Representation of Deviation From Ideality in Concentrated Aqueous Solutions of Electrolytes Using a Mean Spherical Approximation Molecular Model

A semiempirical expression for the Helmholtz energy of mixed electrolyte solutions in solvents mixtures is obtained from the solution of the mean spherical approximation given by Planche and Renon (1981) for a nonprimitive model of interactions. A consistent set of analytical equations for the related thermodynamic properties was further derived and used to represent osmotic coefficient data of strong aqueous electrolytes at 25°C. Data correlation was performed on more than 80 systems up to a 6 M molality using generally one adjustable parameter for each single electrolyte; from these parameters the properties of mixtures can be calculated in a predictive manner without additional parameters.

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SCOPE

The computation of phase equilibria involving electrolyte systems requires versatile representations of thermodynamic properties of electrolyte solutions. The method devised by Pitzer (Pitzer, 1973; Pitzer and Mayorga, 1973; Pitzer and Kim, 1974) from a virial-type expression for the excess Gibbs energy has provided chemical engineers with a convenient tool and has given rise to extensive data treatment. But this model does not actually account for the molecular nature of the solvent, which is treated as dielectric continuum. Further developments by Cruz and Renon (1978) and Chen et al. (1982), using the NRTL equation, has shown that the formalism of nonelectrolytes could also help modeling nonideality in ionic solutions. However, application of all these approaches must go through the adjustment of at least two parameters for each single electrolyte. More recently, Kondo and Eckert (1983) proposed a one-parameter model for representing activity coefficients in electrolyte solutions, but the corresponding equations involve numerical integration and were only applied up to an ionic strength of 3.

The objective of this work is to give a new method for representing excess properties of electrolyte solutions, from the solution of the mean spherical approximation given by Planche and Renon (1981) for a nonprimitive model of interactions.

The applicability of the model was investigated through the study of many strong aqueous electrolyte systems, taking particular interest in the number of required parameters.

CONCLUSIONS AND SIGNIFICANCE

From an analytical expression of the Helmholtz energy, a consistent set of equations has been derived for representing thermodynamic properties of electrolyte solutions. Data of osmotic coefficients of single and mixed strong aqueous electrolytes at 25°C have been successfully correlated up to a 6 M molality, using one adjustable parameter for each salt and two parameters for each cation. The latter parameters are common to all salts including the same cation and can generally be estimated from the values of Stokes radii for representing data with reasonable accuracy. No ternary parameter is involved in the equations and the osmotic coefficients of mixtures can be predicted from the values of binary parameters without additional parameters. Another advantage of this representation is that the solvent is not limited to water. Compositions are calculated as concentrations and accordingly, for each component—solute or solvent—the limiting case of pure substance can be treated within the framework of the same theory.

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INTRODUCTION

Significant theoretical advances in the understanding of ionic solutions have been made in recent years, due to the rapid development of statistical mechanics methods (Friedman, 1981). However, advances made since the major progress achieved by Pitzer (1973) do not seem to have actually promoted new practical methods useful for engineers. One reason for this is that it is quite difficult to obtain simple representations from advanced theories without losing either thermodynamic consistency or most of the information conveyed by the models.

Triolo et al. (1976) have used the analytical solution of the mean spherical approximation (MSA) given by Blum (1975) for the primitive model as an empirical equation to fit osmotic coefficient data of 1-1 single electrolytes. Using only one adjustable parameter for each salt, they obtained a good agreement up to a 2 M concentration. Unfortunately, the model was not tested for predictivity and thermodynamic consistency.

An analytical solution of the MSA was also given (Planche and Renon, 1981) for a mixture of charged and neutral hard spheres with additional short-range and coulombic interactions. It is this theory which underlies the approach presented here.

THEORETICAL BACKGROUND

The model of Planche is based on the following expression for the interaction between two species i and j:

$$u_{ij}(r)/kT = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 D r k T} + \frac{W_{ij}}{2\pi r N}\,\delta'(r - \sigma_{ij}) \quad \text{for } r > \sigma_{ij} = (\sigma_i + \sigma_j)/2$$
$$u_{ij}(r) = \infty \quad \text{for } r < \sigma_{ij} \qquad (1)$$

where Z_i and σ_i are respectively the ionic charge and the diameter of species i; D is the dielectric constant of the solution; and δ' stands for the derivative of the Dirac function.

This potential accounts for long-range coulombic forces as well as short-range interactions. The contribution from short-range interactions combines hard sphere repulsions and contact interactions characterized by parameter W_{ij}.

It must be emphasized that the potential given by Eq. 1 is not an interionic potential of mean force as the quantity used within the framework of the McMillan-Mayer theory. It applies to both ionic and nonionic species and enables the properties of pure substances to be represented.

The parameters W_{ij} are assumed to be temperature-dependent, and in this work the following form of variation was selected for the liquid phase:

$$W_{ij} = \frac{A_{ij}^0}{T}(1 - \alpha_{ij}T + 2\,\alpha_{ij}\gamma T^2)\exp[\alpha_{ij}T(1 - \gamma T)] \qquad (2)$$

with $\gamma = 10^{-5}\,K^{-1}$ and $\alpha_{ij} \geq 0$.

Accordingly, the parameters of the model are A_{ij}, σ_{ij} and σ_i. The constant γ is small enough to have practically no influence over the temperature range 100–500 K and yet it allows W_{ij} to go to zero *at infinite* temperature.

