosen reference system.

There are various ways to expand the properties of the real system about a chosen reference system. The most widely used and highly successful perturbation method (Eyring et al, 1982) was derived by Barker and Henderson (1967). In their approach, the pair potential is separated into two portions:

$$\Phi_{ij}(r) = (\Phi_{ij})_0(r) + \lambda(\Phi_{ij})_1(r) \quad (2.1)$$

where

$(\Phi_{ij})_0(r)$ = pair-potential energy of reference system

$(\Phi_{ij})_1(r)$ = pair-potential energy of perturbation

λ = a parameter which can vary from zero to unity.

The configurational Helmholtz free energy is expanded in a power series in λ to give:

$$A = A_0 + \lambda(\partial A/\partial \lambda)_{\lambda=0} + \lambda^2/2 (\partial^2 A/\partial \lambda^2)_{\lambda=0} + \dots \quad (2.2)$$

where A_0 = the configurational Helmholtz energy of the reference fluid with potential $(\Phi_{ij})_0$

For a pairwise potential:

$$\beta A = \ln \int \text{EXP}(-\beta \sum_{i < j} \Phi_{ij}(r)) d\bar{r}, \dots d\bar{r}_N \quad (2.3)$$

where $\beta = 1/kT$

$\bar{r}$ = vector distance r

The integral in equation (2.3) is the configurational integral.

Substituting equation (2.1) into equation (2.3) yields:

$$\beta A = \ln \int \text{EXP}(-\beta \sum_{i < j} (\Phi_{ij})_0 + \lambda (\Phi_{ij})_1) d\bar{r}, \dots d\bar{r}_N \quad (2.4)$$

Differentiating equation (2.4) with respect to λ (Gubbins, 1973) gives

$$(\partial A / \partial \lambda)_{\lambda=0} = 2\pi\rho^2 V \sum \sum x_i x_j \int_0^\infty (\Phi_{ij})_1(r) (g_{ij})_0(r) r^2 dr \quad (2.5)$$

where

V = total system volume

$(g_{ij})_0(r)$ = radial distribution function of the reference system

Therefore, equation (2.2) becomes (with $\lambda=1$ to recover the real system):

$$A = A_0 + 2\pi\rho^2 V \sum \sum x_i x_j \int_0^\infty (\Phi_{ij})_1(r) (g_{ij})_0(r) r^2 dr \quad (2.6)$$

The salient feature of the second term in equation (2.6) is that the radial distribution function of the reference system is used to calculate the thermodynamic properties. Many common equations of state can be derived from equation (2.6) (see McQuarrie, 1976 for a derivation of the van der Waal's equation of state) by making reasonable assumptions about the radial distribution functions of the reference system.

The second-order term in the perturbation expansion is highly complex (Donohue and Prausnitz, 1977), involving three and four body radial distribution functions. Henderson and Barker (1971) obtained a tractable expression.

The second-order term is:

$$\begin{aligned}
 \beta A_2 = & - \pi \rho \sum_i \sum_j x_i x_j \int \phi_{ij}^2(r) (g_{ij})_0(r) r^2 dr \\
 & - 2\pi \rho^2 \sum_i \sum_j \sum_k x_i x_j x_k \int \phi_{ij}(r_{12}) \phi_{ik}(r_{23}) \\
 & ((g_{ij})_0(r_{12})(g_{jk})_0(r_{23})(g_{ik})_0(r_{13}) - (g_{ij})_0(r_{12}) \\
 & (g_{jk})_0(r_{23})) r_{12}^2 dr_{12} (2\pi r_{31} r_{32} / (r_{12}) dr_{31} dr_{32}) \\
 & - (\pi/2) \rho^3 \sum_i \sum_j \sum_k \sum_l x_i x_j x_k x_l \int \Omega dr^4
 \end{aligned} \tag{2.7}$$

where the integral in the last term is a complicated function of radial distribution functions and pair potentials integrated over a complex $\underline{r}$ vector. As stated by Donohue and Prausnitz (1977), the two higher-order terms in equation (2.7) have little engineering utility, as they would be extremely difficult to evaluate. However, perturbation theory is useful as a guide in the development of both pure fluid and mixture equations of state for engineering calculations (Henderson, 1979).

3. Derivation of the Primitive Mean-Spherical-Approximation Model for Non-Equal Diameters

The Mean-Spherical-Approximation (MSA) model was first solved analytically by Waisman and Lebowitz (1970, 1972) for the primitive case with equal-size ions. (The "primitive" case is defined as charged hard sphere ions imbedded in a continuum dielectric.) The solution of the MSA for the primitive case with arbitrary-sized ions was obtained by Blum (1975) using Baxter's factorization (1970). The MSA model provides a "screened" radial distribution function for inclusion into the energy equation:

$$U = 2\pi\rho^2 \sum_i \sum_j x_i x_j \int_0^\infty \Phi_{ij} g_{ij}(r) r_{ij}^2 dr_{ij} \quad (3.1)$$

where

- U = configurational internal energy/per unit volume
- ρ = density
- Φ_{ij} = pair potential energy
- $g_{ij}(r)$ = radial distribution function
- r = radial distance from the center of molecule i to the center of molecule j

For the coulombic potential:

$$\Phi_{ij} = \frac{e^2 Z_i Z_j}{Dr_{ij}} \quad (3.2)$$

- e = elementary charge
- Z = charge number
- D = dielectric constant of the solution
- r = center to center molecule distance

we have

$$U = (2\pi\rho^2 e^2 / D) \sum_i \sum_j x_i x_j Z_i Z_j \int_0^\infty g_{ij}(r) r_{ij} dr_{ij} \quad (3.3)$$

The goal is to obtain an analytical expression for the "screened" g_{ij} which reflects the collective effect of the ions on the solution properties. The derivation of the MSA begins with the following definitions of the total and direct correlation functions:

$$h_{ij}(r) = g_{ij}(r) - 1 \quad (3.4)$$

where

$$h_{ij}(r) = \text{total correlation function}$$

and

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \sum_k \rho_k \int h_{ik}(r_{23}) c_{jk}(r_{13}) d\bar{r}_3 \quad (3.5)$$

where

$$c_{ij}(r) = \text{direct correlation function}$$

$$d\bar{r}_3 = \text{differential volume element}$$

Equation 3.5 is the Ornstein-Zernike (1914) equation which describes the total correlation between molecules 1 and 2 with a direct effect of molecule 1 on molecule 2, and an indirect effect through molecule 3. The first term on the right side of equation 3.5 is the direct effect and the second term is the indirect effect.

The basic assumptions in the MSA model are:

$$h_{ij}(r) = -1 \text{ for } r < \sigma_{ij} \quad (3.6)$$

and

$$c_{ij}(r) = -\beta\phi_{ij} \text{ for } r > \sigma_{ij} \quad (3.7)$$

Equation 3.6 is exact for a potential with hard-sphere repulsion.

Equation 3.7 is derived from the asymptotic behavior of $c_{ij}(r)$ at large r from the Hypernetted Chain relation. The Hypernetted Chain relation is (see Reed and Gubbins, 1973):

$$c_{ij}(r) = g_{ij}(r) - 1 - \ln g_{ij}(r) - \beta\phi_{ij} \quad (3.8)$$

As r gets large, $g_{ij}(r)$ approaches unity. The asymptotic approximation is reasonable since the energy equation (equation 3.1), and hence thermodynamic properties, involve the integral of $g_{ij}(r)$ (or analogously $h_{ij}(r)$) from zero to infinity.

The basic procedure will be to transform the Ornstein-Zernike equation into Fourier space and factor the equation into functions which are analytic in selected domains of the complex plane. The inverse Fourier transform will then provide the desired relations for substitution into equation (3.3) for g_{ij} .

The three dimensional spherical Fourier transform of a function $\Psi(r)$ is given by

$$\Psi(k) = \int d\vec{r} \text{EXP}(ik \cdot \vec{r}) \Psi(r) \quad (3.9)$$

Performing integrations over the angles (Eyring, et al., 1982) yields:

$$\Psi(k) = 4\pi \int_0^{\infty} dr (r/k) \sin(kr) \Psi(r) \quad (3.10)$$

The Fourier transform of $h_{ij}(r)$ and $c_{ij}(r)$ are defined by:

$$C_{ij}(k) = 4\pi(\rho_i \rho_j)^{1/2} \int_0^{\infty} dr_{ij} (r_{ij}/k) \sin(kr_{ij}) c_{ij}(r) \quad (3.11)$$

and

$$H_{ij}(k) = 4\pi(\rho_i \rho_j)^{1/2} \int_0^{\infty} dr_{ij} (r_{ij}/k) \sin(kr_{ij}) h_{ij}(r) \quad (3.12)$$

Multiplying the Ornstein-Zernike equation by $4\pi(\rho_i \rho_j)^{1/2}$
 $(r_{ij}/k) \sin(kr_{ij})$ and integrating over dr_{ij} (in bipolar
 coordinates) yields

$$H_{ij}(k) - C_{ij}(k) = 4\pi(\rho_i \rho_j)^{1/2} (r_{ij}/k) \sin(kr_{ij}) dr_{ij} \\ 2\pi \left[\sum \rho_k \int_0^{\infty} \int_0^{\infty} (r_{ik} r_{kj} / r_{ij}) dr_{ik} dr_{kj} h_{ik}(r) c_{kj}(r) \right] \quad (3.13)$$

Reversing the order of integration yields:

$$H_{ij}(k) - C_{ij}(k) = 2\pi \sum \rho_k \int_0^{\infty} r_{ik} h_{ik}(r) dr_{ik} \int_0^{\infty} r_{kj} c_{kj}(r) dr_{kj} \\ \left[\int \frac{(r_{ik} + r_{kj})}{|r_{ik} - r_{kj}|} dr_{ij} 4\pi(\rho_i \rho_j)^{1/2} \sin(kr_{ij}) / k \right] \quad (3.14)$$

The integral over dr_{ij} can be performed easily:

$$\int_{|r_{ik} - r_{kj}|}^{(r_{ik} + r_{kj})} dr_{ij} \sin(kr_{ij})/k = k^{-2}(\cos(k(r_{ik} - r_{kj})) - \cos(k(r_{ik} + r_{kj}))) \quad (3.15)$$

where

$$k^{-2}(\cos(k(r_{ik} - r_{kj})) - \cos(k(r_{ik} + r_{kj}))) = 2k^{-2}\sin(kr_{ik})\sin(kr_{kj}) \quad (3.16)$$

The Fourier-transformed Ornstein-Zernike equation becomes

$$H_{ij}(k) - C_{ij}(k) = 16\pi^2(\rho_i\rho_j)^{1/2}\Sigma\rho_k \int_0^\infty (r_{ik}/k)\sin(kr_{ik})h_{ik}(r)dr_{ik} \\ \int_0^\infty (r_{kj}/k)\sin(kr_{kj})c_{kj}(r)dr_{kj} \quad (3.17)$$

Substituting equations 3.11 and 3.12 into equation 3.17:

$$H_{ij}(k) - C_{ij}(k) = \Sigma H_{ik}(k) C_{kj}(k) \quad (3.18)$$

An equivalent form incorporating Kronecker deltas ($\delta_{ij} = 1$ for $i = j$ and $= 0$ for $i \neq j$) is derived as follows from equation 3.18:

$$\Sigma H_{ik}(k)\delta_{kj} - \Sigma C_{kj}(k)\delta_{ik} + \delta_{ij} - \Sigma H_{ik}(k)C_{kj}(k) = \delta_{ij} \quad (3.19)$$

or

$$\Sigma (H_{ik}(k)\delta_{kj} - C_{kj}(k)\delta_{ik} + \delta_{ik}\delta_{kj} - H_{ik}(k)C_{kj}(k)) = \delta_{ij} \quad (3.20)$$

or

$$\Sigma (H_{ik}(k) + \delta_{ik}) (\delta_{kj} - C_{kj}(k)) = \delta_{ij} \quad (3.21)$$

Equation 3.21 is the starting point for application of Baxter's factorization. The Fourier transformed total-correlation function must be finite and therefore $\delta_{kj} - C_{kj}(k)$ must be non-singular.

Separating $c_{kj}(r)$ into short (hard sphere) and long-range contributions:

$$c_{kj}(r) = c_{kj}^0(r) - \frac{\beta e^2 Z_k Z_j}{Dr_{kj}} \quad (3.22)$$

and adding a factor on the long-range term to ensure a non-singular transformed equation; equation (3.22) becomes

$$c_{kj}(r) = c_{kj}^0(r) - \lim_{\tau \rightarrow 0} \frac{\beta e^2 Z_k Z_j}{Dr_{kj}} \text{EXP}(-\tau|r|) \quad (3.23)$$

where τ = a constant

The Fourier transformed equation (3.23) becomes

$$C_{kj}(k) = C_{kj}^0(k) - \lim_{\tau \rightarrow 0} 4\pi(\rho_k \rho_j)^{1/2} \beta e^2 Z_k Z_j / (kD) \int_0^\infty \sin(kr_{kj}) \text{EXP}(-\tau|r|) dr_{kj} \quad (3.24)$$

From the Laplace transform tables in Arfken (1970):

$$\int_0^\infty \sin(kr_{kj}) \text{EXP}(-\tau|r_{kj}|) dr_{kj} = \frac{k}{\tau^2 + k^2} \quad (3.25)$$

Equation (3.24) becomes

$$C_{kj}(k) = C_{kj}^0(k) - \lim_{\tau \rightarrow 0} 4\pi(\rho_k \rho_j)^{1/2} (\beta e^2 Z_k Z_j) / (D(\tau^2 + k^2)) \quad (3.26)$$

The poles of equation (3.26) are at $k=i\tau$ and $-i\tau$, rather than on the real k axis. Baxter's factorization of equation (3.21) is shown in equation (3.27):

$$\delta_{ij} - C_{ij}^0 + \lim_{\tau \rightarrow 0} 4\pi(\rho_i \rho_j)^{1/2} \beta e^2 Z_i Z_j / (D(\tau^2 + k^2)) = \Sigma Q_{ik}(k)_+ Q_{jk}(k)_- \quad (3.27)$$

where

$$Q_{ik}(k)_+ = \delta_{ik} + (\rho_i \rho_k)^{1/2} \left(- \int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(ikr)_+ Q_{ik}(r) \right. \\ \left. + A_{ik} \int_{\lambda_{ji}}^{\infty} dr_{ik} \text{EXP}(r_{ik}(ik-\tau)_+) \right) \quad (3.28)$$

$$Q_{jk}(k)_- = \delta_{jk} + (\rho_j \rho_k)^{1/2} \left(- \int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} \text{EXP}(ikr)_- Q_{jk}(r) \right. \\ \left. + A_{jk} \int_{\lambda_{kj}}^{\infty} dr_{jk} \text{EXP}(r_{jk}(ik-\tau)_-) \right) \quad (3.29)$$

In the above equations, the subscript $+$ denotes a positive k domain and $-$ denotes a negative k domain. The first two terms on the right side of equations (3.28) and (3.29) were first deduced by Baxter. Blum (1975) added the last terms into the equations to account for the long-range contribution. Note that $Q(k)$ has singularities only in the lower k plane. If $k=-i\tau$, the third term diverges (after integration). Using the Laplace transform tables in Arfken (1970), a term with $1/(ik-\tau)$ is obtained. Also note that integration on the lower-half plane produces a divergence in the second term for Q_+ , which can most easily be observed on the imaginary axis.

On the imaginary axis in the lower half plane, the exponential factor for Q_+ in the integral becomes

$$\text{EXP}^{ikz} = \text{EXP}^{-ky} \quad (3.30)$$

As y approaches $-\infty$, an integration on the semicircle in the lower half plane would diverge. Conversely Q_- approaches unity.

One property of $Q(r)$ should be noted:

$Q(r)$ must approach zero as r approaches infinity for Jordan's Lemma (Arfken, 1970) to be valid for definite integrals of the Fourier type in the complex plane. This is reasonable, since $Q_{ij}(r)$ is a factorization of $C_{ij}^0(r)$.

The constants σ_{ij} and λ_{ij} are "range parameters" for integration of equations (3.28) and (3.29)

where

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \quad (3.31)$$

$$\lambda_{ij} = (\sigma_i - \sigma_j)/2 \quad (3.32)$$

The upper limit of the second terms in equation (3.28) and (3.29) is set to σ_{ij} since $C_{ij}^0(r) = 0$ for $r > \sigma_{ij}$ (consistent with hard sphere repulsion). The upper limit of the third terms in equations (3.28) and (3.29) is set to ∞ , since the long-range contribution to C_{ij} decays slowly with increasing r .

Useful constraints on $Q_{ij}(r)$ and $A_{ij}(r)$ can be derived by taking the Fourier inverse of equation (3.27). Substituting equations (3.28) and (3.29) into equation (3.27):

$$\begin{aligned}
\delta_{ij} - C_{ij}^0(k) + 4\pi(\rho_i\rho_j)^{1/2}Be^2Z_iZ_j/(D(\tau^2+k^2)) = \\
\Sigma\delta_{ik}\delta_{jk} + \Sigma\delta_{jk}(\rho_i\rho_k)^{1/2}(-\int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(ikr_{ik}) + Q_{ik}(r) + \\
A_{ik} \int_{\lambda_{ki}}^{\infty} dr_{ik} \text{EXP}(r_{ik}(-\tau+ik)_+)) \\
+ \Sigma\delta_{ik}(\rho_j\rho_k)^{1/2}(-\int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} \text{EXP}(ikr_{jk}) - Q_{jk}(r) + \\
A_{jk} \int_{\lambda_{kj}}^{\infty} dr_{jk} \text{EXP}(r_{jk}(-\tau+ik)_-)) \\
+ \Sigma(\rho_i\rho_k)^{1/2}(\int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(ikr_{ik}) + Q_{ik}(r))(\rho_j\rho_k)^{1/2} \\
(\int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} \text{EXP}(ikr_{jk}) - Q_{jk}(r)) \\
+ \Sigma(\rho_i\rho_k)^{1/2}(-\int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(ikr_{ik}) + Q_{ik}(r))A_{jk} \int_{\lambda_{kj}}^{\infty} dr_{jk} \text{EXP}(r_{jk}(-\tau+ik)_-) \\
+ \Sigma A_{ik} \int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(r_{ik}(-\tau+ik)_+)(\rho_j\rho_k)^{1/2}(-\int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} \text{EXP}(-ikr) - Q_{jk}(r)) \\
+ \Sigma A_{ik} \int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(r_{ik}(-\tau+ik)_+) A_{jk} \int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} \text{EXP}(r_{jk}(-\tau+ik)_-) \quad (3.33)
\end{aligned}$$

Noting that terms with $\Sigma \delta_{ik}(\dots)_{jk}$ equal $(\dots)_{ij}$ and $\Sigma \delta_{jk}(\dots)_{ik}$ equal $(\dots)_{ij}$, equation (3.33) becomes

$$\begin{aligned}
& -C_{ij}^0(k) + 4\pi(\rho_i \rho_j)^{1/2} \beta e^2 Z_i Z_j / (D(\tau^2 + k^2)) = \\
& (\rho_i \rho_j)^{1/2} \left(-\int_{\lambda_{ji}}^{\sigma_{ji}} dr_{ij} \text{EXP}(ikr_{ij})_+ Q_{ij}(r) + A_{ij} \int_{\lambda_{ji}}^{\infty} \text{EXP}(r_{ij}(-\tau + ik)_+) \right) \\
& + (\rho_i \rho_j)^{1/2} \left(-\int_{\lambda_{ij}}^{\sigma_{ij}} dr_{ji} \text{EXP}(-ikr_{ji})_- Q_{ji}(r) + A_{ji} \int_{\lambda_{ij}}^{\infty} \text{EXP}(r_{ji}(-\tau + ik)_-) \right) \\
& + \Sigma(\rho_i \rho_k)^{1/2} \left(\int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(ikr_{ik})_+ Q_{ik}(r) \right) (\rho_j \rho_k)^{1/2} \\
& \quad \left(\int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} \text{EXP}(ikr_{jk})_- Q_{jk}(r) \right) \\
& + \Sigma(\rho_i \rho_k)^{1/2} \left(-\int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(ikr_{ik})_+ Q_{ik}(r) \right) \left(A_{jk} \int_{\lambda_{kj}}^{\infty} dr_{jk} \text{EXP}(r_{jk}(-\tau + ik)_-) \right) \\
& + \Sigma A_{ik} \left(\int_{\lambda_{ki}}^{\infty} dr_{ik} \text{EXP}(r_{ik}(-\tau + ik)_+) \right) (\rho_i \rho_k)^{1/2} \left(-\int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} \text{EXP}(-ikr_{jk})_- Q_{jk}(r) \right) \\
& + \Sigma A_{ik} \left(\int_{\lambda_{ki}}^{\infty} dr_{ik} \text{EXP}(r_{ik}(-\tau + ik)_+) \right) \left(A_{jk} \int_{\lambda_{kj}}^{\infty} dr_{jk} \text{EXP}(r_{jk}(-\tau + ik)_-) \right) \quad (3.34)
\end{aligned}$$

Multiplying equation (3.34) by $(2\pi)^{-1}(\rho_i \rho_j)^{-1/2} \text{EXP}(-ikr'_{ij})$ and

integrating from $-\infty$ to ∞ yields the appropriate inverse Fourier transform. The inverse transform of the first term is obtained by:

$$\begin{aligned}
& -(2\pi)^{-1}(\rho_i \rho_j)^{-1/2} \int_{-\infty}^{\infty} C_{ij}^0(k) \text{EXP}(-ikr'_{ij}) dk = \\
& -2 \int_{-\infty}^{\infty} \text{EXP}(-ikr'_{ij}) dk \int_0^{\infty} dr_{ij} \sin(kr_{ij}) (r_{ij}/k) c_{ij}^0(r) \quad (3.35)
\end{aligned}$$

Noting from Butkov (1968) for analytical functions:

$$\int_{\gamma}^{\beta} h(Z) dZ \int_a^b F(Z,s) ds = \int_a^b ds \int_{\gamma}^{\beta} h(Z) f(Z,s) dZ \quad (3.36)$$

Equation (3.35) becomes

$$=-2 \int_0^{\infty} dr_{ij} r_{ij} c_{ij}^0(r) \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) \sin(kr_{ij})/k \quad (3.37)$$

Using the identity:

$$\sin(kt) = (\text{EXP}(ikt) - \text{EXP}(-ikt))/2i \quad (3.38)$$

where $t = r_{ij}$

equation (3.37) becomes

$$= -2 \int_{r'_{ij}}^{\infty} dt t c_{ij}^0(t) \int_{-\infty}^{\infty} dk \text{EXP}(-ik(r'_{ij}-t)) - \text{EXP}(-ik(r'+t))/2ik \quad (3.39)$$

For $t > r'_{ij}$ and $t < r'_{ij}$, the integral over dk is zero since the integral over the arc in the lower half plane is zero by Jordan's Lemma and the individual residues of each exponential term cancel. However at $t = r'_{ij}$, a $2\pi i$ residue results, yielding

$$= -2\pi \int_{r'_{ij}}^{\infty} dt t c_{ij}^0(t) \quad (3.40)$$

The inverse transform of the second term in equation (3.34) is

$$\begin{aligned}
& (2\pi)^{-1}(\rho_i \rho_j)^{-1/2} \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) 4\pi(\rho_i \rho_j)^{1/2} \beta e^2 Z_i Z_j / (D(\tau^2 + k^2)) \\
& = 2 \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) \beta e^2 Z_i Z_j / (D(\tau^2 + k^2)) \quad (3.41)
\end{aligned}$$

The poles of equation (3.41) are at $k=i\tau$ and $k=-i\tau$. Integrating in the lower halfplane yields only one pole at $k=-i\tau$. There is no contribution to the integral along the arc in the halfplane by Jordan's Lemma. The residue is $2\pi i \text{EXP}(-\tau r'_{ij}) / (2i\tau)$ or $\pi \text{EXP}(-\tau r'_{ij}) / \tau$ yielding

$$= 2 \pi \beta e^2 Z_i Z_j / D \text{EXP}(-\tau r'_{ij}) / \tau \quad (3.42)$$

The inverse transform of the third term is

$$\begin{aligned}
& -(2\pi)^{-1} \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) \int_{\lambda_{ji}}^{\sigma_{ji}} dr_{ij} \text{EXP}(ikr_{ij}) Q_{ij}(r) = \\
& \dots = -(2\pi)^{-1}(\rho_i \rho_j)^{-1/2} \int_{\lambda_{ji}}^{\sigma_{ji}} dr_{ij} Q_{ij}(r) \int_{-\infty}^{\infty} dk \text{EXP} ik(r_{ij} - r'_{ij}) \quad (3.43)
\end{aligned}$$

The integral over dk is $2\pi U(r'_{ij})$ (see Mathews and Walker, 1970) where $U(r'_{ij}) = 1$ for $r_{ij} = r'_{ij}$ and 0 otherwise,

$$= - \int_{\lambda_{ji}}^{\sigma_{ji}} dr_{ij} Q_{ij}(r) U(r'_{ij}) \quad (3.44)$$

$$= - Q_{ij}(r) S(r'_{ij} - \lambda_{ji}) \quad (3.45)$$

where $S(r'_{ij} - \lambda_{ji}) = 1$ for any $r_{ij} = r'_{ij}$ larger than λ_{ji} ,

The inverse transform of the fourth term is

$$\begin{aligned}
 & (2\pi)^{-1} \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) \int_{\lambda_{ji}}^{\infty} dr_{ij} \text{EXP}(r_{ij}(-\tau + ik)) A_{ij} \\
 & = (2\pi)^{-1} A_{ij} \int_{\lambda_{ji}}^{\infty} dr_{ij} \text{EXP}(-\tau r_{ij}) \int_{-\infty}^{\infty} dk \text{EXP}(ik(r_{ij} - r'_{ij})) \quad (3.46)
 \end{aligned}$$

Again evaluating the integral over dk as $2\pi U(r'_{ij})$, equation (3.46) becomes:

$$= A_{ij} \int_{\lambda_{ji}}^{\infty} dr_{ij} \text{EXP}(-\tau r_{ij}) U(r'_{ij}) \quad (3.47)$$

Integrating equation (3.47) gives

$$= A_{ij} \text{EXP}(-\tau r'_{ij}) S(r'_{ij} - \lambda_{ji}) \quad (3.48)$$

Likewise, the inverse transform of the fifth and sixth terms are

$$= -Q_{ji}(r) S(r'_{ji} - \lambda_{ij}) \quad (3.49)$$

and

$$= A_{ji} \text{EXP}(-\tau r'_{ji}) S(r'_{ji} - \lambda_{ij}) \quad (3.50)$$

respectively.

The inverse transform of the seventh term is

$$\begin{aligned}
& \Sigma(2\pi)^{-1}(\rho_i\rho_j)^{-1/2} \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij})(\rho_i\rho_k)^{1/2} \\
& \int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(ikr_{ik}) Q_{ik}(r) (\rho_j\rho_k)^{1/2} \\
& \int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} \text{EXP}(ikr_{jk}) Q_{jk}(r) \\
& = \Sigma\rho_k \int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} Q_{ik}(r) \int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} Q_{jk}(r) U(r'_{ij}) \quad (3.51)
\end{aligned}$$

The inverse transform of the eighth term is

$$\begin{aligned}
& -\Sigma(2\pi)^{-1}(\rho_i\rho_j)^{-1/2} \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij})(\rho_i\rho_k)^{1/2} \\
& \int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} \text{EXP}(ikr_{ik}) Q_{ik}(r) (\rho_j\rho_k)^{1/2} \int_{\lambda_{kj}}^{\infty} dr_{jk} \text{EXP}(r_{ij}(-\tau+ik)) A_{jk} \\
& = -\Sigma\rho_k \int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} Q_{ik}(r) \int_{\lambda_{kj}}^{\infty} dr_{jk} A_{jk} \text{EXP}(-\tau r_{jk}) U(r'_{ij}) \quad (3.52)
\end{aligned}$$

Likewise, the inverse transform of the ninth term is

$$= -\Sigma\rho_k \int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} Q_{jk}(r) \int_{\lambda_{ki}}^{\infty} dr_{ik} A_{ik} \text{EXP}(-\tau r_{ik}) U(r'_{ij}) \quad (3.53)$$

Finally, the inverse transform of the tenth term is

$$\begin{aligned} & \Sigma (2\pi)^{-1} (\rho_i \rho_j)^{-1/2} \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) A_{ik} \int_{\lambda_{ki}}^{\infty} dr_{ik} \text{EXP}(r_{ik}(-\tau+ik)) A_{jk} \\ & \int_{\lambda_{kj}}^{\infty} dr_{jk} \text{EXP}(r_{jk}(-\tau+ik)) (\rho_i \rho_k)^{1/2} (\rho_j \rho_k)^{1/2} \\ & = \Sigma \rho_k A_{ik} A_{jk} \int_{\lambda_{ki}}^{\infty} dr_{ik} \text{EXP}(-\tau r_{ik}) \int_{\lambda_{kj}}^{\infty} dr_{jk} \text{EXP}(-\tau r_{jk}) U(r'_{ij}) \end{aligned} \quad (3.54)$$

$$= \Sigma \rho_k A_{ik} A_{jk} \int_{\lambda_{ki}}^{\infty} dr_{ik} \text{EXP}(-\tau r_{ik}) \text{EXP}(\tau r'_{ij} - \tau r_{ik}) \quad (3.55)$$

$$= \Sigma \rho_k A_{ik} A_{jk} \text{EXP}(\tau r'_{ij}) \text{EXP}(-2\tau \lambda_{ki}) / 2\tau \quad (3.56)$$

The total inverse transformed equation is

$$\begin{aligned}
& -2\pi \int_{r'_{ij}}^{\infty} dt \, t c^{\circ}_{ij}(t) + 2\pi\beta e^2 Z_i Z_j / D \, \text{EXP}(-\tau r'_{ij}) / \tau = \\
& -Q_{ij}(r) S(r'_{ij} - \lambda_{ji}) + A_{ij} \text{EXP}(-\tau r'_{ij}) S(r'_{ij} - \lambda_{ji}) \\
& -Q_{ji}(r) S(r'_{ji} - \lambda_{ij}) + A_{ji} \text{EXP}(-\tau r'_{ji}) S(r'_{ji} - \lambda_{ij}) \\
& + \Sigma \rho_k \int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} Q_{ik}(r) \int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} Q_{jk}(r) U(r'_{ij}) \\
& - \Sigma \rho_k \int_{\lambda_{ki}}^{\sigma_{ki}} dr_{ik} Q_{ik}(r) \int_{\lambda_{kj}}^{\infty} dr_{jk} A_{jk} \text{EXP}(-\tau r_{jk}) U(r'_{ij}) \\
& - \Sigma \rho_k \int_{\lambda_{kj}}^{\sigma_{kj}} dr_{jk} Q_{jk}(r) \int_{\lambda_{ki}}^{\infty} dr_{ik} A_{ik} \text{EXP}(-\tau r_{ik}) U(r'_{ij}) \\
& + \Sigma \rho_k A_{ik} A_{jk} \text{EXP}(\tau r'_{ij}) \text{EXP}(-2\tau \lambda_{ki}) / 2\tau
\end{aligned} \tag{3.57}$$

As noted by Blum (1980), various conditions and relationships between the parameters exist. First, letting τ approach zero (to recover the original system) yields

$$4\pi\beta e^2 Z_i Z_j / D = \Sigma \rho_k A_{ik} A_{jk} \tag{3.58}$$

Next, define the constant α as

$$\alpha^2 = 4\pi\beta e^2 / D \tag{3.59}$$

The A's in equation (3.58) represent unknowns, in our derivation and by noting some important properties of the $\underline{\alpha Z}$ and $\underline{A}$ matrices, an important factorization can be obtained.

For a binary system:

$$\alpha^2 \begin{bmatrix} Z_1 Z_1 & Z_1 Z_2 \\ Z_2 Z_1 & Z_2 Z_2 \end{bmatrix} = \begin{bmatrix} \rho_1 A_{11} A_{11} + \rho_2 A_{12} A_{12} & \rho_1 A_{11} A_{21} + \rho_2 A_{12} A_{22} \\ \rho_1 A_{21} A_{11} + \rho_2 A_{22} A_{12} & \rho_1 A_{21} A_{21} + \rho_2 A_{22} A_{22} \end{bmatrix} \quad (3.60)$$

We would like to define a new unknown parameter a by the following relation

$$Z_i a_k = A_{ik} \quad (3.61)$$

The validity of the indices of $\underline{Z}$ and $\underline{a}$ is shown below.

Substituting equation (3.61) into equations (3.58) and (3.59) yields

$$\alpha^2 Z_i Z_j = \sum \rho_k Z_i a_k Z_j a_k \quad (3.62)$$

The Z's in equation 3.62 can be pulled out of the summation to give:

$$\alpha^2 Z_i Z_j = Z_i Z_j \sum \rho_k a_k a_k \quad (3.63)$$

which verifies the assumed Z index in equation (3.61).

The eigenvalue relation of the left side of equation (3.60) is

$$\lambda^2 - \lambda(Z_1 Z_1 + Z_2 Z_2) = 0 \quad (3.64)$$

yielding only one non-zero eigenvalue.

The eigenvalue relation of the right side of equation (3.60) is

$$\begin{aligned} \lambda^2 - \rho_1 Z_1 Z_1 a_1 a_1 \lambda - \rho_2 Z_1 Z_1 a_2 a_2 \lambda - \rho_2 Z_2 Z_2 a_2 a_2 \\ - \rho_1 Z_2 Z_2 a_1 a_1 \lambda = 0 \end{aligned} \quad (3.65)$$

Equation (3.65) also has one non-zero eigenvalue.

Equation (3.57) provides two more useful relations. At $r'_{ij} = \sigma_{ij}$, the first term is continuous, however the integrals on the right side terminate at σ_{ij} , and to preserve continuity

$$Q_{ij}(\sigma) = 0 \quad (3.66)$$

Finally, by exchanging the i and j indices in equation (3.57) in the limit as $\tau \rightarrow 0$ at $r_{ij} = \lambda_{ij}$ yields the following symmetry relation:

$$-Q_{ij}(\lambda) + A_{ij} = -Q_{ji}(\lambda) + A_{ji} \quad (3.67)$$

Now, the inverse Fourier transform of the Ornstein-Zernike equation in terms of the Weiner-Hopf (Baxter, 1970) factorization is:

$$\Sigma_k (\delta_{ik} + H_{ik}(k)) (\Sigma_l Q_{kl}(k) Q_{jl}^{-1}(k)) = \delta_{ij} \quad (3.68)$$

As an example, for the 1,1 element of a binary mixture:

$$\begin{aligned} (\delta_{11} + H_{11}(k)) (Q_{11}(k) Q_{11}^{-1}(k) + Q_{12}(k) Q_{12}^{-1}(k) + \\ (\delta_{12} + H_{12}(k)) (Q_{21}(k) Q_{11}^{-1}(k) + Q_{22}(k) Q_{12}^{-1}(k)) = \delta_{11} \end{aligned} \quad (3.69)$$

Equation (3.68) can be written in matrix notation as:

$$(\underline{\delta} + \underline{H}(k)) \underline{Q}(k) \underline{Q}^-(k)^T = \underline{\delta} \quad (3.70)$$

Or, analogously:

$$(\underline{\delta} + \underline{H}(k)) \underline{Q}(k) = \underline{\delta} (\underline{Q}^-(k)^T)^{-1} \quad (3.71)$$

The goal is to take the inverse Fourier transform of equation (3.71).

The right side of equation (3.71) is given (for a binary) by

$$\underline{\delta} (\underline{Q}^-(k)^T)^{-1} = \left[\frac{1}{Q_{11}^-(k)Q_{22}^-(k) - Q_{12}^-(k)Q_{21}^-(k)} \right] \begin{bmatrix} Q_{22}^-(k) & -Q_{12}^-(k) \\ -Q_{21}^-(k) & Q_{11}^-(k) \end{bmatrix} \quad (3.71a)$$

Taking the inverse transform of the right side of equation (3.71) yields zero, as noted by Blum (1980) since the integrand has no singularities in the lower half complex plane. The inverse transform of the elements on the left side of equation (3.71) is

$$(2\pi)^{-1}(\rho_i \rho_j)^{-1/2} \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) \Sigma_k(\delta_{ik} + H_{ik}(k)) Q_{kj}(k) = 0 \quad (3.72)$$

Substituting equation (3.28) into equation (3.72) yields

$$\begin{aligned}
& (2\pi)^{-1} (\rho_i \rho_j)^{-1/2} \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) \left[\delta_{ij} - (\rho_i \rho_j)^{-1/2} \right. \\
& \int_{\lambda_{ji}}^{\sigma_{ji}} dr_{ij} \text{EXP}(ikr_{ij}) Q_{ij}(r) + (\rho_i \rho_j)^{1/2} A_{ij} \int_{\lambda_{ji}}^{\infty} dr_{ij} \text{EXP}(r_{ij}(ik-\tau)) \\
& + H_{ij}(k) - \Sigma_k H_{ik} (\rho_k \rho_j)^{1/2} \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} \text{EXP}(ikr_{kj}) Q_{kj}(r) \\
& \left. + \Sigma_k H_{ik}(k) (\rho_k \rho_j)^{1/2} A_{kj} \int_{\lambda_{jk}}^{\infty} dr_{kj} \text{EXP}(r_{kj}(ik-\tau)) \right] = 0 \quad (3.73)
\end{aligned}$$

The inverse transform of the first term in equation (3.73) is zero, while the inverse transform of the second term is $-Q_{ij}(r')$ (see the derivation of equation (3.44)). Letting τ approach zero, the inverse transform of the third term is A_{ij} .

The inverse transform of the fourth term is obtained by substituting in equation (3.12) for $H_{ij}(k)$ and noting the analogy with equation (3.35). The inverse transform is analogous to equation (3.40):

$$2\pi \int_{r'_{ij}}^{\infty} dt \, t \, h_{ij}(t) \quad (3.74)$$

The inverse transform of the final terms require the definition of the Fourier convolution. From Butkov (1968):

$$F^{-1}(L(k)M(k)) = \int_{-\infty}^{\infty} l(r) m(r'-r) dr \quad (3.75)$$

where F^{-1} denotes the inverse Fourier transform

The inverse of the fifth term is

$$\begin{aligned}
 & 2\Sigma\rho_k \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) \left[\int_0^{\infty} dr_{ik} \sin(kr_{ik}) (k/r_{ik}) h_{ik}(r) \right. \\
 & \left. \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) \text{EXP}(ikr_{kj}) \right] \\
 & \Sigma\rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) \left[2\pi \int_{|r'_{ik}-r_{kj}|}^{\infty} dt t h_{ik}(t) \right] \quad (3.76)
 \end{aligned}$$

Note that the limits on the outer integral on the right side of equation (3.76) are not $-\infty$ to ∞ , but rather λ_{kj} to σ_{kj} .

These limits are consistent with the change of order of integration step in Butkov's (1968) derivation.

The inverse transform of the sixth term is

$$\begin{aligned}
 & 2\Sigma\rho_k \int_{-\infty}^{\infty} dk \text{EXP}(-ikr'_{ij}) \left[\int_0^{\infty} dr_{ik} \sin(kr_{ik}) (k/r_{ik}) h_{ik}(r) \right. \\
 & \left. \int_{\lambda_{jk}}^{\infty} dr_{kj} A_{kj} \text{EXP}(ikr_{kj}) \right] \\
 & \Sigma\rho_k \int_{\lambda_{jk}}^{\infty} dr_{kj} A_{kj} \left[2\pi \int_{|r'_{ik}-r_{kj}|}^{\infty} dt t h_{ik}(t) \right] \quad (3.77)
 \end{aligned}$$

The inverse transform of equation (3.73) is therefore:

$$\begin{aligned}
 2\pi \int_{r'_{ij}}^{\infty} dt \, t \, h_{ij}(t) - Q_{ij}(r') + A_{ij} = \\
 \Sigma \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) \left[2\pi \int_{|r'_{ik}-r_{kj}|}^{\infty} dt \, t \, h_{ik}(t) \right] + \\
 -\Sigma \rho_k \int_{\lambda_{jk}}^{\infty} dr_{kj} A_{kj} \left[2\pi \int_{|r'_{ik}-r_{kj}|}^{\infty} dt \, t \, h_{ik}(t) \right]
 \end{aligned} \tag{3.78}$$

The electroneutrality condition presented by Blum (1980) is

$$4\pi \Sigma_k \rho_k Z_k \int_0^{\infty} dr_{ik} r_{ik}^2 h_{ik}(r) = -Z_i \tag{3.79}$$

Multiplying equation (3.79) by a_j and using equation (3.61)

$$4\pi \Sigma_k \rho_k A_{kj} \int_0^{\infty} dr_{ik} r_{ik}^2 h_{ik}(r) = -A_{ij} \tag{3.80}$$

Using integration by parts, equation (3.80) can be written as:

$$\Sigma_k \rho_k A_{kj} \int_0^{\infty} dr'_{ik} \, 2\pi \int_{r'_{ik}}^{\infty} dt \, t \, h_{ik}(t) = A_{ij}/2 \tag{3.81}$$

Changing variables in equation (3.81) using $r'_{ik} = |r'_{ik}-r_{kj}|$ yields

$$\Sigma_k \rho_k A_{kj} \int_{r'_{ik}}^{\infty} dr_{kj} \, 2\pi \int_{|r'_{ik}-r_{kj}|}^{\infty} dt \, t \, h_{ik}(t) = A_{ij}/2 \tag{3.82}$$

Using the above relation in equation (3.78), equation (3.78) becomes

$$\begin{aligned}
 2\pi \int_{r'_{ij}}^{\infty} dt \, t \, h_{ij}(t) - Q_{ij}(r') + A_{ij}/2 = \\
 \sum \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) \left[2\pi \int_{|r'_{ik}-r_{kj}|}^{\infty} dt \, t \, h_{ik}(t) \right] - \\
 \sum \rho_k A_{kj} \int_{\lambda_{jk}}^{r'_{ki}} dr_{kj} \left[2\pi \int_{|r'_{ik}-r_{kj}|}^{\infty} dt \, t \, h_{ik}(t) \right] \quad (3.83)
 \end{aligned}$$

Now, expanding $Q_{ij}(r)$ in a Taylor series about $Q_{ij}(\sigma)$ yields

$$Q_{ij}(r) = Q_{ij}(\sigma) + (r'_{ij} - \sigma_{ij}) \frac{\partial Q_{ij}}{\partial r'_{ij}} + 1/2 (r'_{ij} - \sigma_{ij})^2 \frac{\partial^2 Q_{ij}}{\partial (r'_{ij})^2} + \dots \quad (3.84)$$

The first and second derivatives of equation (3.83) will be taken using Liebnitz's rule. Liebnitz's rule is written as follows:

$$\frac{d}{dx} \int_{a(x)}^{b(x)} Y(t,x) dt = \int_{a(x)}^{b(x)} \frac{\partial Y(t,x)}{\partial x} dt + Y(b(x),x) \frac{db(x)}{dx} - Y(a(x),x) \frac{da(x)}{dx} \quad (3.85)$$

Taking the first derivative of the first term (with respect to r') in equation (3.83) yields:

$$\frac{d}{dr'_{ij}} \left[2\pi \int_{r'_{ij}}^{\infty} dt \, t \, h_{ij}(t) \right] = -2\pi r'_{ij} h_{ij}(r') \quad (3.86)$$

The first derivative of the second term in equation (3.83) is $\partial Q_{ij}(r')/\partial r'_{ij}$ while that of the third term is zero.