The method of solution is an extension of the procedure used by Blum (1975) to solve the MSA for the primitive model. It chiefly involves the calculation in the vicinity of σ_{ij}, using Baxter's (1970) decomposition of integrals and derivatives of the distribution function $g_{ij}(r)$, as characterized by the exact Ornstein-Zernike equation and the mean spherical closure approximation. The internal energy can be calculated from $g_{ij}(r)$ through the energy equation, and further integration at constant volume yields the Helmholtz energy. Detailed derivations have already been given by Planche (1981) and we proceed directly to the resulting expression for the molar Helmholtz energy of a multicomponent system at temperature T:

$$\begin{aligned}(a - a_0^T)/RT = {} & \sum_i \frac{x_i}{RT}\left[h_i - (s_i + R)T - \frac{3}{2}C_i RT\ln(T/T_0)\right] \\ & + \sum_i x_i \ln\left(\frac{x_i RT}{P_0 v\Delta}\right) + 3\sum_i x_i \frac{\sigma_i^2}{\Delta}\left(\zeta_1 + \frac{\zeta_2^2}{2\Delta}\right) \\ & - \sum_i\sum_j \frac{x_i x_j}{\Delta v}A_{ij}\left(1 + \frac{3}{\Delta}\zeta_2\sigma_j\right) \\ & - \frac{\alpha^2}{4\pi}\sum_j x_j z_j \frac{z_j\Gamma_j + F_j p}{1 + \Gamma_j\sigma_j} + \frac{\Gamma^3 v}{3\pi N}\cdot\end{aligned} \qquad (3)$$

The reference state is defined as the ideal gas at one atmosphere pressure (101.325 kPa) and temperature T. The composition is characterized by the mole fractions x_i, and v stands for the molar volume of the solution.

The other quantities involved in Eq. 3 are defined by:

$$\zeta_n = N\frac{\pi}{6}\sum_i \frac{x_i}{v}\sigma_i^n \qquad (4)$$

$$\Delta = 1 - \zeta_3 \qquad (5)$$

$$T_0 = 298.15\ \text{K}$$

$$\alpha^2 = e^2 N/\epsilon_0 DRT\ (\text{m}) \qquad (6)$$

$$p = N\sum_k \frac{z_k\sigma_k x_k}{v(1 + \Gamma_k\sigma_k)}\ (\text{m}^{-2}) \qquad (7)$$

$$A_{ij} = \frac{A_{ij}^0}{T}\exp[\alpha_{ij}T(1 - \gamma T)]\ (\text{m}^3\cdot\text{mol}^{-1}) \qquad (8)$$

The first term in Eq. 3, including the parameters h_i, s_i, and C_i, is introduced to account for the difference in reference states for a given molecule in the gas and liquid phases; it therefore applies only to volatile components. Γ_k is a scaling quantity which has the dimension of an inverse length. For neutral species, $\Gamma_k = 0$, and for all ions Γ_k has the common value Γ, determined by solving the algebraic equation:

$$4\Gamma^2 = \alpha^2 N\sum_k \frac{x_k}{v}\left(\frac{z_k - \sigma_k F_k p}{1 + \Gamma_k\sigma_k}\right)^2 \qquad (9)$$

with:

$$F_j = B_j + A_j\left(1 - \sum_k \frac{x_k}{v}N\frac{\sigma_k^2 B_k}{(1 + \Gamma_k\sigma_k)}\right)\Bigg/\left(1 + \sum_k \frac{x_k}{v}N\frac{\sigma_k^2 A_k}{(1 + \Gamma_k\sigma_k)}\right) \qquad (10)$$

$$A_j = \frac{\pi}{\Delta}\left(\frac{\sigma_j}{2} + \sum_k \frac{x_k}{v}\sigma_k W_{kj}\right) \qquad (11)$$

$$B_j = \frac{1}{p}\sum_k \frac{x_k z_k \Gamma_k W_{kj}}{v(1 + \Gamma_k\sigma_k)} \qquad (12)$$

Equation 9 can be easily solved by an iterative method of substitution, in generally less than five iterations, from an initial guess value of $\Gamma = 0$.

APPROXIMATION TO THE HELMHOLTZ ENERGY

In order to calculate thermodynamic properties from the expression of the Helmholtz energy, Planche (1981) used approximate values for the derivatives of Γ but retained the complete Eq. 9 for determining Γ itself. Indeed, although Γ can easily be calculated, a rigorous determination of its derivatives would require a quite involved and time-consuming calculation procedure. Planche avoided such difficulties, but he had to integrate the Gibbs-Duhem equation for determining the properties of both solvent and solutes.

We have therefore chosen to start from a simplified expression for the Helmholtz energy and to perform the subsequent derivations without making additional approximations. Thus the equations for the thermodynamic properties derived from A have an analytical form, and thermodynamic consistency is automatically satisfied.

The approximation used consists in neglecting the terms $F_j r \sigma_j$—which are small compared to z_j or $\Gamma \sigma_j$—in Eqs. 3 and 9. Therefore the following expression is obtained as an approximation to the molar Helmholtz energy:

$$
\begin{aligned}
(a - a_0^T)/RT = {} & \sum_i \frac{x_i}{RT}\left[h_i - (s_i + R)T - \frac{3}{2} C_i RT \ln(T/T_0)\right] \\
& + \sum_i x_i \ln\left(\frac{x_i RT}{P_0 v \Delta}\right) + 3 \sum_i x_i \frac{\sigma_i^2}{\Delta}\left(\zeta_1 + \frac{\zeta_2^2}{2\Delta}\right) \\
& - \sum_{i,j} \frac{x_i x_j}{\Delta v} A_{ij}\left(1 + \frac{3}{\Delta} \zeta_2 \sigma_j\right) \\
& - \frac{\alpha^2}{4\pi} \sum_j \left(\frac{x_j z_j^2 \Gamma_j}{1 + \Gamma_j \sigma_j}\right) + \frac{\Gamma^3 v}{3\pi N} \qquad (13)
\end{aligned}
$$

with

$$4\Gamma^2 = \alpha^2 N \sum_k \frac{x_k}{v}\left(\frac{z_k}{1 + \Gamma_k \sigma_k}\right)^2 \cdot \qquad (14)$$

OTHER THERMODYNAMIC PROPERTIES

Equation 13 can now be used to calculate by appropriate derivations other thermodynamic properties, such as the pressure and the chemical potentials of the liquid mixture.

Equation of State

Pressure is calculated from:

$$P = -\left(\frac{\partial\left(\sum_i n_i\right)\left(a - a_0^T\right)}{\partial V}\right)_{T, n_1, \ldots, n_i, n_n} \qquad (15)$$

The resulting equation of state is:

$$
\begin{aligned}
P/RT = {} & \frac{6}{\pi N}\left(\frac{\zeta_0}{\Delta} + \frac{3\zeta_1\zeta_2}{\Delta^2} + \frac{3\zeta_2^3}{\Delta^3}\right) \\
& - \sum_i \sum_j \frac{x_i x_j A_{ij}}{v^2 \Delta^2}\left(1 + \frac{6\zeta_2 \sigma_j}{\Delta}\right) - \frac{\Gamma^3}{3\pi N} \\
& - \frac{\alpha^2}{4\pi D}\left(\frac{\partial D}{\partial V}\right)_{T, n_1, \ldots, N_n} \sum_j \left(\frac{n_j z_j^2 \Gamma_j}{1 + \Gamma_j \sigma_j}\right) \cdot \qquad (16)
\end{aligned}
$$

Chemical Potential

For any component i of the mixture, the chemical potential can be calculated according to:

$$\mu_i - \mu_{i0}^T = \left(\frac{\partial\left(\sum n_i\right)\left(a - a_0^T\right)}{\partial n_i}\right)_{T, V, n_{j \neq i}} \qquad (17)$$

We introduce the auxiliary quantities P_{HS} and P_{SR}, which are respectively the contributions to the pressure of the hard spheres effects and of the short range effects parametrized by A_{ij}:

$$P_{HS}/RT = \frac{6}{\pi N}\left(\frac{\zeta_0}{\Delta} + \frac{3\zeta_1\zeta_2}{\Delta^2} + \frac{3\zeta_2^3}{\Delta^3}\right) \qquad (18)$$

$$P_{SR}/RT = -\sum_{i,j} \frac{x_i x_j A_{ij}}{v^2 \Delta^2}\left(1 + \frac{6\zeta_2 \zeta_j}{\Delta}\right) \qquad (19)$$

Combination of Eqs. 13, 17, 18, and 19 yields:

$$
\begin{aligned}
(\mu_i - \mu_{i0}^T)/RT = {} & \frac{1}{RT}\left[h_i - s_i T - \frac{3}{2} C_i RT \ln\left(\frac{T}{T_0}\right)\right] \\
& + \ln \frac{x_i RT}{P_0 v \Delta} + \frac{N\pi}{6} \sigma_i^3 (P_{HS} + P_{SR})/RT + \frac{\sigma_i^2}{\Delta}\left(3\zeta_1 + \frac{9\zeta_2^2}{2\Delta}\right) \\
& + 3\sigma_i \frac{\zeta_2}{\Delta} - \frac{1}{\Delta}\left[\sum_k \frac{x_k}{v} A_{ki}\left(2 + \frac{3\zeta_2}{\Delta}\sigma_i\right) + 3\sum_k \frac{A_{ki} x_k}{v\Delta} \zeta_2 \sigma_k\right. \\
& \left. + \frac{\pi}{2\Delta} N \sum_l \sum_k \frac{x_k x_l}{v^2} A_{lk}^{L} \sigma_i^2 \sigma_k\right] + \frac{\alpha^2}{4\pi D}\left(\frac{\partial D}{\partial n_i}\right)_{T,V} \sum_j \left(\frac{n_j z_j^2 \Gamma_j}{1 + \Gamma_j \sigma_j}\right) \\
& - \frac{\alpha^2}{4\pi} \frac{z_i^2 \Gamma_i}{(1 + \Gamma_i \sigma_i)} \cdot \qquad (20)
\end{aligned}
$$

For a given composition, Eqs. 14, 16, and 20 should be simultaneously solved to obtain the values of chemical potentials at constant temperature, composition and pressure; the molar volume is involved in both Eqs. 14 and 16 and can be calculated from the algebraic equation of state. Note that Eqs. 16 and 20 include derivatives of the dielectric constant D. Indeed, we recall that the model of Planche takes into account the variation of D with ionic concentration; the explicit form of this concentration dependence is given in the next section.