Taking the first derivative of the fourth term in equation (3.83) yields

$$\begin{aligned} \frac{\partial}{\partial r'_{ij}} \Sigma \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) \left[2\pi \int_{-\infty}^{\infty} \frac{dt}{|r'_{ik}-r_{kj}|} t h_{ik}(t) \right] = \\ 2\pi \Sigma \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) \frac{\partial}{\partial r'_{ij}} \int_{-\infty}^{\infty} \frac{dt}{|r'_{ik}-r_{kj}|} t h_{ik}(t) = \\ -2\pi \Sigma \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) (\bar{r}'_{ik}-r_{kj}) h_{ik}(r'-r) \end{aligned} \quad (3.87)$$

Taking the first derivative of the last term in equation (3.83) yields:

$$\begin{aligned} - \frac{\partial}{\partial r'_{ij}} \Sigma \rho_k A_{kj} \int_{\lambda_{jk}}^{r'_{ik}} dr_{kj} \left[2\pi \int_{-\infty}^{\infty} \frac{dt}{|r'_{ik}-r_{kj}|} t h_{ik}(t) \right] = -2\pi \Sigma \rho_k A_{kj} \int_0^{\infty} dt t h_{ik}(t) \\ + 2\pi \Sigma \rho_k A_{kj} \int_{\lambda_{jk}}^{r'_{ik}} dr_{kj} (r'_{ik}-r_{kj}) h_{ik}(r'-r) \end{aligned} \quad (3.88)$$

The first derivative of equation (3.83) is therefore

$$\begin{aligned}
-2\pi r'_{ij} h_{ij}(r') - \partial Q_{ij}(r') / \partial r'_{ij} &= -2\pi \Sigma \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) (r'_{ik} - r_{kj}) h_{ik}(r' - r) \\
-2\pi \Sigma \rho_k A_{kj} \int_0^{\infty} dt \, t \, h_{ik}(t) + 2\pi \Sigma \rho_k A_{kj} \int_{\lambda_{jk}}^{r'_{ik}} dr_{kj} (r'_{ik} - r_{kj}) h_{ik}(r' - r) & \quad (3.89)
\end{aligned}$$

We now restrict r' to be less than σ and note that $h = -1$ at that condition. Equation (3.89) becomes

$$\begin{aligned}
2\pi r'_{ij} - \partial Q_{ij}(r') / \partial r'_{ij} &= 2\pi \Sigma \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) (r'_{ik} - r_{kj}) \\
-2\pi \Sigma \rho_k A_{kj} \int_0^{\infty} dt \, t \, h_{ik}(t) - 2\pi \Sigma \rho_k A_{kj} \int_{\lambda_{jk}}^{r'_{ik}} dr_{kj} (r'_{ik} - r_{kj}) & \quad (3.90)
\end{aligned}$$

The subsequent derivative of equation (3.90) is

$$2\pi - \partial^2 Q_{ij}(r') / \partial r'_{ij}{}^2 = 2\pi \Sigma \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} dr_{kj} Q_{kj}(r) - 2\pi \Sigma \rho_k A_{kj} \int_{\lambda_{jk}}^{r'_{ik}} dr_{kj} \quad (3.91)$$

Once more, taking the derivative of equation (3.91) yields

$$-\partial^3 Q_{ij}(r') / \partial r'_{ij}{}^3 = 2\pi \Sigma \rho_k A_{kj} \quad (3.92)$$

Noting that the right side of equation (3.92) is zero by electroneutrality, and equation (3.92) becomes

$$\partial^3 Q_{ij}(r') / \partial r'_{ij}{}^3 = 0 \quad (3.93)$$

Convenient definitions are presented in equations (3.94) to (3.97), following Blum (1975)

$$J'_{ij} = \int_{\lambda_{ij}}^{\sigma_{ij}} dr_{ij} Q_{ij}(r) \quad (3.94)$$

$$J''_{ij} = \int_{\lambda_{ij}}^{\sigma_{ij}} dr_{ij} Q_{ij}(r) r_{ij} \quad (3.95)$$

$$B_i = \Sigma \rho_k Z_k \int_0^{\infty} dt \, t \, h_{ki}(t) \quad (3.96)$$

$$\chi_n = \Sigma \rho_k \sigma_k^2 Z_k \quad (3.97)$$

Equations (3.90) and (3.91) can be rewritten using equations (3.94) through (3.96) as:

$$\begin{aligned} 2\pi r'_{ij} - \partial Q_{ij}(r') / \partial r'_{ij} &= 2\pi \Sigma \rho_k J'_{kj} r'_{ik} - 2\pi \Sigma \rho_k J''_{kj} \\ &- a_j B_i - 2\pi \Sigma \rho_k a_j Z_k \int_{\lambda_{jk}}^{r'_{ik}} dr_{kj} (r'_{ik} - r_{kj}) \end{aligned} \quad (3.98)$$

and

$$2\pi - \partial^2 Q_{ij}(r') / \partial r'_{ij}{}^2 = 2\pi \Sigma \rho_k J'_{kj} - 2\pi \Sigma \rho_k a_j Z_k \int_{\lambda_{jk}}^{r'_{ik}} dr_{kj} \quad (3.99)$$

At $r' = \sigma'_{ij}$ equations (3.98) and (3.99) become

$$\begin{aligned} 2\pi \sigma_{ij} - \partial Q_{ij}(r') / \partial r'_{ij} &= 2\pi \Sigma \rho_k J'_{kj} \sigma_{ij} - 2\pi \Sigma \rho_k J''_{kj} \\ &- a_j B_i - a_j 2\pi \Sigma \rho_k Z_k (\sigma_{ij} (\sigma_{ij} - \lambda_{kj}) - 1/2 (\sigma_{ij}^2 - \lambda_{kj}^2)) \end{aligned} \quad (3.100)$$

and

$$2\pi - \partial^2 Q_{ij}(r') / \partial r'_{ij}{}^2 = 2\pi \Sigma \rho_k J'_{kj} - a_j \pi \Sigma \rho_k Z_k (\sigma_{ij} - \lambda_{kj}) \quad (3.101)$$

Using equation (3.97), equations (3.100) and (3.101) become

$$2\pi\sigma_{1j} - \partial Q_{1j}(r')/\partial r'_{1j} = 2\pi\Sigma\rho_k J'_{k1}\sigma_{1j} - 2\pi\Sigma\rho_k J'_{k2} - a_j B_1 - \frac{\pi}{2}\sigma_1 a_j X_1 - \frac{\pi}{4}a_j X_2 \quad (3.102)$$

and

$$2\pi - \partial^2 Q_{1j}(r')/\partial r'^2_{1j} = 2\pi\Sigma\rho_k J'_{k1} - a_j \pi X_1 \quad (3.103)$$

Substituting equation (3.84) into equations (3.94) and (3.95) and noting that the first and second derivatives with respect to r' at $r'_{1j}=\sigma_{1j}$ are constant yields

$$J'_{1j} = \partial Q_{1j}/\partial r'_{1j} \int_{\lambda_{j1}}^{\sigma_{j1}} dr_{1j} (r_{1j}-\sigma_{1j}) + \partial^2 Q_{1j}/\partial r'^2_{1j} \int_{\lambda_{j1}}^{\sigma_{j1}} dr_{1j} (r_{1j}-\sigma_{1j})^2/2 \quad (3.104)$$

and

$$J'_{1j} = \partial Q_{1j}/\partial r'_{1j} \int_{\lambda_{j1}}^{\sigma_{j1}} dr_{1j} r_{1j} (r_{1j}-\sigma_{1j}) + \partial^2 Q_{1j}/\partial r'^2_{1j} \int_{\lambda_{j1}}^{\sigma_{j1}} dr_{1j} r_{1j} (r_{1j}-\sigma_{1j})^2/2 \quad (3.105)$$

Integrating equations (3.104) and (3.105) yields

$$J'_{1j} = \partial Q_{1j}/\partial r'_{1j} (r_{1j}^2/2 - \sigma_{1j} r_{1j}) \Big|_{\lambda_{j1}}^{\sigma_{j1}} + \partial^2 Q_{1j}/\partial r'^2_{1j} (r_{1j}^3/3 - r_{1j}^2 \sigma_{1j} + r_{1j} \sigma_{1j}^2)/2 \Big|_{\lambda_{j1}}^{\sigma_{j1}} \quad (3.106)$$

and

$$J'_{ij} = \partial Q_{ij} / \partial r'_{ij} (r_{ij}^3 / 3 - \sigma_{ij} r_{ij}^2 / 2) \Big|_{\lambda_{ij}}^{\sigma_{ij}} +$$

$$\partial^2 Q_{ij} / \partial r'^2_{ij} (r_{ij}^4 / 4 - 2/3 \sigma_{ij} r_{ij}^3 + \sigma^2_{ij} r_{ij}^2 / 2) \Big|_{\lambda_{ij}}^{\sigma_{ij}} \quad (3.107)$$

Evaluating the limits in equations (3.106) and (3.107) yields

$$J'_{ij} = -\sigma_i^2 / 2 (\partial Q_{ij} / \partial r'_{ij}) + \sigma_i^3 / 6 (\partial^2 Q_{ij} / \partial r'^2_{ij}) \quad (3.108)$$

and

$$J''_{ij} = -(3\sigma_j \sigma_i^2 - \sigma_i^3) / 12 (\partial Q_{ij} / \partial r'_{ij}) + (\sigma_i^4 / 12) \partial^2 Q_{ij} / \partial r'^2_{ij} \quad (3.109)$$

Substituting equations (3.108) and (3.109) into equations (3.102) and (3.103) yields:

$$\partial Q_{ij} / \partial r'^2_{ij} = \frac{\pi}{\Delta} \left(2 + \frac{\epsilon_2 \sigma_j \pi}{\Delta} + a_j (\chi_1 + \sum \rho_k N_k \sigma_k^2) \right) \quad (3.110)$$

$$J'_{ij} = -\sigma_i^2 \left(\frac{\pi \sigma_i}{6\Delta} + \frac{\pi \sigma_j}{2\Delta} + \frac{\epsilon_2 \sigma_i \sigma_j \pi^2}{12\Delta^2} + \frac{a_j N_i}{2} + \frac{a_j \pi \sigma_i}{12\Delta} (\chi_1 + \sum \rho_k N_k \sigma_k^2) \right) \quad (3.111)$$

where

$$\Delta = 1 - \pi \epsilon_3 / 6 \quad (3.112)$$

$$\epsilon_m = \sum \rho_k \sigma_k^m \quad (3.113)$$

$$N_1 = \Sigma \rho_k Z_k 2\pi \int_0^\infty dt \, t \, h_{k,1}(t) + \frac{\pi}{4} \chi_2 + \frac{\pi}{6} \Sigma \rho_k \sigma_k^3 N_k \quad (3.114)$$

Further progress is made by multiplying the inverse Fourier transform (equation (3.83)) by $\rho_i Z_i$ and summing over the index i for $r_{i,j}=0$:

$$2\pi \Sigma \rho_k Z_k \int_0^\infty dt \, t \, h_{k,j}(t) = \Sigma \rho_k Z_k Q_{k,j} - a_j / 2 \Sigma \rho_k Z_k^2 + \Sigma \rho_i Z_i (\Sigma \rho_k J'_{k,j} 2\pi \int_0^\infty dt \, t \, h_{i,k}(t) - 2\pi \Sigma \rho_k A_{k,j} \int_0^\infty dt \, t \, h_{i,k}(t) \int_{\lambda_{j,k}}^0 dr_{k,j}) \quad (3.115)$$

Using the following definition

$$B_j = \Sigma \rho_k Z_k 2\pi \int_0^\infty dt \, t \, h_{k,j}(t) \quad (3.116)$$

and substituting equation (3.116) into equation (3.115) yields

$$B_j = \Sigma \rho_k Z_k Q_{k,j} - \frac{a_j}{2} \Sigma \rho_k Z_k^2 + \Sigma \rho_k B_k (J'_{k,j} + A_{k,j} \lambda_{j,k}) \quad (3.117)$$

Substituting equation (3.84) into equation (3.117) yields

$$a_j = 2(N_j + \sigma_j \Lambda \pi / 2\Delta) / d \quad (3.118)$$

where

$$d = \Sigma \rho_k (Z_k + N_k \sigma_k)^2 \quad (3.119)$$

and

$$\Lambda = \Sigma (\rho_k \sigma_k Z_k + \rho_k \sigma_k^2 N_k) \quad (3.120)$$

Now that we have an expression for a_j , we can determine the coefficients to the Baxter correlation function by substituting equations (3.118) and (3.119) into equations (3.110), (3.111) and using equation (3.108). The resulting equations are:

$$\partial^2 Q_{ij} / \partial r_{ij}^2 = \frac{\pi}{\Delta} \left(2 + \frac{\epsilon_2 \sigma_j \pi}{\Delta} + a_j \Delta \right) \quad (3.121)$$

and

$$\partial Q_{ij} / \partial r_{ij} = \frac{\pi}{\Delta} \left(\frac{\sigma_i + \sigma_j + \sigma_i \sigma_j \epsilon_2 \pi}{2\Delta} \right) - da_i a_j \quad (3.122)$$

The symmetry relation (equation (3.67) enables us to reduce the number of unknown parameters (a_j at this point). Writing $A_{ji} - Q_{ji}(\lambda_{ij})$ in terms of the derivatives of Q (equation (3.84)) and substituting in equations (3.121) and (3.122) yields

$$A_{ji} - Q_{ji}(\lambda_{ij}) = \frac{\pi}{\Delta} \sigma_i \sigma_j - a_i (\sigma_j N_j + Z_j) \quad (3.123)$$

Note that for all pairs of ions

$$a_i (N_j \sigma_j + Z_j) = a_j (N_i \sigma_i + Z_i) \quad (3.124)$$

or

$$(N_j \sigma_j + Z_j) / a_j = \text{constant} = (N_i \sigma_i + Z_i) / a_i \quad (3.125)$$

Using equation (3.118) and defining a new constant Γ , yields

$$(N_j \sigma_j + Z_j) / a_j = d / (2\Gamma) \quad (3.126)$$

Rearranging equation (3.126) and using equation (3.118) yields

$$\Gamma (N_j \sigma_j + Z_j) = -(N_j + \sigma_j \Lambda \frac{\pi}{2\Delta}) \quad (3.127)$$

Further rearrangement yields

$$N_j \sigma_j + Z_j = (Z_j - \sigma_j^2 \Lambda \frac{\pi}{2\Delta}) / (1 + \sigma_j \Gamma) \quad (3.128)$$

Multiplying equation (3.128) by $\rho_j \sigma_j$ and summing over index j yields

$$\sum \rho_k \sigma_k (N_k \sigma_k + Z_k) = \sum \frac{\rho_k \sigma_k Z_k}{1 + \sigma_k \Gamma} - \frac{\pi \Lambda}{2\Delta} \sum \frac{\rho_k \sigma_k^3}{1 + \sigma_k \Gamma} \quad (3.129)$$

or

$$\Lambda = \left(\sum \frac{\rho_k \sigma_k Z_k}{1 + \sigma_k \Gamma} \right) / \left(1 + \frac{\pi}{2\Delta} \sum \frac{\rho_k \sigma_k^3}{1 + \sigma_k \Gamma} \right) \quad (3.130)$$

Therefore, equations (3.128) and (3.126) can be shown to provide a_j in terms of known parameters

$$a_j = \frac{2\Gamma}{D} (Z_j - \sigma_j^2 \Lambda \frac{\pi}{2\Delta}) / (1 + \sigma_j \Gamma) \quad (3.131)$$

The energy equation (in terms of the total correlation function) for a mixture of ions (described by the primitive coulombic potential) is

$$U_{ion} = 2\pi \frac{e^2}{D} \sum \rho_i \rho_j Z_i Z_j \int_0^\infty dr_{ij} r_{ij} (h_{ij}(r) - 1) \quad (3.132)$$

Noting electroneutrality, and substituting equation (3.116) into equation (3.132) yields

$$U_{ion} = \frac{e^2}{D} \sum \rho_j Z_j B_j \quad (3.133)$$

Substituting equation (3.114) into equation (3.133) and again observing electroneutrality yields

$$U_{ion} = \frac{e^2}{D} \sum \rho_j Z_j N_j \quad (3.134)$$

Substituting equation (3.128) into equation (3.134) yields

$$U_{ion} = \frac{e^2}{D} \sum \rho_j Z_j \left((Z_j/\sigma_j - \sigma_j \Lambda \frac{\pi}{2\Delta}) / (1 + \sigma_j \Gamma) - Z_j/\sigma_j \right) \quad (3.135)$$

or

$$U_{ion} = \frac{e^2}{D} \sum \left(\rho_j Z_j^2 / \sigma_j (1/(1 + \sigma_j \Gamma) - 1) - \frac{\pi \Lambda}{2\Delta} \left(\frac{\rho_j \sigma_j Z_j}{1 + \sigma_j \Gamma} \right) \right) \quad (3.136)$$

or

$$U_{ion} = \frac{-e^2}{D} \left(\sum \left(\frac{\rho_j Z_j^2 \Gamma}{1 + \sigma_j \Gamma} \right) + \frac{\pi}{2\Delta} \Lambda^2 \Omega \right) \quad (3.137)$$

where

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum \frac{\rho_k \sigma_k^3}{1 + \sigma_k \Gamma} \quad (3.138)$$

which is the result presented by Blum (1975).

4. Discussion of Non-Equal Diameter Mean-Spherical-Approximation Model

The derivation of the non-equal diameter Mean Spherical Approximation (MSA) model for electrolyte mixtures involves considerable mathematical manipulation. This section summarizes the derivation and presents a physical interpretation of the resulting relations.

Equations of state for mixtures can be derived from the energy equation (equation (3.1)), once an expression for the radial distribution function (g_{ij}) is known, by integrating over temperature to obtain the Helmholtz free energy and differentiating with respect to volume to obtain the pressure. In electrolyte mixtures, one cannot assume a simple value or expression for g_{ij} (e.g., unity) because the coulombic potential is long-range, and that leads to a divergent integral. Fortunately, the electrostatic force felt by an ion j some distance away from ion i is attenuated (or screened) by the electrostatic forces of other nearby ions. This "many-body" effect, once treated properly, eliminates the apparent divergence. The derivation presented in section 3 was based on a Fourier transform of the Ornstein-Zernike equation to obtain a "screened radial distribution function".

Free-volume effects on mixture properties are properly accounted for in the MSA model (unlike the Debye-Huckel model and its many variations) as a result of the definitions of the total correlation function $\langle h_{ij} \rangle$ and the direct correlation function $\langle c_{ij} \rangle$ in equations (3.6) and (3.7). Hard-sphere repulsion is assumed to exist for all ionic and uncharged species.

The MSA internal energy is obtained to be the sum of uncharged-hard-sphere and ionic contributions. An implicit screening-factor (Γ) relation arises for mixtures with ions of different diameters, requiring iteration to obtain the screening factor. Table 4.1 presents a comparison between Debye-Huckel and the ionic-term in the MSA.

The ion internal energy of both the Debye-Huckel and MSA models becomes zero as the density or the ionic strength approaches zero. The ion internal energy of the Debye-Huckel and equal-diameter MSA becomes zero as the temperature becomes infinite. The ion internal energy of the non-equal diameter MSA approaches a non-zero limit as the temperature becomes infinite.

Table 4.1

Comparison of MSA and Debye Huckel Equations

MSA

Screening
Factor

$$2\Gamma = \left(\frac{4\pi\beta e^2}{D} \sum \rho_i \left(\frac{Z_i - \pi\sigma_i^2\Lambda/(2\Delta)}{1+\sigma_i\Gamma} \right)^2 \right)^{1/2}$$

$$* \quad 2\Gamma(1+\sigma\Gamma) = \left(\frac{4\pi\beta e^2}{D} \sum \rho_k Z_k^2 \right)^{1/2}$$

U_{ion}

$$U_{ion} = \frac{-e^2}{D} \left(\sum \left(\frac{\rho_i Z_i^2 \Gamma}{1+\sigma_i \Gamma} \right) + \frac{\pi}{2\Delta} \Lambda^2 \Omega \right)$$

$$* \quad U_{ion} = \frac{-e^2}{D\sigma^2} \left(\sum \rho_k Z_k^2 \right) \left(\frac{4\pi\beta e^2}{D} \sum \rho_k Z_k^2 \right)^{-1/2} \left(1 + \sigma \left(\frac{4\pi\beta e^2}{D} \sum \rho_k Z_k^2 \right)^{1/2} \right. \\ \left. - \left(1 + 2\sigma \left(\frac{4\pi\beta e^2}{D} \sum \rho_k Z_k^2 \right)^{1/2} \right)^{1/2} \right)$$

Debye-Huckel

Screening
Factor

$$K = \left(\frac{4\pi\beta e^2}{D} \sum \rho_k Z_k^2 \right)^{1/2}$$

U_{ion}

$$U_{ion} = - \left(\frac{4\pi\beta e^2}{D} \sum \rho_k Z_k^2 \right)^{3/2} / 8\pi\beta$$

* all ion diameters equal

5. Explicit MSA Screening Factor

As noted in Section 4, an implicit screening factor arises for mixtures of ions of different sizes. Thus an iterative solution is required, and the Helmholtz free energy can not be obtained from direct integration of

$$A = \beta^{-1} \int_0^\beta U_{\text{ion}}(\beta) d\beta \quad (5.1)$$

because the ion internal energy is a function of the implicit screening factor (Γ). Rather, the complex method of Høye and Stell (1977) using manipulations in Fourier space has been used by Blum and Høye (1977) to obtain an analytical expression for the Helmholtz free energy, and hence an expression for activity coefficients.

An explicit MSA screening factor relation would enable more straightforward derivation of expressions for thermodynamic properties, would facilitate analysis of the behavior of the MSA and require minimal computational expense. An asymptotic form of the MSA screening factor will be derived, about the Debye-Hückel limit, by starting with equation 3.126

$$Z_j + N_j \sigma_j = d a_j / 2\Gamma \quad (3.126)$$

Squaring equation 3.126, followed by multiplying both sides by ρx_j yields

$$\rho x_j (Z_j + \sigma_j N_j)^2 = \rho x_j a_j^2 d^2 / (4\Gamma^2) \quad (5.2)$$

Summing over all j in equation 5.2 yields

$$\rho \sum x_j (Z_j + \sigma_j N_j)^2 = \rho d^2 (\sum x_j a_j^2) / (4\Gamma^2) \quad (5.3)$$

Substituting 3.63 into equation 5.3 gives

$$\rho \sum x_j (Z_j + \sigma_j N_j)^2 = \alpha^2 d^2 / (4\Gamma^2) \quad (5.4)$$

Therefore, the MSA screening factor is given by:

$$\Gamma = (\alpha/2) (\rho \sum x_j (Z_j + \sigma_j N_j)^2)^{1/2} \quad (5.5)$$

Note that in the limit of small diameters, the MSA screening factor approaches the Debye-Huckel limit divided by two (see Table 4.1).

The MSA and Debye Huckel ion internal energies do become equal in this limit, however. To calculate the screening factor for finite-size ions, the parameter N_j must be known. An implicit expression was presented for N_j in Section Three as equation 3.114.

$$N_j = \sum \rho_k Z_k 2\pi \int_0^\infty dt \, t \, h_{kj} + \frac{\pi}{4} X_2 + \frac{\pi}{6} \sum \rho_k \sigma_k^3 N_k \quad (3.114)$$

To simplify the derivation in Section Three, a variable B_j was defined as

$$B_j = \sum \rho_k Z_k 2\pi \int_0^\infty dt \, t \, h_{kj} \quad (3.116)$$

Equation 3.114 becomes

$$N_j = B_j + \frac{\pi}{4} X_2 + \frac{\pi}{6} \sum \rho_k \sigma_k^3 N_k \quad (5.6)$$

Equation 5.6 can be easily inverted. Multiplying equation 5.6 by $\rho x_j \sigma_j^3$

and summing over j yields

$$\rho \sum x_j \sigma_j^3 N_j = \rho \sum x_j \sigma_j^3 B_j + (\rho \sum x_j \sigma_j^3) \left(-\frac{\pi}{4} \chi_2 + \frac{\pi}{6} \rho \sum x_k \sigma_k^3 N_k \right) \quad (5.7)$$

Substituting equation 3.112 into equation 5.7 yields

$$0 = \rho \sum x_k \sigma_k^3 B_k + (1-\Delta) (3/2 \rho \sum x_k Z_k \sigma_k^2) - \Delta \rho \sum x_k \sigma_k^3 N_k \quad (5.8)$$

Substituting equation 5.8 into equation 5.6 yields

$$N_j = B_j + \frac{\pi}{4\Delta} \rho \sum x_k Z_k \sigma_k^2 + \frac{\pi}{6\Delta} \rho \sum x_k \sigma_k^3 B_k \quad (5.9)$$

Now, in the Debye-Huckel limit, the total correlation function is

$$h_{jk} = - \frac{\beta e^2}{D r} Z_j Z_k \text{EXP}^{-\kappa r} \quad (5.10)$$

Substituting equation 5.10 into equation 3.116 yields

$$B_j = -(2\pi\rho\beta e^2/D) Z_j \sum x_k Z_k^2 \int_0^\infty dr \text{EXP}^{-\kappa r} \quad (5.11)$$

Integrating equation 5.11 gives

$$B_j = - \frac{Z_j 2\pi\rho\beta e^2}{DK} \sum x_k Z_k^2 \quad (5.12)$$

or, more simply

$$B_j = - \frac{Z_j K}{2} \quad (5.13)$$

Therefore, equation 5.9 becomes

$$N_j = -Z_j \frac{K}{2} + \frac{\pi}{4\Delta} \rho \sum x_k Z_k \sigma_k^2 - \frac{\pi}{12\Delta} K \rho \sum x_k \sigma_k^3 Z_k \quad (5.14)$$

Equation 5.14 is substituted into equation 5.5 to give the explicit screening factor

$$\Gamma = \frac{\alpha}{2} \left(\rho \sum x_j \left(Z_j + \sigma_j \left(\frac{\pi}{4\Delta} \rho \sum x_k Z_k \sigma_k^2 - Z_j \frac{K}{2} - \frac{\pi}{12\Delta} K \rho \sum x_k \sigma_k^3 Z_k \right) \right)^2 \right)^{1/2} \quad (5.15)$$

Tables 5.1 and 5.2 compare the screening factor and ion internal energy predicted by Debye-Huckel, MSA and explicit asymptotic MSA for single salt in a solvent similar to water. Various ion sizes, ion charges, temperatures, densities, and dielectric constants are selected. The explicit MSA internal energy is calculated using only the first term in equation 3.137. For ion diameters near that of water, the second term is negligible. At small ion diameters, the MSA and explicit MSA screening factors agree closely and are one-half the Debye-Huckel value; the internal energies predicted by all of the methods agree closely. The Debye-Huckel screening factor, unlike both MSA models, is not a function of ion diameters. The explicit MSA becomes progressively worse, as expected, with increasing ion diameters. For fixed ion diameters, the deviation between predictions is larger at higher charge numbers. The MSA screening factor and internal energy decrease as the ion diameter of component two increases. The explicit MSA shows this trend only at charge numbers of unity and low ionic strengths. It should be noted that

the prediction of internal energy (and the other macroscopic properties) is of key interest to chemical-process design calculations; the screening factor is an intermediate quantity.

Inaccurate predictions of the explicit asymptotic MSA arise from the terms in equation 5.10 involving B_j , which were based on the Debye-Huckel radial distribution function. Remembering that the MSA total-correlation function is unknown (the Ornstein-Zernike transformation only provides an integral, over dr , of the value times r), an empirical correction factor can be formulated for the explicit MSA using the comparisons to the behavior of the MSA in Tables 5.1 and 5.2.

As the ionic strength increases, B_j should increase less rapidly than given by equation 5.13. Equation 5.17 presents a simple empirically-corrected expression for B_j

$$B_j = -Z_j \frac{K}{2(1+K)} \quad (5.17)$$

Equation 5.17 approaches equation 5.13 at low ionic strength, low density or high temperature. Tables 5.3 and 5.4 summarize the predictions of the explicit MSA using the above equation. The proper variation of both the screening factor and internal energy as a function of ion size is observed. However, the predicted screening factor decreases too rapidly with increasing ion size. To improve predictions for ion sizes near that of water, a slight variation of equation 5.17 is presented in equation 5.18.

$$B_j = -Z_j \frac{K}{2 (1 + \alpha (\rho \sum_i x_i Z_i^2 \sigma_i^2)^{1/2})} \quad (5.18)$$

Tables 5.5 and 5.6 summarize the predictions of the explicit MSA using the above equation. The predicted screening factor and ion internal energy generally decrease with increasing ion sizes, similar to the behavior predicted by the MSA. At higher ion sizes, the explicit MSA does predict a slight increase in screening factor with increasing ion size. However, the ion internal energy predicted by both the MSA and explicit MSA decrease with increasing ion size at these conditions. The explicit-MSA and MSA screening-factor and ion-internal-energy predictions differ by a maximum of 35% and 17%, respectively.

Figures 5.1, 5.2, 5.3 and 5.4 illustrate screening-factor and ion-internal-energy predictions of the Debye Huckel, MSA, and explicit MSA (based on equation 5.18) for 1-1 and 2-2 electrolytes in a solvent similar to water at 298 K. A constant density of 0.055 gmole/cm³, 20 mole percent of ions in solution, and a constant cation hard-sphere diameter of 1.0 Å were assumed for these figures. The anion hard-sphere diameter was varied from nearly zero to 3 Å. The MSA and explicit MSA agree closely (within 1%) at the lower ion sizes, independent of the cation to anion diameter ratio. At larger ion sizes (1 Å cation and 3 Å anion), the methods agree to within 10% to 15%. The agreement between the MSA and explicit MSA is a function of both average ion size and size difference between ions.

Figures 5.3 and 5.4 present ion-internal-energy predictions for 1-1 and 2-2 electrolytes, respectively, at the same conditions assumed in Figures 5.1 and 5.2. Similar agreement between the models is observed. It should be noted that the MSA and explicit MSA do not approach the Debye Huckel limit as the anion diameter approaches zero because the cation diameter is fixed at a non-negligible size of $1\text{\AA}$.

The explicit MSA, based on equation 5.18, provides reasonable screening-factor and ion-internal-energy predictions for ion sizes comparable to (or less than) that of water. While equation 5.18 is strictly valid only in this region, predictions for equal-size ions are accurate to much larger ion sizes. Table 5.7 and Figures 5.5, 5.6, 5.7 and 5.8 present a comparison of the explicit MSA to the MSA for 1-1 and 2-2 electrolytes. Equal-size ions, 20 mole percent of ions in solution, and a constant Δ of 0.53 were used. A constant Δ was used rather than a constant density since a large increase in ion size can result in a non-physical negative Δ for a constant density. In this case, the density decreases as the ion sizes increase. Again the explicit MSA and MSA predictions agree well (with maximum deviations of 22% for screening factor and 10% for ion internal energy). Debye Huckel predicted screening factors and ion internal energies are much higher than the MSA models, as in the previous cases.

An explicit MSA screening-factor relation has been derived in this section based on the asymptotic behavior of the ion total-correlation function in the limit of small ion sizes. This development is based on the MSA theory for electrolytes, rather than the more typical approach to extend the Debye-Huckel theory, such as Pitzer (1973). To improve predictions for ion sizes comparable to that of water, an empirical correction function was developed for the explicit MSA by comparison to the predictions of the (implicit) MSA. Screening factor and ion internal energy predictions of the explicit MSA agree well with the MSA for ion sizes near that of water and for much larger ion sizes when the ions have equal diameters. The explicit MSA (based on equation 5.18) will be used in the development of an equation of state for electrolytes in Section 6.

Table 5.1

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 298 K

 $\rho = 0.055$ gmole/cm³

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	K_D	Screening Factor	
							Γ_M	Γ_N
1	-1	0.1	0.1	0.01	0.01	0.773	0.385	0.386
1	-1	0.1	0.1	1	1	0.773	0.298	0.237
1	-1	0.1	0.1	1	2	0.773	0.277	0.179
1	-1	0.1	0.1	1	3	0.773	0.263	0.171
1	-1	0.2	0.2	1	1	1.094	0.392	0.248
1	-1	0.2	0.2	1	2	1.094	0.361	0.177
1	-1	0.2	0.2	1	3	1.094	0.342	0.319
1	-1	0.3	0.3	1	1	1.340	0.459	0.221
1	-1	0.3	0.3	1	2	1.340	0.419	0.226
1	-1	0.3	0.3	1	3	1.340	0.396	0.570
2	-2	0.1	0.1	1	1	1.547	0.512	0.175
2	-2	0.1	0.1	1	2	1.547	0.467	0.327
2	-2	0.1	0.1	1	3	1.547	0.443	0.782
2	-2	0.2	0.2	1	1	2.188	0.659	0.103
2	-2	0.2	0.2	1	2	2.188	0.597	0.947
2	-2	0.2	0.2	1	3	2.188	0.569	2.761
2	-2	0.3	0.3	1	1	2.679	0.761	0.455
2	-2	0.3	0.3	1	2	2.679	0.687	1.682
2	-2	0.3	0.3	1	3	2.679	0.651	3.419
2	-1	0.1	0.2	1	1	1.340	0.459	0.221
2	-1	0.1	0.2	1	2	1.340	0.419	0.226
2	-1	0.1	0.2	1	3	1.340	0.396	0.570
2	-1	0.2	0.4	1	1	1.894	0.594	0.050
2	-1	0.2	0.4	1	2	1.894	0.558	0.513
2	-1	0.2	0.4	1	3	1.894	0.539	0.539
1	-1	0.1	0.1	3	2	0.773	0.242	0.075
1	-1	0.1	0.1	3	3	0.773	0.229	0.062
1	-1	0.1	0.1	3	4	0.773	0.220	0.171
2	-2	0.1	0.1	3	2	1.547	0.395	0.813
2	-2	0.1	0.1	3	3	1.547	0.368	1.021
2	-2	0.1	0.1	3	4	1.547	0.350	1.463

 Γ_N Non-Iterative MSA Screening Factor (uncorrected) Γ_M MSA Screening Factor K_D Debye-Huckel Screening Factor

Component 3 = Water

D = 78

 $\sigma(3) = 3 \text{ \AA}^{\circ}$

Table 5.1 (Continued)

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 298 K

 $\rho = 0.055$ gmole/cm³

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	U_D	Internal Energy	
							U_M	U_N
1	-1	0.1	0.1	0.01	0.01	-329.2	-326.5	-327.0
1	-1	0.1	0.1	1	1	-329.2	-195.4	-163.1
1	-1	0.1	0.1	1	2	-329.2	-168.4	-120.6
1	-1	0.1	0.1	1	3	-329.2	-152.5	-110.3
1	-1	0.2	0.2	1	1	-931.2	-479.6	-337.9
1	-1	0.2	0.2	1	2	-931.2	-405.6	-239.5
1	-1	0.2	0.2	1	3	-931.2	-364.5	-334.4
1	-1	0.3	0.3	1	1	-1710.6	-803.3	-462.3
1	-1	0.3	0.3	1	2	-1710.6	-671.0	-433.4
1	-1	0.3	0.3	1	3	-1710.6	-600.7	-732.1
2	-2	0.1	0.1	1	1	-2633.7	-1152.4	-507.5
2	-2	0.1	0.1	1	2	-2633.7	-953.6	-755.9
2	-2	0.1	0.1	1	3	-2633.7	-849.4	-1144.9
2	-2	0.2	0.2	1	1	-7449.2	-2704.9	-2119.0
2	-2	0.2	0.2	1	2	-7449.2	-2202.0	-2769.2
2	-2	0.2	0.2	1	3	-7449.2	-1953.2	-3379.5
2	-2	0.3	0.3	1	1	-13674.0	-4410.7	-3192.3
2	-2	0.3	0.3	1	2	-13674.0	-3562.0	-5169.3
2	-2	0.3	0.3	1	3	-13674.0	-3152.6	-5500.4
2	-1	0.1	0.2	1	1	-1710.6	-803.3	-462.3
2	-1	0.1	0.2	1	2	-1710.6	-713.5	-433.4
2	-1	0.1	0.2	1	3	-1710.6	-664.2	-732.1
2	-1	0.2	0.4	1	1	-4838.4	-1902.1	-243.1
2	-1	0.2	0.4	1	2	-4838.4	-1671.4	-1586.5
2	-1	0.2	0.4	1	3	-4838.4	-1551.3	-2348.5
1	-1	0.1	0.1	3	2	-329.2	-129.4	-54.1
1	-1	0.1	0.1	3	3	-329.2	-115.6	-44.4
1	-1	0.1	0.1	3	4	-329.2	-106.2	-91.4
2	-2	0.1	0.1	3	2	-2633.7	-683.5	-929.1
2	-2	0.1	0.1	3	3	-2633.7	-595.2	-855.3
2	-2	0.1	0.1	3	4	-2633.7	-539.3	-825.3

 U_N Non-Iterative MSA Ionic Internal Energy (uncorrected) U_M MSA Ionic Internal Energy U_D Debye-Huckel Ionic Internal Energy

Component 3 = Water

D = 78

 $\sigma(3) = 3 \text{ \AA}^\circ$

Table 5.2

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 500 K

 $\rho = 0.055$ gmole/cm³

D = 78

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	K_D	Screening Factor	
							Γ_M	Γ_N
1	-1	0.1	0.1	1	1	0.597	0.241	0.209
1	-1	0.1	0.1	1	2	0.597	0.225	0.171
1	-1	0.1	0.1	1	3	0.597	0.214	0.150

T = 298 K

 $\rho = 0.065$ gmole/cm³

D = 78

1	-1	0.1	0.1	1	1	0.841	0.319	0.244
1	-1	0.1	0.1	1	2	0.841	0.295	0.179
1	-1	0.1	0.1	1	3	0.841	0.281	0.187

T = 373 K

 $\rho = 0.055$ gmole/cm³

D = 56

1	-1	0.1	0.1	1	1	0.816	0.311	0.241
1	-1	0.1	0.1	1	2	0.816	0.288	0.179
1	-1	0.1	0.1	1	3	0.816	0.274	0.181

T = 298 K

 $\rho = 0.045$ gmole/cm³

D = 78

1	-1	0.1	0.1	1	1	0.700	0.275	0.227
1	-1	0.1	0.1	1	2	0.700	0.256	0.177
1	-1	0.1	0.1	1	3	0.700	0.243	0.160

Γ_N Non-Iterative MSA Screening Factor (uncorrected)
 Γ_M MSA Screening Factor
 K_D Debye-Huckel Screening Factor

Component 3 = Water

D = 78

 $\sigma(3) = 3 \text{ \AA}$

Table 5.2 (Continued)

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 500 K		gmole/cm ³					Internal Energy	
$\rho = 0.055$							U_M	U_N
D = 78								
Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	U_D		
1	-1	0.1	0.1	1	1	-254.2	-165.1	-147.3
1	-1	0.1	0.1	1	2	-254.2	-144.7	-116.6
1	-1	0.1	0.1	1	3	-254.2	-132.3	-99.6
T = 298 K		gmole/cm ³						
$\rho = 0.065$								
D = 78								
1	-1	0.1	0.1	1	1	-357.9	-205.6	-166.7
1	-1	0.1	0.1	1	2	-357.9	-176.4	-120.4
1	-1	0.1	0.1	1	3	-357.9	-159.5	-117.8
T = 373 K		gmole/cm ³						
$\rho = 0.055$								
D = 56								
1	-1	0.1	0.1	1	1	-483.7	-281.2	-230.6
1	-1	0.1	0.1	1	2	-483.7	-241.7	-167.9
1	-1	0.1	0.1	1	3	-483.7	-218.6	-160.0
T = 298 K		gmole/cm ³						
$\rho = 0.045$								
D = 78								
1	-1	0.1	0.1	1	1	-297.8	-183.8	-157.7
1	-1	0.1	0.1	1	2	-297.8	-159.0	-119.7
1	-1	0.1	0.1	1	3	-297.8	-144.3	-104.7
U _N Non-Iterative MSA Ionic Internal Energy (uncorrected)								
U _M MSA Ionic Internal Energy								
U _D Debye-Huckel Ionic Internal Energy								

Component 3 = Water

D = 78

 $\sigma(3) = 3 \text{ \AA}$

Table 5.3

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 298 K

 $\rho = 0.055$ gmole/cm³

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	K_D	Screening Factor	
							Γ_M	Γ_N
1	-1	0.1	0.1	0.01	0.01	0.773	0.385	0.386
1	-1	0.1	0.1	1	1	0.773	0.298	0.302
1	-1	0.1	0.1	1	2	0.773	0.277	0.265
1	-1	0.1	0.1	1	3	0.773	0.263	0.240
1	-1	0.2	0.2	1	1	1.094	0.392	0.404
1	-1	0.2	0.2	1	2	1.094	0.361	0.343
1	-1	0.2	0.2	1	3	1.094	0.342	0.304
1	-1	0.3	0.3	1	1	1.340	0.459	0.478
1	-1	0.3	0.3	1	2	1.340	0.419	0.397
1	-1	0.3	0.3	1	3	1.340	0.396	0.347
2	-2	0.1	0.1	1	1	1.547	0.512	0.539
2	-2	0.1	0.1	1	2	1.547	0.467	0.439
2	-2	0.1	0.1	1	3	1.547	0.443	0.385
2	-2	0.2	0.2	1	1	2.188	0.659	0.718
2	-2	0.2	0.2	1	2	2.188	0.597	0.565
2	-2	0.2	0.2	1	3	2.188	0.569	0.500
2	-2	0.3	0.3	1	1	2.679	0.761	0.852
2	-2	0.3	0.3	1	2	2.679	0.687	0.655
2	-2	0.3	0.3	1	3	2.679	0.651	0.588
2	-1	0.1	0.2	1	1	1.340	0.459	0.478
2	-1	0.1	0.2	1	2	1.340	0.419	0.397
2	-1	0.1	0.2	1	3	1.340	0.396	0.347
2	-1	0.2	0.4	1	1	1.894	0.594	0.637
2	-1	0.2	0.4	1	2	1.894	0.558	0.555
2	-1	0.2	0.4	1	3	1.894	0.539	0.515
1	-1	0.1	0.1	3	2	0.773	0.242	0.182
1	-1	0.1	0.1	3	3	0.773	0.229	0.137
1	-1	0.1	0.1	3	4	0.773	0.220	0.100
2	-2	0.1	0.1	3	2	1.547	0.395	0.218
2	-2	0.1	0.1	3	3	1.547	0.368	0.069
2	-2	0.1	0.1	3	4	1.547	0.350	0.135

 Γ_N Non-Iterative MSA Screening Factor (using equation 5.17) Γ_M MSA Screening Factor K_D Debye-Huckel Screening Factor

Component 3 = Water

D = 78

 $\sigma(3) = 3 \text{ \AA}$

Table 5.3 (Continued)

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 298 K

 $\rho = 0.055$ gmole/cm³

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	U_0	Internal Energy	
							U_M	U_N
1	-1	0.1	0.1	0.01	0.01	-329.2	-326.5	-327.0
1	-1	0.1	0.1	1	1	-329.2	-195.4	-197.5
1	-1	0.1	0.1	1	2	-329.2	-168.4	-162.9
1	-1	0.1	0.1	1	3	-329.2	-152.5	-141.7
1	-1	0.2	0.2	1	1	-931.2	-479.6	-489.7
1	-1	0.2	0.2	1	2	-931.2	-405.6	-390.2
1	-1	0.2	0.2	1	3	-931.2	-364.5	-333.8
1	-1	0.3	0.3	1	1	-1710.6	-803.3	-825.6
1	-1	0.3	0.3	1	2	-1710.6	-671.0	-644.9
1	-1	0.3	0.3	1	3	-1710.6	-600.7	-545.7
2	-2	0.1	0.1	1	1	-2633.7	-1152.4	-1191.3
2	-2	0.1	0.1	1	2	-2633.7	-953.6	-916.6
2	-2	0.1	0.1	1	3	-2633.7	-849.4	-776.6
2	-2	0.2	0.2	1	1	-7449.2	-2704.9	-2845.8
2	-2	0.2	0.2	1	2	-7449.2	-2202.0	-2130.5
2	-2	0.2	0.2	1	3	-7449.2	-1953.2	-1814.7
2	-2	0.3	0.3	1	1	-13674.0	-4410.7	-4696.6
2	-2	0.3	0.3	1	2	-13674.0	-3562.0	-3469.2
2	-2	0.3	0.3	1	3	-13674.0	-3152.6	-2976.4
2	-1	0.1	0.2	1	1	-1710.6	-803.3	-825.6
2	-1	0.1	0.2	1	2	-1710.6	-713.5	-703.7
2	-1	0.1	0.2	1	3	-1710.6	-664.2	-637.7
2	-1	0.2	0.4	1	1	-4838.4	-1902.1	-1987.0
2	-1	0.2	0.4	1	2	-4838.4	-1671.4	-1662.8
2	-1	0.2	0.4	1	3	-4838.4	-1551.3	-1500.6
1	-1	0.1	0.1	3	2	-329.2	-129.4	-107.0
1	-1	0.1	0.1	3	3	-329.2	-115.6	-81.2
1	-1	0.1	0.1	3	4	-329.2	-106.2	-63.2
2	-2	0.1	0.1	3	2	-2633.7	-683.5	-482.7
2	-2	0.1	0.1	3	3	-2633.7	-595.2	-194.1
2	-2	0.1	0.1	3	4	-2633.7	-539.3	-312.6

 U_N Non-Iterative MSA Ionic Internal Energy (using equation 5.17) U_M MSA Ionic Internal Energy U_0 Debye-Huckel Ionic Internal Energy

Component 3 = Water

D = 78

 $\sigma(3) = 3 \text{ \AA}$

Table 5.4

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 500 K $\rho = 0.055$ gmole/cm ³ D = 78								
Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	K _D	Screening Factor	
							Γ_M	Γ_N
1	-1	0.1	0.1	1	1	0.597	0.241	0.243
1	-1	0.1	0.1	1	2	0.597	0.225	0.218
1	-1	0.1	0.1	1	3	0.597	0.214	0.202
T = 298 K $\rho = 0.065$ gmole/cm ³ D = 78								
1	-1	0.1	0.1	1	1	0.841	0.319	0.324
1	-1	0.1	0.1	1	2	0.841	0.295	0.283
1	-1	0.1	0.1	1	3	0.841	0.281	0.258
T = 373 K $\rho = 0.055$ gmole/cm ³ D = 56								
1	-1	0.1	0.1	1	1	0.816	0.311	0.316
1	-1	0.1	0.1	1	2	0.816	0.288	0.276
1	-1	0.1	0.1	1	3	0.816	0.274	0.249
T = 298 K $\rho = 0.045$ gmole/cm ³ D = 78								
1	-1	0.1	0.1	1	1	0.700	0.275	0.278
1	-1	0.1	0.1	1	2	0.700	0.256	0.245
1	-1	0.1	0.1	1	3	0.700	0.243	0.222
Γ_N Non-Iterative MSA Screening Factor (using equation 5.17) Γ_M MSA Screening Factor K_D Debye-Huckel Screening Factor								

Component 3 = Water
 D = 78
 $\sigma(3) = 3 \text{ \AA}$

Table 5.4 (Continued)

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 500 K
 $\rho = 0.055$ gmole/cm³
D = 78

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	U_D	Internal Energy	
							U_M	U_N
1	-1	0.1	0.1	1	1	-254.2	-165.1	-166.2
1	-1	0.1	0.1	1	2	-254.2	-144.7	-140.8
1	-1	0.1	0.1	1	3	-254.2	-132.3	-124.9

T = 298 K
 $\rho = 0.065$ gmole/cm³
D = 78

1	-1	0.1	0.1	1	1	-357.9	-205.6	-208.4
1	-1	0.1	0.1	1	2	-357.9	-176.4	-170.8
1	-1	0.1	0.1	1	3	-357.9	-159.5	-149.2

T = 373 K
 $\rho = 0.055$ gmole/cm³
D = 56

1	-1	0.1	0.1	1	1	-483.7	-281.2	-284.8
1	-1	0.1	0.1	1	2	-483.7	-241.7	-233.5
1	-1	0.1	0.1	1	3	-483.7	-218.6	-202.4

T = 298 K
 $\rho = 0.045$ gmole/cm³
D = 78

1	-1	0.1	0.1	1	1	-297.8	-183.8	-185.0
1	-1	0.1	0.1	1	2	-297.8	-159.0	-153.9
1	-1	0.1	0.1	1	3	-297.8	-144.3	-133.9

U_N Non-Iterative MSA Ionic Internal Energy (using equation 5.17)
 U_M MSA Ionic Internal Energy
 U_D Debye-Huckel Ionic Internal Energy

Component 3 = Water
D = 78
 $\sigma(3) = 3 \text{ \AA}$

Table 5.5

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 298 K

 $\rho = 0.055$ gmole/cm³

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	K_D	Screening Factor	
							Γ_M	Γ_N
1	-1	0.1	0.1	0.01	0.01	0.773	0.385	0.386
1	-1	0.1	0.1	1	1	0.773	0.298	0.302
1	-1	0.1	0.1	1	2	0.773	0.277	0.290
1	-1	0.1	0.1	1	3	0.773	0.263	0.294
1	-1	0.2	0.2	1	1	1.094	0.392	0.404
1	-1	0.2	0.2	1	2	1.094	0.361	0.390
1	-1	0.2	0.2	1	3	1.094	0.342	0.409
1	-1	0.3	0.3	1	1	1.340	0.459	0.478
1	-1	0.3	0.3	1	2	1.340	0.419	0.464
1	-1	0.3	0.3	1	3	1.340	0.396	0.496
2	-2	0.1	0.1	1	1	1.547	0.512	0.539
2	-2	0.1	0.1	1	2	1.547	0.467	0.532
2	-2	0.1	0.1	1	3	1.547	0.443	0.529
2	-2	0.2	0.2	1	1	2.188	0.659	0.718
2	-2	0.2	0.2	1	2	2.188	0.597	0.710
2	-2	0.2	0.2	1	3	2.188	0.569	0.758
2	-2	0.3	0.3	1	1	2.679	0.761	0.852
2	-2	0.3	0.3	1	2	2.679	0.687	0.851
2	-2	0.3	0.3	1	3	2.679	0.651	0.924
2	-1	0.1	0.2	1	1	1.340	0.459	0.478
2	-1	0.1	0.2	1	2	1.340	0.419	0.472
2	-1	0.1	0.2	1	3	1.340	0.396	0.479
2	-1	0.2	0.4	1	1	1.894	0.594	0.637
2	-1	0.2	0.4	1	2	1.894	0.558	0.637
2	-1	0.2	0.4	1	3	1.894	0.539	0.686
1	-1	0.1	0.1	3	2	0.773	0.242	0.267
1	-1	0.1	0.1	3	3	0.773	0.229	0.252
1	-1	0.1	0.1	3	4	0.773	0.220	0.258
2	-2	0.1	0.1	3	2	1.547	0.395	0.482
2	-2	0.1	0.1	3	3	1.547	0.368	0.455
2	-2	0.1	0.1	3	4	1.547	0.350	0.471

 Γ_N Non-Iterative MSA Screening Factor (using equation 5.18) Γ_M MSA Screening Factor K_D Debye-Huckel Screening Factor

Component 3 = Water

D = 78

 $\sigma(3) = 3 \text{ \AA}^{\circ}$

Table 5.5 (Continued)

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 298 K

 $\rho = 0.055$ gmole/cm³

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	U_0	Internal Energy	
							U_M	U_N
1	-1	0.1	0.1	0.01	0.01	-329.2	-326.5	-327.0
1	-1	0.1	0.1	1	1	-329.2	-195.4	-197.5
1	-1	0.1	0.1	1	2	-329.2	-168.4	-173.6
1	-1	0.1	0.1	1	3	-329.2	-152.5	-163.2
1	-1	0.2	0.2	1	1	-931.2	-479.6	-489.7
1	-1	0.2	0.2	1	2	-931.2	-405.6	-425.4
1	-1	0.2	0.2	1	3	-931.2	-364.5	-403.1
1	-1	0.3	0.3	1	1	-1710.6	-803.3	-825.6
1	-1	0.3	0.3	1	2	-1710.6	-671.0	-712.5
1	-1	0.3	0.3	1	3	-1710.6	-600.7	-677.6
2	-2	0.1	0.1	1	1	-2633.7	-1152.4	-1191.3
2	-2	0.1	0.1	1	2	-2633.7	-953.6	-1019.8
2	-2	0.1	0.1	1	3	-2633.7	-849.4	-949.4
2	-2	0.2	0.2	1	1	-7449.2	-2704.9	-2845.8
2	-2	0.2	0.2	1	2	-7449.2	-2202.0	-2411.6
2	-2	0.2	0.2	1	3	-7449.2	-1953.2	-2255.0
2	-2	0.3	0.3	1	1	-13674.0	-4410.7	-4696.6
2	-2	0.3	0.3	1	2	-13674.0	-3562.0	-3954.2
2	-2	0.3	0.3	1	3	-13674.0	-3152.6	-3702.0
2	-1	0.1	0.2	1	1	-1710.6	-803.3	-825.6
2	-1	0.1	0.2	1	2	-1710.6	-713.5	-752.0
2	-1	0.1	0.2	1	3	-1710.6	-664.2	-731.4
2	-1	0.2	0.4	1	1	-4838.4	-1902.1	-1987.0
2	-1	0.2	0.4	1	2	-4838.4	-1671.4	-1801.4
2	-1	0.2	0.4	1	3	-4838.4	-1551.3	-1765.7
1	-1	0.1	0.1	3	2	-329.2	-129.4	-137.0
1	-1	0.1	0.1	3	3	-329.2	-115.6	-122.0
1	-1	0.1	0.1	3	4	-329.2	-106.2	-115.9
2	-2	0.1	0.1	3	2	-2633.7	-683.5	-752.8
2	-2	0.1	0.1	3	3	-2633.7	-595.2	-654.9
2	-2	0.1	0.1	3	4	-2633.7	-539.3	-609.8

 U_N Non-Iterative MSA Ionic Internal Energy (using equation 5.18) U_M MSA Ionic Internal Energy U_0 Debye-Huckel Ionic Internal Energy

Component 3 = Water

D = 78

 $\sigma(3) = 3 \text{ \AA}^*$

Table 5.6

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 500 K

 $\rho = 0.055$ gmole/cm³

D = 78

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	K_D	Screening Factor	
							Γ_M	Γ_N
1	-1	0.1	0.1	1	1	0.597	0.241	0.243
1	-1	0.1	0.1	1	2	0.597	0.225	0.233
1	-1	0.1	0.1	1	3	0.597	0.214	0.236

T = 298 K

 $\rho = 0.065$ gmole/cm³

D = 78

1	-1	0.1	0.1	1	1	0.841	0.319	0.324
1	-1	0.1	0.1	1	2	0.841	0.295	0.312
1	-1	0.1	0.1	1	3	0.841	0.281	0.325

T = 373 K

 $\rho = 0.055$ gmole/cm³

D = 56

1	-1	0.1	0.1	1	1	0.816	0.311	0.316
1	-1	0.1	0.1	1	2	0.816	0.288	0.303
1	-1	0.1	0.1	1	3	0.816	0.274	0.309

T = 298 K

 $\rho = 0.045$ gmole/cm³

D = 78

1	-1	0.1	0.1	1	1	0.700	0.275	0.278
1	-1	0.1	0.1	1	2	0.700	0.256	0.266
1	-1	0.1	0.1	1	3	0.700	0.243	0.266

 Γ_N Non-Iterative MSA Screening Factor (using equation 5.18) Γ_M MSA Screening Factor K_D Debye-Huckel Screening Factor

Component 3 = Water

D = 78

 $\sigma(3) = 3 \text{ \AA}^\circ$

Table 5.6 (Continued)

Comparison of Predicted Screening Factor and Ion Internal Energy

T = 500 K
 $\rho = 0.055$ gmole/cm³
D = 78

Z(1)	Z(2)	x(1)	x(2)	$\sigma(1)$	$\sigma(2)$	U_D	Internal Energy U_M	U_N
1	-1	0.1	0.1	1	1	-254.2	-165.1	-166.2
1	-1	0.1	0.1	1	2	-254.2	-144.7	-147.9
1	-1	0.1	0.1	1	3	-254.2	-132.3	-139.9

T = 298 K
 $\rho = 0.065$ gmole/cm³
D = 78

1	-1	0.1	0.1	1	1	-357.9	-205.6	-208.4
1	-1	0.1	0.1	1	2	-357.9	-176.4	-183.0
1	-1	0.1	0.1	1	3	-357.9	-159.5	-174.3

T = 373 K
 $\rho = 0.055$ gmole/cm³
D = 56

1	-1	0.1	0.1	1	1	-483.7	-281.2	-284.8
1	-1	0.1	0.1	1	2	-483.7	-241.7	-249.7
1	-1	0.1	0.1	1	3	-483.7	-218.6	-234.8

T = 298 K
 $\rho = 0.045$ gmole/cm³
D = 78

1	-1	0.1	0.1	1	1	-297.8	-183.8	-185.0
1	-1	0.1	0.1	1	2	-297.8	-159.0	-163.0
1	-1	0.1	0.1	1	3	-297.8	-144.3	-152.3

U_N Non-Iterative MSA Ionic Internal Energy (using equation 5.18)
 U_M MSA Ionic Internal Energy
 U_D Debye-Huckel Ionic Internal Energy

Component 3 = Water
D = 78
 $\sigma(3) = 3 \text{ \AA}$

Table 5.7

Comparison of Predicted Screening Factor and Ion Internal Energy
for Equal-Diameter Ions

T = 298 K

$\Delta = 0.53$

$x(1) = x(2) = 0.1$

Z(1)	Z(2)	$\sigma_1 (= \sigma_2)$	Screening Factor			Internal Energy		
			K_D	Γ_M	Γ_N	U_D	U_M	U_N
1	-1	1	0.862	0.325	0.331	- 366.9	- 208.7	- 211.7
1	-1	4	0.686	0.193	0.217	- 292.1	- 92.8	- 98.9
1	-1	8	0.361	0.100	0.113	- 153.8	- 47.3	- 50.6
1	-1	12	0.210	0.0608	0.0675	- 89.4	- 29.9	- 31.7
1	-1	16	0.139	0.0417	0.0455	- 59.1	- 21.3	- 22.4
2	-2	1	1.724	0.554	0.589	-2934.9	-1213.7	-1261.7
2	-2	4	1.372	0.308	0.396	-2336.8	- 469.3	- 521.6
2	-2	8	0.723	0.159	0.207	-1230.2	- 238.1	- 265.4
2	-2	12	0.420	0.0971	0.1225	- 715.6	- 152.6	- 168.8
2	-2	16	0.278	0.0669	0.0821	- 472.5	- 110.0	- 120.8

Γ_N Non-Iterative MSA Screening Factor (using equation 5.18)
 Γ_M MSA Screening Factor
 K_D Debye-Huckel Screening Factor
 U_N Non-Iterative MSA Ionic Internal Energy
 U_M MSA Ionic Internal Energy
 U_D Debye-Huckel Ionic Internal Energy

Component 3 = Water

D = 78

$\sigma(3) = 3 \text{ \AA}$

FIGURE 5.1
 DEBYE HUCKEL, MSA AND EXPLICIT MSA
 SCREENING FACTOR
 1-1 SALT IN WATER AT 298 K

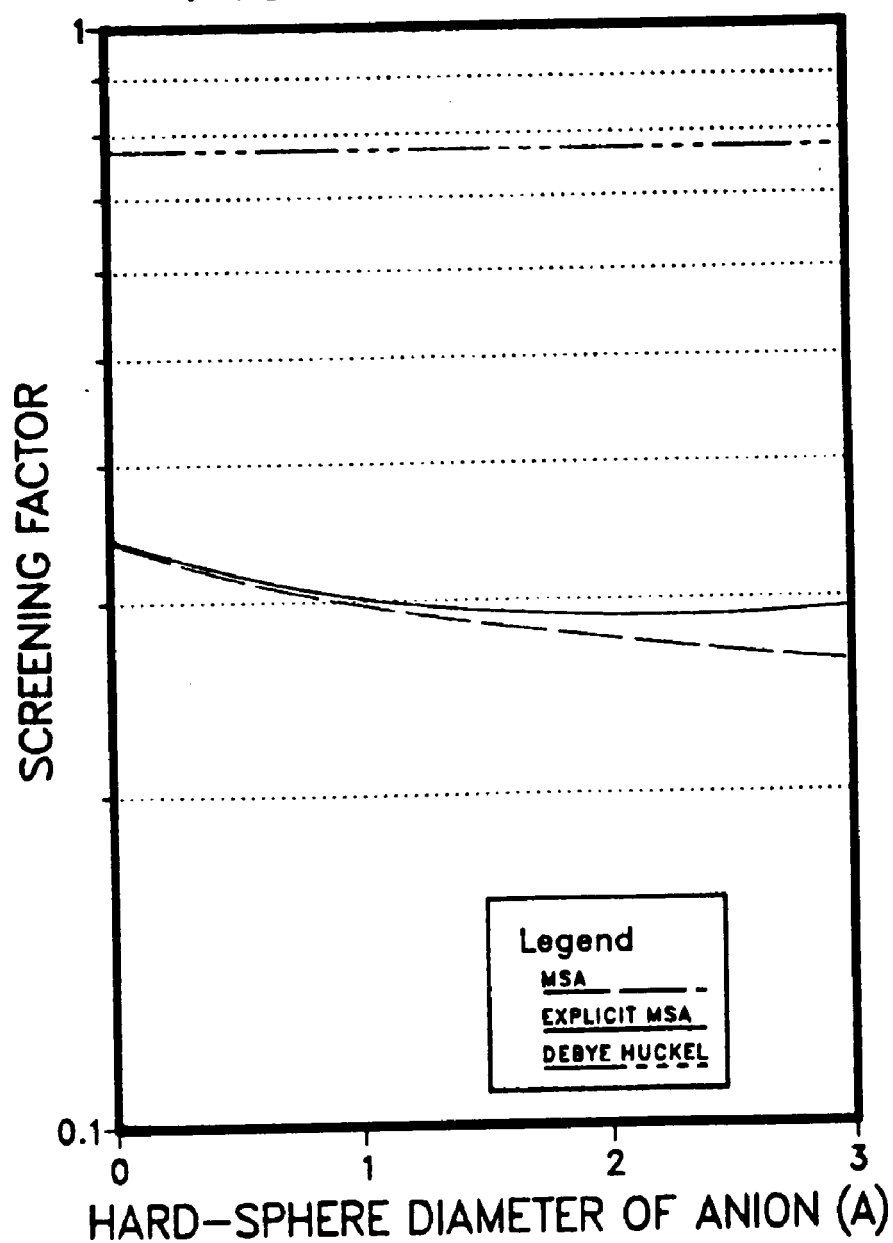


FIGURE 5.2
 DEBYE HUCKEL, MSA AND EXPLICIT MSA
 SCREENING FACTOR
 2-2 SALT IN WATER AT 298 K

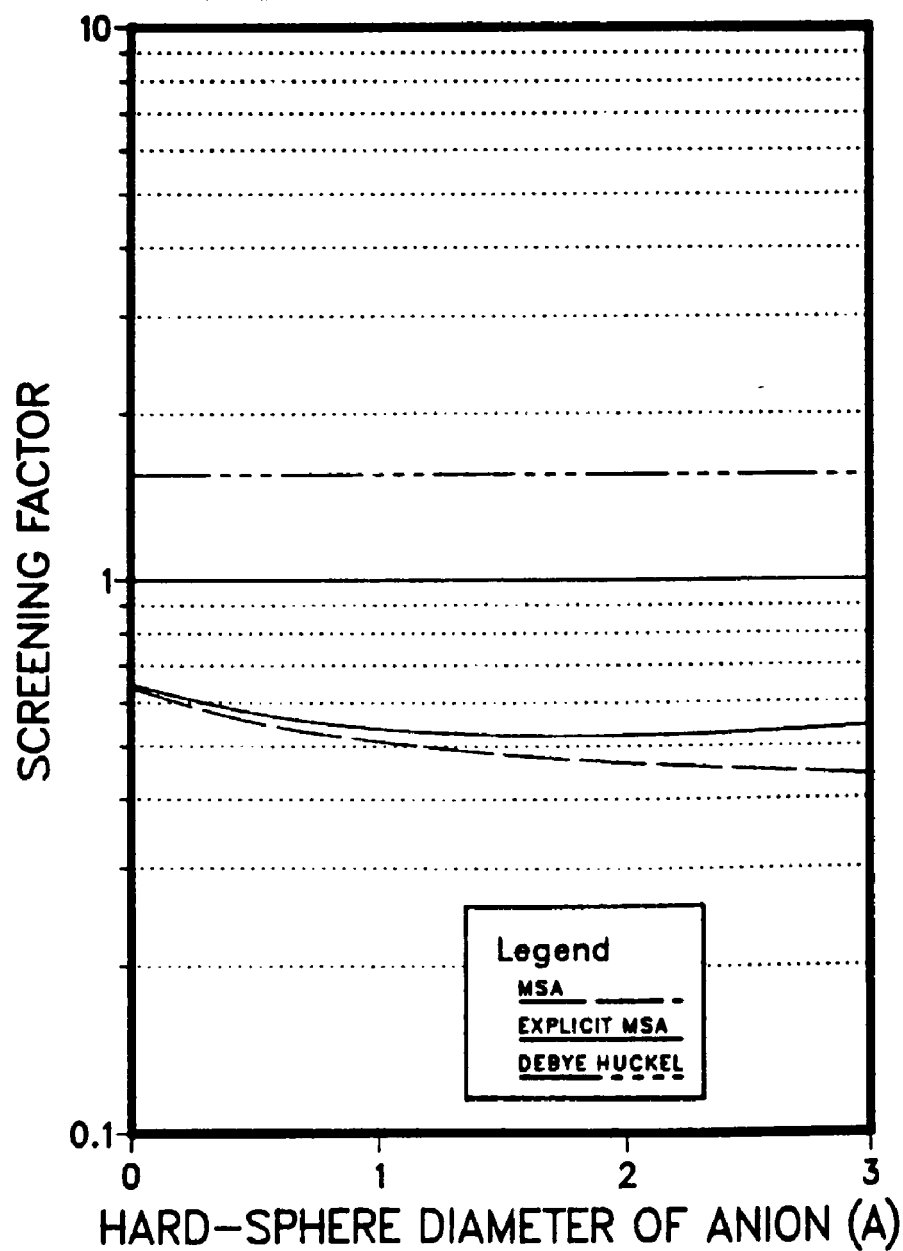


FIGURE 5.3
 DEBYE HUCKEL, MSA AND EXPLICIT MSA
 ION INTERNAL ENERGY
 1-1 SALT IN WATER AT 298 K

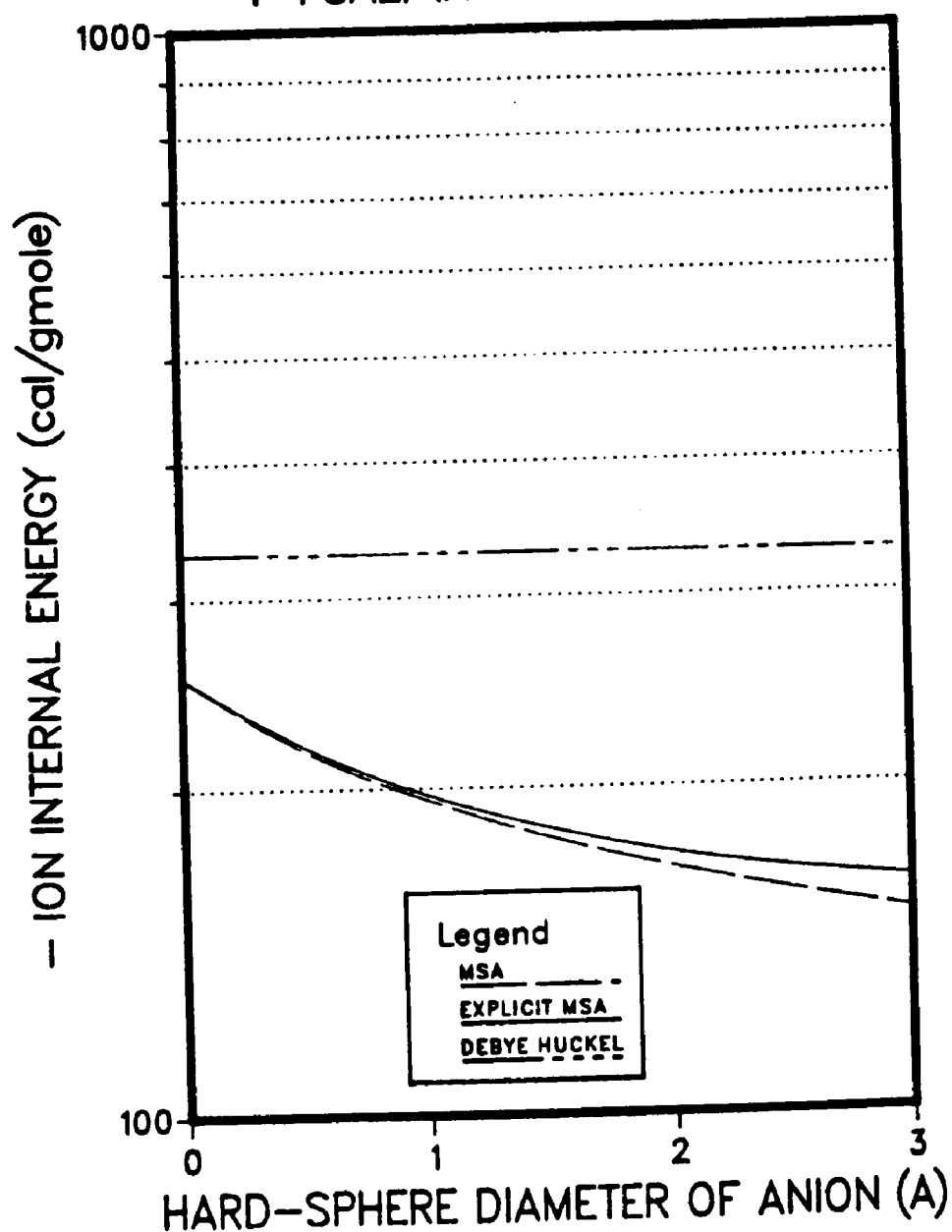


FIGURE 5.4
 DEBYE HUCKEL, MSA AND EXPLICIT MSA
 ION INTERNAL ENERGY
 2-2 SALT IN WATER AT 298 K

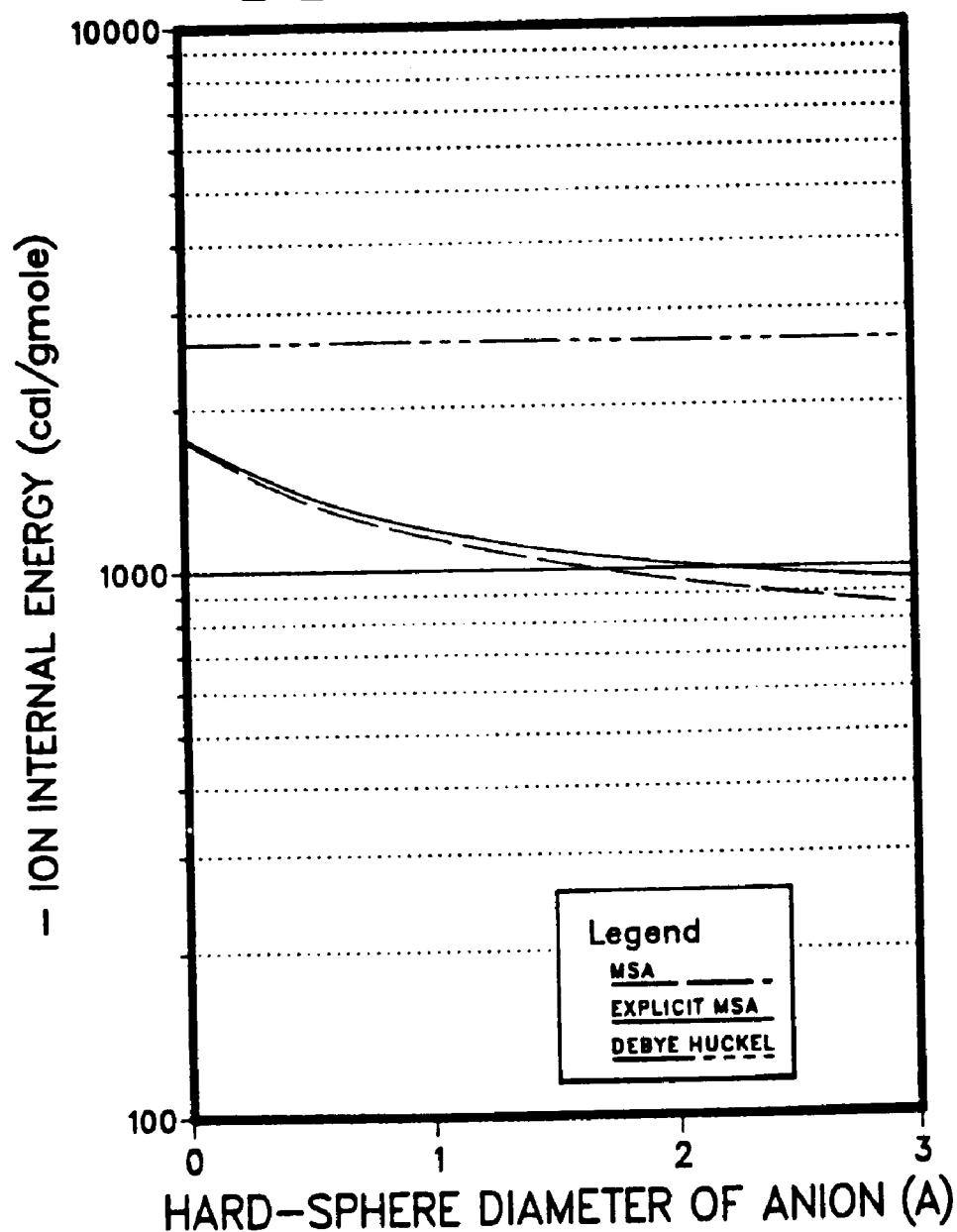


FIGURE 5.5
 DEBYE HUCKEL, MSA AND EXPLICIT MSA
 SCREENING FACTOR
 1-1 SALT IN WATER AT 298 K

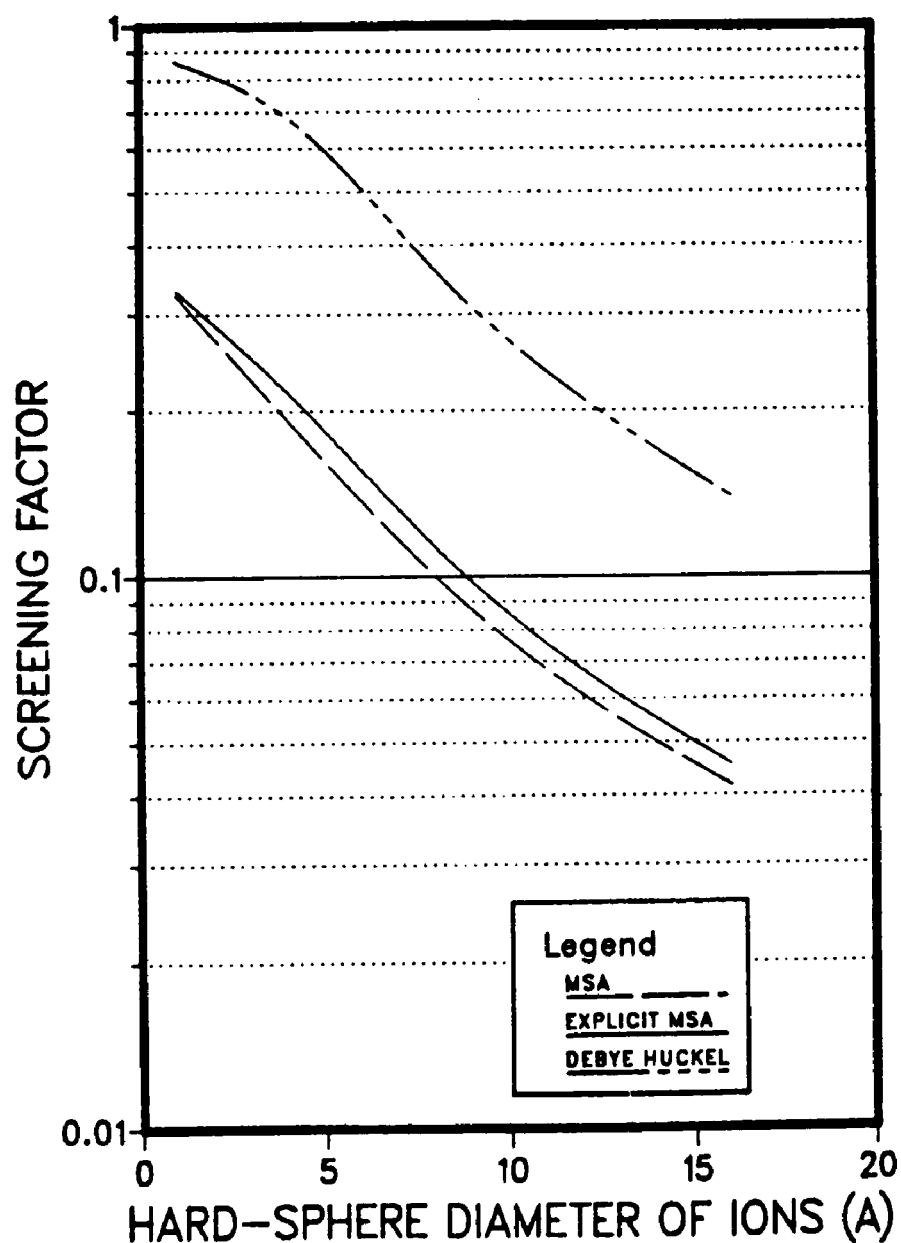


FIGURE 5.6
 DEBYE HUCKEL, MSA AND EXPLICIT MSA
 SCREENING FACTOR
 2-2 SALT IN WATER AT 298 K

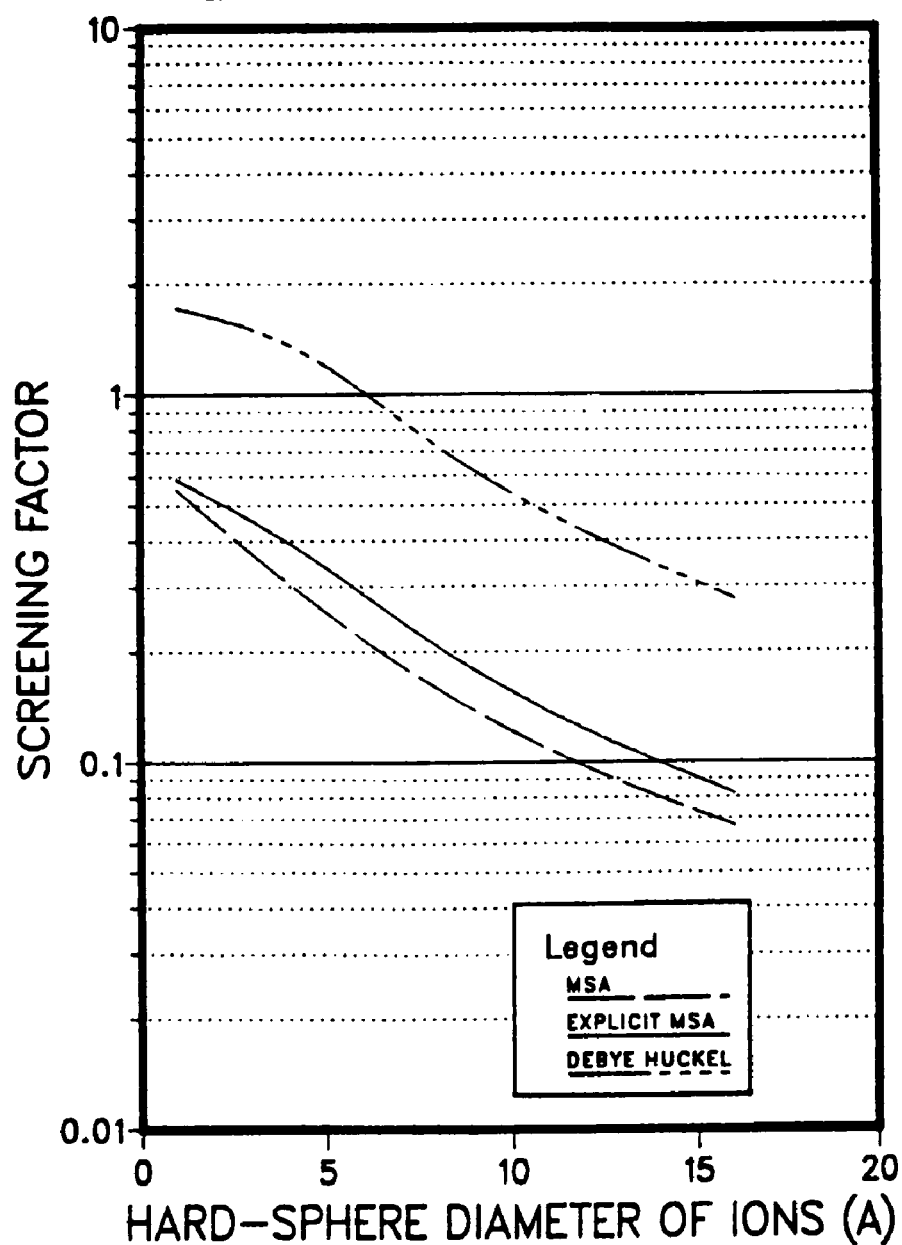


FIGURE 5.7
 DEBYE HUCKEL, MSA AND EXPLICIT MSA
 ION INTERNAL ENERGY
 1-1 SALT IN WATER AT 298 K

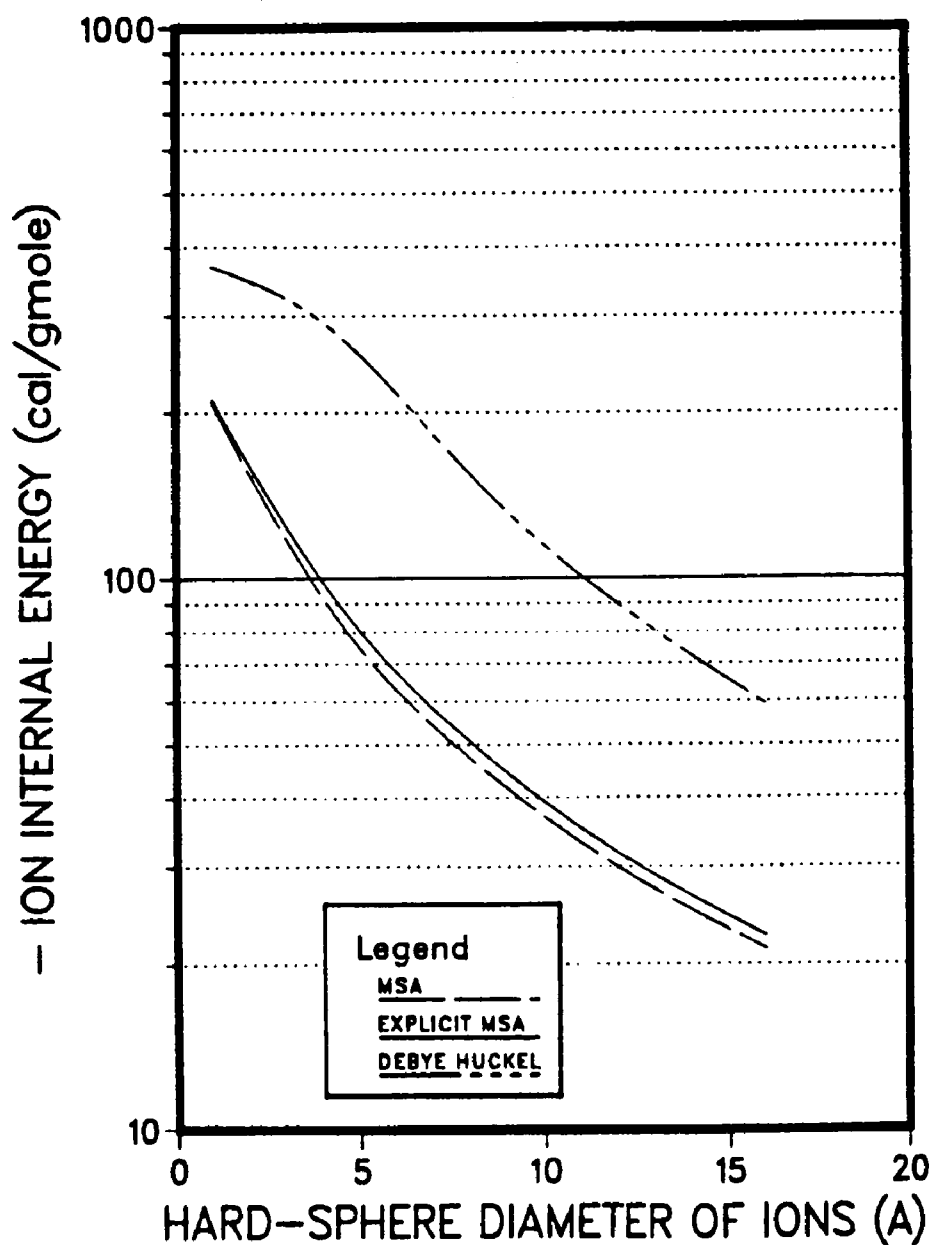
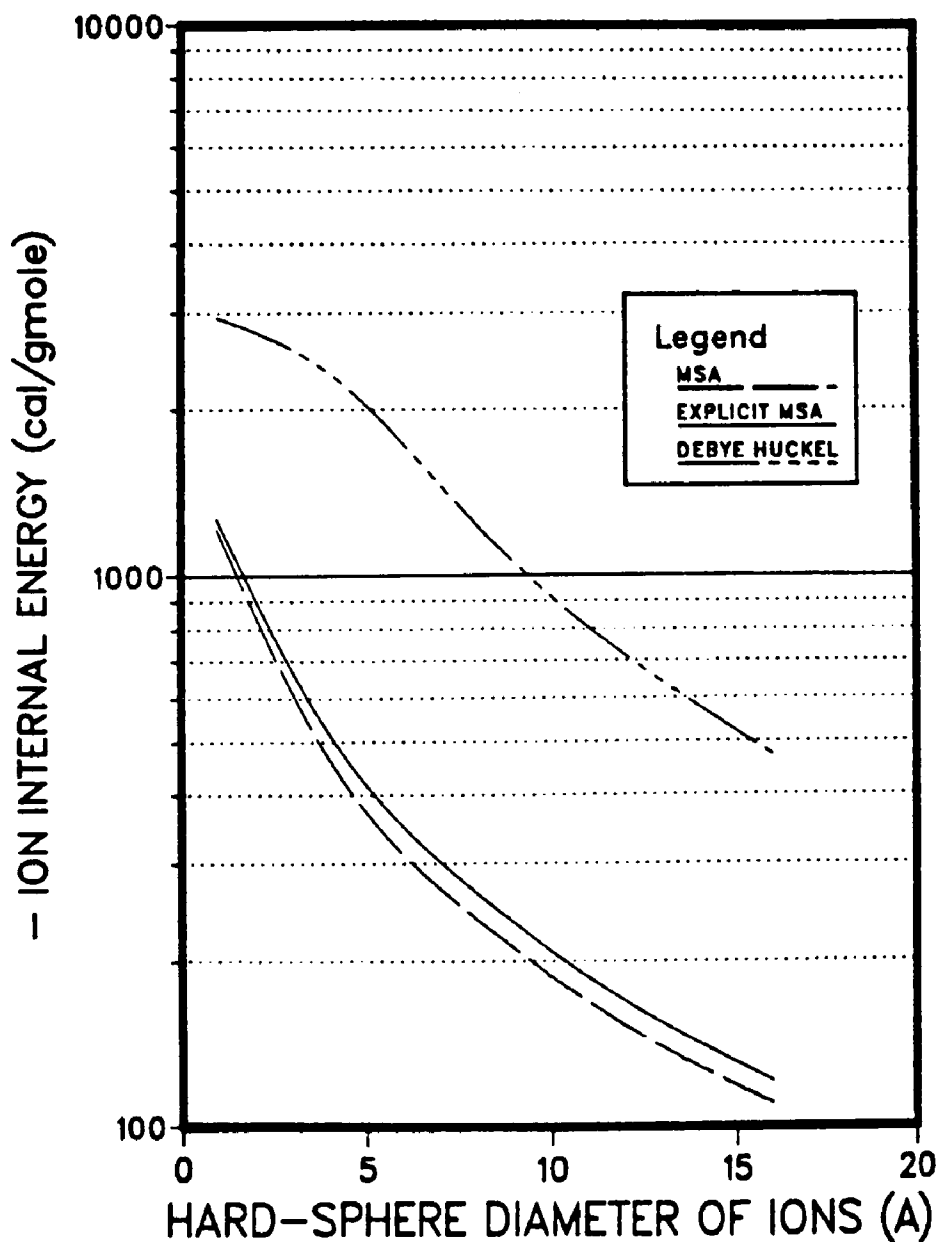


FIGURE 5.8
 DEBYE HUCKEL, MSA AND EXPLICIT MSA
 ION INTERNAL ENERGY
 2-2 SALT IN WATER AT 298 K



6. Perturbed MSA Equation of State

An equation of state for mixtures of electrolytes and non-ionic solvent molecules is developed in this section using ideas from perturbation theory. The Helmholtz free energy of the fluid is assumed to consist of hard-sphere, electrostatic (in the explicit MSA approximation), and attractive contributions. Equation 6.1 summarizes the basic form of the equation of state

$$A = A_{\text{hard sphere}} + A_{\text{explicit MSA}} + A_{\text{attractive forces}} \quad (6.1)$$

The MSA derivation in Section 3 provides an expression for the electrostatic excess over a hard-sphere fluid in the Percus-Yevick approximation (Blum, 1980). The Percus-Yevick equation of state for hard-sphere mixtures is therefore used in equation 6.1. The form of the equation derived using the compressibility equation

$$kT \left[\frac{\partial P}{\partial \rho_i} \right]_{T, \rho_j \neq i} = 1 - 4\pi \rho \sum x_i \int_0^\infty c_{ij} r^2 dr \quad (6.2)$$

is chosen, since predictions agree with molecular-dynamics data better than the form derived using the pressure equation (Reed and Gubbins, 1973).