Osmotic Coefficient

The osmotic coefficient of a solution of ions in a solvent S, at temperature T and pressure P, is related to the chemical potential of the solvent according to:

$$\varphi(P, T, x_1, \ldots, x_i, \ldots, x_S) = -\frac{1}{RT} \frac{x_S}{\sum_{\text{ions}} x_i}\left[\mu_S(P, T, x_1, \ldots, x_S) - \mu_S^*(P, T, x_S = 1)\right]. \qquad (21)$$

Using Eqs. 16 and 20, the osmotic coefficient can then be written:

$$
\begin{aligned}
\varphi = 1 - {} & \frac{\Gamma^3 v (1 - \zeta_3'')}{3\pi N \sum_{\text{ions}} x_i} \\
& - \frac{\alpha^2 v (1 - \zeta_3'')}{4\pi D \sum_{\text{ions}} x_i}\left(\frac{\partial D}{\partial v}\right)_{T, n_1, \ldots, n_n} \sum_j \left(\frac{n_j z_j^2 \Gamma_j}{1 + \Gamma_j \sigma_j}\right) \\
& + \varphi_{HS} + \varphi_{SR} + \varphi_{\text{vol.}} \qquad (22)
\end{aligned}
$$

with

$$\varphi_{HS} = \frac{6}{\pi N} \frac{v}{\sum_{\text{ions}} x_i}\left(\frac{3\zeta_1''\zeta_2''}{\Delta} + \frac{3\zeta_2''^3}{\Delta^2} + \frac{9}{2} \frac{\zeta_2^0 \zeta_2''^2}{\Delta^2}\right) \qquad (23)$$

$$\varphi_{SR} = -\frac{v}{\sum_{\text{ions}} x_i}\left[3 \sum_{l,k} \frac{x_k x_l}{v^2 \Delta^2} A_{lk} \zeta_2'' \sigma_k - \frac{3x_S^2}{v^2 \Delta^2} A_{SS} \zeta_2'' \sigma_s\right.$$

$$+ \sum_{\text{ions}} \frac{x_k x_l}{v^2 \Delta} A_{lk} \left(1 + \frac{3\zeta_2 \sigma_k}{\Delta}\right)\Bigg] \quad (24)$$

$$\varphi_{\text{vol}} = -\frac{x_S}{\sum_{\text{ions}} x_i} \Bigg\{ \ln\left(\frac{x_S v^* \Delta^*}{v\Delta}\right) - \frac{1}{\Delta}\left(\frac{x_S v^*}{v} - 1 + \zeta_3''\right) + \left(\frac{x_S v^*}{v} - 1 + \zeta_3''\right)^2 \left[\frac{Pv}{\Delta x_S RT} + \left(\frac{v}{v^* x_S \Delta\Delta^*}\right)^2 \times \left(\frac{3}{2}\zeta_3^{02} - 3\zeta_3^0 \frac{A_{SS} x_S}{v}\right)\right]\Bigg\} \quad (25)$$

$$\zeta_n^0 = \frac{N\pi}{6} x_S \sigma_S^n \quad (26)$$

$$\zeta_n'' = \frac{N\pi}{6} \sum_{\text{ions}} \frac{x_i}{v} \sigma_i^n . \quad (27)$$

The superscript $*$ refers to the pure solvent at the temperature and pressure of the system. An alternative way of calculating φ is to use Eq. 20 directly for μ_S and to determine μ_S^* by computing the limiting value of μ_S when the ionic concentration goes to zero. Both methods were used and were found to be in complete agreement.

ESTIMATION OF THE DIELECTRIC CONSTANT

While the concentration dependence of the dielectric constant of ionic solutions has been recognized for a long time from experimental evidence, few attempts have been made to take into account this effect when modeling deviations from ideality in electrolyte solutions. Triolo et al. (1976) tried to improve the primitive model within the framework of the MSA, using either a two-parameter density-dependent dielectric constant or an adjustable but not density-dependent dielectric constant. They obtained good agreement with osmotic coefficient data up to a 2 M molality, but the calculated values of the dielectric constant are not realistic, since they are greater than the pure solvent constant.

The equation used in the present model was designed to represent the experimental trend of the dielectric constant in terms of concentrations and ionic sizes:

$$D = 1 + (D_S - 1)\left(\frac{1 - \zeta_3''}{1 + \frac{\zeta_3''}{2}} - \sum_{\text{ions}} \frac{E_i x_i \Delta''^2}{T v \sigma_{P_i}}\right) \cdot \quad (28)$$

Here D_S is the dielectric constant of pure solvent and σ_{P_i} is the Pauling diameter of the ions i. This formula is an extension of the equation proposed by Giese et al. (1970).

Ions in solution are assumed to be dielectric holes, polarizing the surrounding solvent molecules in inverse proportion to the Pauling radii. For each mixture, the parameters E_i should be fitted to experimental data of dielectric constants. However, in view of the scarcity of reliable data and for the sake of simplicity, only two different values were assigned in the present study to the parameters E_i. For aqueous electrolytes at 25°C it was found suitable to set E_i equal to zero in the case of anions, and to use the common value $E_c = 30 \cdot 10^{-13}$ K·m^4·mol^{-1} for cations.