The hard-sphere contribution to the Helmholtz free energy is

$$A_{\text{hard sphere}} = RT \ln \rho - RT \ln (1 - \pi/6\epsilon_3) +$$

$$\frac{\pi RT}{6\rho} \left(\frac{3 \epsilon_1 \epsilon_2}{1 - \pi/6\epsilon_3} + \frac{\pi \epsilon_2^3}{4(1 - \pi/6\epsilon_3)^2} \right) \quad (6.3)$$

The MSA electrostatic internal energy, presented in equation 3.137, consists of two terms. The second term involving Λ is zero for equal size ions and small for ion-diameter ratios less than about five (Lee, 1983). In Tables 5.1 - 5.6, the term involving Λ was always less than 2% of the total electrostatic energy, therefore the electrostatic internal energy is assumed to be

$$U_{\text{ION}} = \frac{-e^2}{D} \left(\sum \frac{\rho_j Z_j^2 \Gamma}{1 + \sigma_j \Gamma} \right) \quad (6.4)$$

The ionic Helmholtz free energy can be obtained from equation 5.1

$$A_{\text{ION}} = \beta^{-1} \int_0^\beta U_{\text{ION}}(\beta') d\beta' \quad (5.1)$$

Substituting equation 6.4 into equation 5.1 yields

$$A_{\text{ION}} = \frac{-e^2 \rho}{D\beta} \sum x_i Z_i^2 \int_0^\beta \frac{\Gamma d\beta'}{1 + \sigma_i \Gamma} \quad (6.5)$$

The explicit-MSA screening factor is a complex function of temperature arising from various terms with a $\beta^{1/2}$ factor and from the temperature dependence of the dielectric constant. In the development of electrolyte models the variation of the dielectric constant with temperature is generally ignored in equation 5.1; occasionally the Born-Bjerrum correction is used (Blum, 1980).

In light of the various assumptions used to derive the explicit MSA such as assuming all of the species are effectively spherical and the Debye-Huckel pair-correlation functions can be used in equation 5.9, only a simple treatment of the temperature dependence in equation 6.5 appears to be warranted. Therefore, the temperature dependence of the numerator in equation 6.5 is assumed to be $\beta^{1/2}$ and the denominator is assumed to be a weak function of temperature. Integrating equation 6.5 with these assumptions yields

$$A_{\text{ION}} = \frac{-2e^2\rho}{3D} \sum \frac{x_i Z_i^2 \Gamma}{1 + \sigma_i \Gamma} \quad (6.6)$$

Equation 6.6 reduces to the Debye-Huckel Helmholtz free energy in the limit of small ion diameters.

The attractive-force contribution to the Helmholtz free energy is based on ideas from perturbation theory (see Section two for a discussion of perturbation theory). Equations 2.6 and 2.7 present the first and second order expansion terms, respectively, about a reference system. The first-order perturbation has a quadratic dependence on mole fraction, while the second-order perturbation has three terms with a quadratic, cubic, and higher dependence on mole fraction, respectively. The basic form of the attractive-contribution to the equation of state is presented in equation 6.7

$$A_{\text{attractive}} = - \left(\left(\sum \sum x_i x_j a_{ij} \right) / v + \left(\sum \sum x_i x_j (x_i \ell_{ji} + x_j \ell_{ij}) \right) / (v^2 RT) \right) \quad (6.7)$$

where $\ell_{ii} = \ell_{jj} = 0$

The first term in equation 6.7 is assumed to arise from the first-order perturbation (with a quadratic dependence on mole fraction). The second term in equation 6.7 is assumed to arise from the term in the second-order perturbation with a cubic dependence on mole fraction.

Equation 6.7 was suggested recently by Ludecke and Prausnitz (1985) in their work on density-dependent mixing rules for the correlation of vapor-liquid and liquid-liquid equilibria of polar systems. These mixing rules are similar to those developed by Mathias and Copeman (1983) from a Taylor-series expansion of density dependent local-composition mixing rules.

For non-ionic species, a_{ij} will be determined from regression of vapor pressure and density data (similar to the procedure used by Ludecke and Prausnitz). As stated in Section 2, the cubic (and higher) terms in the second order perturbation would be extremely difficult to evaluate from equation 2.7. Therefore, ϕ_{ij} (for any binary pair) will be evaluated from regression of phase equilibrium data (similar to the procedure used by Ludecke and Prausnitz).

The determination of a_{ij} for ionic species is considerably less straightforward. Conventional methods for obtaining a_{ij} based on vapor pressure, cannot be followed, because the vapor pressure of individual charged species cannot be determined. Further, the vapor pressures of salts in aqueous solutions at most conditions of interest are extremely small and are difficult to obtain experimentally. Therefore, a_{ij} for ions must be established by some alternate method.

The MSA model developed by Ball, et al. (1985) assumes $a_{ij}=0$. It is more reasonable to assume that the electron clouds of ionic species are polarizable and that dispersion forces exist between them. Shoor and Gubbins (1969) use the Mavroyannis and Stephan theory (1962) of dispersion forces in their model for predicting salting effects. The pair-potential dispersion energy from the Mavroyannis and Stephan theory is

$$\Phi_{ij} = \frac{3a_0^{1/2}e^2 (\alpha_i\alpha_j) (\eta_i\eta_j)^{1/2}}{2r^6((\alpha_i\eta_j)^{1/2} + (\alpha_j\eta_i)^{1/2})} \quad (6.8)$$

where $a_0 = 0.5292\text{\AA}$

α = polarizability

η = number of electrons

Substituting equation 6.8 into equation 2.6, assuming $(g_{ij})_0 = 0$ for $r < \sigma_{ij}$ and $(g_{ij})_0 = 1$ for $r \geq \sigma_{ij}$ and integrating yields

$$A_{\text{attractive}} = \rho \sum \sum x_i x_j \frac{\pi a_0^{1/2} e^2 \alpha_i \alpha_j (\eta_i \eta_j)^{1/2}}{\sigma_{ij}^3 ((\alpha_i \eta_j)^{1/2} + (\alpha_j \eta_i)^{1/2})} \quad (6.9)$$

or

$$a_{ij} = \frac{\pi a_0^{1/2} e^2 \alpha_i \alpha_j (\eta_i \eta_j)^{1/2}}{\sigma_{ij}^3 ((\alpha_i \eta_j)^{1/2} + (\alpha_j \eta_i)^{1/2})} \quad (6.10)$$

Equation 6.10 is used for all ion-ion dispersion forces. Equation 6.11 is assumed for ion - uncharged species interactions

$$a_{ij} \Big|_{\text{ion-uncharged}} = (a_{ii} a_{jj})^{1/2} P_{k_{ij}} \quad (6.11)$$

where $P_{k_{ij}}$ = binary interaction parameter

The total configurational Helmholtz free energy of the perturbed-hard-sphere MSA equation of state is presented in Appendix B.

The pressure predicted by the equation-of-state was derived from the Helmholtz free energy expression by standard manipulations. Appendix C shows the resulting expression for pressure. Temperature, pressure and composition are usually known in engineering calculations. Consequently, the density must be obtained by iteration. The method of Mathias et al. (1984) was used in this study.

Regression of Pure Component Data

The pure-component parameters a and σ in the equation of state (see Appendix C) are obtained for non-ionic components from regression of vapor-pressure and liquid-density data. Pure-component property correlations were developed for water, methanol, and aniline. Experimental vapor-pressure and liquid-density data for water (Keenan and Keyes, 1955) range from 273.15 K to 588.71 K. Experimental vapor-pressure and liquid-density data for methanol (Machado and Streett, 1983) range from 298.15 K to 473.15 K. Experimental vapor-pressure data for aniline (Stull, 1947) range from 307.95 to 457.55 K, while experimental liquid-density data (Timmermans, 1950) range from 273.15 K to 398.15 K.

Given the experimental temperature and density, the liquid-density residuals are defined by

$$(p_{\text{PMsA}} - p_{\text{experimental}})/p_{\text{experimental}} = \text{residual}_n \quad (6.12)$$

for the n^{th} data point. Given experimental vapor pressure and temperature, the vapor-pressure residuals are defined by

$$(\ln\phi_{\text{liquid}} - \ln\phi_{\text{vapor}})_{\text{PMsA}} = \text{residual}_n \quad (6.13)$$

for the n^{th} data point. The residual in equation 6.13 is related to the equality of chemical potential across the pure-component vapor-liquid phase boundary. At a given experimental temperature and

pressure, the vapor and liquid chemical potentials (or equivalently fugacity coefficients) are equal. However, difference in the chemical potentials predicted by the equation of state, at the experimental conditions, will be non zero, unless, of course, the equation of state fits the data exactly.

The perturbed MSA equation of state (PMSA) parameters $\underline{a}$ and σ were fit to the vapor pressure and liquid density using the IMSL parameter-estimation software ZXSSQ(1982). ZXSSQ minimizes the sum of squares of a set of residuals using the Marquardt (1963) minimization method. By varying the equation of state parameters, ZXSSQ minimizes the sum of squares of the residuals defined in equations 6.12 and 6.13. The parameters $\underline{a}$ and σ are assumed to vary linearly with temperature, as shown in equations 6.14 and 6.15

$$\underline{a} = \psi (L + MT) \quad (6.14)$$

$$\sigma = \psi (L + MT) \quad (6.15)$$

Therefore, four parameters are obtained for each pure (non-ionic) component by regressing vapor pressure and liquid density data.

Tables 6.1, 6.2 and 6.3 present the experimental data for water, methanol, and aniline, respectively. The residuals, averages of the residuals and parameters are also presented in the tables. The averages of the residuals for vapor pressure and density of water are

0.483% and 1.36% respectively. The averages of the residuals for vapor pressure and density of methanol are 0.153% and 0.170%, respectively. For aniline, the averages of the vapor-pressure and density residuals are 4.72% and 2.85%, respectively. Figures 6.1 through 6.6 show the residuals as a function of temperature. The deviations of the model from the data for water and methanol had smooth trends with temperature, while those for aniline showed some scatter. The corresponding averages of the residuals for water and methanol are lower than those for aniline.

Regression of Mean Ionic Activity Coefficient Data

The phase equilibrium of single fully-dissociated salts in water is described using the PMSA equation of state by correlating mean-ionic activity coefficients of the salts. The salts chosen for this study are KOH, NaOH, LiBr, NH_4NO_3 , CaCl_2 , CaBr_2 , KBr, NaCl, KCl, NaBr, NH_4Cl , and Na_2SO_4 , representing 1-1, 1-2 and 2-1 salts with various degrees of non-ideality. Equation 6.10 for $a_{\pm}$ requires the number of electrons (η), polarizability (α) and hard-sphere diameter (σ) of the ions. Table 6.4 presents a summary of the hard-sphere diameters and polarizabilities for the ions of the above salts. The hard sphere diameters of Li^+ , Na^+ , K^+ , Cl^- , Br^- , and Ca^{++} were obtained from Pauling (1939). The hard sphere diameters of NH_4^+ , OH^- , NO_3^- and SO_4^{--} were estimated from van der Waals volumes (see Bondi, 1968). The polarizabilities

for all ions were obtained from Landolt - Bornstein, (1950). The dielectric constant of pure water at the system temperature was assumed ($D = 78$ for 298 K). Appendix A discusses dielectric constants in more depth.

Experimentally-derived mean-ionic activity coefficients for KOH, NaOH, LiBr, NH_4NO_3 , KBr, NaCl, NaBr, KCl, and NH_4Cl in water at 298 K were obtained from Hamer and Wu (1972). While those for CaCl_2 and CaBr_2 in water at 298 K were obtained from Robinson and Stokes (1968), those for Na_2SO_4 in water at 298 K from Goldberg (1981), and those for KOH in water at 353 K from Harned and Owen (1964). The experimentally-derived mean ionic activity coefficients presented by the above authors were obtained from analysis of data from different sources.

The mean-ionic activity-coefficient data were first fit with one parameter (P_k). In this case, $P_{k\text{cation-water}} = P_{k\text{anion-water}}$ was assumed since the two parameters are highly correlated and regression of both at one time results in a non-unique set of parameters. It must be noted that these constraints on the cation and anion parameters limit the application to single salts dissolved in multicomponent solvent mixtures. The mean-ionic activity coefficient residuals are defined as

$$\ln \gamma_{\text{data}}^{\pm} - \ln \gamma_{\text{PMSA}}^{\pm} = \text{residual}_i \quad (6.16)$$

for the n^{th} data point. The mean-ionic activity coefficient predicted by the equation of state is calculated based on ratio of the fugacity coefficient at the mixture composition to the infinite-dilution fugacity coefficient.

$$\ln \gamma_{\text{PMSA}}^{\pm} = \frac{v_{\text{cation}}}{v_{\text{cation}} + v_{\text{anion}}} \ln (\phi_{\text{cation}} / \phi_{\text{cation}}^{\infty}) + \frac{v_{\text{anion}}}{v_{\text{cation}} + v_{\text{anion}}} \ln (\phi_{\text{anion}} / \phi_{\text{anion}}^{\infty}) \quad (6.17)$$

Tables 6.5 to 6.22 present the mean-ionic activity-coefficient data and PMSA predicted values. The average of the residuals and corresponding interaction parameters are also summarized on the tables. Table 6.23 summarizes the average of the residuals, interaction parameters, and maximum mole fraction of the ions in solution. It should be noted that most of the data used significantly exceed 6 molal (the typical limit used by most previous researchers).

Figures 6.7 to 6.30 compare PMSA predictions to the data. Figure 6.7 compares the one parameter PMSA fit to the experimental data for KOH in water at 298 K. At zero mole fraction of ions, the mean ionic activity coefficients of both the data and PMSA are unity, as expected. The activity coefficient first decreases rapidly with increasing ion mole fraction, and then increases rapidly. The PMSA

predictions are too high at low ion concentration and too low at high ion concentrations. This trend is observed, in varying degrees, with the one parameter fit to all of the salts studied. The Bromley (1972), Meissner (1972), Pitzer (1973), and Chen (1982) activity coefficient models were evaluated in the excellent compilation by Zemaitis, et al. (1986). The compilation of Zemaitis, et al. enables a straightforward comparison of these models to the PMSA model for selected systems. Figure 6.8 presents a comparison of the above mentioned models to the one-parameter PMSA fit and the experimental data of Hamer and Wu (1972). Below an ion mole fraction of 0.3, the PMSA predicts values that are too high. The other models predict values in good agreement below an ion mole fraction of 0.2, but deviations become larger at higher ion concentrations. It must be noted that the Bromley and Meissner methods are based on a one parameter fit, while the Chen model is based on a two parameter fit, and the Pitzer method is based on a three parameter fit. The Bromley, Meissner and Pitzer models have been specifically developed to describe the behavior of salts in water in the low concentration region, by the use of empirical functions of ion concentration or ionic strength.

At high ion concentrations, Pitzer predictions are significantly too high, while Chen predictions are significantly too low. Predictions of the PMSA, Bromley and Meissner methods are comparable at these conditions. As will be shown later, the PMSA predictions near 0.1 ion mole fraction can be improved significantly by taking into account the second-order perturbation term.

A comment on the sensitivity of the predictions to the hard-sphere diameter and polarizability of an ionic species is warranted at this point. The experimental data for KOH in water were refit using a K^+ hard-sphere-diameter 1.1 times the Pauling value (Table 6.4). The average of the residuals was 22.5% with $P_{K_{ion-water}} = 1.41$. The experimental data were again refit with the Pauling diameter for K^+ , and the polarizability of K^+ was set to 1.1 times the Landolt-Bornstein value. The average of the residuals was 15.8% with $P_{K_{ion-water}} = 1.42$. Both fits to the data are similar to those obtained with the base values. It should be noted that the predictions were more sensitive to the hard sphere diameter than the polarizability. This result is not surprising since the hard sphere diameter is present to a higher power in equation 6.10 than the polarizability.

Figure 6.9 illustrates a PMSA one parameter fit to the data for NaOH in water at 298 K. PMSA predictions deviate on the high side at low ion concentrations, on the low side at higher ion concentrations, and again on the high side at ion mole fractions near to 0.5.

Figure 6.10 adds the predictions of the Bromley, Meissner, Chen and Pitzer models to the plot in figure 6.9. Above an ion mole fraction of 0.3, all of the models, except PMSA, deviate substantially from the data. Of the activity coefficient models, Bromley predicts the most reasonable values at these conditions.

Figures 6.11 to 6.15 present a PMSA one parameter fit to the data for KBr, NaBr, NaCl, KCl and NH_4Cl in water at 298 K, respectively.

The mean ionic activity coefficient decreases below unity with increasing ion concentration and, unlike KOH and NaOH, increases slowly at higher ion concentrations. The same trend is observed in deviations from data as seen in the KOH and NaOH systems. The one parameter PMSA predicts values too high at low ion concentrations and too low at higher ion concentrations. Overall, the PMSA predictions agree closely with the data for these systems.

Figure 6.16 presents a PMSA one parameter fit to the data for NH_4NO_3 in water at 298 K. Unlike the other systems presented previously, the mean ionic activity coefficient decreases with increasing ion concentration, including the high ion concentration range. PMSA predictions are again reasonable, showing the proper trend with ion concentrations.

Figure 6.17 presents a PMSA one parameter fit to the data for the extremely non-ideal LiBr – water system at 298 K. The PMSA predictions deviate in the same manner as observed with the other systems. The deviations are much larger, however because of the extremely rapid increase in activity coefficient with ion concentration.

To illustrate predictions for 1-2 and 2-1 salts, Figures 6.18 to 6.22 present PMSA one-parameter fits to the data for CaCl_2 , CaBr_2 , and Na_2SO_4 . The behavior of the CaCl_2 and CaBr_2 systems is similar to KOH and NaOH, while the behavior of the Na_2SO_4 system is similar to KBr and KCl. The one-parameter PMSA fits to these data are similar to the 1-1 salt systems. For CaCl_2 , Bromley, Meissner, Pitzer and Chen predictions are available and are shown along with the PMSA and the data in Figure 6.19. The activity coefficient predictions are similar to those for 1-1 salt systems, being increasingly inaccurate as ion concentration increases. Also, as observed previously, the predictions of the Pitzer method are too high and the predictions of the Chen method are too low at high ion concentrations. Figure 6.22 presents a comparison of the predictions of the activity coefficient models to the one-parameter PMSA and the data for Na_2SO_4 . In this case, Bromley predictions are much too low at the higher ion concentrations. The three-parameter Pitzer model provides the best overall fit to these data. At the highest ion concentration (about 0.21), the PMSA model predicts values less accurately than Pitzer, but better than the other methods.

To check that the predictions of the PMSA are reasonable at temperatures other than 298 K, KOH in water at 353 K was studied. A dielectric constant of 61.2 for water was assumed. Ion hard-sphere diameter and polarizability were assumed to be independent of temperature. Figure 6.23 illustrates a one parameter fit to the data.

The predictions are similar to those at 298 K (Figure 6.7), and the $PK_{\text{ion-water}}$, found by the regression, is equal to that obtained at 298 K (see Table 6.23).

As noted in the previous discussion, predictions of the one-parameter PMSA are too high (in varying degrees) at ion mole fractions near to 0.1. These deviations are reasonable because the equation of state does not explicitly account for ion induced-dipole effects on all species and the ion-dipole (of water) interaction is accounted for by a fixed dielectric constant. Because the basic trends in the data are described well by the one-parameter PMSA model, the deviations of the one-parameter fit from data will be treated through the second order perturbation term in equation 6.7. $\ell_{\text{water-cation}} = \ell_{\text{water-anion}}$ was assumed. Similar to the procedure of Ludecke and Prausnitz (1985), the $\ell_{\text{water-ion}}$ parameter was scaled by $\alpha_{\text{cation-anion}}^2$ to make ℓ dimensionless, and is regressed along with $PK_{\text{ion-water}}$.

Figures 6.24 to 6.30 illustrate two-parameter PMSA fits to experimental data for various systems in water at 298 K. The systems showing the greatest deviation with the one-parameter PMSA fits were chosen. In all cases, the two-parameter PMSA predictions are substantially better than the one parameter PMSA predictions.

Figure 6.24 illustrates the predictions of the two-parameter PMSA for KOH. The agreement of the two parameter PMSA with the data is much

closer than the one parameter PMSA. Figure 6.25 presents the Bromley, Meissner, Chen and Pitzer predictions along with the two parameter PMSA and data (Hamer and Wu, 1972). The PMSA predictions are better than the other models overall.

Figure 6.26 presents the improvement possible with a two parameter PMSA fit for the NH_4NO_3 system. The deviations are similar to those of the one-parameter fit, however they are smaller.

Figure 6.27 illustrates the predictions of the two parameter PMSA for LiBr . The two parameter fit is substantially better than the one parameter fit for this extremely non-ideal system. The ℓ parameter obtained by regression is large, compared to those obtained for the other systems (see Table 6.23). Caution must be exercised in applying this result to multicomponent solvent systems.

Figure 6.28 presents two-parameter PMSA predictions for CaCl_2 . Again, the predictions are significantly better than the one parameter fit. Figure 6.29 presents the predictions of the Bromley, Meissner, Pitzer and Chen models for the same system. The PMSA fits the data better than the other methods, overall.

Figure 6.30 presents the predictions of the two-parameter PMSA for CaBr_2 in water. Again the two parameter fit agrees with the data better than the one-parameter fit.

Analysis of Interaction Parameters

The PMSA equation of state is capable of describing the mean-ionic-activity-coefficient behavior of single fully-dissociated electrolytes in water. Further, it can be shown that the $P_{K_{ion-water}}$ interaction parameters obtained by regression follow a definite trend with ion size. Figure 6.31 presents $P_{K_{ion-water}}$ as a function of $\sigma_{cation-anion}$, or $(\sigma_{cation} + \sigma_{anion})/2$, for the one-parameter fits. Overall, the interaction parameters, P_k , decrease with increasing average cation-anion hard-sphere diameter.

Figure 6.32 shows $P_{K_{ion-water}}$ as a function of $\sigma_{cation-anion}$ for the one and two parameter fits. KOH, NH_4NO_3 , LiBr, $CaCl_2$, $CaBr_2$ were based on two-parameter fits, while the others were based on one-parameter fits. The scatter is lower than in Figure 6.31. Further, the $P_{K_{ion-water}}$ obtained from the two parameter fit were closer to unity than those obtained from the one-parameter fit. The solid line on Figure 6.32 is based on a two constant least squares fit

$$P_{K_{ion-water}} = 0.434 + 2.383/\sigma_{cation-anion} \quad (6.18)$$

This correlation predicts a $P_{K_{ion-water}}$ of 1.34 for KOH (the value obtained from regression of data is 1.29). If the $P_{K_{ion-water}}$ was set to 1.34 and the $\ell_{water-ion}$ was set to that obtained previously from regression of data, the resulting average of residuals is 21.7%. The average of residuals obtained previously

with a $P_{K_{ion-water}} = 1.29$ was 2.2%, indicating a reasonable change of about 20% in the average fit with a variation of 0.05 in $P_{K_{ion-water}}$.

The results shown in Figures 6.31 and 6.32 are particularly encouraging since the salts chosen for the study exhibit a wide range of non-ideality. Approximate predictions of mean ionic activity coefficients of fully-dissociated salts dissolved in water (for $\sigma_{cation-anion}$ from $2.2\text{\AA}$ to $3.6\text{\AA}$) can be obtained with the PMSA equation of state and equation 6.18.

Fugacity Coefficients of Ions

Some comments on the fugacity coefficient of ions in solution are necessary. Equations of state, unlike activity coefficient models, provide residual properties such as fugacity coefficients and enthalpy departures. The low-dilution fugacity coefficients of Na^+ and OH^- in water predicted by a perturbed-hard-sphere equation of state using dispersion theory in the attractive term will be roughly EXP (13) and EXP (-17), respectively. While the equation of state may provide a good fit to mean-ionic activity-coefficient data, it would predict that Na^+ would vaporize from solution, because its fugacity is so large. Electrical work could be produced by flashing the solution and separating the phases. Since this phenomena is not observed in nature, some important effect must be missing from the

description of the residual properties. The MSA electrostatic term describes the internal energy required to charge ions from zero to their full charge in an electrically neutral mixture. As with the Debye Huckel model, the electroneutrality condition was imposed in the derivation. The configurational energy of an ion (i) in solution, however, must account for the energy required to keep the mixture electrically neutral. Consider the case where an NA^+ vaporizes from an aqueous solution with a nearby OH^- remaining in solution. The internal energy required to remove one NA^+ ion from its associated OH^- is

$$U_{\text{NA}^+} = -e^2 \int_a^\infty \frac{Z_i Z_j}{D r^2} dr \quad (6.19)$$

where a is the distance of separation in solution. As an example, if a is assumed to be $3\text{\AA}$ and the NA^+ and OH^- are assumed to be near to the vapor-liquid interface (D can be approximated as unity throughout the integration), the resulting energy to remove the NA^+ ion is 1.1×10^5 cal/gmole. Assuming the energy required to remove all NA^+ from their associated OH^- is the same, the total energy is $(nU)_{\text{NA}^+}$. Taking the mole number derivative and setting the standard state to be infinite separation in the vapor phase yields

$$\ln \phi_{\text{NA}^+ \text{ electrical separation}} = -186.7 \text{ at } 298 \text{ K} \quad (6.20)$$

This contribution to the ionic fugacity coefficients is extremely large and ensures that for liquids far from the mixture critical point, the vapor pressure of ions is negligible. With the above simple development, the electrical-separation fugacity coefficient is composition independent. Therefore, a composition-independent electrical-separation contribution can be added to an equation of state expression for fugacity coefficients of ions when predicting vapor-liquid equilibrium of mixtures with electrolytes dissolved in the liquid phase.

Liquid Density

One benefit of the equation of state approach is that expressions for fugacity, density and residual thermal properties are obtained by standard analytical derivation. Internally consistent values are predicted for all of these properties. Fugacity of the individual species is generally key to the design of separation processes and mixture density is usually of less interest. Nevertheless, the liquid density predicted by the equation of state should be at least qualitatively reasonable. Therefore, experimental data for NaCl and CaCl₂ in water at 298.15 K were compared to PMSA model predictions. The same physical constants and interaction parameters established for the mean-ionic activity coefficient correlations were used (the two-parameter fit for CaCl₂ was chosen).

The equation of state predicts molar volumes on a fully-dissociated salt basis. Assuming this same basis in calculating the average molecular weight, densities, on a gr/cm^3 basis, were calculated.

The experimental and predicted liquid densities (gr/cm^3) for NaCl are

<u>m</u>	<u>ρ_{Data}</u>	<u>ρ_{PMSA}</u>
1.02	1.037	1.030
4.99	1.166	1.095

The experimental and predicted liquid densities for CaCl_2 are

<u>m</u>	<u>ρ_{Data}</u>	<u>ρ_{PMSA}</u>
1.01	1.082	1.054
4.98	1.341	1.182

The PMSA equation of state predicts an increase in liquid density with increasing salt concentration, as observed with the experimental data.

Table 6.1

Vapor Pressure and Liquid Density for Water
Experimental Data and Four Parameter Fit

Temp.(K)	Vap. Pres.(Atm)	Residual (Eqn 6.13)	Liq. Density (gmole/cm ³)	Residual (Eqn. 6.12)
273.15	0.00602	0.008702	0.05556	0.02986
283.15	0.0121	0.005186	0.05552	0.02229
297.04	0.0292	0.002191	0.05537	0.01353
310.93	0.0646	-0.001888	0.05519	0.005286
324.82	0.132	-0.002494	0.05488	-0.000677
338.71	0.253	-0.005123	0.05448	-0.005135
352.59	0.457	-0.006491	0.05400	-0.008297
366.48	0.784	-0.006411	0.05350	-0.01131
394.26	2.029	-0.006048	0.05235	-0.01536
422.04	4.559	-0.004870	0.05102	-0.01737
449.82	9.159	-0.002134	0.04948	-0.01703
477.59	16.824	0.000457	0.04775	-0.01506
505.37	28.748	0.003360	0.04558	-0.01303
533.15	46.313	0.005969	0.04373	-0.08639
560.93	71.102	0.007911	0.04083	0.08708
588.71	104.96	0.008820	0.03772	0.02602
Average (%)		0.483		1.36

$$a = (8.254 - 0.00549T)10^6$$

$$\sigma = 3.229 - 0.000536 T$$

Table 6.2

Vapor Pressure and Liquid Density for Methanol
Experimental Data and Four Parameter Fit

Temp.(K)	Vap. Pres.(Atm)	Residual (Eqn 6.13)	Liq. Density (gmole/cm ³)	Residual (Eqn. 6.12)
298.15	0.167	0.008702	0.02458	-0.0003223
313.15	0.348	0.000961	0.02414	-0.0000436
323.15	0.546	0.001966	0.02383	0.0004569
333.15	0.830	0.003688	0.02352	0.0006024
343.15	1.230	0.003026	0.02321	0.000307
353.15	1.777	0.002596	0.02288	0.0004451
363.15	2.513	-0.000747	0.22550	0.0000168
373.15	3.478	-0.000242	0.02221	-0.0005946
383.15	4.727	-0.001852	0.02185	-0.001016
393.15	6.303	-0.001566	0.02148	-0.001789
403.15	8.266	0.000358	0.02108	-0.002088
413.15	10.692	0.000382	0.02066	-0.002485
423.15	13.662	0.000374	0.02021	-0.002628
433.15	17.261	0.000189	0.01973	-0.002669
443.15	21.569	0.000648	0.01921	-0.002286
453.15	26.670	0.000679	0.01862	-0.000099
463.15	32.650	0.000122	0.01797	0.003185
473.15	39.611	0.000792	0.01722	0.009596
Average (%)		0.153		0.170

$$a = (16.59 - 0.01624T)10^6$$

$$\sigma = 4.199 - 0.000853 T$$

Table 6.3

Vapor Pressure and Liquid Density for Aniline
Experimental Data and Four Parameter Fit

Temp. (K)	Vap. Pres. (Atm)	Residual (Eqn 6.13)	Liq. Density (gmole/cm ³)	Residual (Eqn. 6.12)
307.95	0.00132	0.1015		
331.05	0.00656	0.001174		
342.55	0.0132	-0.04059		
355.15	0.0263	-0.06905		
369.85	0.0526	-0.06085		
379.15	0.0789	-0.05731		
393.05	0.132	-0.05647		
413.25	0.263	0.04312		
435.05	0.526	0.05029		
457.55	1.000	0.04273		
273.15			0.01116	0.04417
293.15			0.01098	0.02526
303.15			0.01088	0.01685
313.15			0.01079	0.00755
333.15			0.01060	-0.01001
353.15			0.01042	-0.02848
398.15			0.00998	-0.06270
Average (%)		4.72		2.85

$$a = (43.46 - 0.01304T)10^6$$

$$\sigma = 5.123 + 0.0007135 T$$

Table 6.4

Hard Sphere Diameter and Polarizability of Selected Ions

Ion	Hard Sphere Diameter ($\text{\AA}$)	Polarizability ($\text{\AA}^3$) ³
K^+	2.66	0.84
Na^+	1.92	0.18
Li^+	1.21	0.029
NH_4^+	3.20	2.04
Ca^{++}	1.98	0.47
OH^-	2.60	2.04
Br^-	3.90	4.81
NO_3^-	4.02	4.36
Cl^-	3.61	3.69
SO_4^{--}	4.45	6.0

Hard sphere diameter for K^+ , Na^+ , Li^+ , Cl^- , Br^- and Ca^{++} obtained from Pauling (1939).

Hard sphere diameter for NH_4^+ , OH^- , NO_3^- and SO_4^{--} estimated from Bondi (1968).

Polarizability for all ions obtained from Landolt-Bornstein (1950).

Table 6.5

Mean Ionic Activity Coefficients of KOH in Water at 298 K

<u>X_{ion}</u>	<u>γ_{data}</u>	<u>γ_{PMSA}</u>
0.0003599	0.9023	0.9103
0.0007195	0.8716	0.8798
0.001797	0.8225	0.8325
0.003587	0.7818	0.7958
0.007149	0.7453	0.7667
0.01068	0.7298	0.7589
0.01420	0.7233	0.7606
0.01768	0.7228	0.7680
0.02114	0.7264	0.7793
0.02458	0.7320	0.7934
0.02779	0.7387	0.8099
0.03138	0.7485	0.8283
0.03475	0.7594	0.8484
0.04141	0.7845	0.8931
0.04798	0.8130	0.9432
0.05446	0.8461	0.9983
0.06086	0.8817	1.058
0.06716	0.9219	1.123
0.08257	1.035	1.306
0.09747	1.172	1.520
0.1119	1.333	1.769
0.1259	1.523	2.054
0.1394	1.744	2.381
0.1525	2.002	2.752
0.1653	2.304	3.172
0.1776	2.651	3.645
0.2103	3.531	4.767
0.2236	4.701	6.158
0.2447	6.263	7.856
0.2647	8.310	9.902
0.2837	10.97	12.34
0.3017	14.32	15.21
0.3188	18.64	18.54
0.3351	24.06	22.39
0.3506	30.65	26.79
0.3655	38.30	31.77
0.3797	47.39	37.36
0.3932	57.52	43.60
0.4062	68.37	50.50
0.4186	79.81	58.08

Average of Residuals = 16.3%

 $PK_{ion-water} = 1.43$

Table 6.6

Mean Ionic Activity Coefficients of NaOH in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm data}$</u>	<u>$\gamma_{\pm PMSA}$</u>
0.0003599	0.9023	0.9079
0.0007195	0.8706	0.8753
0.001797	0.8205	0.8227
0.003587	0.7778	0.7786
0.007149	0.7363	0.7367
0.01068	0.7156	0.7172
0.01420	0.7840	0.7077
0.01768	0.6973	0.7041
0.02114	0.6937	0.7042
0.02458	0.6930	0.7072
0.02779	0.6934	0.7122
0.03138	0.6948	0.7189
0.03475	0.6983	0.7270
0.04141	0.7073	0.7467
0.04798	0.7185	0.7703
0.05446	0.7319	0.7970
0.06086	0.7475	0.8266
0.06716	0.7654	0.8589
0.08257	0.8164	0.9507
0.09747	0.8798	1.058
0.1119	0.9537	1.181
0.1259	1.042	1.320
0.1394	1.147	1.477
0.1525	1.270	1.653
0.1653	1.415	1.850
0.1776	1.583	2.069
0.2103	2.014	2.582
0.2236	2.599	3.208
0.2447	3.388	3.965
0.2647	4.431	4.874
0.2837	5.786	5.956
0.3017	7.505	7.235
0.3188	9.624	8.737
0.3351	12.16	10.49
0.3506	15.09	12.52
0.3655	18.36	14.85
0.3797	21.92	17.53
0.3932	25.66	20.57
0.4062	29.50	24.02
0.4186	33.39	27.90
0.4305	37.31	32.25
0.4402	41.27	37.10

Table 6.6 (Continued)

Mean Ionic Activity Coefficients of NaOH in Water at 298 K

<u>χ_{ion}</u>	<u>$\gamma_{\pm data}$</u>	<u>$\gamma_{\pm PMSA}$</u>
0.4530	45.30	42.48
0.4635	49.43	48.44
0.4737	53.69	54.99
0.4835	58.00	62.16
0.4929	62.08	70.00
0.5020	65.40	78.53
0.5108	67.17	87.77

Average of Residuals = 11.6%

 $P_{K_{ion-water}} = 1.59$

Table 6.7

Mean Ionic Activity Coefficients of KBr in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm data}$</u>	<u>$\gamma_{\pm PMSA}$</u>
0.0003599	0.9023	0.9098
0.0007195	0.8706	0.8784
0.001797	0.8185	0.8274
0.003587	0.7738	0.7834
0.007149	0.7272	0.7380
0.01068	0.7005	0.7128
0.01420	0.6827	0.6963
0.01768	0.6698	0.6848
0.02114	0.6600	0.6765
0.02458	0.6531	0.6702
0.02779	0.6471	0.6656
0.03138	0.6422	0.6621
0.03475	0.6392	0.6593
0.04141	0.6343	0.6564
0.04798	0.6323	0.6551
0.05446	0.6324	0.6552
0.06086	0.6336	0.6562
0.06716	0.6357	0.6579
0.08257	0.6453	0.6641
0.09747	0.6593	0.6719
0.1119	0.6756	0.6806
0.1259	0.6956	0.6895
0.1394	0.7170	0.6986
0.1525	0.7387	0.7076
0.1653	0.7631	0.7165

Average of Residuals = 2.5%

 $P_{K_{ion-water}} = 1.12$

Table 6.8

Mean Ionic Activity Coefficients of NaBr in Water at 298 K

<u>X_{ion}</u>	<u>Y_{data}</u>	<u>Y_{PMSA}</u>
0.0003599	0.9033	0.9101
0.0007195	0.8736	0.8792
0.001797	0.8255	0.8301
0.003587	0.7858	0.7899
0.007149	0.7473	0.7527
0.01068	0.7278	0.7361
0.01420	0.7162	0.7286
0.01768	0.7095	0.7262
0.02114	0.7069	0.7272
0.02458	0.7053	0.7305
0.02779	0.7068	0.7356
0.03138	0.7082	0.7420
0.03475	0.7116	0.7496
0.04141	0.7209	0.7671
0.04798	0.7321	0.7874
0.05446	0.7467	0.8096
0.06086	0.7635	0.8335
0.06716	0.7826	0.8588
0.08257	0.8371	0.9269
0.09747	0.9041	1.001
0.1119	0.9807	1.079
0.1259	1.068	1.161
0.1394	1.168	1.247
0.1525	1.278	1.335
0.1653	1.400	1.426
0.1776	1.533	1.519
0.2103	1.834	1.710
0.2236	2.182	1.907
0.2447	2.580	2.107

Average of Residuals = 5.5%

P_{K_{ion-water}} = 1.23

Table 6.9

Mean Ionic Activity Coefficients of NaCl in Water at 298 K

<u>X_{ion}</u>	<u>Y_{data}</u>	<u>Y_{PMSA}</u>
0.0003599	0.9033	0.9090
0.0007193	0.8726	0.8771
0.001797	0.8235	0.8255
0.003587	0.7818	0.7818
0.007149	0.7393	0.7387
0.01068	0.7167	0.7166
0.01420	0.7030	0.7039
0.01768	0.6933	0.6965
0.02114	0.6875	0.6924
0.02458	0.6838	0.6908
0.02779	0.6811	0.6908
0.03138	0.6804	0.6922
0.03475	0.6807	0.6947
0.04141	0.6833	0.7020
0.04798	0.6891	0.7117
0.05446	0.6959	0.7232
0.06086	0.7049	0.7360
0.06716	0.7161	0.7500
0.08257	0.7499	0.7884
0.09747	0.7911	0.8307
0.1119	0.8400	0.8756
0.1259	0.8958	0.9225
0.1394	0.9598	0.9710
0.1525	1.031	1.021
0.1653	1.112	1.071
0.1776	1.1199	1.123
0.1811	1.226	1.138

Average of Residuals = 2.4%

P_{K_{ion-water}} = 1.27

Table 6.10

Mean Ionic Activity Coefficients of KCl in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm data}$</u>	<u>$\gamma_{\pm PMSA}$</u>
0.0003599	0.9013	0.9092
0.0007195	0.8696	0.8773
0.001797	0.8175	0.8252
0.003587	0.7708	0.7799
0.007149	0.7222	0.7326
0.01068	0.6944	0.7057
0.01420	0.6746	0.6880
0.01768	0.6607	0.6753
0.02114	0.6497	0.6658
0.02458	0.6418	0.6585
0.02799	0.6348	0.6528
0.03138	0.6298	0.6484
0.03475	0.6258	0.6448
0.04141	0.6197	0.6398
0.04798	0.6155	0.6368
0.05446	0.6134	0.6352
0.06086	0.6133	0.6346
0.06716	0.6143	0.6347
0.08257	0.6191	0.6371
0.09747	0.6293	0.6413
0.1119	0.6429	0.6465
0.1259	0.6589	0.6520
0.1394	0.6786	0.6578
0.1474	0.6908	0.6612
0.1525	0.6997	0.6634

Average of Residuals = 2.4%

 $P_{K_{ion-water}} = 1.15$

Table 6.11

Mean Ionic Activity Coefficients of NH_4Cl in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm\text{data}}$</u>	<u>$\gamma_{\pm\text{PMSA}}$</u>
0.0003599	0.9013	0.9101
0.0007195	0.8696	0.8789
0.001797	0.8175	0.8282
0.003587	0.7718	0.7845
0.007149	0.7232	0.7394
0.01068	0.6944	0.7140
0.01420	0.6756	0.6973
0.01768	0.6607	0.6855
0.02114	0.6497	0.6766
0.02458	0.6418	0.6699
0.02799	0.6348	0.6647
0.03138	0.6287	0.6605
0.03475	0.6247	0.6573
0.04141	0.6176	0.6526
0.04798	0.6134	0.6497
0.05446	0.6113	0.6480
0.06086	0.6101	0.6471
0.06716	0.6100	0.6468
0.08257	0.6137	0.6475
0.09747	0.6205	0.6493
0.1119	0.6306	0.6515
0.1259	0.6406	0.6536
0.1394	0.6519	0.6554
0.1525	0.6643	0.6569
0.1653	0.6757	0.6580
0.1776	0.6870	0.6587
0.2013	0.7086	0.6588
0.2105	0.7156	0.6684

Average of Residuals = 3.9%

 $\text{P}k_{\text{ion-water}} = 1.19$

Table 6.12

Mean Ionic Activity Coefficients of NH_4NO_3 Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm \text{data}}$</u>	<u>$\gamma_{\pm \text{PMSA}}$</u>
0.0003599	0.8973	0.9096
0.0007195	0.8626	0.8776
0.001797	0.8024	0.8247
0.003587	0.7467	0.7771
0.007149	0.6829	0.7241
0.01068	0.6439	0.6911
0.01420	0.6147	0.6670
0.01768	0.5925	0.6479
0.02114	0.5731	0.6321
0.02458	0.5577	0.6185
0.02799	0.5432	0.6065
0.03138	0.5317	0.5958
0.03475	0.5201	0.5862
0.04141	0.5018	0.5690
0.04798	0.4853	0.5541
0.05446	0.4717	0.5409
0.06086	0.4600	0.5289
0.06716	0.4492	0.5179
0.08257	0.4262	0.4936
0.09747	0.4077	0.4727
0.1119	0.3930	0.4542
0.1259	0.3798	0.4376
0.1394	0.3672	0.4225
0.1525	0.3575	0.4088
0.1653	0.3486	0.3961
0.1776	0.3405	0.3844
0.2013	0.3268	0.3636
0.2236	0.3156	0.3457
0.2447	0.3058	0.3301
0.2647	0.2992	0.3164
0.2837	0.2918	0.3045
0.3017	0.2864	0.2940
0.3188	0.2819	0.2848
0.3351	0.2782	0.2766
0.3506	0.2757	0.2693
0.3655	0.2726	0.2628
0.3797	0.2708	0.2570
0.3932	0.2686	0.2517
0.4062	0.2661	0.2470
0.4186	0.2649	0.2427

Table 6.12 (Continued)

Mean Ionic Activity Coefficients of NH_4NO_3 Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm \text{data}}$</u>	<u>$\gamma_{\pm \text{PMSA}}$</u>
0.4305	0.2634	0.2388
0.4420	0.2616	0.2352
0.4530	0.2596	0.2320
0.4635	0.2572	0.2289
0.4737	0.2546	0.2261
0.4830	0.2534	0.2237

Average of Residuals = 9.0%

 $\text{PK}_{\text{ion-water}} = 1.21$

Table 6.13

Mean Ionic Activity Coefficients of LiBr in Water at 298 K

<u>X_{ion}</u>	<u>Y_{data}</u>	<u>Y_{PMSA}</u>
0.0003599	0.9053	0.9128
0.0007195	0.8776	0.8846
0.001797	0.8335	0.8437
0.003587	0.7999	0.8170
0.007149	0.7725	0.8075
0.01068	0.7632	0.8197
0.01420	0.7628	0.8425
0.01768	0.7655	0.8722
0.02114	0.7754	0.9072
0.02458	0.9863	0.9466
0.02799	0.8004	0.9901
0.03138	0.8146	1.037
0.03475	0.8319	1.088
0.04141	0.8700	1.200
0.04798	0.9149	1.327
0.05446	0.9656	1.469
0.06086	1.022	1.627
0.06716	1.085	1.802
0.08257	1.271	2.320
0.09747	1.506	2.971
0.1119	1.799	3.778
0.1259	2.163	4.767
0.1394	2.617	5.967
0.1525	3.181	7.410
0.1653	3.884	9.128
0.1776	4.761	11.16
0.2013	7.234	16.29
0.2236	11.14	23.13
0.2447	17.34	31.97
0.2647	27.21	43.14
0.2837	42.76	56.94
0.3017	66.82	73.63
0.3188	103.0	93.47
0.3351	154.9	116.7
0.3506	226.41	143.3
0.3655	316.8	173.6
0.3797	425.6	207.6
0.3932	547.1	245.2
0.4062	680.3	286.5
0.4186	835.9	331.4

Average of Residuals = 43.7%

PK_{ion-water} = 1.59

Table 6.14

Mean Ionic Activity Coefficients of CaCl_2 in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm \text{data}}$</u>	<u>$\gamma_{\pm \text{PMSA}}$</u>
0.005371	0.5208	0.5032
0.01068	0.4771	0.4626
0.01594	0.4624	0.4577
0.02114	0.4577	0.4675
0.02629	0.4601	0.4862
0.03138	0.4677	0.5112
0.03642	0.4774	0.5413
0.04141	0.4903	0.5761
0.04635	0.5075	0.6153
0.05123	0.5270	0.6587
0.06086	0.5739	0.7584
0.07023	0.6314	0.8760
0.07953	0.6996	1.013
0.08859	0.7812	1.170
0.09747	0.8775	1.350
0.1189	1.207	1.912
0.1394	1.723	2.663
0.1590	2.473	3.642
0.1776	3.563	4.891
0.1955	5.183	6.452
0.2126	7.480	8.370
0.2290	10.61	10.69
0.2447	14.71	13.44
0.2598	19.63	16.68
0.2743	25.19	20.42
0.2883	31.09	24.71
0.3017	37.26	29.56
0.3146	43.92	34.99
0.3271	50.82	41.02
0.3391	58.25	47.65
0.3506	66.22	54.89

Average of Residuals = 20.8%

 $\text{PK}_{\text{ion-water}} = 1.42$

Table 6.15

Mean Ionic Activity Coefficients of CaCl_2 in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm \text{data}}$</u>	<u>$\gamma_{\pm \text{PMSA}}$</u>
0.00537	0.5349	0.5205
0.01068	0.4963	0.4921
0.01594	0.4888	0.4996
0.02114	0.4924	0.5232
0.02629	0.5032	0.5571
0.03138	0.5203	0.5992
0.03642	0.5407	0.6486
0.04141	0.5654	0.7051
0.04635	0.5946	0.7686
0.05123	0.6282	0.8393
0.06086	0.7070	1.003
0.07029	0.8024	1.200
0.07953	0.9191	1.434
0.08859	1.062	1.709
0.09747	1.240	2.029
0.1189	1.877	3.066
0.1394	2.940	4.513
0.1590	4.613	6.470
0.1776	7.624	9.046
0.1955	13.23	12.35
0.2126	23.41	16.50
0.2290	41.11	21.60
0.2447	73.75	27.75

Average of Residuals = 30.2%

 $\text{PK}_{\text{ion-water}} = 1.35$

Table 6.16

Mean Ionic Activity Coefficients of Na_2SO_4 in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm \text{data}}$</u>	<u>$\gamma_{\pm \text{PMSA}}$</u>
0.00537	0.4481	0.4784
0.01068	0.3695	0.3979
0.01594	0.3264	0.3527
0.02114	0.2973	0.3217
0.02629	0.2756	0.2983
0.03138	0.2587	0.2797
0.03642	0.2448	0.2643
0.04141	0.2333	0.2514
0.04635	0.2235	0.2403
0.05123	0.2150	0.2308
0.07493	0.1865	0.1979
0.09747	0.1713	0.1805
0.01189	0.1639	0.1716
0.01394	0.1620	0.1677
0.01590	0.1641	0.1663
0.1776	0.1694	0.1658
0.1955	0.1776	0.1650
0.2126	0.1882	0.1634

Average of Residuals = 6.6%

 $\text{PK}_{\text{ion-water}} = 1.14$

Table 6.17

Mean Ionic Activity Coefficients of KOH in Water at 353 K

<u>X_{ion}</u>	<u>γ_{data}</u>	<u>γ_{PMSA}</u>
0.003587	0.7617	0.7712
0.007149	0.7232	0.7323
0.01420	0.6928	0.7098
0.03475	0.7045	0.7479
0.05123	0.7483	0.8200
0.06716	0.8094	0.9121
0.1259	1.193	1.446
0.1776	1.860	2.261
0.2236	2.344	3.415
0.2647	4.651	4.964
0.3017	7.318	6.960
0.3351	10.83	9.439
0.3797	18.38	14.11

Average of Residuals = 12.3%

 $pK_{ion-water} = 1.43$

Table 6.18

Mean Ionic Activity Coefficients of KOH in Water at 298 K

<u>X_{ion}</u>	<u>Y_{±data}</u>	<u>Y_{±PMSA}</u>
0.0003599	0.9023	0.9093
0.0007195	0.8716	0.8778
0.001797	0.8225	0.8279
0.003587	0.7818	0.7870
0.007149	0.7453	0.7500
0.01068	0.7298	0.7344
0.01420	0.7233	0.7285
0.01768	0.7228	0.7281
0.02114	0.7264	0.7315
0.02458	0.7320	0.7376
0.02779	0.7387	0.7458
0.03138	0.7485	0.7557
0.03475	0.7594	0.7671
0.04141	0.7845	0.7937
0.04798	0.8130	0.8246
0.05446	0.8461	0.8594
0.06086	0.8817	0.8978
0.06716	0.9219	0.9396
0.08257	1.035	1.060
0.09747	1.172	1.202
0.1119	1.333	1.370
0.1259	1.523	1.566
0.1394	1.744	1.793
0.1525	2.002	2.056
0.1653	2.304	2.359
0.1776	2.651	2.709
0.2103	3.531	3.574
0.2236	4.701	4.710
0.2447	6.263	6.193
0.2647	8.310	8.115
0.2837	10.97	10.59
0.3017	14.32	13.75
0.3188	18.64	17.75
0.3351	24.06	22.79
0.3506	30.65	29.08
0.3655	38.30	36.86
0.3797	47.39	46.41
0.3932	57.52	58.05
0.4062	68.37	72.12
0.4186	79.81	88.99

Average of Residuals = 2.2%

P_{Kion-water} = 1.29ℓ_{water-ion} = 0.418

Table 6.19

Mean Ionic Activity Coefficients of NH_4NO_3 Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm \text{data}}$</u>	<u>$\gamma_{\pm \text{PMSA}}$</u>
0.0003599	0.8973	0.9082
0.0007195	0.8626	0.8751
0.001797	0.8024	0.8189
0.003587	0.7467	0.7663
0.007149	0.6829	0.7046
0.01068	0.6439	0.6642
0.01420	0.6147	0.6337
0.01768	0.5925	0.6089
0.02114	0.5731	0.5879
0.02458	0.5577	0.5698
0.02799	0.5432	0.5539
0.03138	0.5317	0.5397
0.03475	0.5201	0.5268
0.04141	0.5018	0.5044
0.04798	0.4853	0.4855
0.05446	0.4717	0.4693
0.06086	0.4600	0.4551
0.06716	0.4492	0.4426
0.08257	0.4262	0.4172
0.09747	0.4077	0.3977
0.1119	0.3930	0.3824
0.1259	0.3798	0.3701
0.1394	0.3672	0.3601
0.1525	0.3575	0.3518
0.1653	0.3486	0.3447
0.1776	0.3405	0.3387
0.2013	0.3268	0.3289
0.2236	0.3156	0.3211
0.2447	0.3058	0.3145
0.2647	0.2992	0.3088
0.2837	0.2918	0.3035
0.3017	0.2864	0.2986
0.3188	0.2819	0.2939
0.3351	0.2782	0.2894
0.3506	0.2757	0.2850
0.3655	0.2726	0.2806
0.3797	0.2708	0.2762
0.3932	0.2686	0.2719
0.4062	0.2661	0.2677
0.4186	0.2649	0.2634

Table 6.19 (Continued)

Mean Ionic Activity Coefficients of NH_4NO_3 Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm \text{data}}$</u>	<u>$\gamma_{\pm \text{PMSA}}$</u>
0.4305	0.2634	0.2592
0.4420	0.2616	0.2551
0.4530	0.2596	0.2509
0.4635	0.2572	0.2468
0.4737	0.2546	0.2428
0.4830	0.2534	0.2389

Average of Residuals = 5.1%

 $\text{PK}_{\text{ion-water}} = 1.19$ $\ell_{\text{water-ion}} = 0.065$

Table 6.20

Mean Ionic Activity Coefficients of LiBr in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm data}$</u>	<u>$\gamma_{\pm PMSA}$</u>
0.0003599	0.9053	0.9091
0.0007195	0.8776	0.8774
0.001797	0.8335	0.8266
0.003587	0.7999	0.7845
0.007149	0.7725	0.7455
0.01068	0.7632	0.7287
0.01420	0.7628	0.7222
0.01768	0.7655	0.7219
0.02114	0.7754	0.7258
0.02458	0.9863	0.7331
0.02799	0.8004	0.7431
0.03138	0.8146	0.7554
0.03475	0.8319	0.7697
0.04141	0.8700	0.8041
0.04798	0.9149	0.8455
0.05446	0.9656	0.8936
0.06086	1.022	0.9486
0.06716	1.085	1.011
0.08257	1.271	1.200
0.09747	1.506	1.445
0.1119	1.799	1.759
0.1259	2.163	2.159
0.1394	2.617	2.666
0.1525	3.181	3.307
0.1653	3.884	4.114
0.1776	4.761	5.129
0.2013	7.234	7.992
0.2236	11.14	12.44
0.2447	17.34	19.24
0.2647	27.21	29.49
0.2837	42.76	44.68
0.3017	66.82	66.80
0.3188	103.0	98.39
0.3351	154.9	142.7
0.3506	226.41	203.5
0.3655	316.8	285.5
0.3797	425.6	393.9
0.3932	547.1	534.5
0.4062	680.3	713.6
0.4186	835.9	937.4

Average of Residuals = 5.8%

 $PK_{ion-water} = 1.30$ $\ell_{water-ion} = 71.3$

Table 6.21

Mean Ionic Activity Coefficients of CaCl_2 in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm \text{data}}$</u>	<u>$\gamma_{\pm \text{PMSA}}$</u>
0.005371	0.5208	0.4882
0.01068	0.4771	0.4362
0.01594	0.4624	0.4202
0.02114	0.4577	0.4187
0.02629	0.4601	0.4255
0.03138	0.4677	0.4379
0.03642	0.4774	0.4546
0.04141	0.4903	0.4750
0.04635	0.5075	0.4988
0.05123	0.5270	0.5258
0.06086	0.5739	0.5892
0.07023	0.6314	0.6655
0.07953	0.6996	0.7558
0.08859	0.7812	0.8615
0.09747	0.8775	0.9842
0.1189	1.207	1.380
0.1394	1.723	1.937
0.1590	2.473	2.708
0.1776	3.563	3.757
0.1955	5.183	5.166
0.2126	7.480	7.030
0.2290	10.61	9.460
0.2447	14.71	12.59
0.2598	19.63	16.55
0.2743	25.19	21.50
0.2883	31.09	27.61
0.3017	37.26	35.06
0.3146	43.92	44.01
0.3271	50.82	54.64
0.3391	58.25	67.13
0.3506	66.22	81.61

Average of Residuals = 8.4%

 $\text{PK}_{\text{ion-water}} = 1.32$ $\ell_{\text{water-ion}} = 0.662$

Table 6.22

Mean Ionic Activity Coefficients of CABr_2 in Water at 298 K

<u>X_{ion}</u>	<u>$\gamma_{\pm \text{data}}$</u>	<u>$\gamma_{\pm \text{PMSA}}$</u>
0.00537	0.5349	0.4897
0.01068	0.4963	0.4379
0.01594	0.4888	0.4228
0.02114	0.4924	0.4232
0.02629	0.5032	0.4326
0.03138	0.5203	0.4488
0.03642	0.5407	0.4706
0.04141	0.5654	0.4974
0.04635	0.5946	0.5293
0.05123	0.6282	0.5662
0.06086	0.7070	0.6561
0.07029	0.8024	0.7704
0.07953	0.9191	0.9134
0.08859	1.062	1.091
0.09747	1.240	1.311
0.1189	1.877	2.109
0.1394	2.940	3.437
0.1590	4.613	5.619
0.1776	7.624	9.151
0.1955	13.23	14.78
0.2126	23.41	23.57
0.2290	41.11	37.06
0.2447	73.75	57.33

Average of Residuals = 11.4%

 $\text{PK}_{\text{ion-water}} = 1.21$ $\ell_{\text{water-ion}} = 0.937$

Table 6.23

Summary of Mean Ionic Activity Coefficient Correlations

Salt	$p_{K_{ion-water}}$	$\ell_{water-ion}$	Average of Residuals (%)	Max X_{ion}
KOH	1.43	0.418	16.3	0.4186
KOH	1.29		2.2	0.4186
NaOH	1.59		11.6	0.5108
KBr	1.12	0.065	2.5	0.1653
NABr	1.23		5.5	0.2447
NaCl	1.27		2.4	0.1811
KCl	1.15		2.4	0.1525
NH ₄ Cl	1.19		3.9	0.2105
NH ₄ NO ₃	1.21		9.0	0.4830
NH ₄ NO ₃	1.19		5.1	0.4830
LiBr	1.59		43.7	0.4186
LiBr	1.30		5.8	0.4186
CaCl ₂	1.42		20.8	0.3506
CaCl ₂	1.32	0.662	8.4	0.3506
CaBr ₂	1.35		30.2	0.2447
CaBr ₂	1.21		11.4	0.2447
Na ₂ SO ₄	1.14	0.937	6.6	0.2126
KOH *	1.43		12.3	0.3797

* at 353 K

FIGURE 6.1
RESIDUAL VALUES:
CORRELATION OF WATER
VAPOR PRESSURE

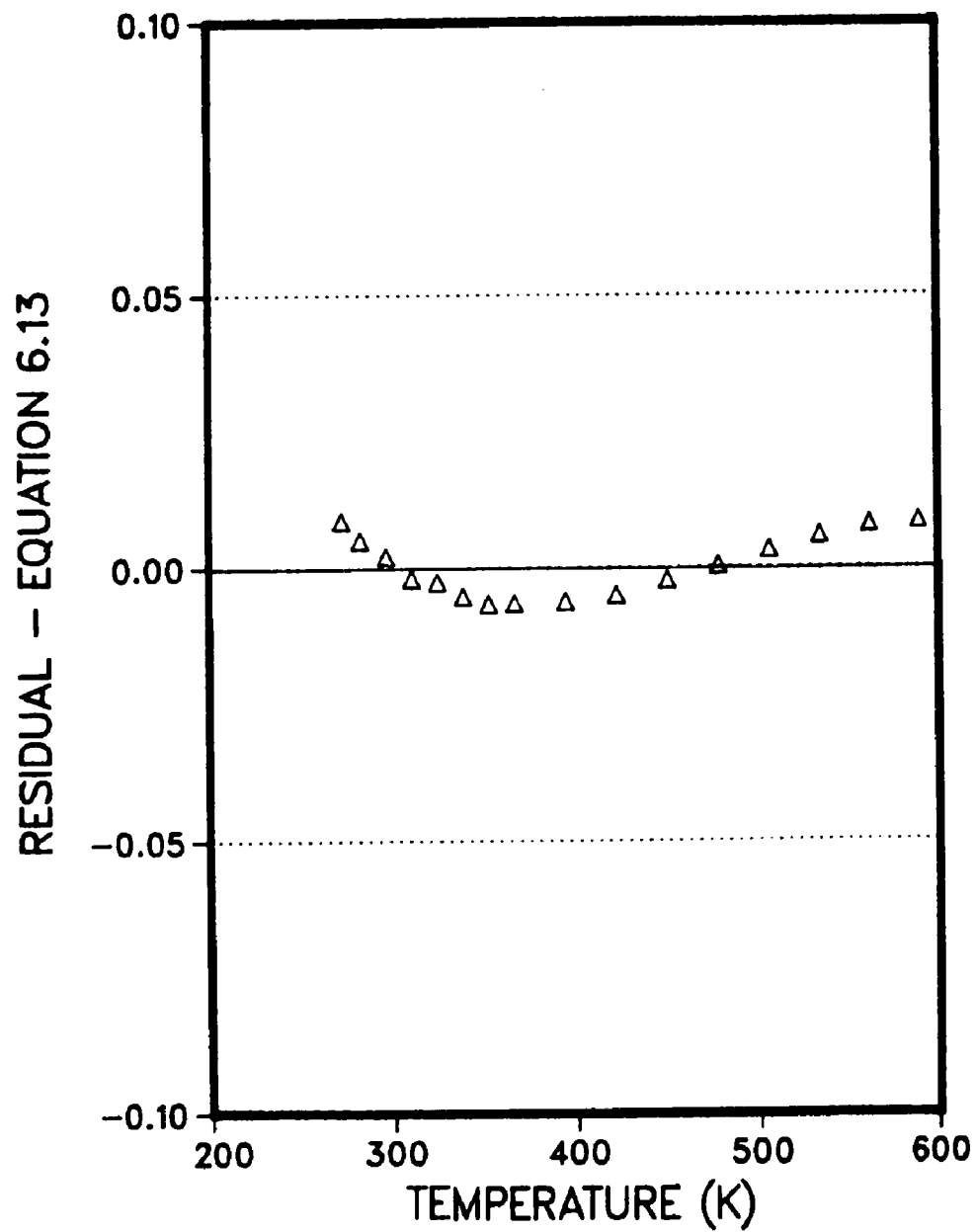


FIGURE 6.2
RESIDUAL VALUES:
CORRELATION OF WATER
LIQUID DENSITY

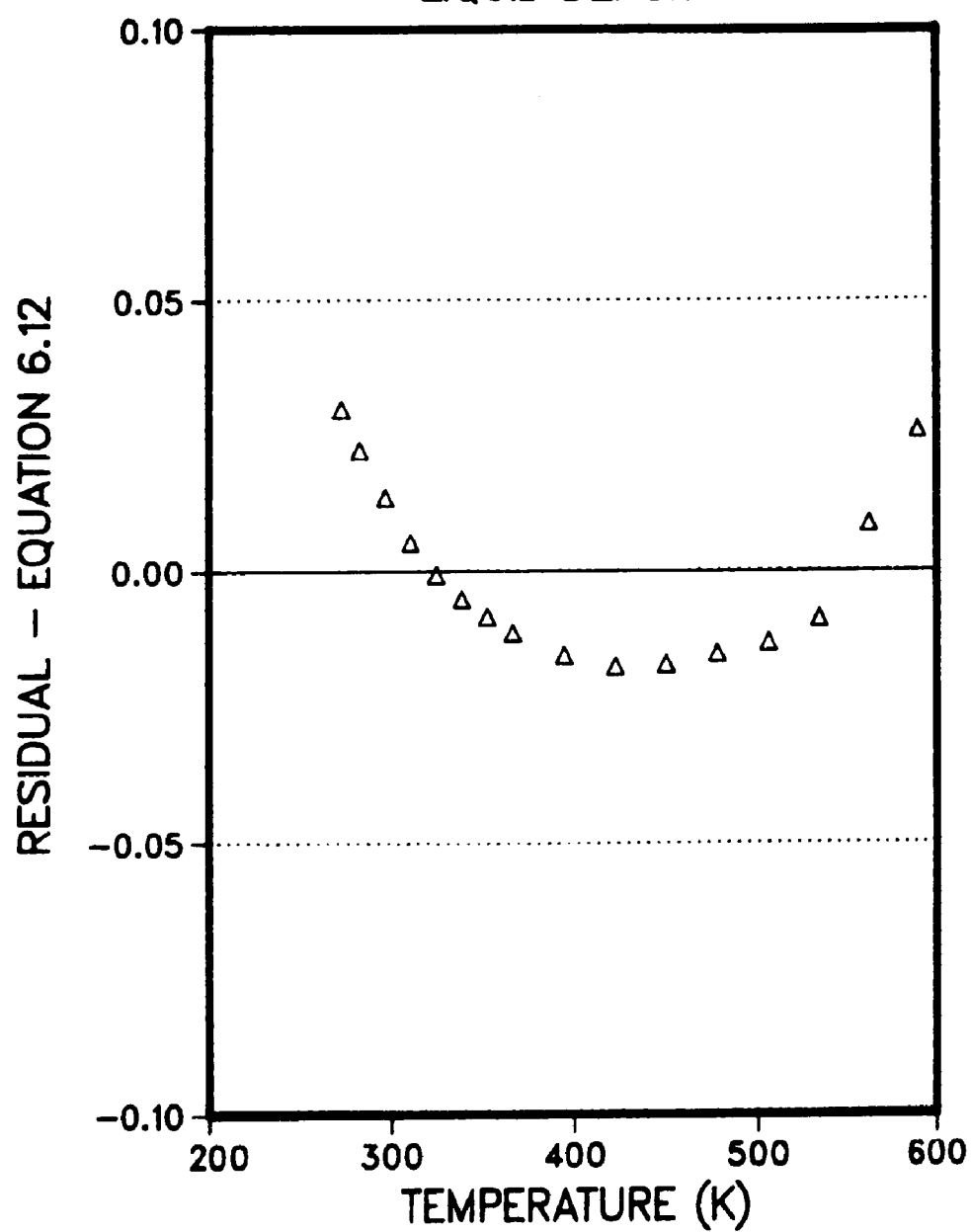


FIGURE 6.3
RESIDUAL VALUES:
CORRELATION OF METHANOL
VAPOR PRESSURE

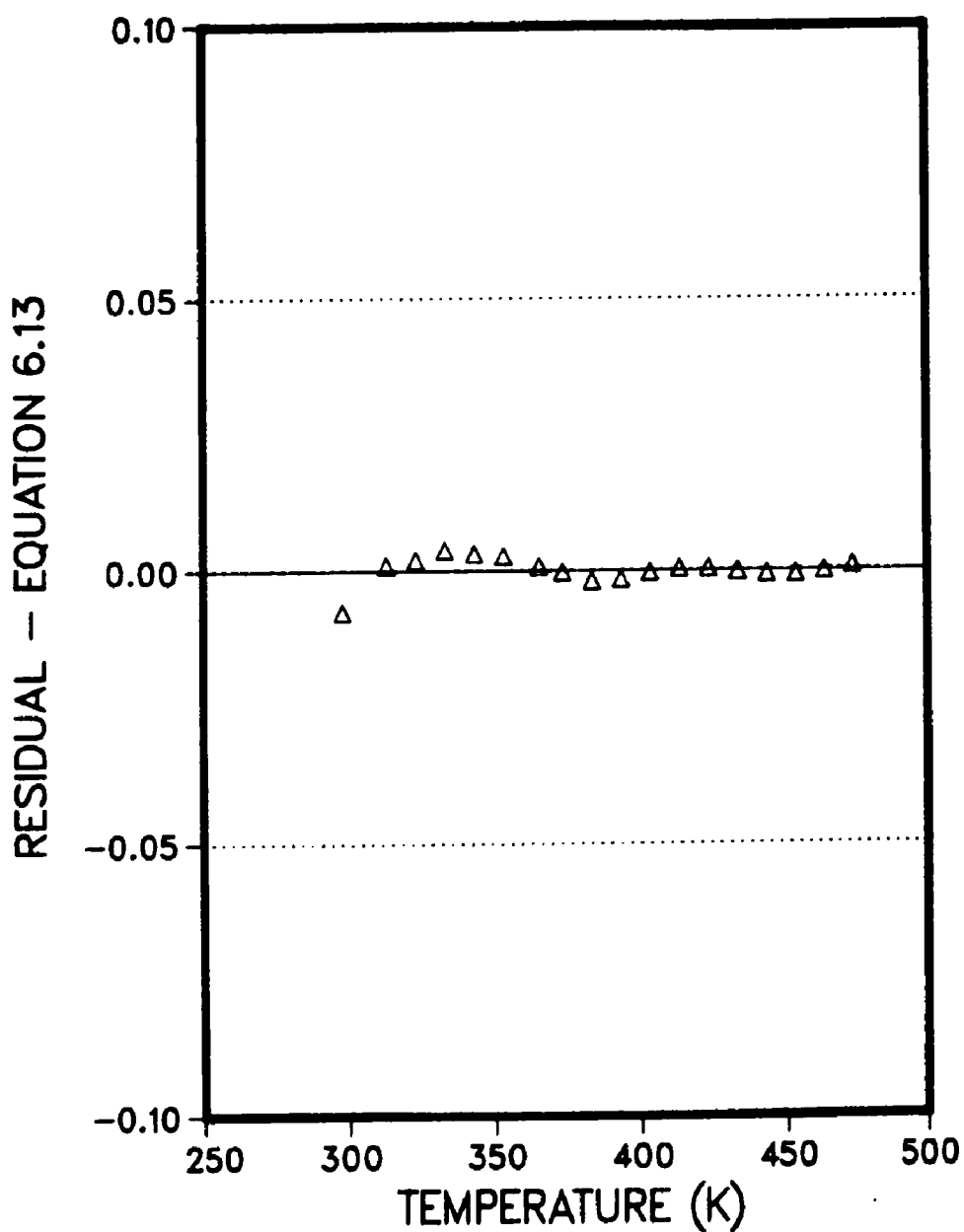


FIGURE 6.4
RESIDUAL VALUES:
CORRELATION OF METHANOL
LIQUID DENSITY

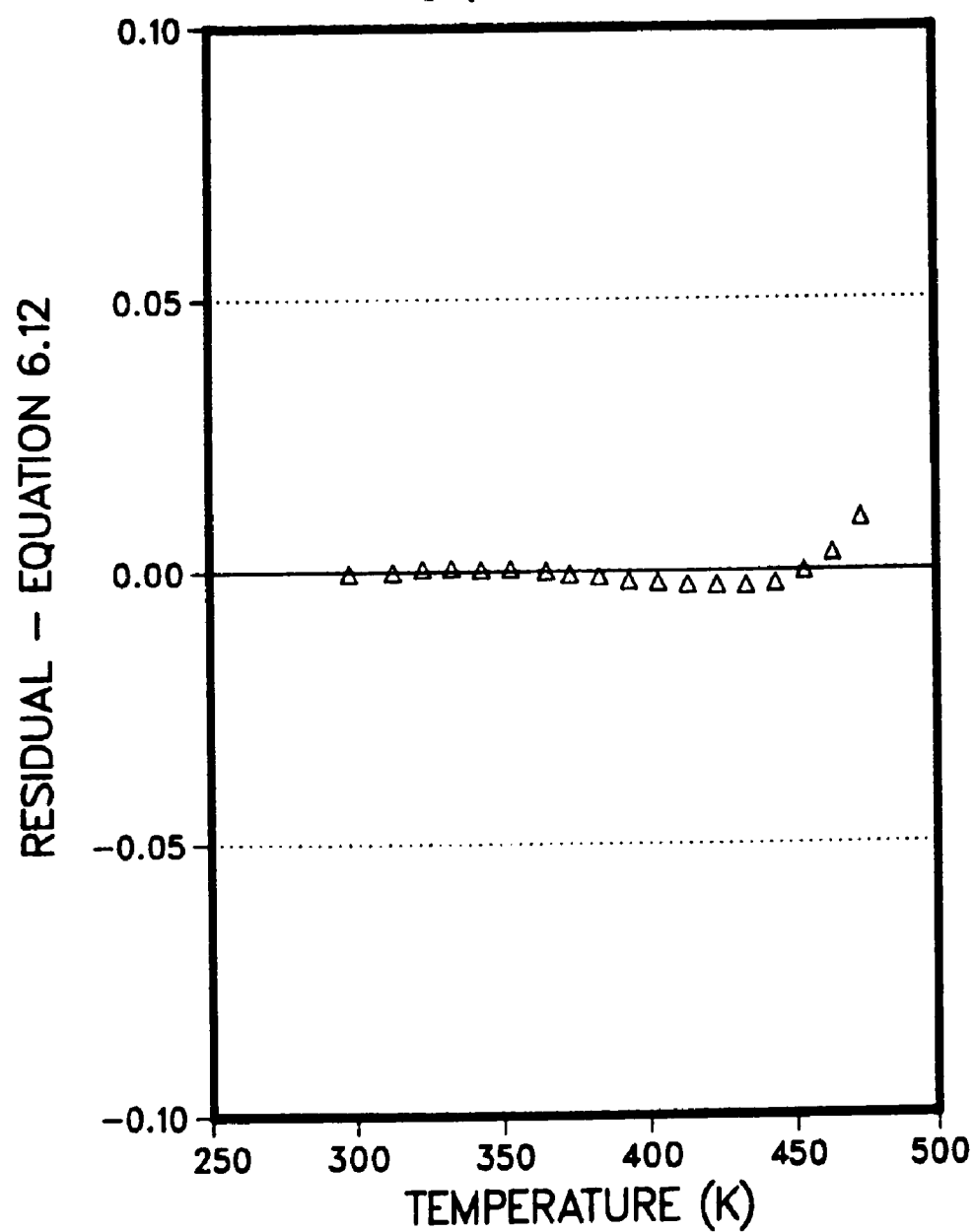


FIGURE 6.5
RESIDUAL VALUES:
CORRELATION OF ANILINE
VAPOR PRESSURE

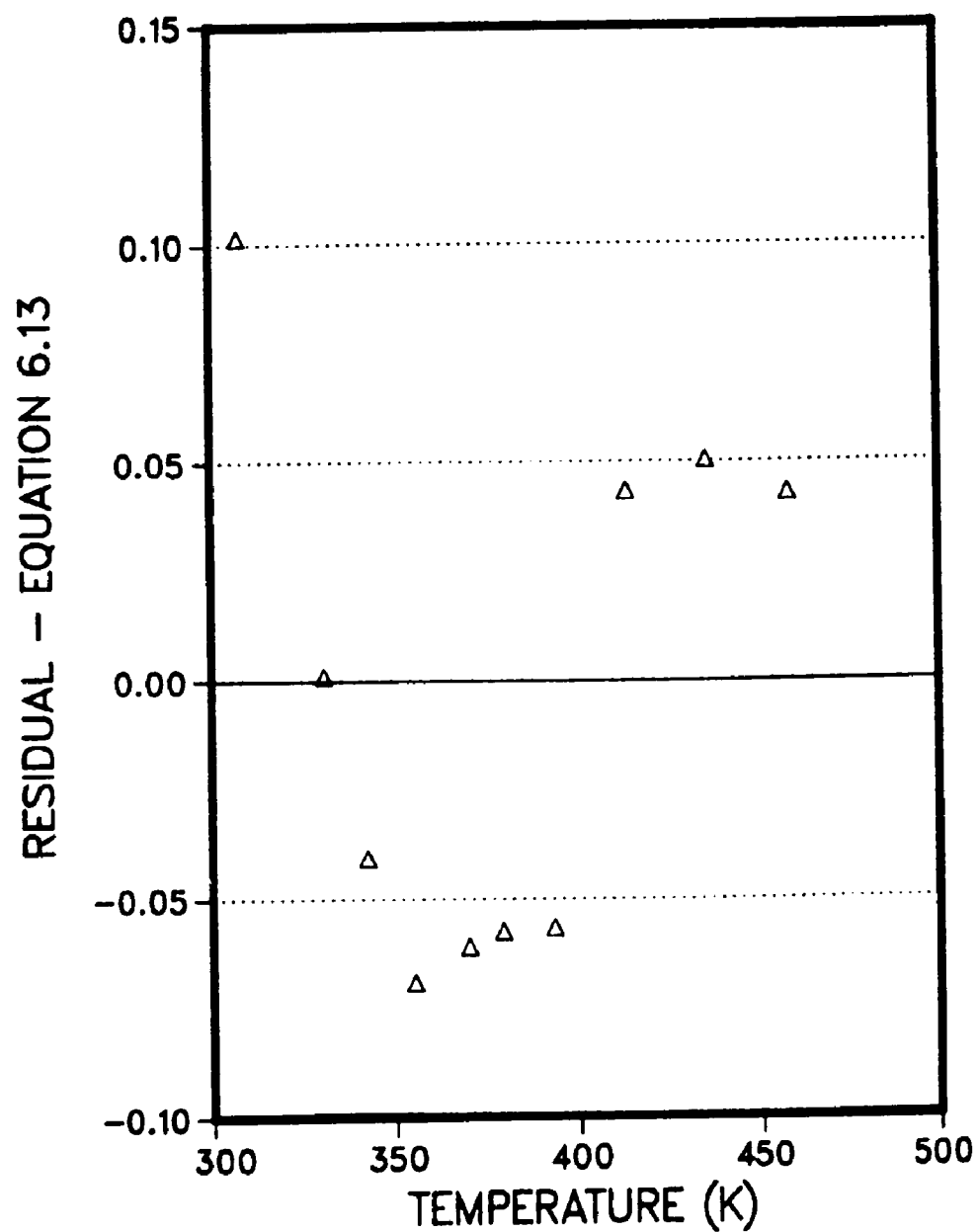


FIGURE 6.6
RESIDUAL VALUES:
CORRELATION OF ANILINE
LIQUID DENSITY

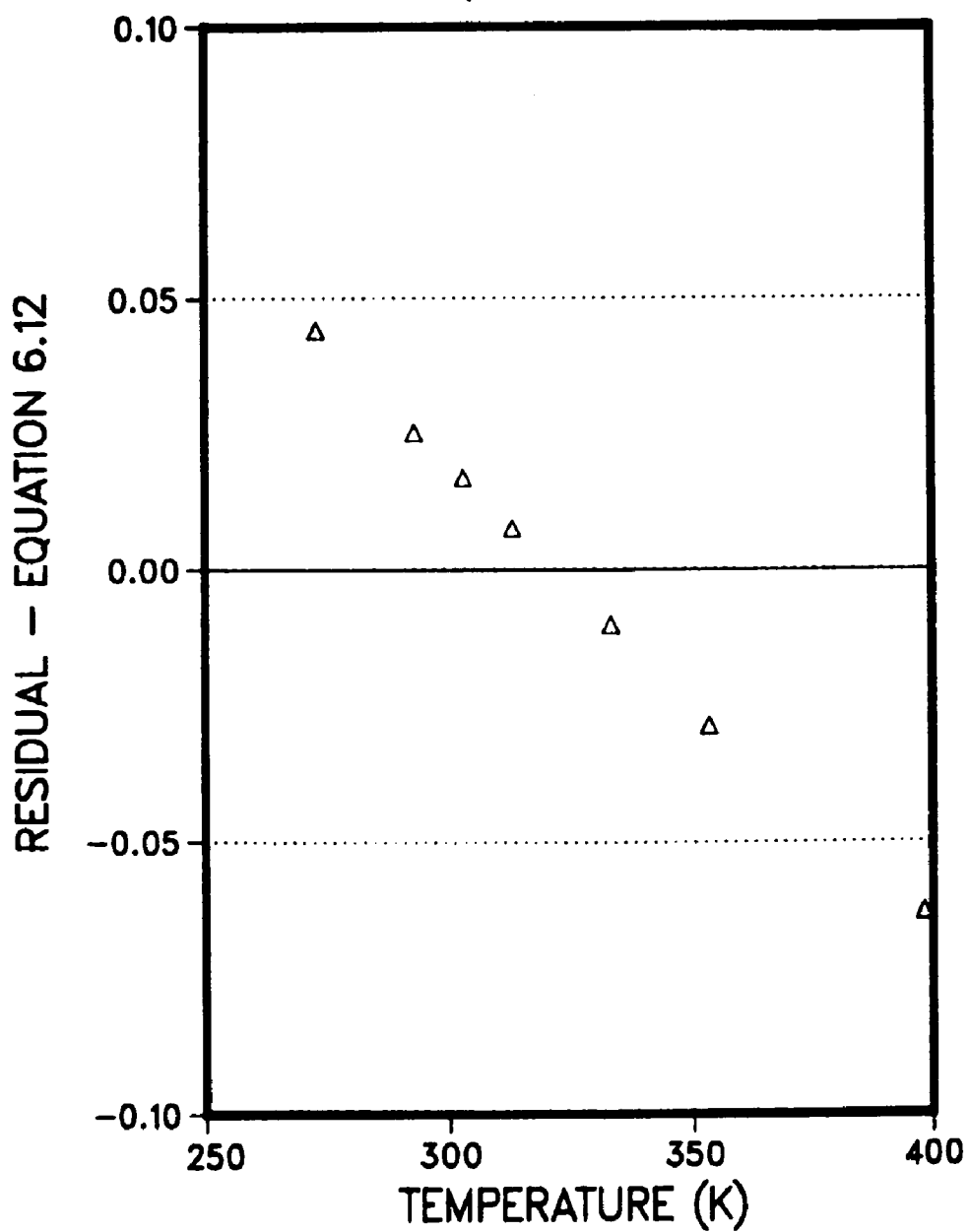


FIGURE 6.7
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR KOH IN WATER AT 298 K

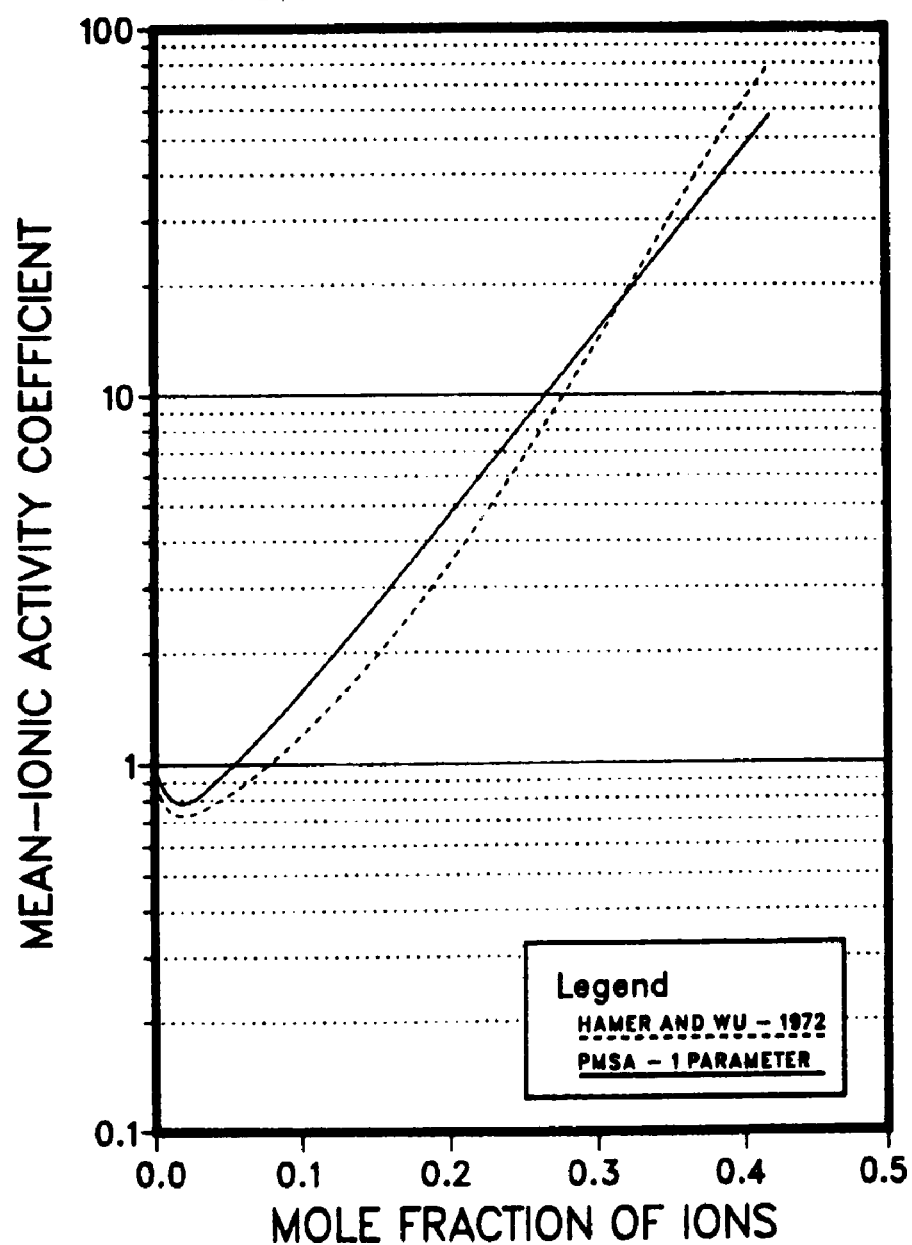


FIGURE 6.8
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR KOH IN WATER AT 298 K