From Eq. 28, the derivatives of D—which appear in the equation of state and the expression of the chemical potential—can now be calculated:

$$\left(\frac{\partial D}{\partial V}\right)_{T, n_i, \ldots, n_i, \ldots, n_S} = \frac{(D-1)(3\zeta_3'' - 1)}{\Delta'' V} + \frac{(D_S - 1)}{V} \frac{(1 - \zeta_3'' - 3\zeta_3''^2/2)}{(1 + \zeta_3''/2)^2} \quad (29)$$

$$\left(\frac{\partial D}{\partial N_i}\right)_{T, V, n_{j \neq i}, n_S} = \frac{(D_S - 1)}{V}\Bigg\{-\frac{N\pi}{4}\sigma_i^3/(1 + \zeta_3''/2)^2 + \frac{\Delta''}{T}\left[\frac{N\pi}{3}\frac{\sigma_i^3}{v}\sum_j \left(\frac{E_j x_j}{\sigma_{p_j}}\right) - \frac{E_i \Delta''}{\sigma_{p_i}}\right]\Bigg\} \cdot \quad (30)$$

DATA CORRELATION FOR STRONG AQUEOUS ELECTROLYTES AT 25°C

The model was applied to the representation of osmotic coefficients of strong pure and mixed aqueous electrolytes at 25°C. The best values of the parameters were determined by least squares analysis on relative deviations between calculated and experimental quantities.

Parameters for Pure Water

The equation of state and the chemical potential of pure molecular substances can be obtained by setting the ionic concentrations equal to zero in Eqs. 16 and 20. In this case, the equation of state includes only the parameters A_{ii}^0, α_{ii} and σ_i. For pure liquid water, using the estimated value of 2.52 Å for the diameter σ_{H_2O}, the parameters A_{H_2O,H_2O} and α_{H_2O,H_2O} were fitted to experimental molar volumes at saturation pressure (Schmidt, 1969) from 20 to 260°C, yielding a relative standard deviation of 0.3%:

$$A_{H_2O,H_2O}^0 = 1.0039 \cdot 10^{-3}\ \text{K} \cdot \text{m}^3 \cdot \text{mol}^{-1}$$

$$\alpha_{H_2O,H_2O} = 0.003715$$

$$\sigma_{H_2O} = 2.52\ \text{Å}.$$

The parameters h_i, s_i and C_i can be estimated from vapor-liquid equilibrium data of pure water and from the equilibrium condition: $\mu_i^{\text{liquid}} = \mu_i^{\text{vapor}}$.

Using for steam the equation of state: $v = (RT/p + B)$ with $B = -2.03372 \cdot 10^{-4}$ m^3·mol^{-1}, the following estimates were found to satisfy the equilibrium condition within 1.2% for saturated water up to 260°C:

$$h_{H_2O} = -50{,}100.55\ \text{J} \cdot \text{mol}^{-1}$$

$$s_{H_2O} = -87.51\ \text{J} \cdot \text{mol}^{-1}$$

$$C_{H_2O} = 2.23162.$$

The latter set of three parameters need not be known for representing osmotic coefficients of aqueous solutions, yet it allows the calculation of vapor-liquid equilibrium.

Parameters for Ionic Solutions

Further estimation of parameters in the case of ionic solutions can be achieved using the following simplifications:

1. As all the data treated here are given at the same temperature, the parameters α_{ij} cannot be obtained.
2. The A_{ij} matrix is assumed to be symmetrical.
3. It is assumed that there are no short-range interactions between ions of the same sign, so that in this case the parameters A_{ij} are equal to zero.

Therefore, at this stage each electrolyte completely dissociated in water must be characterized by three short-range interaction parameters A_{cH_2O}, A_{aH_2O} and A_{ca} (respectively related to cation-water, anion-water, and cation-anion interactions), and two ionic diameters, σ_c and σ_a.

For mixed electrolytes, since there are no parameters A_{ij} for pairs of ions of the same sign, all the parameters can be obtained from the study of binary water-salt systems.

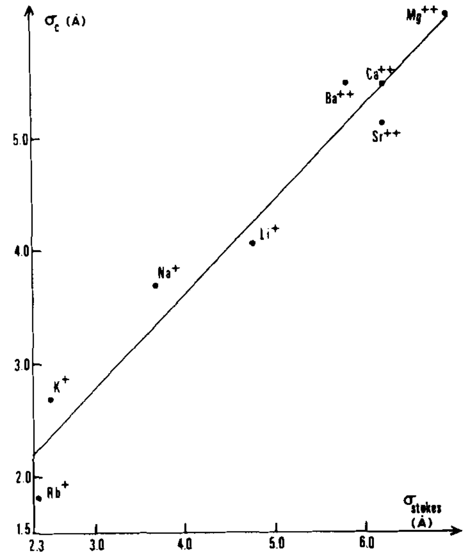

Figure 1. Variation of adjusted cationic diameter with Stokes diameter.

TABLE 1A. RESULTS OF FIT FOR OSMOTIC COEFFICIENT DATA OF SINGLE AQUEOUS ELECTROLYTES AT 25°C

Electrolyte†	Maximum Molality	100 σ_φ*	Electrolyte†	Maximum Molality	100 σ_ϕ*
HCl	6	0.6	KCl	4.5	0.4
HBr	3	0.3	KBr	5.5	0.3
HI	3	0.8	KI	4.5	1.0
HNO_3	3	1.0	KNO_3	3.5	2.9
$HClO_4$	6	1.2	KA_c**	3.5	2.3
LiCl	6	0.7	KF	4	0.5
LiBr	6	1.3	KOH	6	2.3
LiI	3	0.8	RbCl	5	0.5
$LiNO_3$	6	0.3	RbBr	5	0.5
$LiClO_4$	4	1.4	RbI	5	1.1
LiA_c**	4	1.3	$RbNO_3$	4.5	4.6
LiOH	4	5.9	RbA_c**	3.5	2.4
NaCl	6	0.9	CsCl	6	2.0
NaBr	4	0.2	CsBr	5	2.3
NaI	3.5	0.5	CsI	3	1.5
$NaNO_3$	6	3.9	$CsNO_3$	1.4	1.0
$NaClO_4$	6	1.0	CsA_c**	3.5	2.7
NaA_c**	3.5	1.7	CsOH	1	2.1
NaF	1	0.1	NH_4Cl	6	0.6
NaOH	6	1.0	NH_4NO_3	6	2.3

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* σ_φ: Root mean square deviation in osmotic coefficient φ.