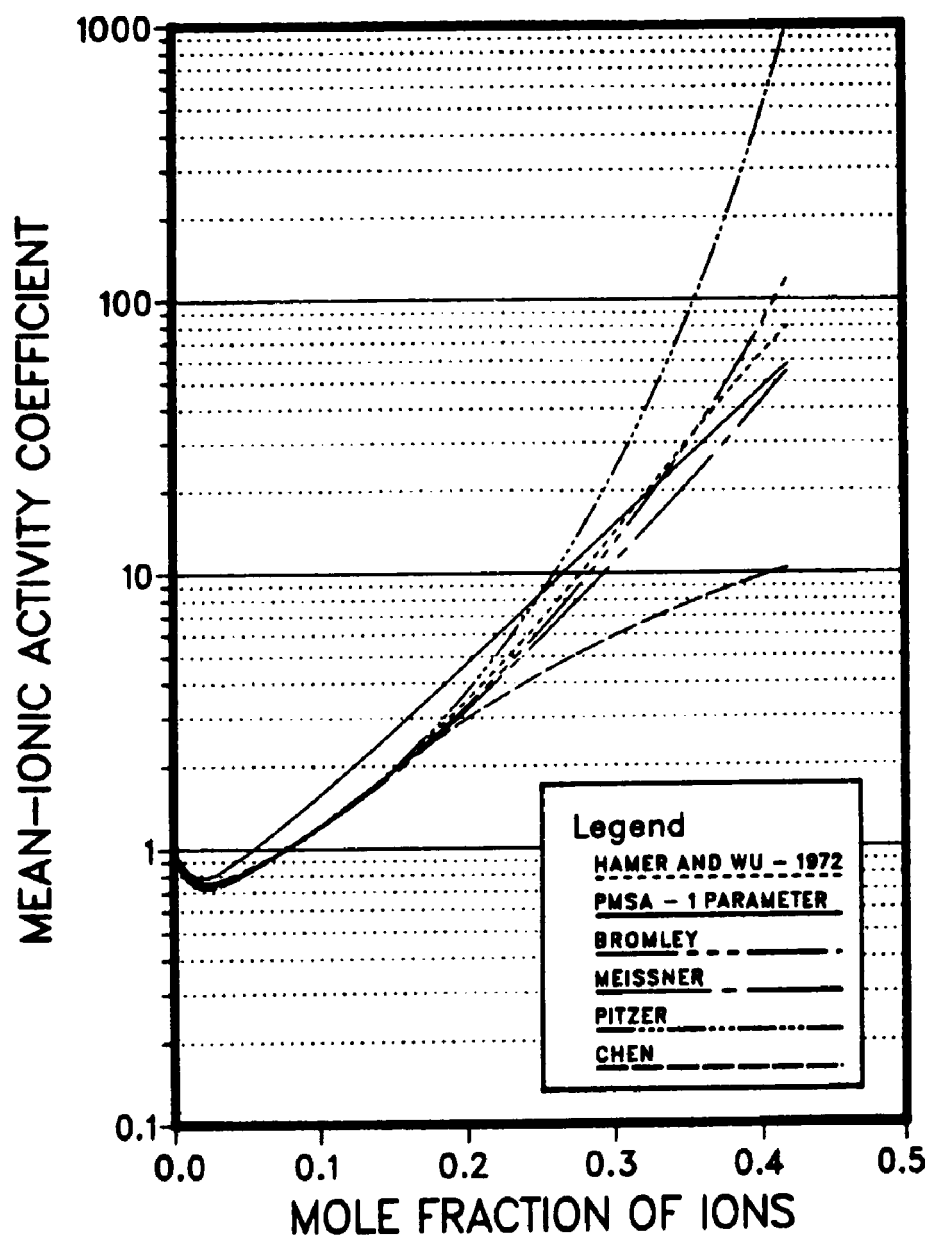


FIGURE 6.9
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR NaOH IN WATER AT 298 K

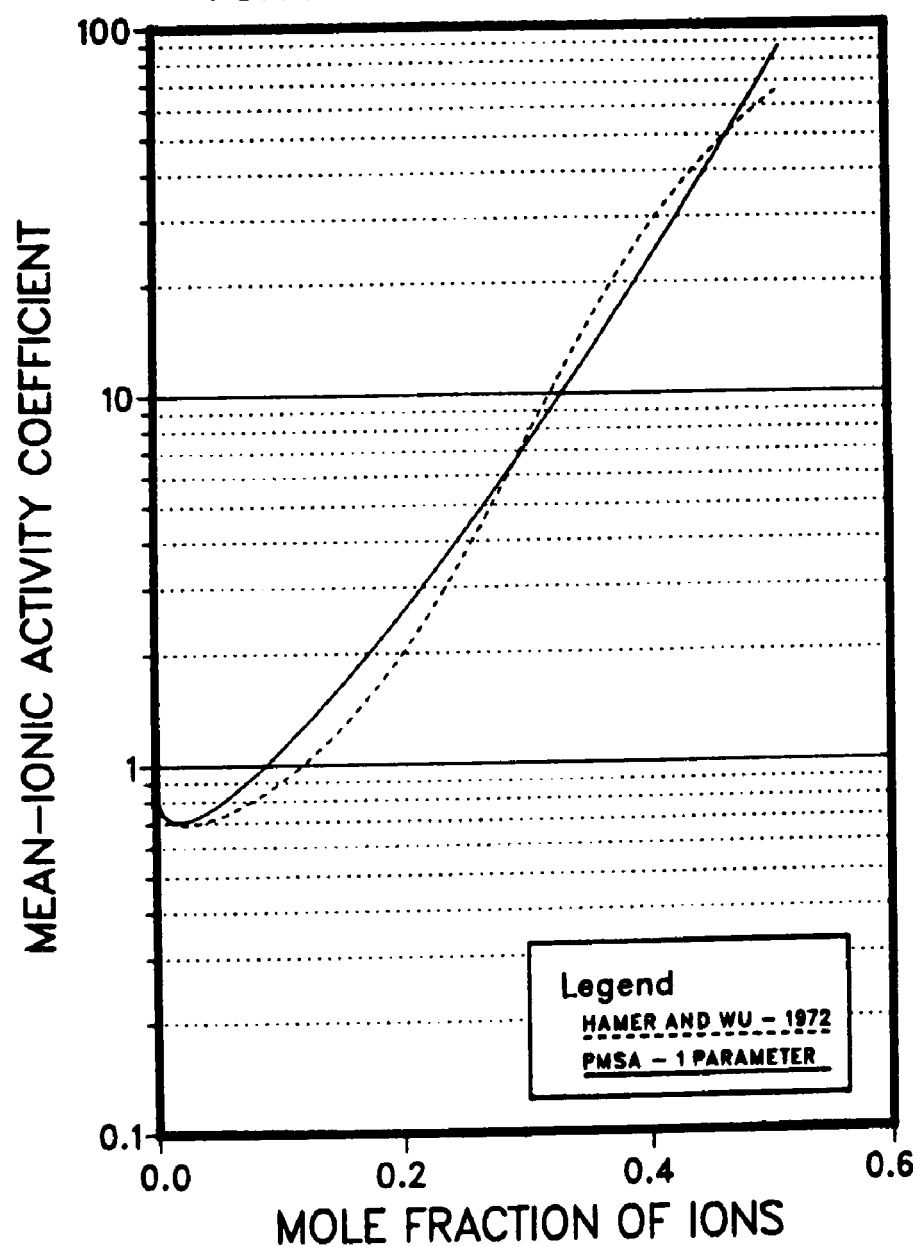


FIGURE 6.10
 PREDICTED AND EXPERIMENTAL
 MEAN-IONIC ACTIVITY COEFFICIENT
 FOR NaOH IN WATER AT 298 K

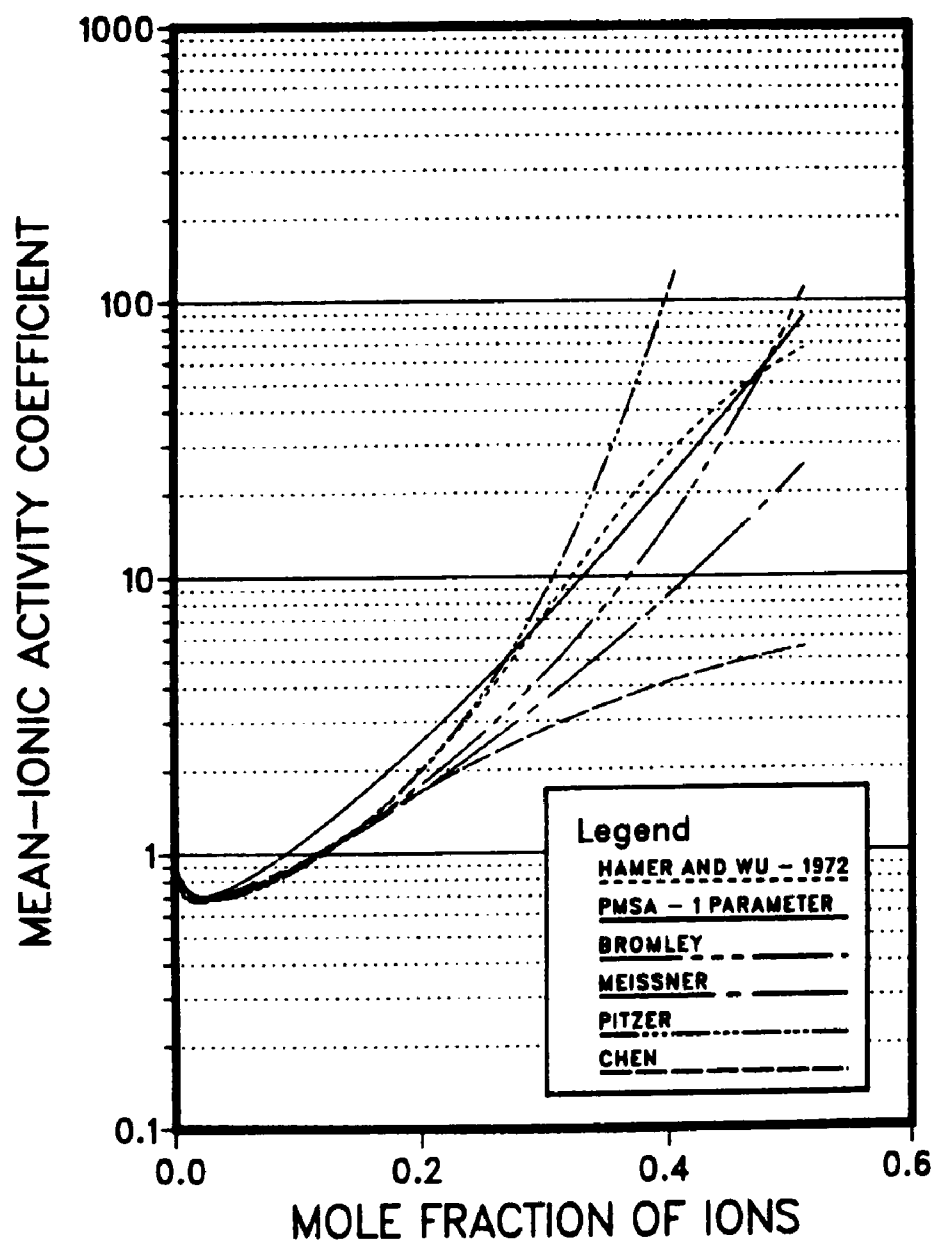


FIGURE 6.11
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR KBR IN WATER AT 298 K

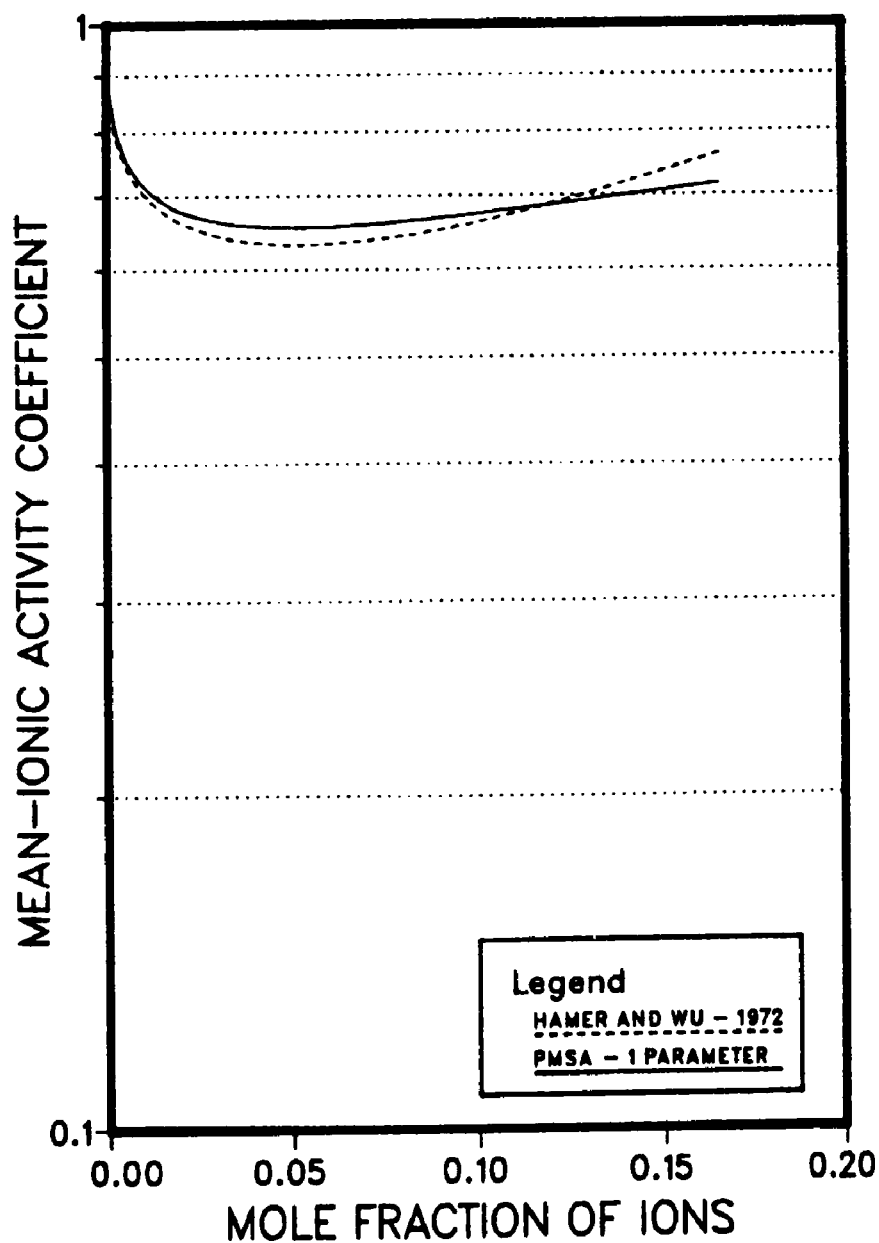


FIGURE 6.12
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR NABR IN WATER AT 298 K

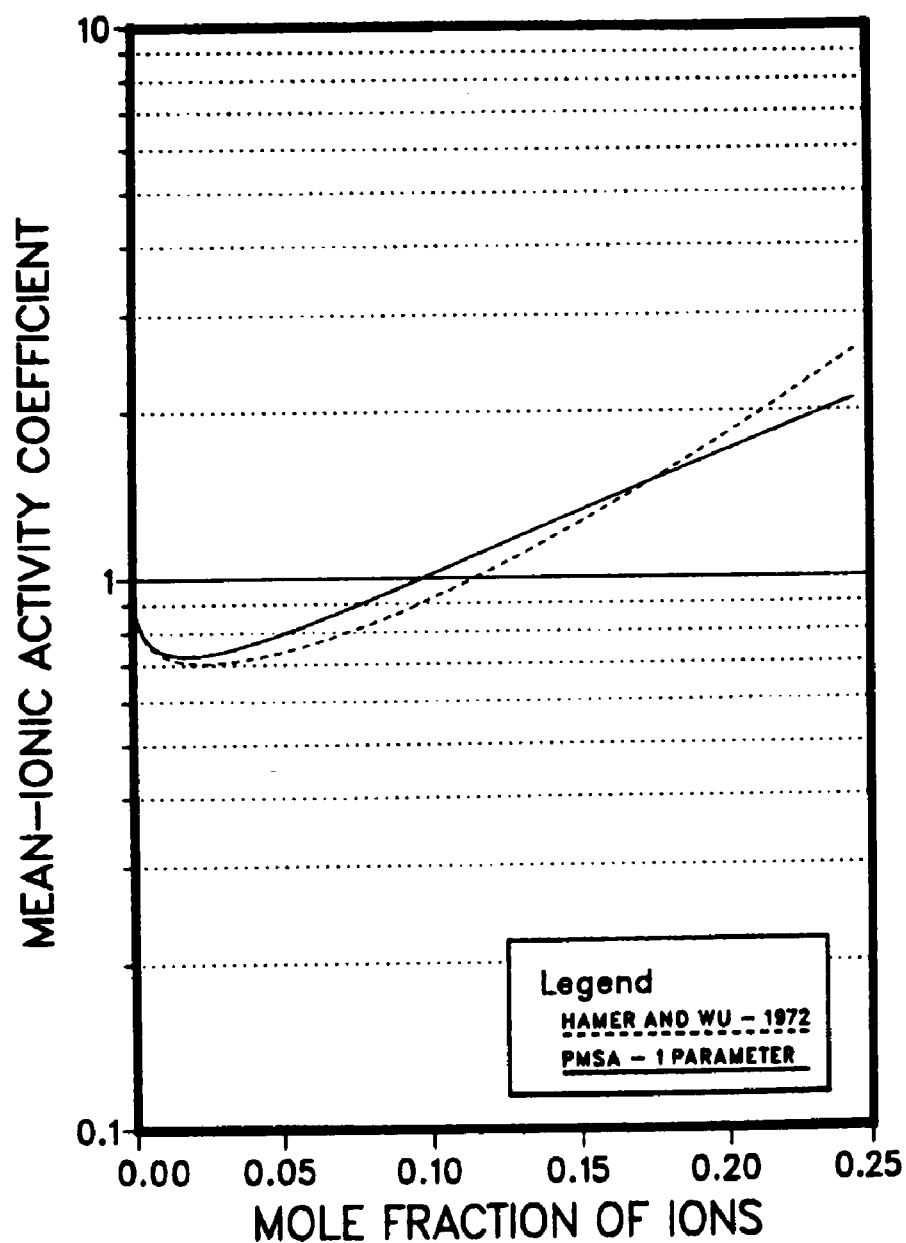


FIGURE 6.13
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR NaCl IN WATER AT 298 K

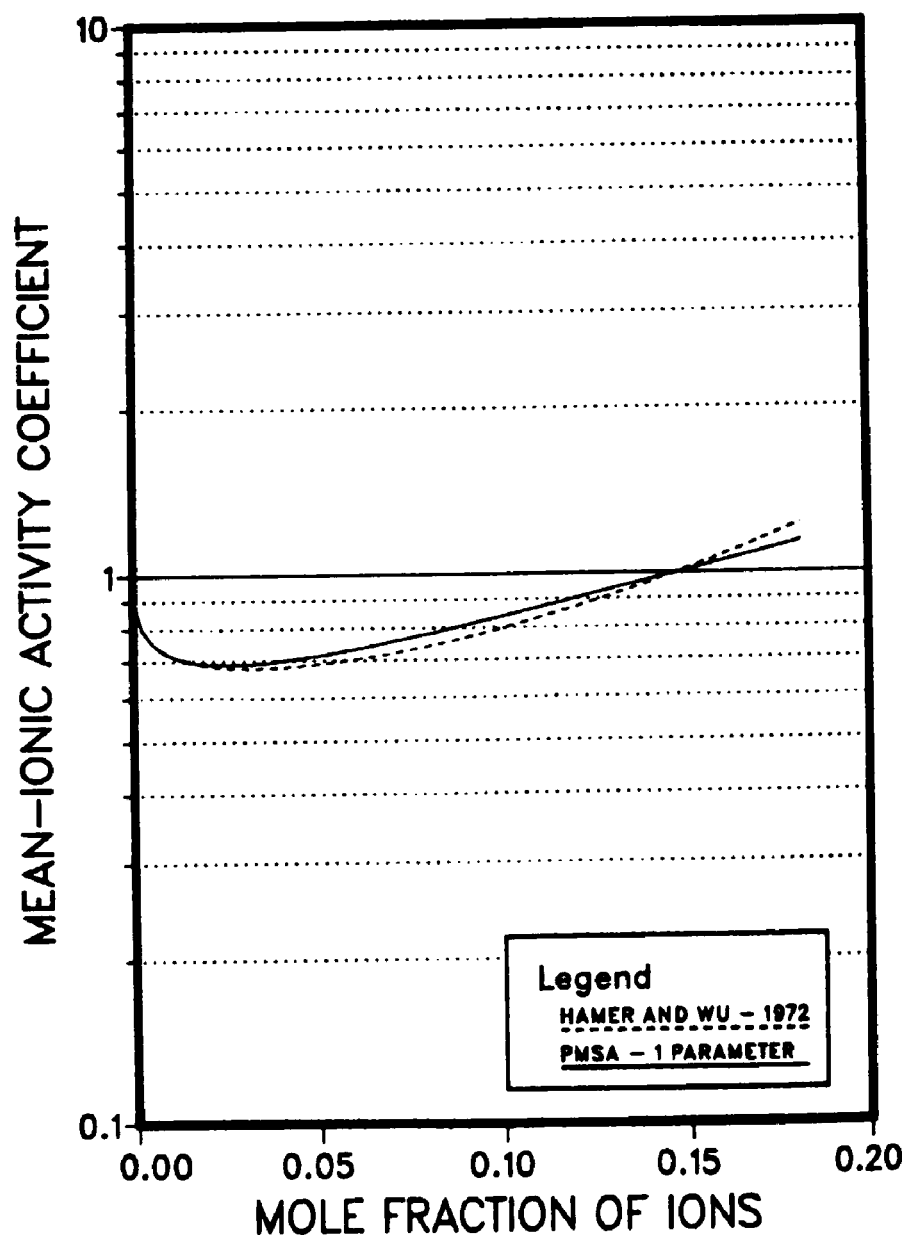


FIGURE 6.14
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR KCL IN WATER AT 298 K

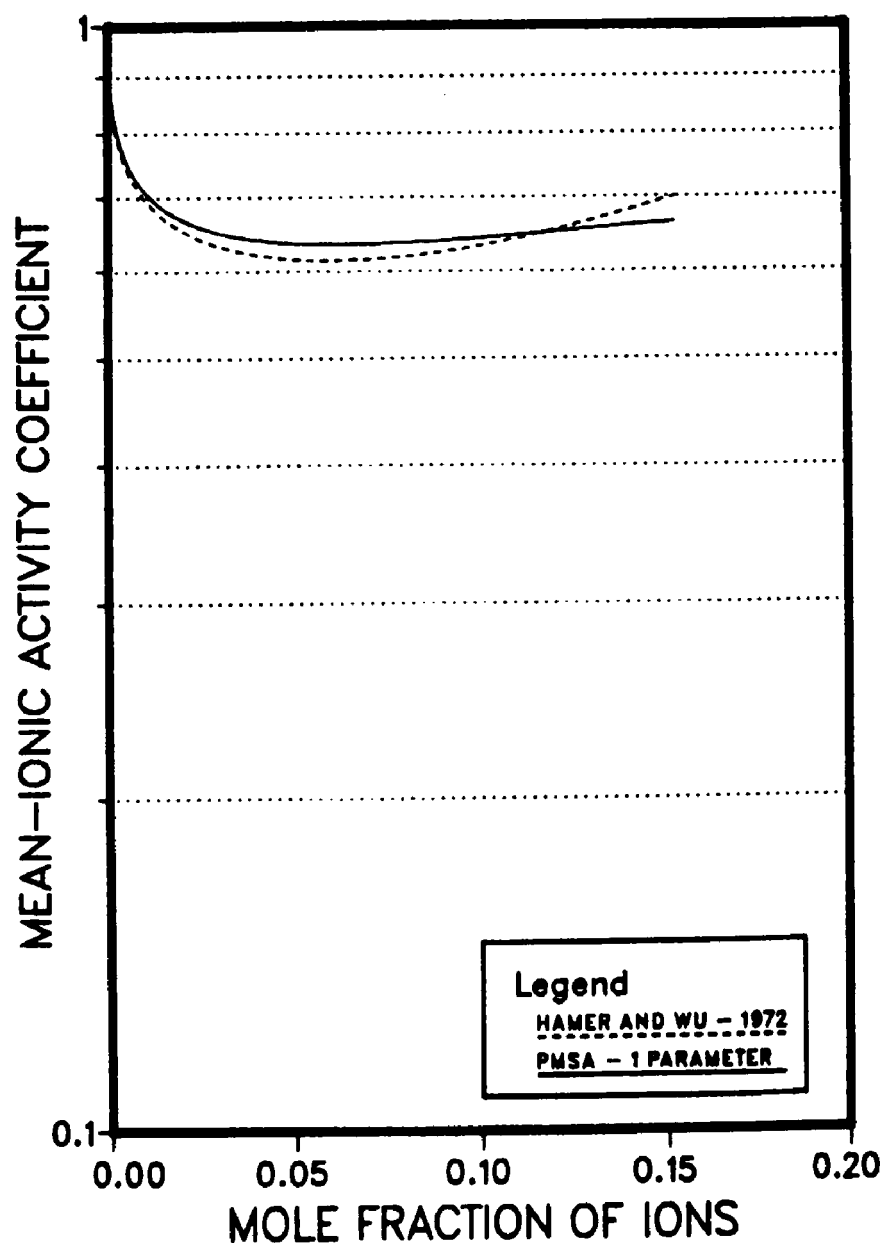


FIGURE 6.15
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR NH_4Cl IN WATER AT 298 K

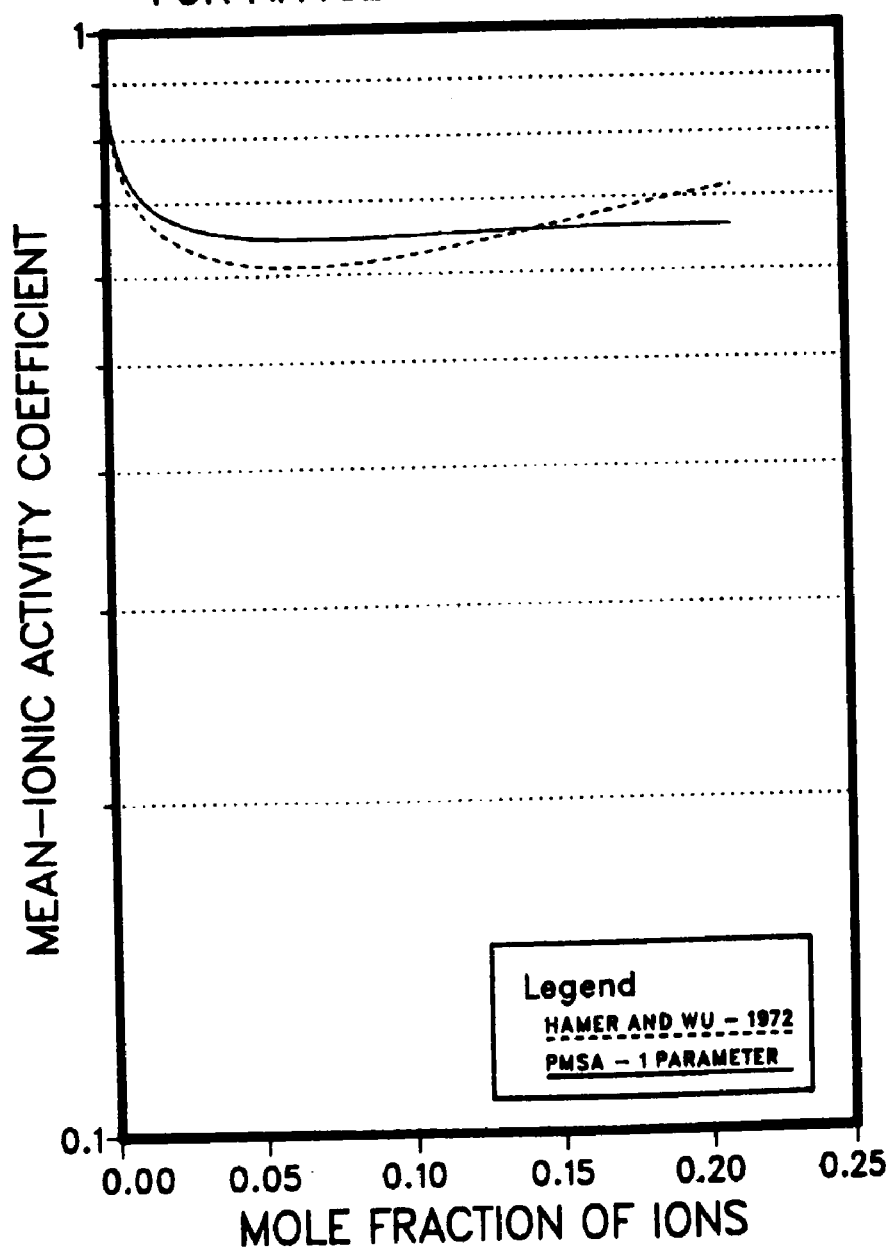


FIGURE 6.16
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR NH_4NO_3 IN WATER AT 298 K

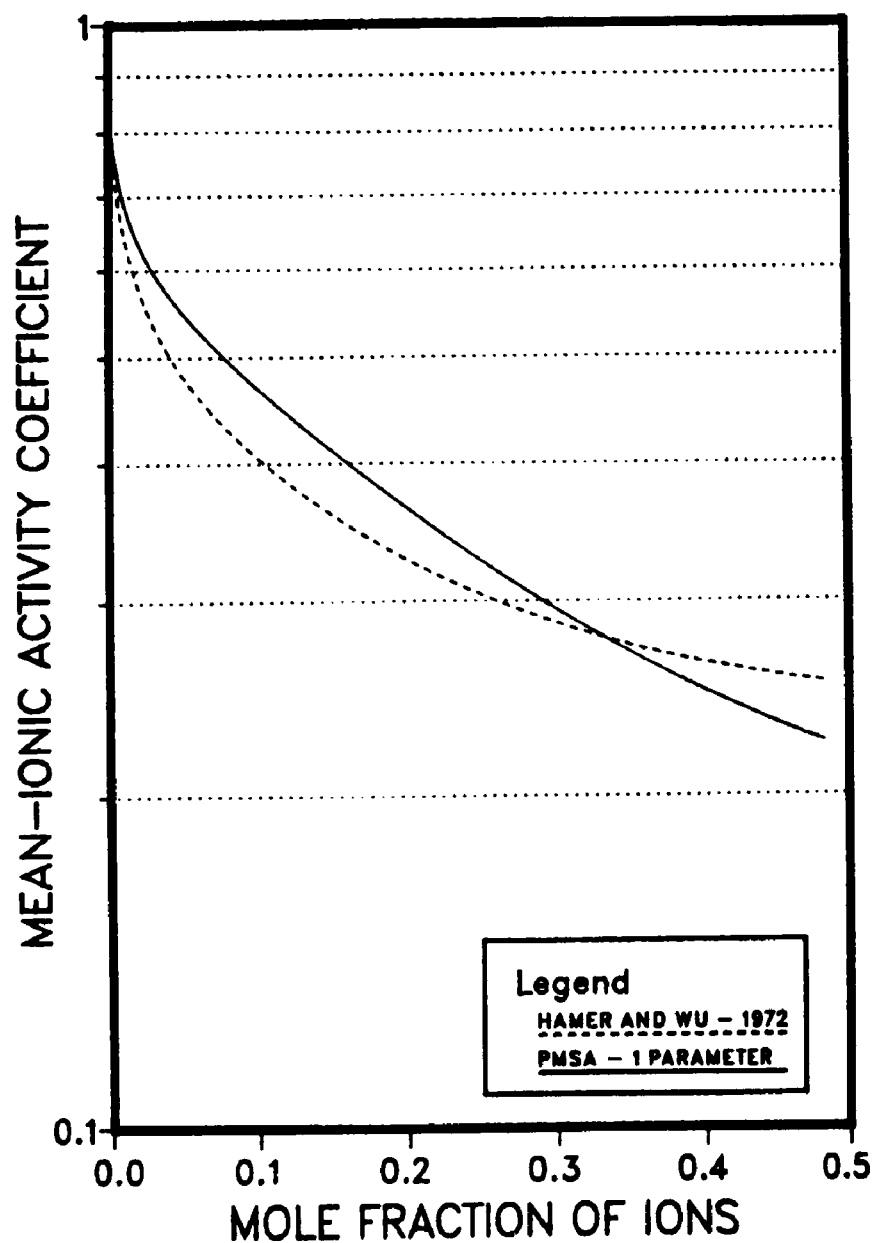


FIGURE 6.17
 PREDICTED AND EXPERIMENTAL
 MEAN-IONIC ACTIVITY COEFFICIENT
 FOR LiBr IN WATER AT 298 K

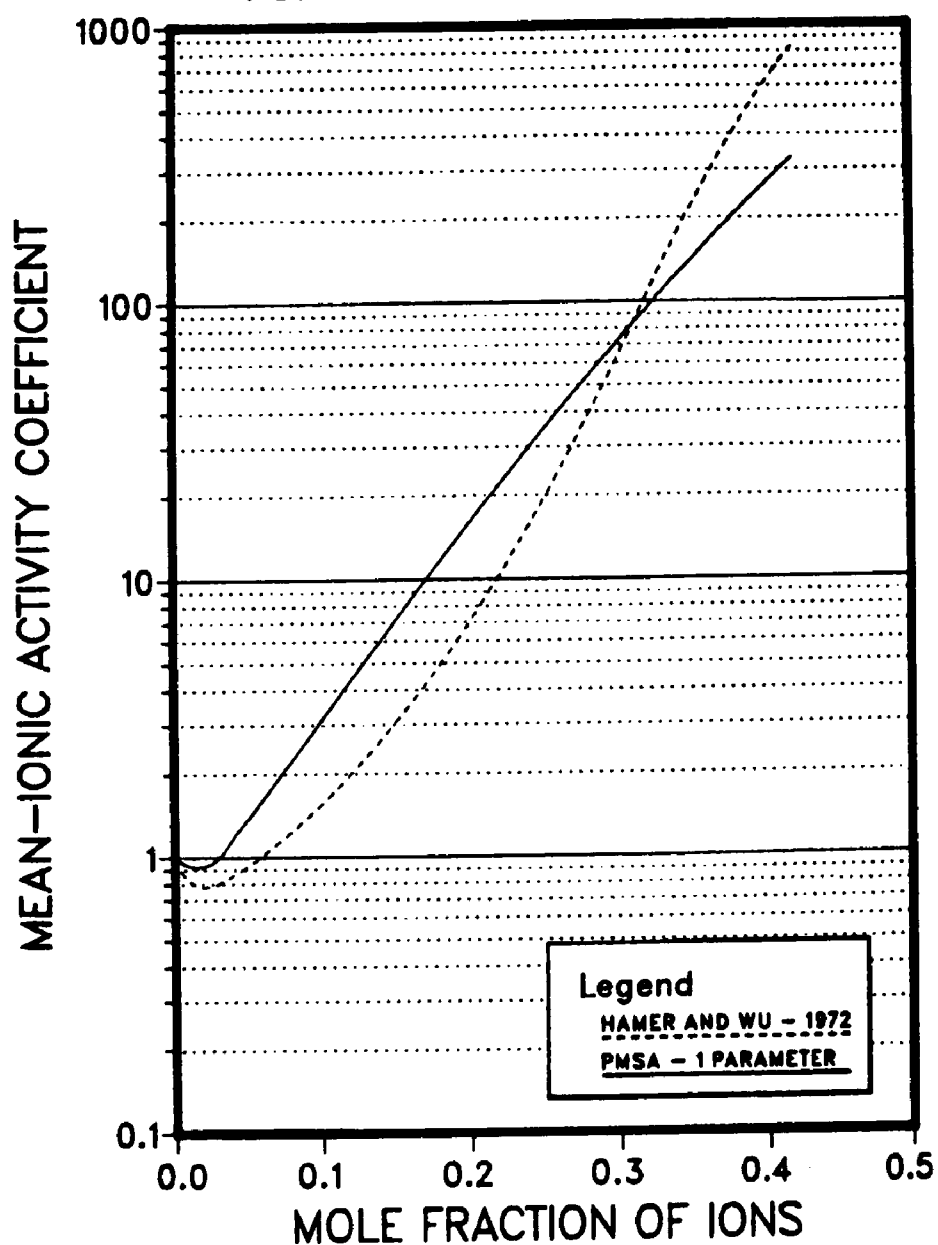


FIGURE 6.18
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR CaCl_2 IN WATER AT 298 K

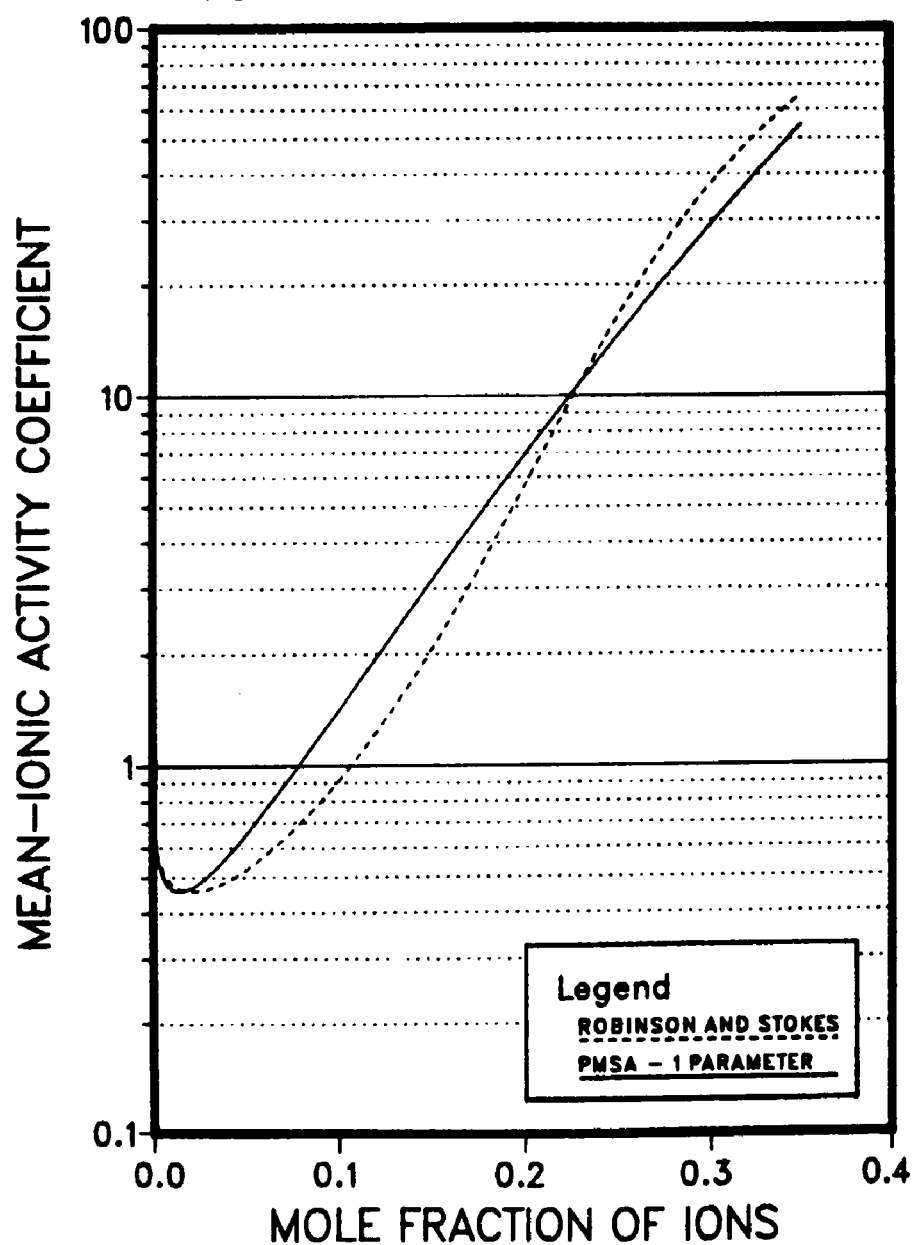


FIGURE 6.19
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR CaCl_2 IN WATER AT 298 K

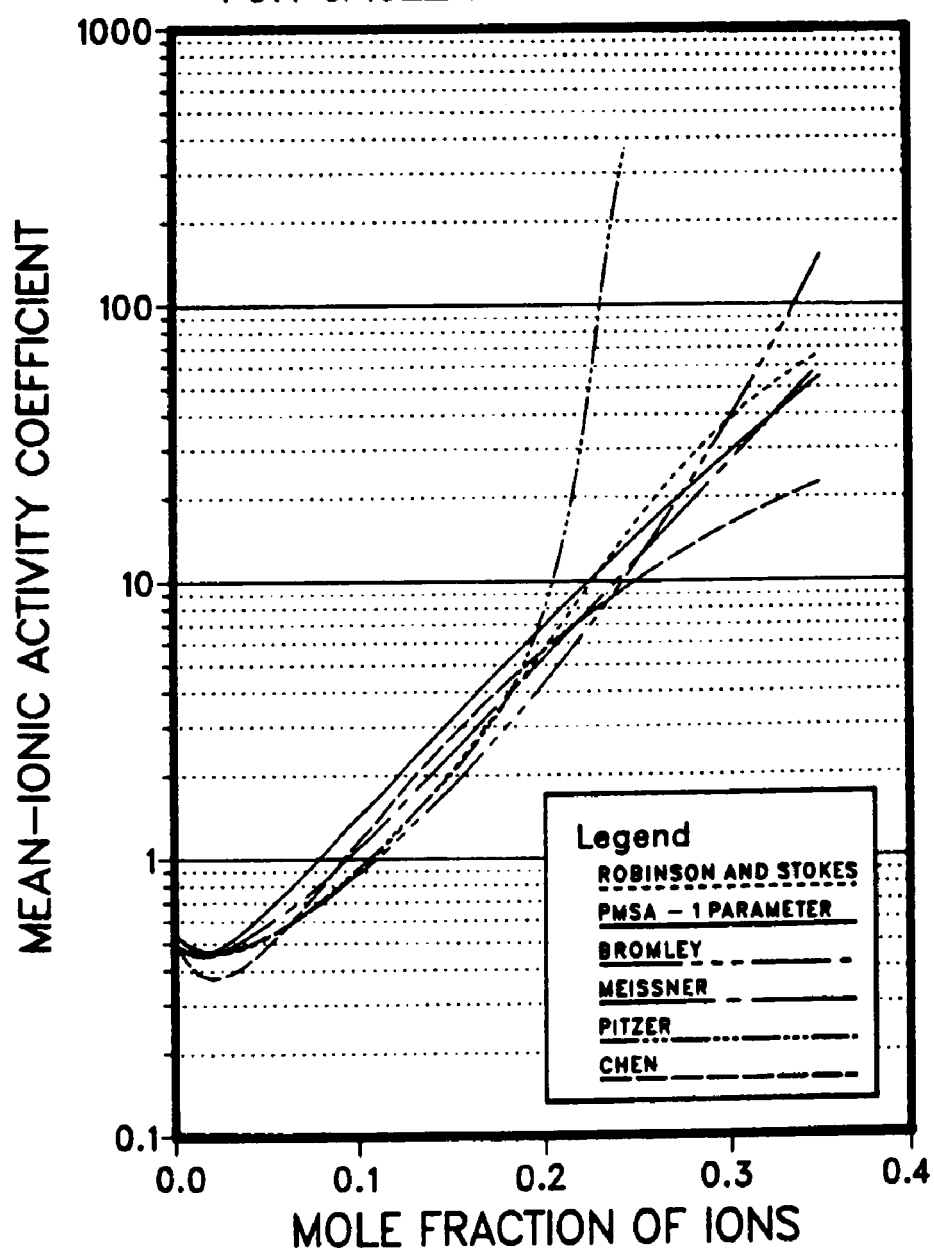


FIGURE 6.20
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR CABR2 IN WATER AT 298 K