** A_c: = Ion acetate.

† 1:1 electrolytes; data from Robinson and Stokes (1970).

Binary Systems

The data treatment was performed by successive stages, with the objective of selecting the most significant parameters. Preliminary calculations showed that the anion-water parameters A_{aH_2O} were always small and had no influence on the data fit; they were therefore set equal to zero: $A_{aH_2O} = 0$.

The influence of the various parameters was first investigated on a limited number of systems, including the following ionic species:

Cations: H^+, Li^+, Na^+, K^+, Cs^+, Rb^+ Ca^{++}, Mg^{++}, Ba^{++}, Sr^{++}.

Anions: Cl^-, Br^-, I^-.

As a first result, it was found that the representation was not very sensitive to the values of the anionic diameters and that a good agreement could be obtained by using the values of the Pauling (1940) diameters for the three anions. Assigning those values to the anionic diameters, the other parameters were then fitted on data of the same systems. To get a consistent set of estimates, for a given cation c, the parameters A_{cCl^-}, A_{cBr^-}, A_{cI^-}, A_{cH_2O} and σ_c were determined by simultaneously treating the three systems cX-H_2O. Adjusting in this way five parameters for each subset of three systems yields a good representation with standard deviations within 0.6% for 1-1 electrolytes and within 1.5% for 2-1 electrolytes.

On the basis of these results, further calculations were then made to investigate the possibility of a more compact method of representation.

Correlations for Cationic Parameters

The values of the cationic diameters which were determined on the 30 systems previously mentioned were found to be related in an approximately linear way to the values of Stokes diameters

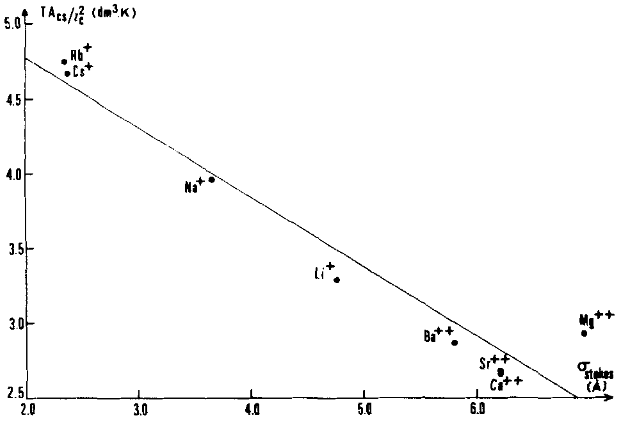

Figure 2. Variation of cation-water parameter A_{CS} with Stokes diameter.

TABLE 1B. RESULTS OF FIT FOR OSMOTIC COEFFICIENT DATA OF SINGLE AQUEOUS ELECTROLYTES AT 25°C

Electrolyte†	Maximum Molality	100 σ_φ*	Electrolyte†	Maximum Molality	100 σ_φ*
Li_2SO_4	2	1.9	CaI_2	2	0.7
Na_2SO_4	4	6.8	$Ca(NO_3)_2$	6	2.4
K_2SO_4	0.7	1.0	$Ca(ClO_4)_2$	3	1.4
Rb_2SO_4	1.8	2.2	$SrCl_2$	4	2.0
Cs_2SO_4	1.8	2.7	$SrBr_2$	2	1.2
$MgSO_4$	2	7.9	SrI_2	2	0.5
$BaCl_2$	1.8	0.9	$Sr(NO_3)_2$	4	3.6
$BaBr_2$	2	0.8	$Sr(ClO_4)_2$	3	1.4
BaI_2	2	0.6	$MgCl_2$	3	1.5
$Ba(NO_3)_2$	0.4	1.0	$MgBr_2$	3	3.6
$Ba(ClO_4)_2$	3.5	1.4	MgI_2	3	5.3
$Ba(A_c)_2$	1.4	2.1	$Mg(NO_3)_2$	3	1.5
$CaCl_2$	3	2.0	$Mg(Ac)_2$	3	4.0
$CaBr_2$	3	0.9	$Mg(ClO_4)_2$	2	1.4
			$Pb(ClO_4)_2$	4	1.5

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* σ_φ: Root mean square deviation.

† 1:2 and 2:1 electrolytes; data from Robinson and Stokes (1970).

TABLE 2. VALUES OF IONIC DIAMETERS ANIONS

$\sigma_a = \sigma_{\text{Pauling}}$ (Å)		Adjusted Values of σ_a	
Cl^-	3.60	NO_3^-	3.12
Br^-	3.90	ClO_4^-	3.64
I^-	4.32	A_c^-*	2.24
F^-	2.72	SO_4^{2-}	3.41
OH^-	3.52		

* A_c^- = Ion acetate cations

	σ_{Pauling} (Å)	σ_{Stokes} (Å)
Na^+	1.90	3.68
Li^+	1.20	4.76
K^+	2.66	2.50
Rb^+	2.96	2.36
Ca^+	3.38	2.38
NH_4^+	2.96	2.50
Ba^{++}	2.70	5.80
Ca^{++}	1.98	6.20
Mg^{++}	1.30	6.94
Sz^{++}	2.26	6.20
Pb^{++}	2.64	5.66

TABLE 3. VALUES OF THE PARAMETERS RELATING TO THE ION H^+

$10^3 \times TA_{H^+,H_2O}$	2.21637
σ_{H^+} (Å)	4.06
σ_{Pauling} (Å)	1.20*

* Estimated

(Nightingale, 1959), as shown in Figure 1. The corresponding equation, obtained by linear regression, is:

$$\sigma_{c\,(\text{Å})} = 0.8286\ \sigma_{\text{Stokes}} + 0.31 \qquad (31)$$

Indeed, calculating σ_c from this relation and adjusting again the other parameters does not result in a significant loss of accuracy. The adjusted diameter of H^+ does not fit this relation and was not used to obtain Eq. 31. In view of the dependence of the Stokes radii on ionic conductivity, this is not unexpected since the hydrogen ion moves in aqueous solution after a special mechanism and has a very high mobility.

Similarly, after inspection of the values of the A_{cH_2O} parameters, it was found suitable to use the following relation:

$$10^3\ T\ A_{cH_2O}/Z_c^2 = -0.4666\ \sigma_{\text{Stokes}\,(\text{Å})} + 5.7053 \qquad (32)$$

where $T = 298.15$ K.

TABLE 5. RESULTS OF THE PREDICTION OF OSMOTIC COEFFICIENTS FOR MIXED ELECTROLYTES, ROOT MEAN SQUARE DEVIATIONS IN φ

Aqueous Solutions at 25°C of Two Salts	100 × σ_φ*	Ref.**	Aqueous Solutions at 25°C of Two Salts	100 × σ_φ*	Ref. **
NaCl-KCl	1.0	a	$NaCl$-$MgCl_2$	1.2	h
NaCl-CsCl	2.1	b	$NaCl$-$CaCl_2$	1.3	i
NaCl-LiCl	2.1	c	$NaCl$-$SrCl_2$	1.8	j
$NaCl$-$NaNO_3$	2.5	d	KCl-$SrCl_2$	3.7	k
NaCl-NaBr	1.0	e	KCl-$CaCl_2$	2.2	l
NaBr-KBr	0.4	e	KCl-$MgCl_2$	1.2	m
$NaNO_3$-KNO_3	4.4	d	KCl-$BaCl_2$	0.9	n
KCl-CsCl	1.0	f	$CsCl$-$BaCl_2$	2.4	o
KCl-KBr	0.3	e	$LiCl$-$BaCl_2$	6.3	o
KCl-KNO_3	2.5	d	$NaCl$-$BaCl_2$	2.8	p
$CaCl_2$-$MgCl_2$	2.1	g			

* Mean value of σ_φ:2.0.
** Reference
a: Robinson (1961)
b: Robinson (1952)
c: Robinson et al. (1971)
d: Bezboruah et al. (1970)
e: Covington et al. (1968)
f: Robinson (1953)
g: Robinson and Bower (1966a)
h: Platford (1968)
i: Robinson and Bower (1966b)
j: Macaskill et al. (1978)
k: Downes (1974)
l: Robinson and Covington (1968)
m: Padova and Saad (1977)
n: Reilly et al. (1971)
o: Lindenbaum et al. (1972)
p: Robinson and Bower (1965)

Comparison with previously calculated values of A_{cH_2O} is illustrated in Figure 2.

Although this procedure can only provide rough estimates of parameters, it proved reliable enough to be incorporated in the method of representation, as shown hereafter.

Final Results for Binary Systems

The 30 systems first selected were expected to be representative of ionic properties in aqueous solutions. Therefore, to test the validity of the above relations, the data treatment was performed on a more extensive set of systems, using the following method.

1. The cationic diameters and the parameters A_{cH_2O} are calculated using Eqs. 31 and 32 except for the hydrogen ion.

TABLE 4. ADJUSTED VALUES OF ANION-CATION PARAMETERS $10^3 TA_{ca}$

c a	Cl^-	Br^-	I^-	F^-	NO_3^-	ClO_4^-	A_c^-	$SO_4^=$	OH^-
Na^+	−3.55250	−2.56352	−0.97175	−3.11863	−1.71860	−1.59408	−15.7695	−4.12175	−5.26314
Li^+	−4.12190	−2.56654	−0.39597	—	−6.32705	−5.81934	−11.2667	−11.64870	2.15830
H^+	−1.78362	−0.71873	2.15087	—	−2.42495	−2.29527	—	—	—
K^+	−4.24782	−3.04244	−1.28777	−11.83975	4.23173	—	−21.0679	−1.83386	−11.84762
Rb^+	−3.76720	−1.84625	0.36893	—	4.02749	—	−21.8671	−2.21437	—
Cs^+	−2.42827	−0.51837	3.21825	—	8.76311	—	−21.3293	−2.95738	−14.95654
NH_4^+	−3.35109	—	—	—	−0.83769	—	—	—	—
Ba^{++}	−8.69884	−11.74663	−16.00186	—	20.13066	−14.01153	−7.5539	—	—
Ca^{++}	−16.24593	−17.47656	−17.26507	—	−8.45619	−23.60827	—	—	—
Mg^{++}	−16.70637	−16.88708	−14.59152	—	−18.79949	−25.53868	−16.0623	−9.36328	—
Sr^{++}	−13.63198	−14.38927	−15.19997	—	−1.78718	−20.09765	—	—	—
Pb^{++}	—	—	—	—	—	−16.95303	—	—	—

2. The anionic diameters are taken equal to the Pauling diameters, when the latter have known values.

3. The only adjusted quantities are the anion-cation parameters and the anionic diameters when the Pauling values are not available.