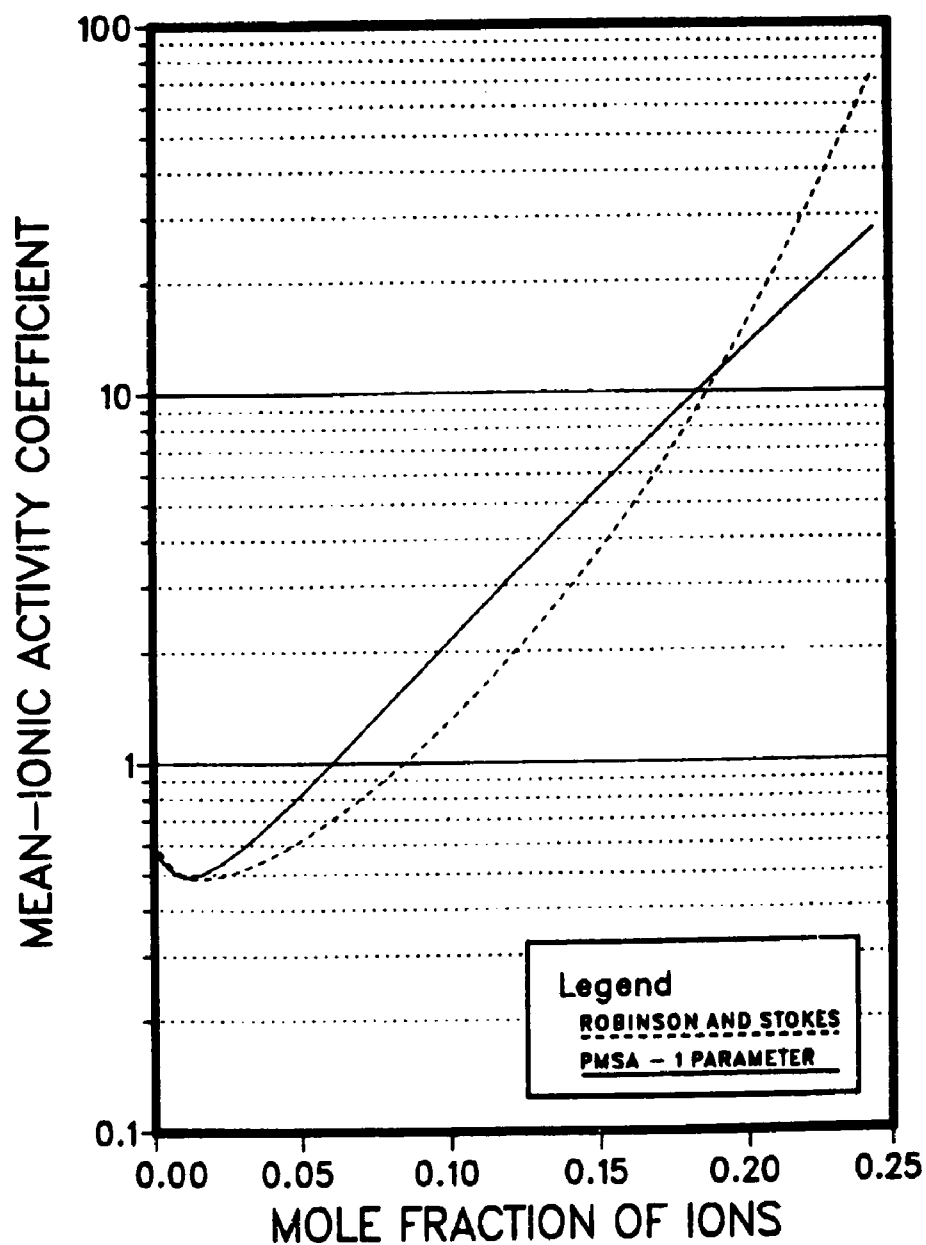


FIGURE 6.21
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR Na_2SO_4 IN WATER AT 298 K

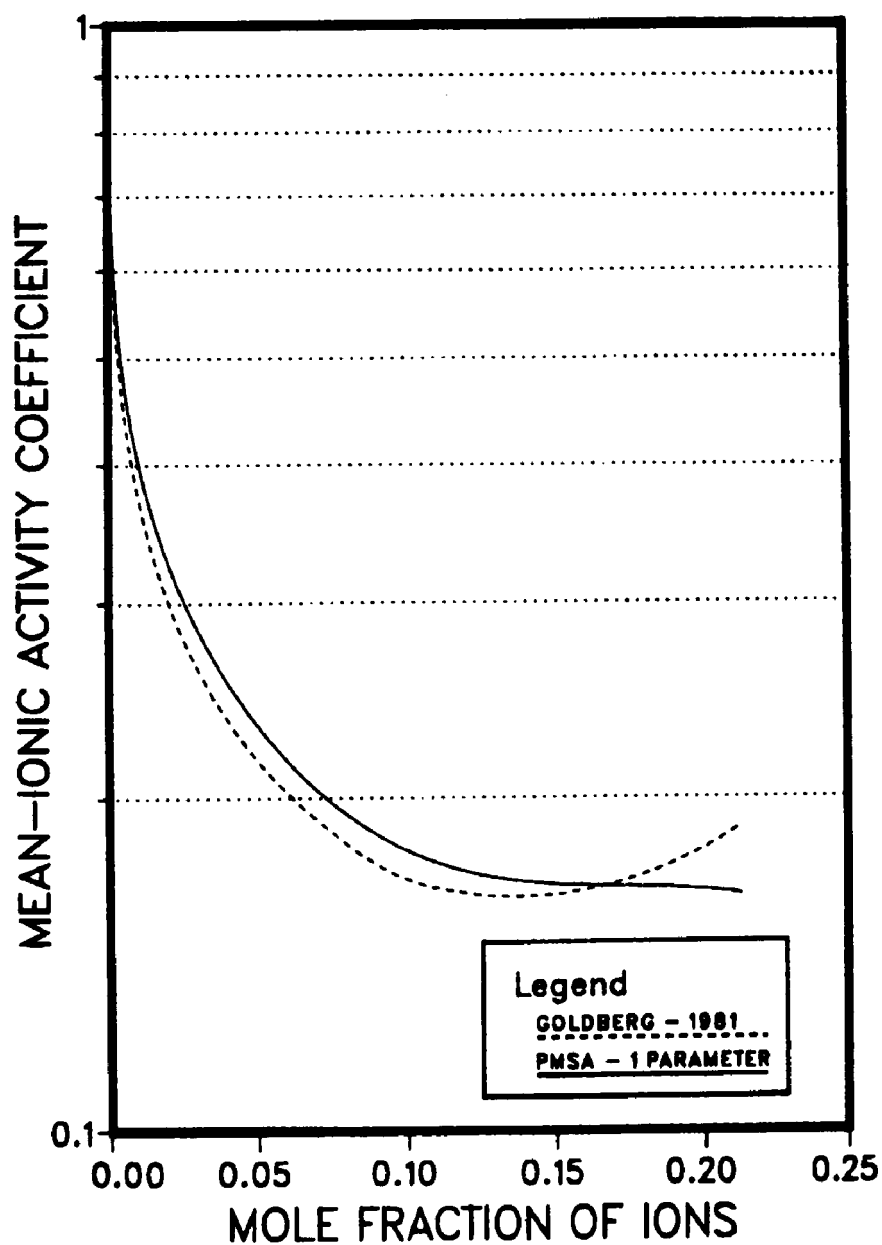


FIGURE 6.22
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR Na_2SO_4 IN WATER AT 298 K

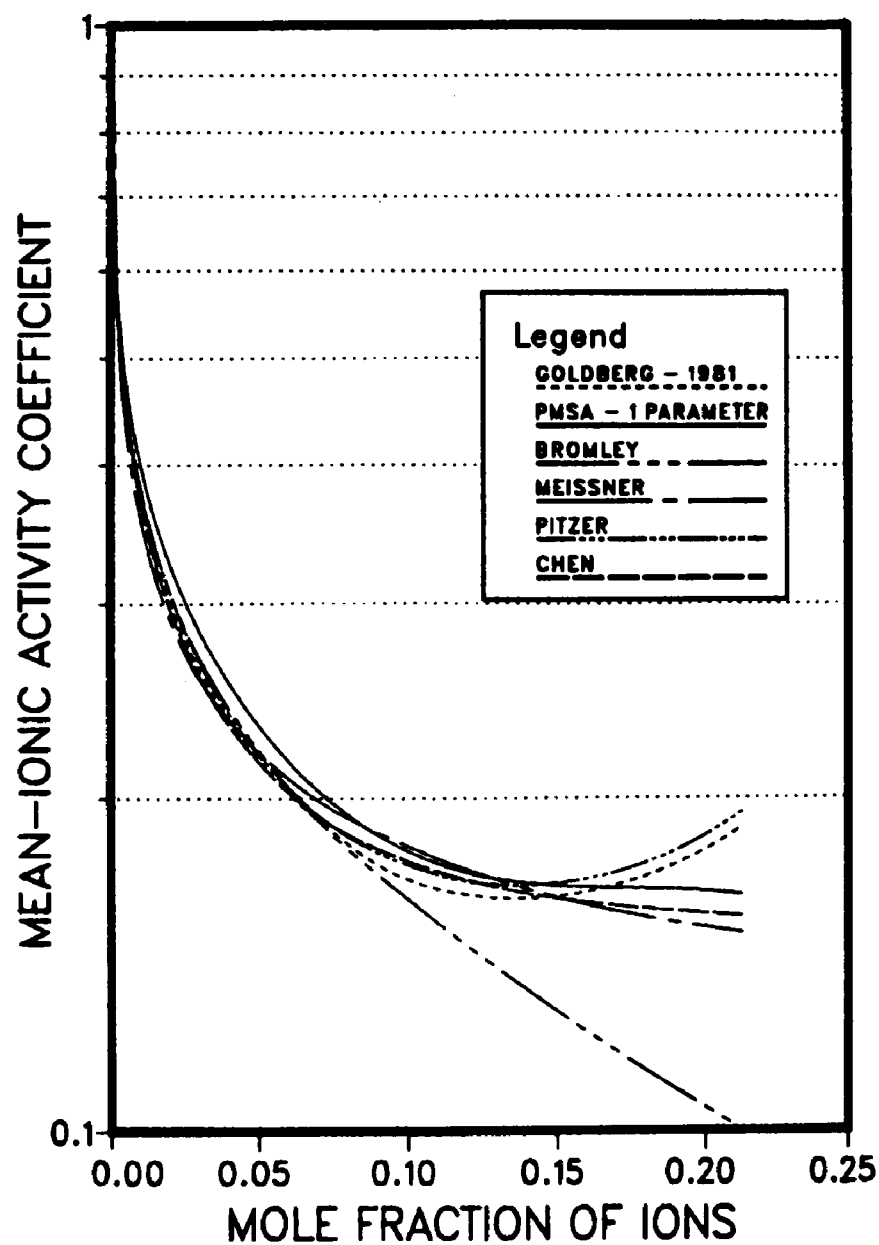


FIGURE 6.23
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR KOH IN WATER AT 353 K

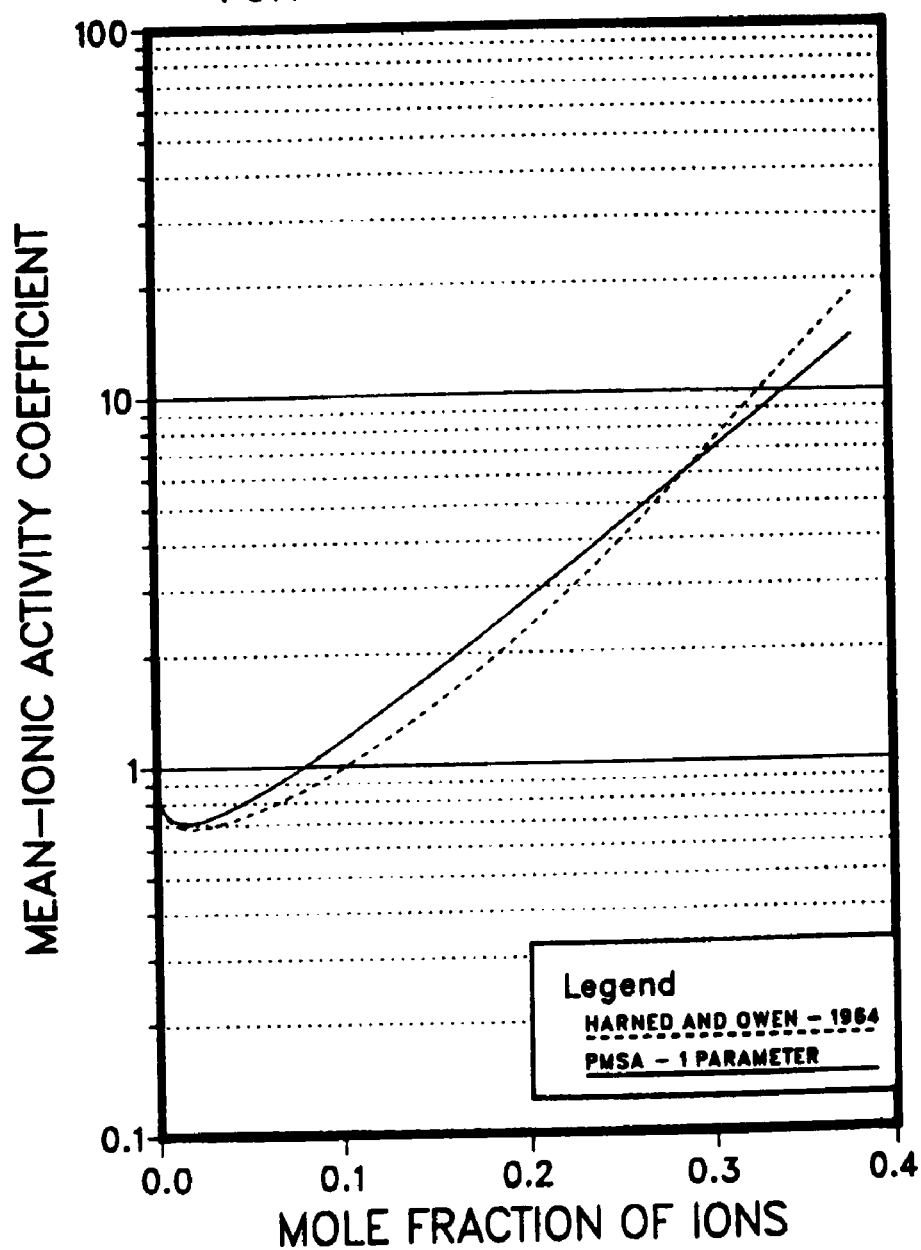


FIGURE 6.24
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR KOH IN WATER AT 298 K

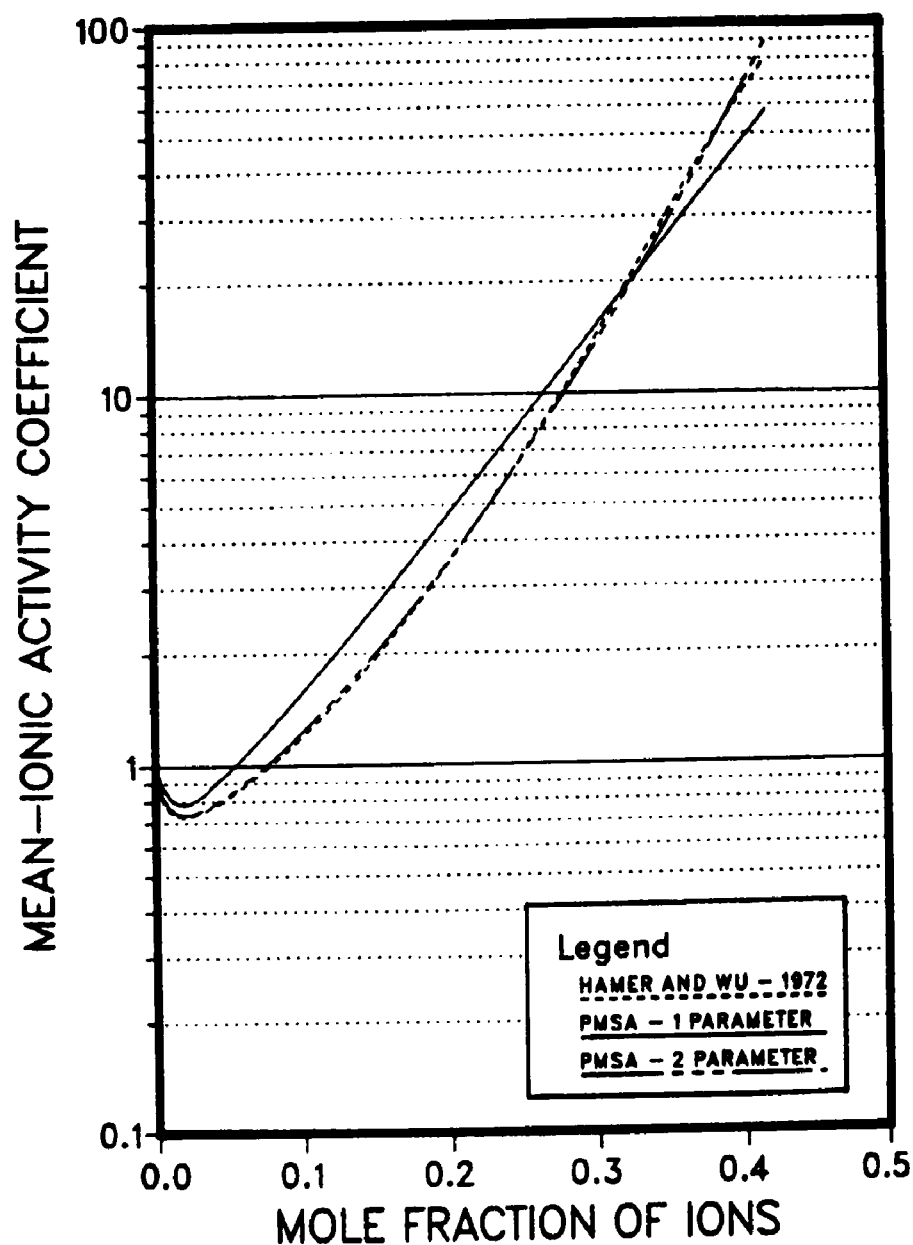


FIGURE 6.25
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR KOH IN WATER AT 298 K

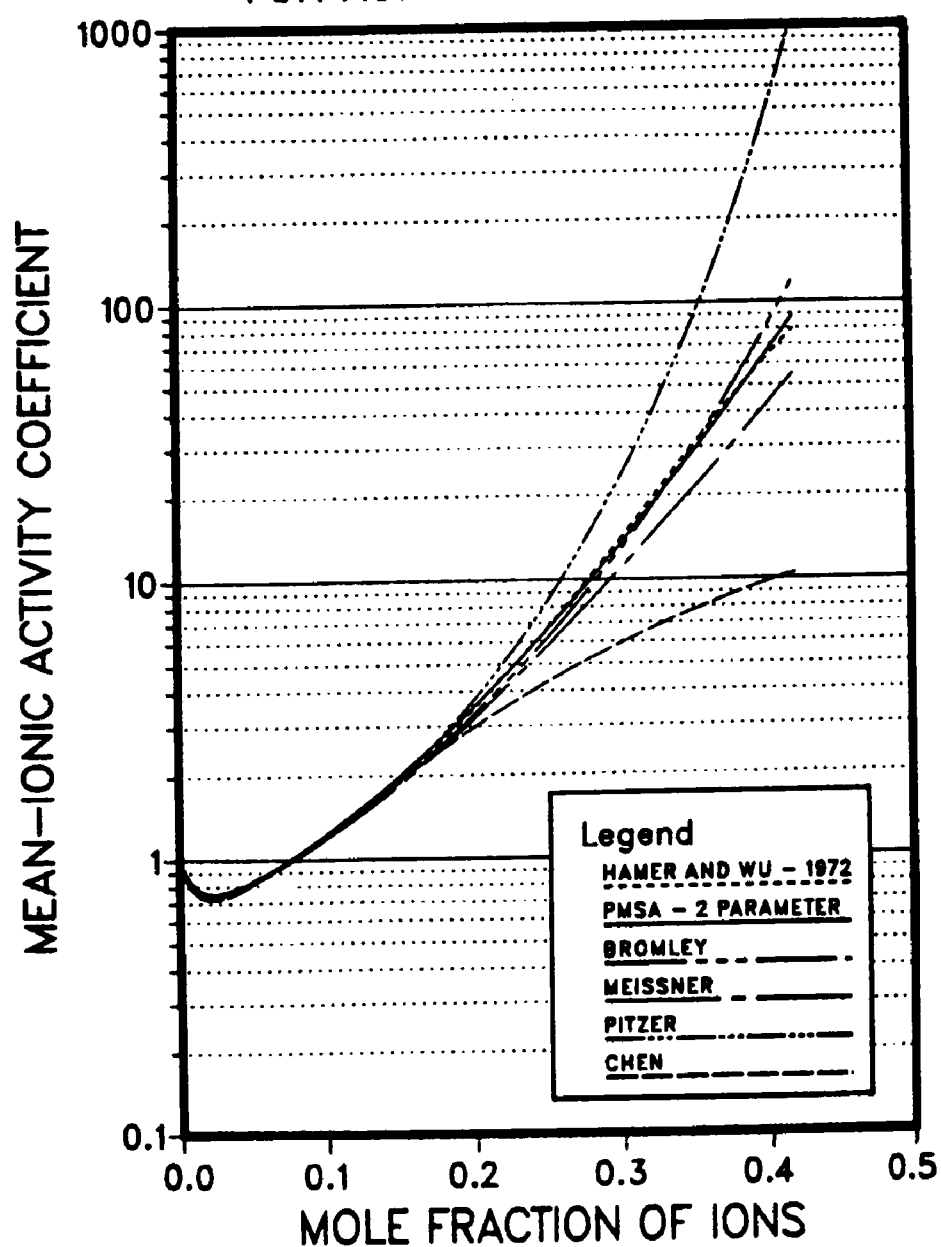


FIGURE 6.26
 PREDICTED AND EXPERIMENTAL
 MEAN-IONIC ACTIVITY COEFFICIENT
 FOR NH_4NO_3 IN WATER AT 298 K

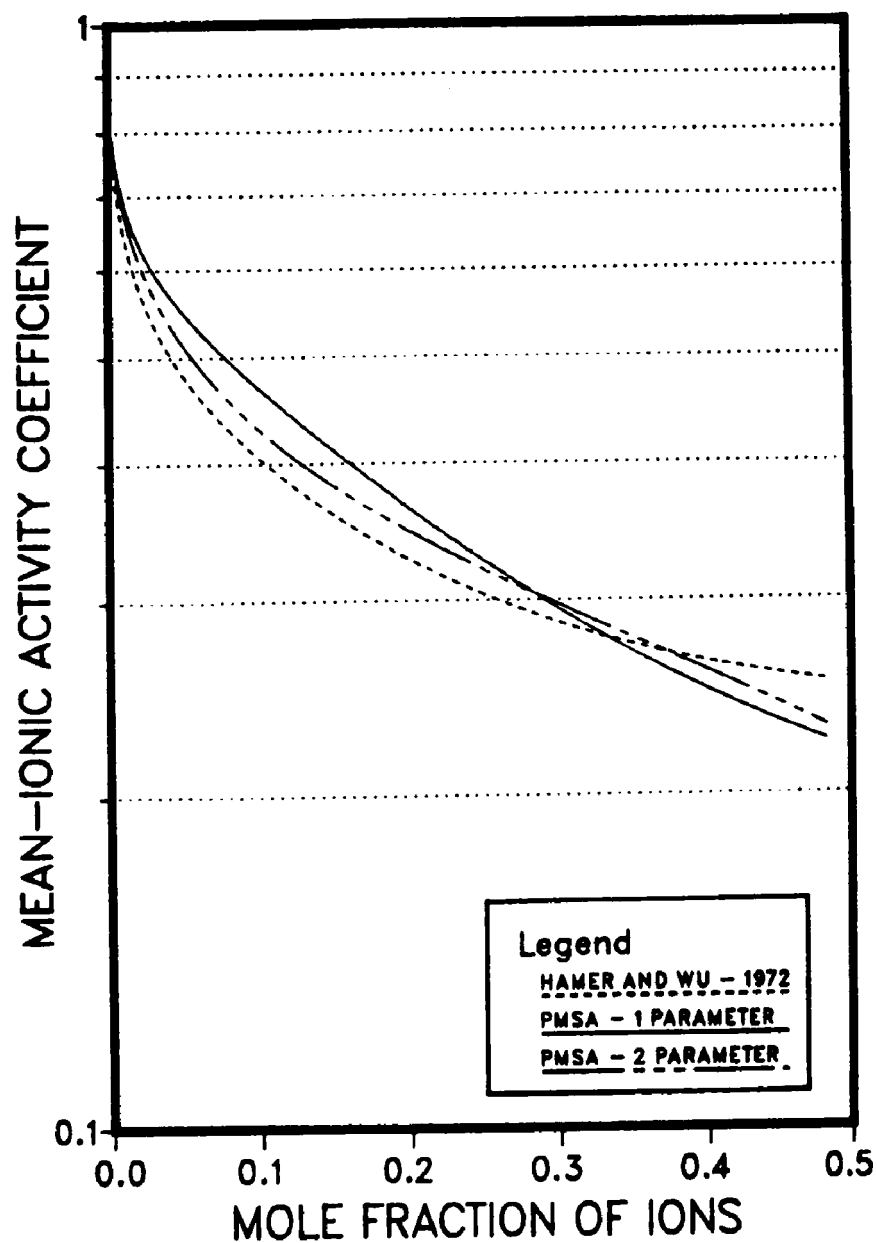


FIGURE 6.27
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR LiBr IN WATER AT 298 K

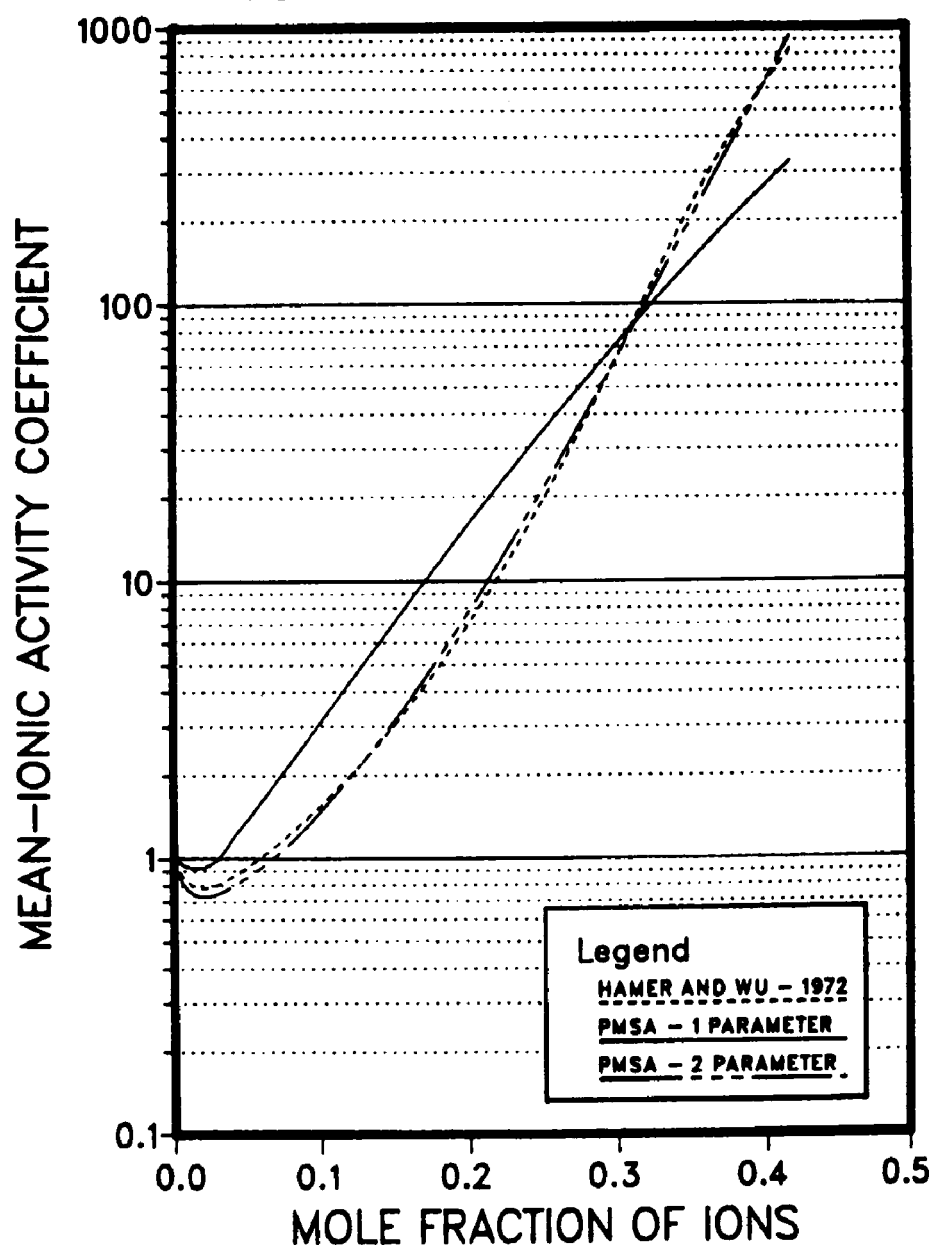


FIGURE 6.28
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR CaCl_2 IN WATER AT 298 K

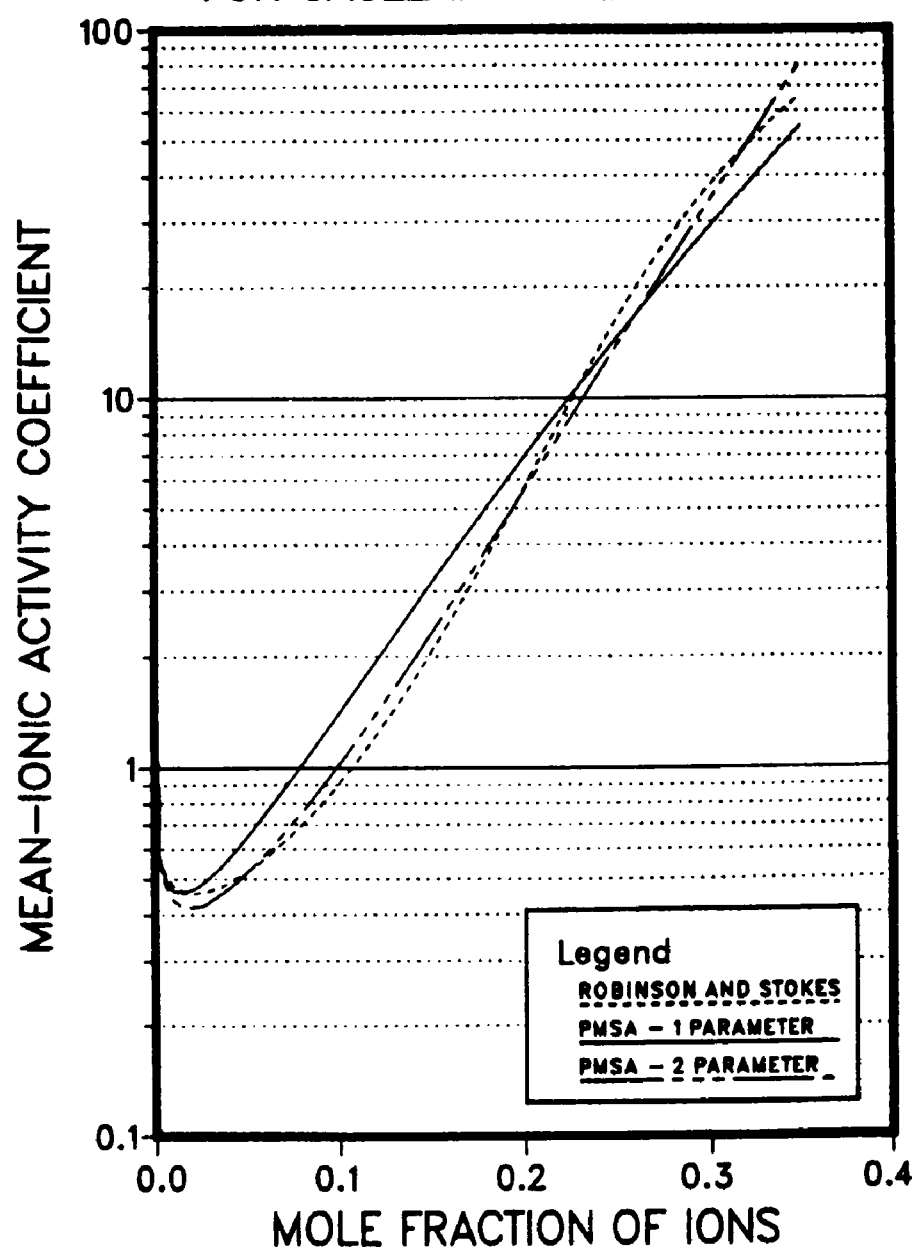


FIGURE 6.29
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR CaCl_2 IN WATER AT 298 K

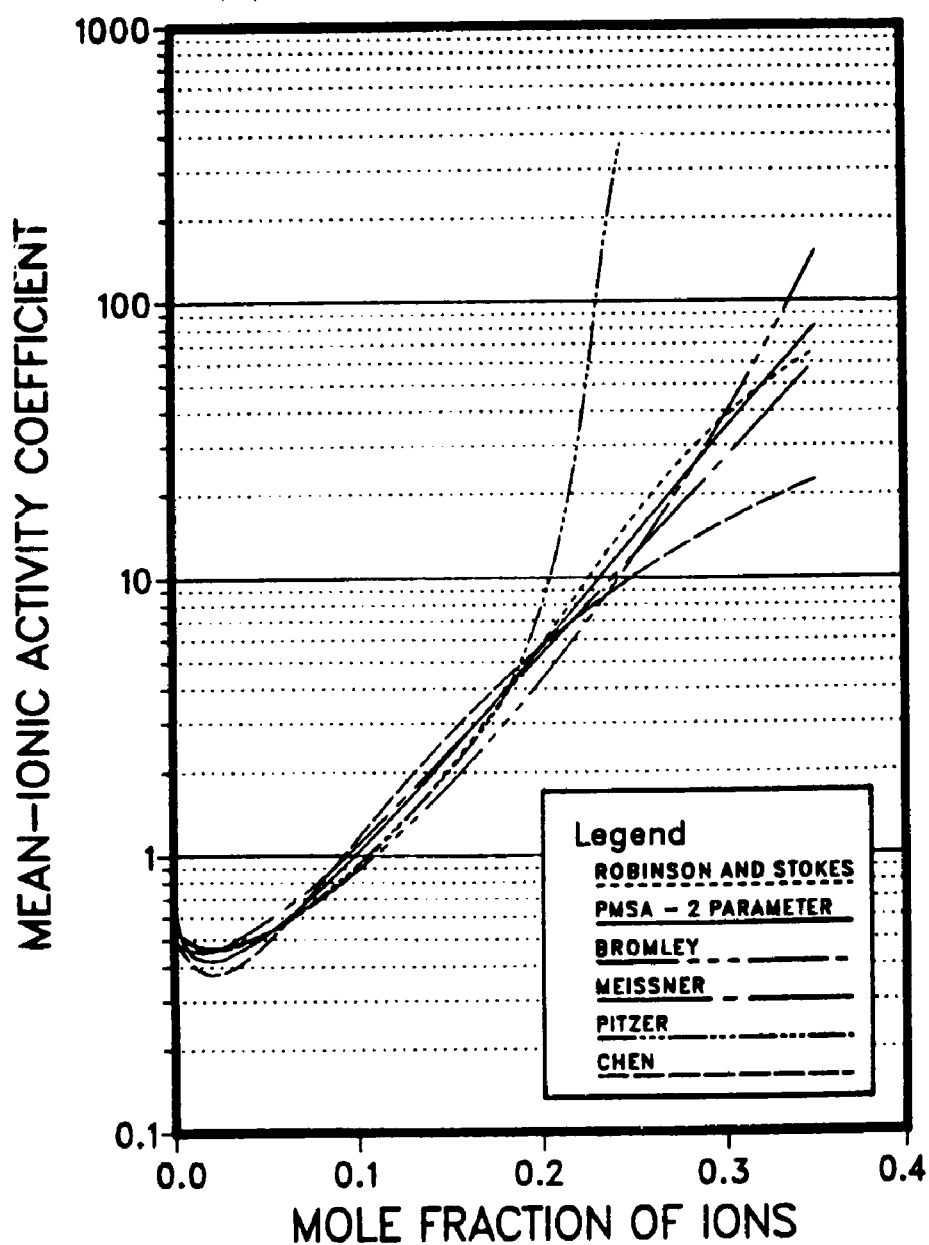


FIGURE 6.30
PREDICTED AND EXPERIMENTAL
MEAN-IONIC ACTIVITY COEFFICIENT
FOR CABR2 IN WATER AT 298 K

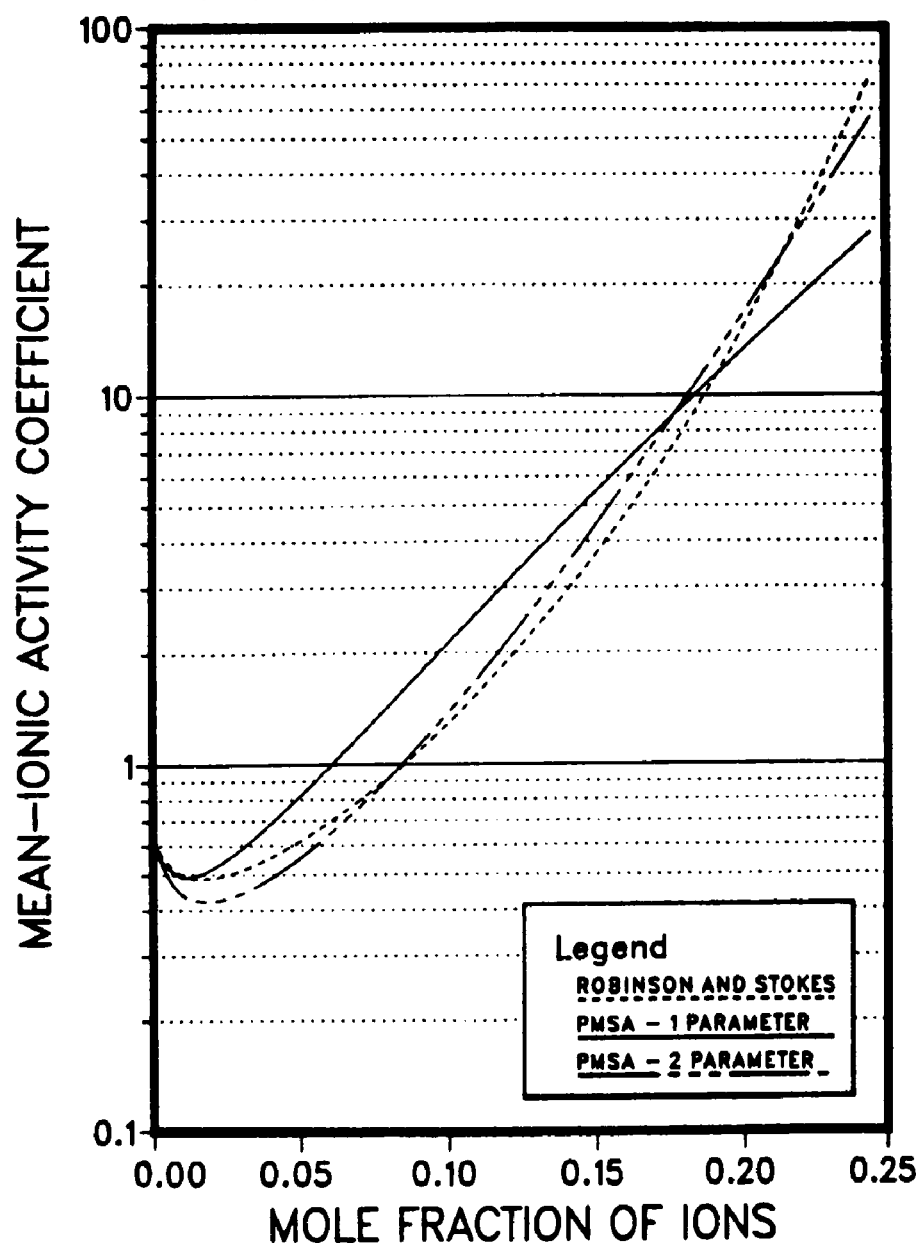


FIGURE 6.31
PK AS A FUNCTION OF AVG. HARD
SPHERE DIA. OF CATION/ANION
(ONE-PARAMETER FITS)

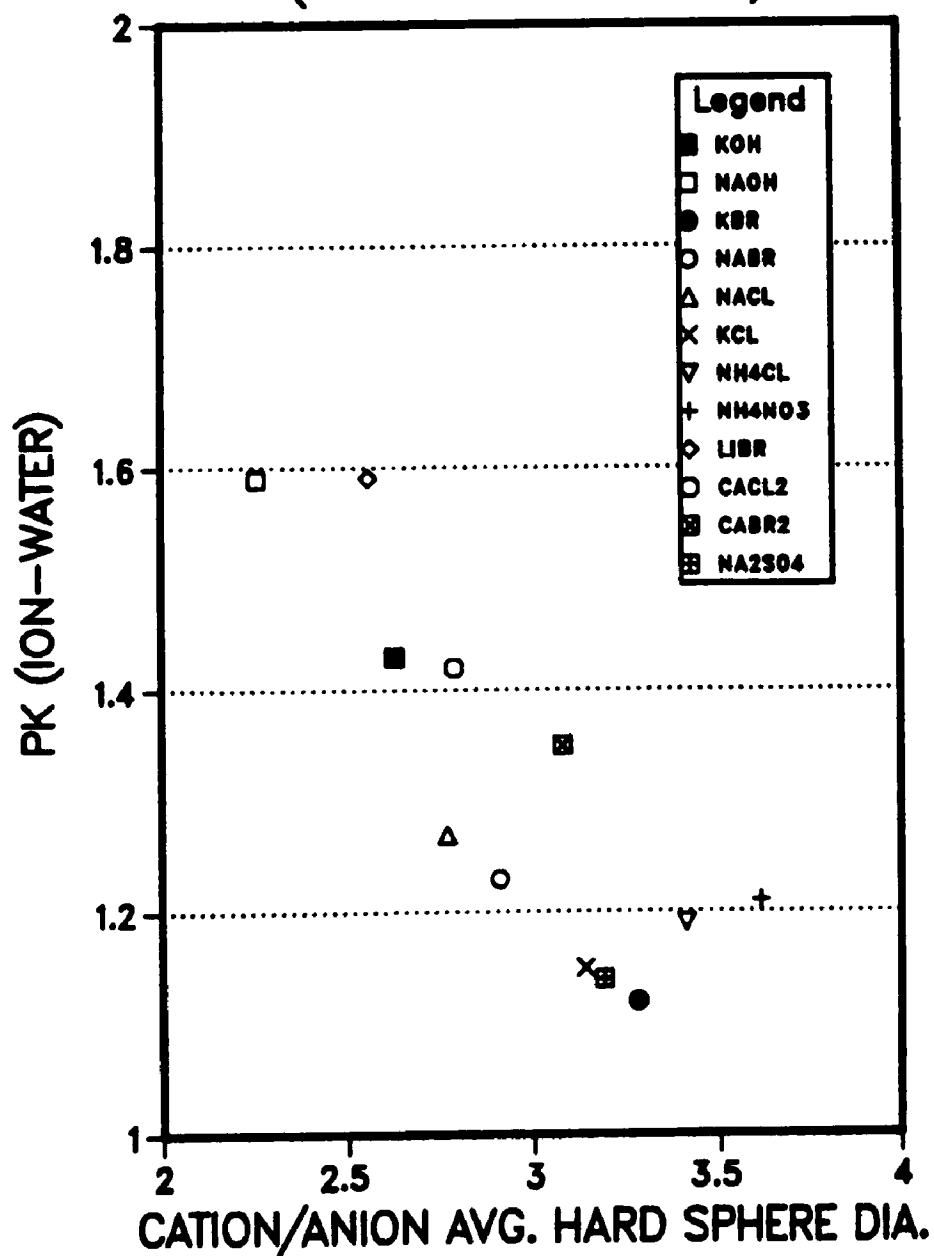
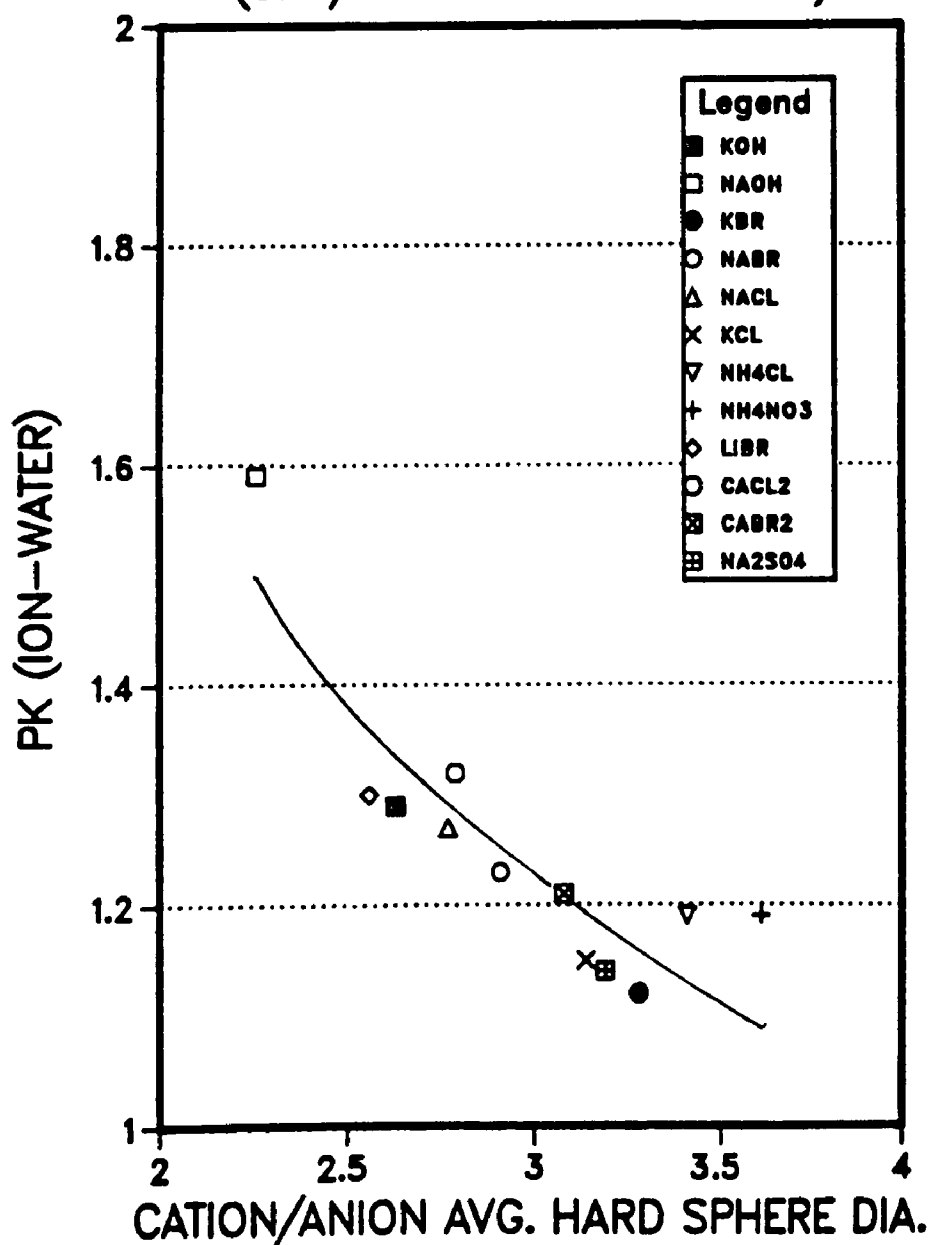


FIGURE 6.32
PK AS A FUNCTION OF AVG. HARD
SPHERE DIA. OF CATION/ANION
(ONE/TWO-PARAMETER FITS)



7. Application to Salting Systems

Addition of non-volatile salts to a liquid phase containing a mixture of solvents alters the phase equilibrium of the solvents. This effect, referred to as a "salting effect", is important when salts are present in reactor product streams which are fed directly to separation units (e.g., distillation columns). Accurate description of phase equilibrium is required to design or simulate the separation units. As mentioned by Furter (1976), addition of small amounts of salts can significantly change the phase equilibrium. For example, Dallos et al. (1983) measured the solubility of aniline in water - NaCl mixtures and reported about a decrease of a factor of 2.6 in aniline solubility as the ion mole fraction was increased to 0.097.