In most cases this procedure requires the adjustment of a single parameter, A_{ca}, for each binary system. Results of the data treatment are reported in Tables 1a and 1b. The average values of root mean square deviations are equal to 1.4% for a set of 40 1-1 electrolytes and to 2.0% for a set of 28 2-1 electrolytes. The values of the parameters which were not calculated from Eqs. 31 and 32 are listed in Tables 2–4. The systems including the ion SO_4^{2-} could not be treated in the same way as the other ones. In this particular case, the parameter $E_{SO_4^{2-}}$ involved in Eq. 28, was set equal to -70.10^{-13} and not to zero as for the other anions. Even after introducing this parameter, only a poor agreement is obtained. This may result from some kind of ionic association (as can be seen, e.g., on the data reported by Harned and Owen, 1958) which is not accounted for by the model.

In view of the approximations which have been made, the parameters cannot actually be assigned any definite physical meaning. We may however notice some regularities. The values of cationic diameters, as given by Eq. 31, are consistent with the usual views on ionic hydration and structure-breaking effects, the highest values corresponding to strongly hydrated ions. From a similar viewpoint it seems realistic to use Pauling's values for the anions, e.g., to assume that they are not really hydrated, since it is known that the mean residence time of water molecules near anions is much less than the value observed in the case of cations. Concerning the quantities A_{ij}, it is noteworthy that for divalent cations, the parameters A_{cH_2O}, as calculated from Eq. 32, are at least twice as large as the parameters relating to monovalent cations. This is in qualitative agreement with the influence of ionic charge on the interactions between water molecules and hydrated ions.

Mixed Electrolytes

The parameters previously estimated from the study of binary systems were used to calculate osmotic coefficients of aqueous mixtures of two salts at 25°C. The prediction results are reported in Table 5 for 21 systems; on an average, the root mean square deviation between calculated and experimental values is of 2%, which is satisfactory in view of the results obtained for binary systems. This further justifies the assumption that short range interactions between ions of same sign can be neglected.

All the correlation results reported here have been obtained from osmotic coefficient data. However we must emphasize that activity coefficient data could have been treated in the same way. The activity coefficient can be calculated from Eq. 20 for the chemical potential and the limiting expression at infinite dilution, and by further performing standard transformations to allow for the appropriate concentration scale. This procedure was successfully tested for consistency, using the values of the parameters obtained from osmotic coefficient data.

NOTATION

A_{ij} = parameter defined by Eq. 8, $m^3 \cdot mol^{-1}$
A_{ij}^o = parameter defined by Eqs. 2 and 8, $m^3 \cdot K \cdot mol^{-1}$
a = molar Helmholtz energy $J \cdot mol^{-1}$
a_o = reference molar Helmholtz energy, $J \cdot mol^{-1}$
C_i = Helmholtz energy parameter, dimensionless
D = dielectric constant of the solution
D_S = dielectric constant of pure solvent
E_i = dielectric parameter, $m^4 \cdot K \cdot mol^{-1}$
e = electron charge, 1.6021×10^{-19} C
g_{ij} = radial distribution function
h_i = Helmholtz energy parameter, $J \cdot mol^{-1}$
k = Boltzmann constant, 1.38054×10^{-23} $J \cdot K^{-1}$
N = Avogadro number, 6.02251×10^{23}, $molecule \cdot mol^{-1}$
n_i = number of moles of component i
P = pressure, Pa
P_o = reference pressure, 101.325 kPa
R = gas constant, 8.3143 $J \cdot K^{-1} \cdot mol^{-1}$
r = distance between species i and j, m
s_i = Helmholtz energy parameter, $J \cdot K^{-1} \cdot mol^{-1}$
T = absolute temperature, K
u_{ij} = potential energy of i and j, J
V = total volume, m^3
v = molar volume of the solution, $m^3 \cdot mol^{-1}$
W_{ij} = potential parameter, $m^3 \cdot mol^{-1}$
x_i = mole fraction of component i in solution
Z_i = ionic charge of species i

Greek Letters

Δ = volumetric fraction defined by Eq. 5
Γ, Γ_i = scaling inverse length, m^{-1}
α = quantity defined by Eq. 6, $m^{1/2}$
α_{ij} = parameter defined in Eqs. 2 and 8, K^{-1}
γ = constant in Eqs. 2 and 8, 10^{-5} K^{-1}
ϵ_o = electric permittivity of free space, 8.854×10^{-12} $F \cdot m^{-1}$
ζ_n = function defined by Eq. 4
ζ_n'' = function defined by Eq. 27
ζ_n^o = function defined by Eq. 26
μ_i = chemical potential of component i, $J \cdot mol^{-1}$
σ_i = diameter of species i, m
σ_{P_i} = Pauling diameter of ion i, m
σ = root mean square deviation
φ = osmotic coefficient

Subscripts

$*$ = pure solvent at the temperature and pressure of the solution

Superscript

a = anion
c = cation
$i,j,k,$ = ion or molecule
s = solvent

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Manuscript received Oct. 30, 1981; revision received July 17, 1984, and accepted July 23.