As mentioned in Section 1, a variety of empirical methods (see Furter, 1976) have been devised to correlate salting effects. However, these methods are not capable of describing phase equilibrium of polar solvents, fugacity of the dissolved salt, and other properties of the mixture, such as density, simultaneously.

The Perturbed-Hard-Sphere MSA (PMSA) equation of state developed in Section 6 has been applied to two salting systems measured recently by Dallos et al. (1983). Aniline solubility in water was measured at 323.15 K as a function of salt concentration in the water phase. NaCl and NH_4Cl significantly affect the aniline solubility and were, therefore, chosen for this study.

To establish a model for salting effects in aniline-water mixtures, the liquid-liquid equilibria of aniline-water binary mixtures must be considered first. Therefore, binary liquid-liquid equilibria and the salting-effects were fit simultaneously (for each salting system). The liquid-liquid equilibrium data presented in Sorensen and Arlt (1979) over a temperature range of 293.15 to 413.15 K were chosen.

The phase equilibrium residuals are defined by

$$\ln(\phi x)_{\text{liquid } 1} - \ln(\phi x)_{\text{liquid } 2} = \text{residual}_n \quad (7.1)$$

for the n^{th} data point.

Liquid 1 is defined as the water-rich phase. Predicted and experimental distribution coefficients defined by

$$K_{DC} = X_{\text{phase } 1} / X_{\text{phase } 2} \quad (7.2)$$

will be discussed below.

The hard-sphere diameters of aniline, water, and ionic species, and the polarizabilities of ionic species were established in Section 6.

Dallos et al. report that the solubility of the salts in aniline is small. Therefore, the electrostatic contributions were calculated only for the water-rich phase. In this phase, the dielectric constant of pure water at the system temperature was assumed. Dallos et al. do not report the composition of the aniline-rich phase, therefore the composition of the aniline-rich phase at 323.15 K was derived by interpolation of the Sorensen and Arlt data at 313.15 K and 333.15 K.

Following Mathias and Copeman (1983), one second-order-perturbation interaction-parameter(ℓ) (equation 6.7) and the first-order-perturbation interaction-parameter (P_k) (equation 6.11) were regressed for the non-ionic liquid-liquid equilibrium. In this case, the P_k was assumed to vary with temperature by

$$P_{k_{\text{aniline-water}}} = \psi (L + M/T) \quad (7.3)$$

One additional P_k was regressed for description of the salting effect; $P_{k_{\text{cation-water}}} = P_{k_{\text{anion-water}}}$ was assumed.

Tables 7.1 and 7.2 present experimental and predicted distribution coefficients for the NaCl and NH₄Cl salting systems, respectively.

The fits to the data are excellent. The average of the residuals is 6.1% and 5.7% for the NaCl and NH₄Cl salting systems, respectively. The interaction parameter, P_k , for aniline-water is a weak function of temperature, and the interaction parameter, P_k for the ions with water, is near unity. It should be noted that the P_k and ℓ for aniline-water obtained for the two different salting systems do differ slightly (beyond the digits reported in Tables 7.1 and 7.2) leading to less than a 0.1% difference in predicted aniline and water distribution coefficients, which was considered to be negligible.

Figure 7.1 illustrates the liquid-liquid equilibrium predictions for the water-aniline binary as a function of temperature. Similar to Mathias and Copeman (1983), and Ludecke and Prausnitz (1985), the correct qualitative trends of solubility with temperature are predicted. Figures 7.2 and 7.3 present experimental and predicted distribution coefficients as a function of the mole fraction of ions in the liquid phase for the NaCl and NH₄Cl salting systems (at 323.15 K), respectively. Dallos et al. (1983) did not report the solubility of aniline in water at zero mole fraction of ions. Therefore, the distribution coefficient of aniline at zero concentration of salt for 323.15 K was derived by linear interpolation of the data of Sorensen and Arlt (1979) and added to Figure 7.2 and 7.3 to verify the agreement between the two sets of data. The predicted and experimental values agree to within 5% in both figures.

To demonstrate application of the PMSA equation of state to a vapor-liquid salting system, correlations were developed for water and methanol with NaBr. The isobaric (1 atm) data of Boone et al. (1976) were selected. The hard-sphere diameters and the other pure component properties were established for water, methanol, Na^+ and Br^- in Section 6. Also, the mean-ionic activity coefficients of NaBr in water were correlated in Section 6 and a $\text{P}K_{\text{ion-water}}$ of 1.23 (see Table 6.23) was used for the NaBr-water system.

The weight-fraction mixing rule, presented as equation A.4 in Appendix A, was used to calculate the dielectric constant of water-methanol mixtures for inclusion into the PMSA equation of state as D. The dielectric constants of methanol and water presented in Maryott and Smith (1951) were used

$$\log_{10} D_{\text{methanol}} = 1.514 - 0.00264 (T - 298.15) \quad (7.4)$$

and

$$\begin{aligned} D_{\text{water}} = & 78.54 (1.0 - 4.579 \times 10^{-3} (T - 298.15) \\ & + 1.19 \times 10^{-5} (T - 298.15)^2 \\ & - 2.80 \times 10^{-8} (T - 298.15)^3) \end{aligned} \quad (7.5)$$

The $\text{P}K_{\text{ion-methanol}}$ and $\text{P}K_{\text{water-methanol}}$ were regressed simultaneously to the vapor-liquid equilibrium data. Table 7.3 summarizes the experimental and predicted K values. The average of the residuals is 5.6%. A $\text{P}K_{\text{ion-methanol}}$ of 0.982 and a $\text{P}K_{\text{water-methanol}}$ of 1.045 were obtained from the regression.

Methanol "salts out" of the liquid phase (K values increase) as the concentration of NaBr increases. Figure 7.4 presents the experimental and predicted K values of methanol as a function of temperature for the three different salt to water molalities (1.0, 2.0, and 4.0). For these conditions, the liquid mole fraction of ions varies from nearly zero, at high liquid mole fractions of methanol, to about 0.13 at high liquid mole fractions of water. The salting effect is larger at the higher temperatures since the methanol is present at low concentrations in the liquid phase with high concentrations of salt.

Table 7.1

Distribution Coefficients for the Water-Aniline
NaCl Salting-Out System
Comparison of Perturbed MSA to Experimental Data

Temperature (K)	X_{IONS}	DATA	PMSA	DATA	PMSA
		K_{DC} WATER	K_{DC} WATER	K_{DC} METHANOL	K_{DC} METHANOL
293.15	0.0	4.663	5.392	0.00856	0.00857
298.15	0.0	4.552	5.044	0.00868	0.00882
313.15	0.0	4.189	4.182	0.00945	0.00984
333.15	0.0	3.742	3.354	0.01152	0.01207
353.15	0.0	3.232	2.749	0.01600	0.01579
373.15	0.0	2.736	2.300	0.02375	0.02275
393.15	0.0	2.230	1.966	0.03651	0.03488
413.15	0.0	1.898	1.694	0.06176	0.05899
323.15	0.01756			0.009186	0.00890
323.15	0.03456			0.007610	0.007348
323.15	0.05100			0.006208	0.006147
323.15	0.06690			0.005354	0.005257
323.15	0.08228			0.004539	0.004549
323.15	0.09720			0.003859	0.003990

Average of residuals = 6.1%

$P_{\text{K}_{\text{aniline-water}}} = 1.078 - 19.6/T$

$\ell_{\text{aniline-water}} = 0.0258$

$P_{\text{K}_{\text{ion-water}}} = 0.940$

Table 7.2

Distribution Coefficients for the Water-Aniline
 NH_4Cl Salting-Out System
 Comparison of Perturbed MSA to Experimental Data

Temperature (K)	X_{IONS}	DATA	PMSA	DATA	PMSA
		K_{DC} WATER	K_{DC} WATER	K_{DC} METHANOL	K_{DC} METHANOL
293.15	0.0	4.663	5.387	0.00856	0.00851
298.15	0.0	4.552	5.040	0.00868	0.00875
313.15	0.0	4.189	4.178	0.00945	0.00977
333.15	0.0	3.742	3.352	0.01152	0.01200
353.15	0.0	3.232	2.749	0.01600	0.01588
373.15	0.0	2.733	2.302	0.02375	0.02265
393.15	0.0	2.320	1.967	0.03651	0.03474
413.15	0.0	1.898	1.694	0.06176	0.05878
323.15	0.01754			0.00997	0.00994
323.15	0.03450			0.00941	0.00928
323.15	0.05090			0.00887	0.00876
323.15	0.06674			0.00835	0.00835
323.15	0.08206			0.00809	0.00806
323.15	0.09690			0.00772	0.00783

Average of residuals = 5.7%

$P_{\text{K}_{\text{aniline-water}}} = 1.078 - 19.5/T$

$\ell_{\text{aniline-water}} = 0.0258$

$P_{\text{K}_{\text{ion-water}}} = 0.921$

Table 7.3

K Values for the Water-Methanol-
NaBr Salting System
Comparison of Perturbed MSA to Experimental Data

Temperature (K)	X_{ions}	DATA	PMSA	DATA	PMSA
		K_{DC} WATER	K_{DC} WATER	K_{DC} METHANOL	K_{DC} METHANOL
366.95	0.0338	0.7560	0.7921	6.849	6.983
362.35	0.0323	0.6700	0.6708	4.779	5.277
358.15	0.0303	0.5496	0.5800	3.843	3.934
354.15	0.0277	0.4679	0.5111	2.969	2.905
347.45	0.0191	0.5275	0.4472	1.578	1.686
343.95	0.0123	0.4527	0.4360	1.301	1.337
340.65	0.0047	0.4910	0.4318	1.081	1.126
339.15	0.0026	0.4530	0.4194	1.033	1.058
366.95	0.0663	0.7528	0.7855	7.154	7.152
361.85	0.0635	0.6362	0.6514	5.327	5.573
357.85	0.0601	0.5143	0.5650	4.347	4.214
353.75	0.0529	0.4544	0.5018	2.843	2.870
347.65	0.0390	0.4190	0.4403	1.782	1.759
344.15	0.0275	0.3823	0.4237	1.423	1.382
340.15	0.0112	0.4146	0.4152	1.118	1.112
339.15	0.0051	0.4687	0.4191	1.045	1.061
370.55	0.1313	0.9315	0.8712	9.456	10.495
364.75	0.1278	0.6861	0.7025	8.936	7.882
358.65	0.1209	0.5863	0.5596	5.452	5.340
353.75	0.1083	0.4471	0.4765	3.548	3.394
342.95	0.0446	0.5111	0.4156	1.277	1.301
340.55	0.0273	0.3812	0.4093	1.212	1.142
338.95	0.0120	0.3614	0.4108	1.067	1.056

Pressure = 1.0 atm

Average of residuals = 5.6%

$Pk_{methanol-water} = 1.045$

$Pk_{ion-water} = 1.230$

$Pk_{ion-methanol} = 0.982$

FIGURE 7.1
ANILINE-WATER LIQUID-LIQUID
EQUILIBRIUM AS A FUNCTION OF
TEMPERATURE

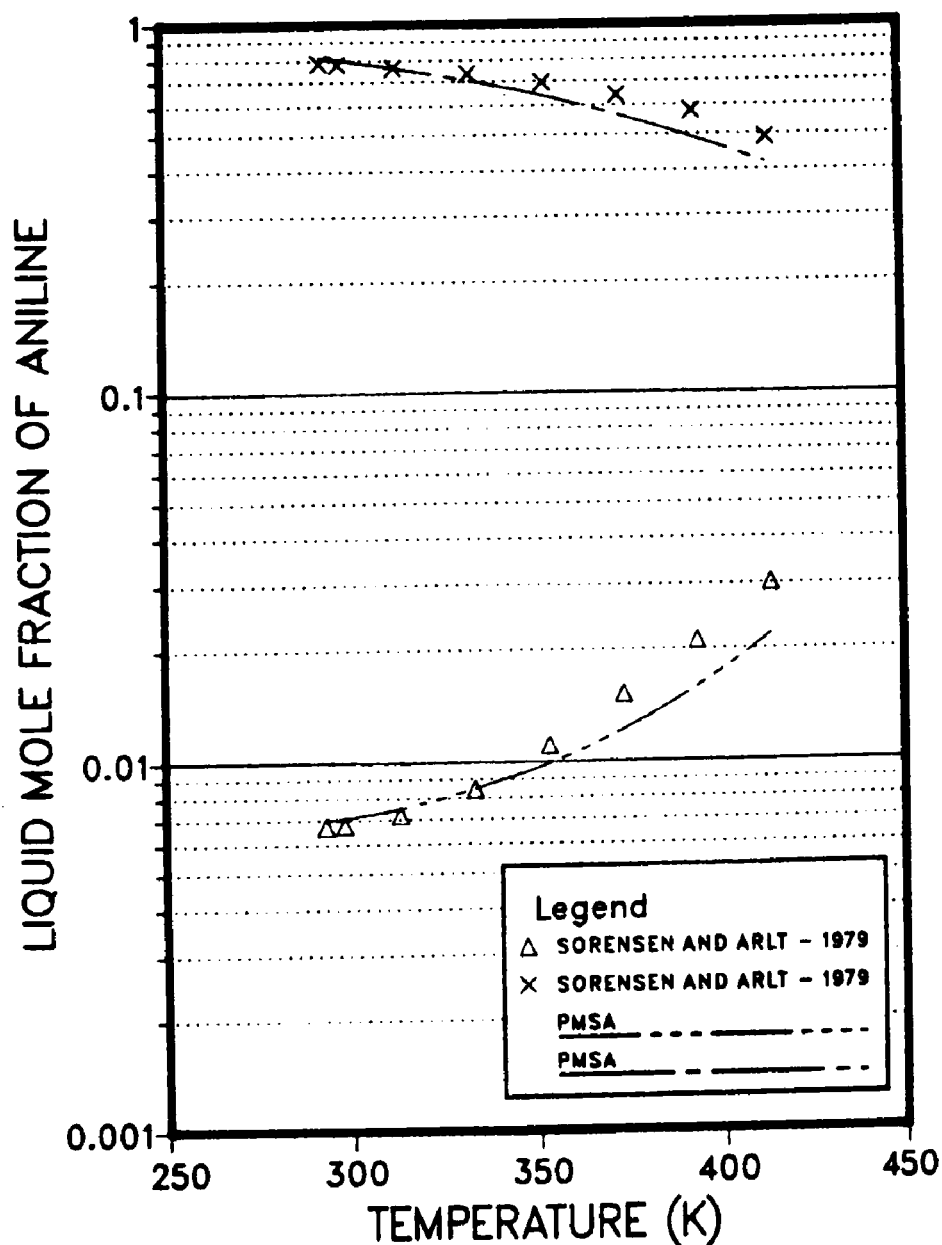


FIGURE 7.2
ANILINE DISTRIBUTION COEFFICIENT
IN WATER AND NaCl AS A FUNCTION
OF ION MOLE FRACTION AT 323.15 K

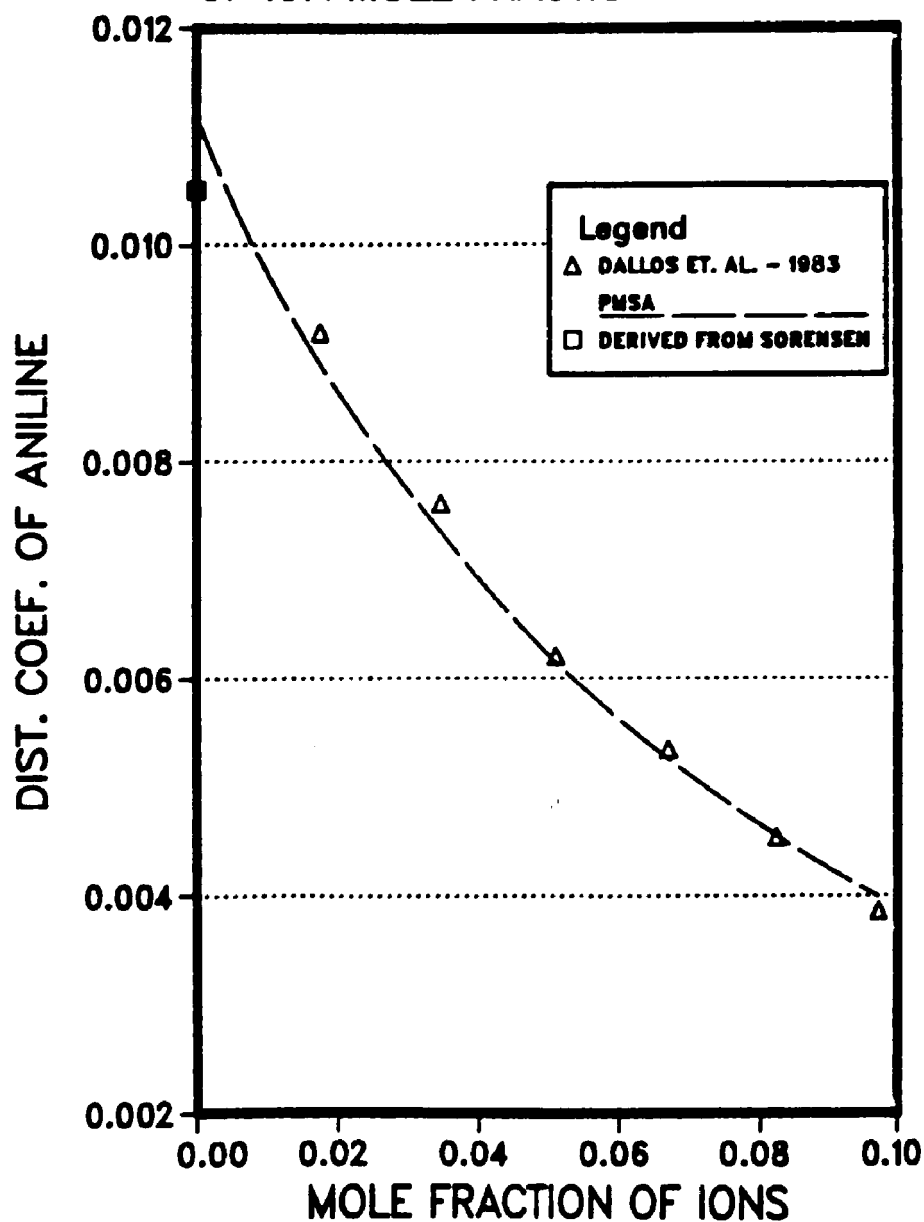


FIGURE 7.3
ANILINE DISTRIBUTION COEFFICIENT
IN WATER AND NH₄CL AS A FUNCTION
OF ION MOLE FRACTION AT 323.15 K

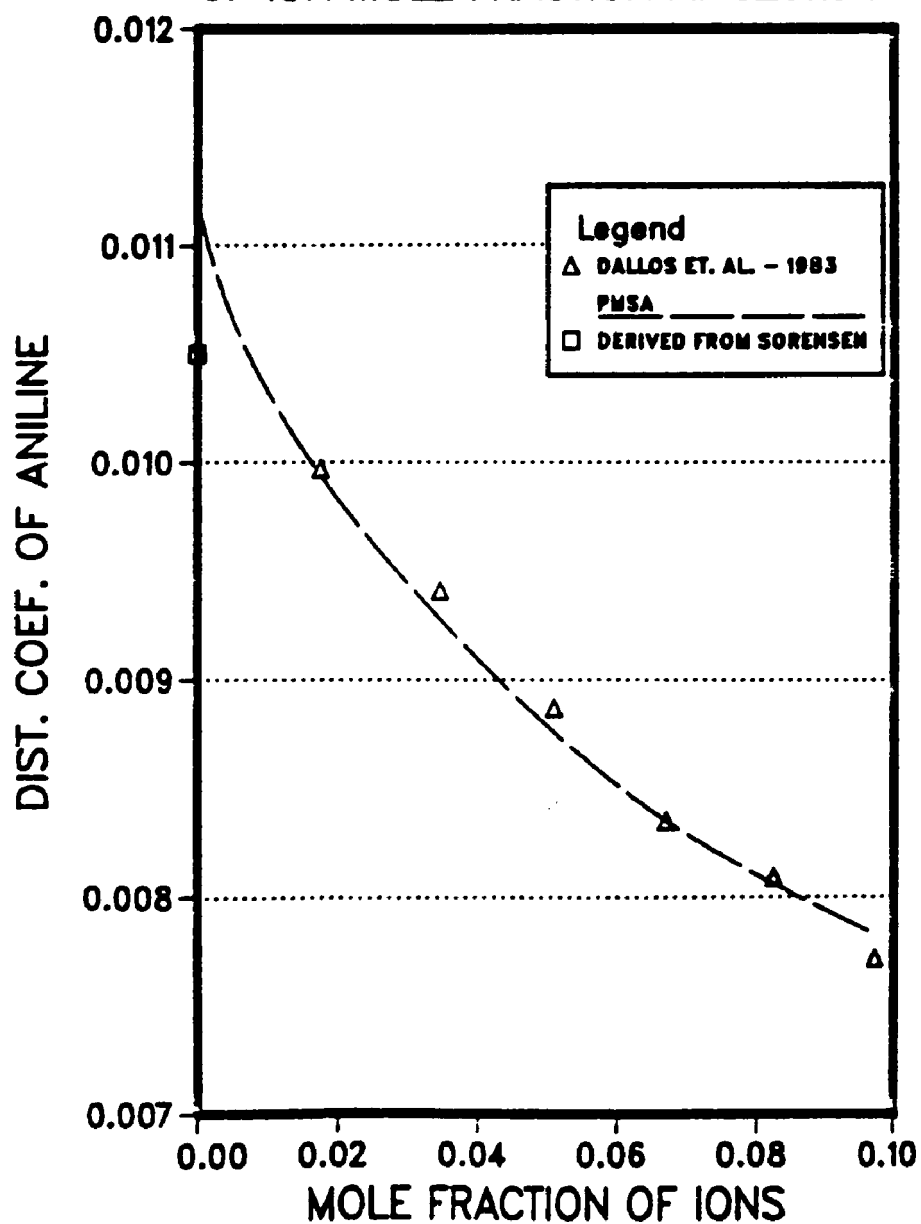
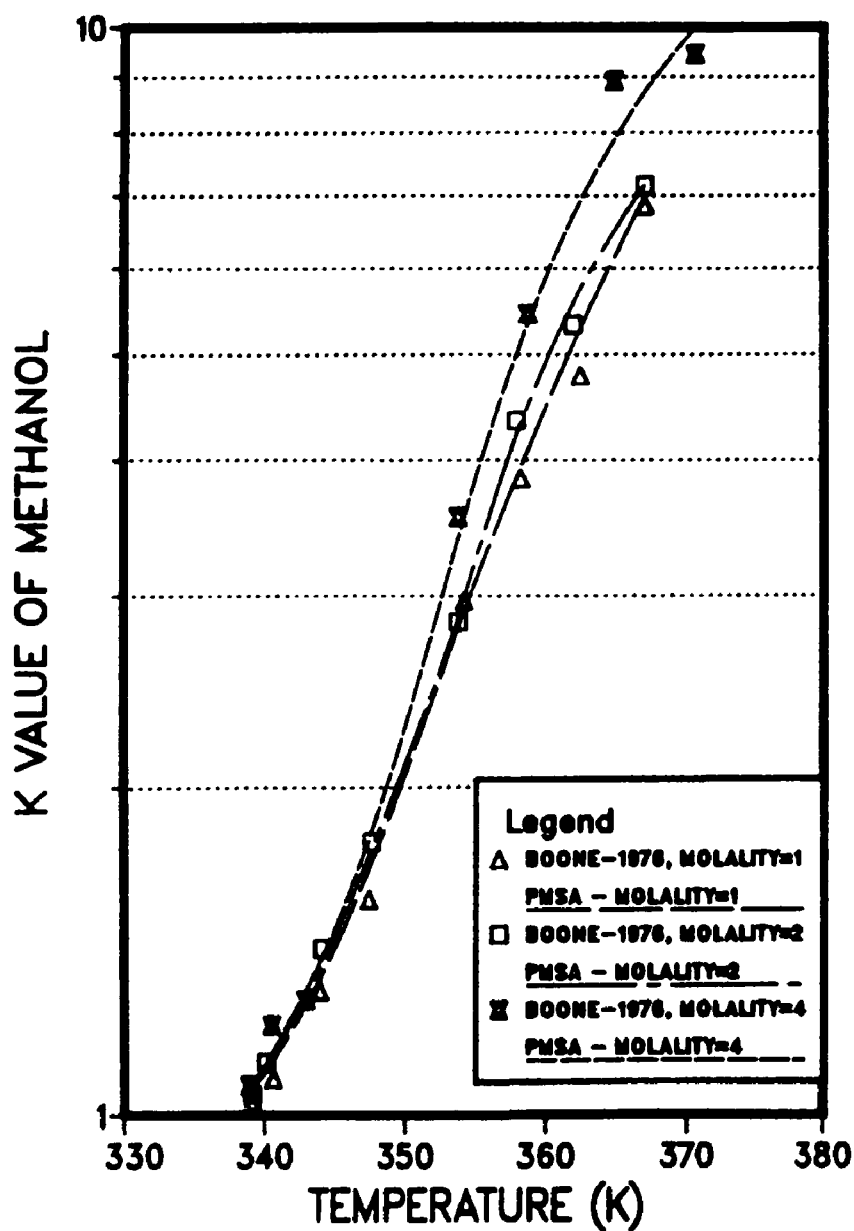


FIGURE 7.4
METHANOL K VALUE IN WATER-NABR
AS A FUNCTION TEMPERATURE
AT 1 ATM



List of Symbols

Upper Case

A =	Helmholtz free energy, subscripted MSA parameter, Pitzer-Debye-Huckel constant
B =	second virial coefficient, MSA parameter
C =	direct correlation function in k space
D =	dielectric constant
G =	Gibbs free energy
H =	total correlation function in k space
I =	ionic strength
J =	integral function of Baxter factorization function
K =	Debye-Huckel screening factor, K value
L =	constant
M =	constant
N =	MSA ion function defined by equation 3.114
P =	pressure
Q =	Baxter's factorization function
R =	gas constant
S =	unit step function
T =	temperature
U =	internal energy, Dirac delta function
V =	total system volume
Z =	charge number

Lower Case

a =	Debye-Huckel central-ion size, MSA parameter, van der Waals attractive parameter
b =	Debye-Huckel parameter
c =	direct correlation function in r space
d =	defined by equation 3.119
e =	elementary charge
f =	fugacity
g =	radial distribution function
h =	total correlation function in r space
i =	complex i
k =	Boltzmann constant
m =	molality
r =	radial distance r
t =	dummy integration variable
v =	molar volume
w =	weight fraction
x =	mole fraction

Greek

β	=	$1/kT$
γ	=	activity coefficient
Γ	=	MSA screening factor
Δ	=	defined by equation 3.112
η	=	number of electrons
ρ	=	density
ϕ	=	fugacity coefficient
Φ	=	pair-potential energy
λ	=	Pitzer parameter, Perturbation-theory parameter
μ	=	Pitzer parameter, chemical potential
ψ	=	function
δ	=	Kronecker's delta
σ	=	hard sphere diameter
α	=	constant in MSA derivation (defined by equation 3.59), polarizability
∂	=	partial derivative
ε	=	defined by equataion 3.113
Λ	=	defined by equation 3.120
ℓ	=	binary interaction parameter
χ	=	defined by equation 3.97
Ω	=	functions of radial distribution functions and pair potentials equation 2.7
ν	=	number of species per molecule of salt

Subscripts

i	=	component i
j	=	component j
k	=	component k
l	=	component l
o	=	reference fluid
+	=	positive k domain
-	=	negative k domain
s	=	solvent

Superscripts

/	=	specified value of
$\pm$	=	mean ionic
E	=	excess
T	=	transpose
//	=	specified value of
∞	=	infinite dilution

Special Symbols

K_{oc}	=	liquid-liquid distribution coefficient
N_o	=	Avogadro's number
P_k	=	binary interaction parameter
a_o	=	$0.5292 \text{ \AA}$
$\vec{r}$	=	vector distance r
∇^2	=	Laplacian operator
<u>underscore</u>	=	two dimensional matrix
$r^{\ddagger}$	=	effective electrostatic radius
ρ_c	=	charge density

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APPENDIX A

Consideration of Dielectric Constants

Dielectric Constants for Mixed Solvents

The dielectric constant (D) is a key property in electrostatic systems because it arises in the pair potential and contributes directly to derived properties, such as activity coefficients. Harned and Owen (1958) state that the dielectric constant of pure components can be expressed as a simple function of temperature, for example

$$\ln D = L - MT \quad (A.1)$$

For mixtures, Bottcher (1973) presents a multicomponent form of the Clausius-Mosotti equation relating mixture dielectric constants to pure-component polarizabilities and volume fractions.

$$(D-1)/(D+2) = 4/3 \pi \sum v_i \alpha_i \quad (A.2)$$

The Clausius-Mosotti equation is strictly valid for non-polar components, and Bottcher further recommends a simple mixing rule based loosely on equation A.2

$$D = \sum v_i D_i \quad (A.3)$$

Harned and Owen (1958) present the mixture dielectric constant data of Wyman and Engals (1938). A simple mixing rule, based on weight fraction, appears to describe the mixture data reasonably well (see Table A.1).

$$D = \sum_i w_i D_i \quad (A.4)$$

The mixing rule describes the mixture dielectric constant best at high concentrations of water. It should be noted that an interaction parameter would be necessary to improve the fit to the data in a few of the systems (like dioxane-water). The maximum deviation does not occur in the mid-composition region and a binary interaction parameter could only provide a limited improvement with these mixing rules.

TABLE A.1

Dielectric Constants of Water Mixtures
(298 K)

W (WA)	Methanol	Calc/Exp	Ethanol	Calc/Exp	n-Propanol	Calc/Exp
	D mix		D mix		D mix	
1	78.54	1.0	78.54	1.0	78.54	1.0
0.9	74.1	0.996	72.8	1.004	71.8	1.012
0.8	69.2	0.999	67.0	1.010	64.9	1.030
0.7	64.3	1.002	61.1	1.019	57.7	1.057
0.6	59.6	1.002	55.0	1.034	50.3	1.097
0.5	54.9	1.002	49.0	1.049	43.0	1.147
0.4	50.1	1.004	43.4	1.060	36.4	1.194
0.3	45.0	1.014	38.0	1.068	30.7	1.226
0.2	40.1	1.020	32.8	1.072	26.1	1.218
0.1	35.7	1.014	28.1	1.058	22.7	1.143
0.0	31.5	1.0	24.3	1.0	20.1	1.0

W (WA)	I-Propanol	Calc/Exp	T-Butanol	Calc/Exp	Ethylene Glycol	Calc/Exp
	D mix		D mix		D mix	
1	78.54	1.0	78.54	1.0	78.54	1.0
0.9	71.4	1.015	70.0	1.024	75.6	0.985
0.8	64.1	1.036	61.3	1.057	72.8	0.967
0.7	56.9	1.061	52.6	1.102	69.8	0.950
0.6	49.7	1.093	43.9	1.164	66.6	0.934
0.5	42.5	1.136	35.4	1.249	63.2	0.920
0.4	35.3	1.196	27.9	1.339	59.4	0.910
0.3	28.7	1.260	21.4	1.425	54.7	0.913
0.2	23.7	1.270	16.5	1.432	49.3	0.930
0.1	20.3	1.185	12.4	1.352	43.7	0.956
0.0	18.0	1.0	9.9	1.0	37.7	1.0

W (WA)	Glycerol	Calc/Exp	Acetone	Calc/Exp	Dioxane	Calc/Exp
	D mix		D mix		D mix	
1.0	78.54	1.0	78.54	1.0	78.54	1.0
0.9	75.5	0.989	73.0	0.994	69.69	1.017
0.8	72.9	0.972	67.0	0.995	60.79	1.041
0.7	70.0	0.957	61.0	0.995	51.90	1.071
0.6	67.1	0.941	54.6	1.003	42.98	1.116
0.5	64.0	0.927	48.2	1.013	34.26	1.177
0.4	60.0	0.925	41.8	1.026	25.85	1.264
0.3	55.6	0.929	35.7	1.035	17.69	1.415
0.2	50.6	0.944	29.6	1.047	10.71	1.624
0.1	45.5	0.966	24.0	1.044	5.605	1.739
0.0	40.1	1.0	19.1	1.0	2.101	1.0

Ion Effect on the Dielectric Constant

The Debye-Huckel and other primitive electrolyte models (including the primitive MSA models) require the dielectric constant of the solution. The dielectric constant of the solvent is typically known; however, the dielectric constant of the solution decreases significantly as the ion concentration increases. Attempts have been made to incorporate this effect into electrolyte models and further discussion of this topic is warranted.

The Born contribution, as presented by Cruz and Renon (1978), for the excess Gibbs energy is

$$\Delta G^{Ex} = e^2 N_o / 2 \left(1/D - 1/D_s \right) \left(\sum x_i Z_i^2 / r_i^e \right) \quad (A.3)$$

where D_s = dielectric constant of the solvent

r_i^e = effective electrostatic radius of component i

N_o = Avagadro's number

x_i = mole fraction of component i

e = elementary charge

Z_i = charge number of component i

The Born term provides the net electrical work to transfer the ions from a solvent of dielectric constant D_s to a solution of dielectric constant D . The solvent rather than the solution dielectric constant is then used in an electrolyte model, like Debye-Huckel.

Helgeson, et al. (1981) presented a correlation for the dielectric constant decrease with increasing ion concentration. They propose

$$1/D - 1/D_s = \sum b_i m_i Z_i^2/2 \quad (A.4)$$

where b = an empirical electrostatic parameter

The Helgeson relation assumes that the dielectric constant decrease is given by a linear function of molality. Although that assumption appears to be reasonable at ionic strengths lower than about 10 molal, it cannot be expected to be accurate at higher ionic strengths. Recently, Chen and Renon (private communication) have concluded that the Born term does not generally improve activity coefficient correlations and is not warranted.

APPENDIX B

Total Configurational Helmholtz Free Energy of the Perturbed Hard Sphere MSA Equation of State (Neglecting de Broglie-Wavelength and Internal Partition-Function Contributions)

$$\begin{aligned}
 A = & RT \sum x_i \ln x_i - RT + RT \ln \rho - RT \ln (1 - \pi/6\epsilon_3) \\
 & + \frac{\pi RT}{6\rho} \left(\frac{3 \epsilon_1 \epsilon_2}{1 - \pi/6\epsilon_3} + \frac{\pi \epsilon_2^3}{4(1 - \pi/6\epsilon_3)^2} \right) \\
 & - \frac{2e^2 \rho}{3D} \sum \frac{x_i Z_i^2 \Gamma}{1 + \sigma_i \Gamma} \\
 & - \rho \sum \sum x_i x_j a_{ij} - \rho^2 / (RT) \sum \sum x_i x_j (x_i \ell_{ji} + x_j \ell_{ij})
 \end{aligned} \tag{B.1}$$

where

$$a_{ij} = \frac{\pi a_0^{1/2} e^2 \alpha_i \alpha_j (\eta_i \eta_j)^{1/2}}{\sigma_{ij}^3 ((\alpha_i \eta_j)^{1/2} + (\alpha_j \eta_i)^{1/2})} \tag{B.2}$$

and

$$\begin{aligned}
 \Gamma = & \frac{\alpha}{2} \left(\rho \sum x_j (Z_j + \sigma_j) \left(\frac{\pi}{4\Delta} \rho \sum x_k Z_k \sigma_k^2 - \frac{Z_j K}{2 (1 + \alpha (\rho \sum x_i Z_i^2 \sigma_i^2)^{1/2})} \right. \right. \\
 & \left. \left. - \frac{K \pi \rho \sum x_k \sigma_k^3 Z_k}{12 \Delta (1 + \alpha (\rho \sum x_i Z_i^2 \sigma_i^2)^{1/2})} \right) \right)^{1/2}
 \end{aligned} \tag{B.3}$$

APPENDIX C

Pressure of the Perturbed Hard Sphere

MSA Equation of State

$$\begin{aligned}
 P = & \frac{\rho RT}{1-\pi/6\epsilon_3} + \frac{\pi RT}{6} \left(\frac{3 \epsilon_1 \epsilon_2}{(1-\pi/6\epsilon_3)^2} + \frac{3 \epsilon_2^3}{(1-\pi/6\epsilon_3)^3} \right) \\
 & - \frac{2\rho^2 e^2}{3D} \left(\sum \frac{x_k z_k^2}{1+\sigma_k \Gamma} - \sum \frac{x_k z_k^2 \Gamma \sigma_k}{(1+\sigma_k \Gamma)^2} \right) \partial \Gamma / \partial \rho \\
 & - \rho^2 \sum \sum x_i x_j a_{ij} - \rho^3 / (RT) \sum \sum x_i x_j (x_i c_{ij} + x_j c_{ji}) \quad (C.1)
 \end{aligned}$$

where

$$\begin{aligned}
 \frac{\partial \Gamma}{\partial \rho} = & (\alpha/4) \rho^{-1/2} (\sum x_k (z_k + \sigma_k N_k)^2)^{1/2} + \\
 & (\alpha/2) \rho^{1/2} (\sum x_j (z_j + \sigma_j N_j) \sigma_j (\partial N_j / \partial \rho)) / (\sum x_k (z_k + \sigma_k N_k)^2)^{1/2} \quad (C.2)
 \end{aligned}$$

and

$$\begin{aligned}
\frac{\partial N_j}{\partial \rho} = & \frac{\pi \Sigma x_k \sigma_k^2 z_k}{4 (1 - \pi/6 \epsilon_3)} + \frac{\pi \rho (\Sigma x_k \sigma_k^2 z_k) (\pi/6) (\Sigma x_k \sigma_k^3)}{4 (1 - \pi/6 \epsilon_3)^2} \\
& + \frac{\alpha/2 \rho^{-1/2} (x_k z_k^2 \sigma_k^2)^{1/2} z_j \alpha/2 (\rho \Sigma x_k z_k^2)^{1/2}}{(1 + \alpha (\rho \Sigma x_k z_k^2 \sigma_k^2)^{1/2})^2} \\
& + \frac{\alpha/2 \rho^{-1/2} (x_k z_k^2 \sigma_k^2)^{1/2} (\pi/12) \rho (\Sigma x_k \sigma_k^3 z_k) \alpha (\rho \Sigma x_k z_k^2)^{1/2}}{(1 + \alpha (\rho \Sigma x_k z_k^2 \sigma_k^2)^{1/2})^2 (1 - \pi/6 \epsilon_3)} \\
& - \frac{z_j (\alpha/4) \rho^{-1/2} (\Sigma x_k z_k^2)^{1/2}}{1 + \alpha (\rho \Sigma x_k z_k^2 \sigma_k^2)^{1/2}} \\
& - \frac{(\pi/12) \rho (\Sigma x_k \sigma_k^3 z_k) \alpha (\rho \Sigma x_k z_k^2)^{1/2} (\pi/6) (\Sigma x_k \sigma_k^3)}{(1 + \alpha (\rho \Sigma x_k z_k^2 \sigma_k^2)^{1/2}) (1 - \pi/6 \epsilon_3)^2} \\
& - \frac{(3/2) (\pi/12) (\Sigma x_k \sigma_k^3 z_k) \alpha \rho^{1/2} (\Sigma x_k z_k^2)^{1/2}}{(1 + \alpha (\rho \Sigma x_k z_k^2 \sigma_k^2)^{1/2}) (1 - \pi/6 \epsilon_3)}
\end{aligned} \tag{C.3}$$

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PROFESSIONAL EXPERIENCE

Since 1985, he has been manager of Scientific Systems, responsible for the development of software and models associated with thermodynamics and kinetics. Previously, from 1982 to 1984, he was the project leader of the Thermophysical Properties group of MIS. In this capacity, he was responsible for the development of thermophysical property models and correlations for corporate-wide applications, including cryogenics, gas processing, and organic chemicals. As a staff engineer from 1977 to 1982, he developed thermophysical property models and data correlations for the Process Systems Group. The work focused on thermodynamics for cryogenic and acid-gas scrubbing applications. Major areas of involvement included: (1) research on equations of state for polar mixtures; (2) the impact of thermodynamic uncertainties on process design; (3) software development for process simulation; and (4) thermodynamic data correlations. From 1976 to 1977, his responsibilities encompassed process development for coal-cleaning technology.

EDUCATION

Lehigh University	1986	Ph.D. Chemical Engineering
Lehigh University	1981	M.S. Chemical Engineering
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PUBLICATIONS

Copeman, T. W., and F. P. Stein, "An Explicit Non-Equal Diameter MSA Model for Electrolytes," presented at Fourth International Conference on Fluid Properties and Phase Equilibria for Chemical Process Design, Denmark, May 1986.

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