x = z/L (−)
z = position in the bed, m
(−) = dimensionless quantity

Greek Letters

α = volumetric purge to feed ratio, u_1/u_2 (−)
ϵ = bed porosity (−)
τ = u_2t/L (−)
τ_b = u_2t_B/L
τ_{fH} = k_2L/u_2 (−)
τ_{fL} = k_1L/u_2 (−)

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Manuscript received Apr. 1, 1983; revision received Sept. 7, 1983, and accepted Sept. 7.

An NRTL Model for Representation and Prediction of Deviation from Ideality in Electrolyte Solutions Compared to the Models of Chen (1982) and Pitzer (1973)

A new method of representation of electrolyte solution nonideality is derived, on the basis of similar assumptions, from a model applied by Cruz and Renon (1978) to binary electrolyte solutions. In order to test the validity of the model for representation of strong electrolyte properties, parameters were fitted to osmotic coefficient data for single, completely dissociated salts in aqueous solutions and were used to calculate osmotic coefficients of mixed aqueous electrolytes. Results are compared with those given by Chen's local composition model (Chen et al., 1982; Aspen, 1983) and Pitzer's truncated model (Pitzer, 1973, 1979; Pitzer and Mayorga, 1973; Pitzer and Kim, 1974), the same number of adjustable parameters being used in each case.

The average standard deviations for single electrolytes are within 1% in the case of 1–1 salts for the three models, and within 2% in the other cases, except for Chen's model (5%). As for predicted results, both local-composition models yield standard deviations of less than 2%, while the accuracy given by the Pitzer model is better than 1.5%.

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SCOPE

Simple methods for representing deviations from ideality in electrolyte solutions are needed to design industrial processes, especially for transformation of raw materials and pollution control. Many models have been developed for that purpose on the basis of semiempirical extensions of the Debye-Hückel expression for the excess Gibbs energy.

The ion interaction model of Pitzer (1973) has proved especially useful; it yields accurate results for aqueous salt solutions properties up to a six-molal concentration.

Some years ago Cruz and Renon proposed a system of equa-

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tions for the representation of single electrolyte properties which, in contrast with most previous semiempirical treatments, can be applied over a very large range of concentrations. A particular feature of this model is that the expression of the excess Gibbs energy includes a contribution derived from the NRTL equation (Renon and Prausnitz, 1968). Another approach using the NRTL model with different assumptions was followed by Chen; the resulting equation can be applied to multicomponent systems.

The first aim of this work is to modify the Cruz model so as to obtain equations which use fewer adjustable binary parameters and which may predict the properties of mixtures. In addition, as a first test the model was applied to strong electrolyte solutions. The results are presented together with those given by Chen's local-composition model and Pitzer's truncated model.

Thus a comparison is provided between two treatments using the NRTL equation and the ion interaction model of Pitzer, which is taken here as a reference for comparison.

CONCLUSIONS AND SIGNIFICANCE

A new set of consistent equations for the representation of deviations from ideality in electrolyte solutions is proposed. The expression for the excess Gibbs energy was derived from the model of Cruz and Renon. It includes the same NRTL term, but only two adjustable parameters are needed for the representation of strong single electrolyte properties up to a six-molal concentration. Extension of the equation to mixed electrolytes is readily achieved without using additional parameters.

The model was applied to the representation of osmotic coefficients of 40 single and 21 mixed, completely dissociated electrolyte systems at 25°C, and compared with Chen's local-composition model and Pitzer's model, using the same number of adjustable parameters. For single electrolytes, similar results are given by the three models in the case of 1-1 salts, showing average standard deviations of less than 1%; for the other types of salts the average deviations are around 5% for Chen's model, and 2% for the other models. For mixed electrolyte systems, the agreement between calculated and experimental values is generally better than 2% when using both local-composition models, and better than 1.5% when using the Pitzer model.

INTRODUCTION

From the user's point of view, the main qualities of a model representing deviations from ideality are a small number of adjustable parameters and the ability to predict properties of multicomponent systems without additional parameters. Here three models are considered for the representation of nonideality of strongly concentrated aqueous electrolytes; they all include two parameters for a water-salt system, and no ternary parameter is needed. Thus the Pitzer model is truncated after the second virial term, so that only the parameters β^0 and β^1 are used.

The Debye-Hückel theory has long been the basis for developing semiempirical models to represent the excess properties of electrolyte solutions. Actually, it gives exact results for very dilute solutions and can be somewhat extended by including the effect of the finite sizes of the ions.

Taking into account various other phenomena in ionic solutions has proved useful to correlate data at higher concentrations. Developing a simple theory of electrolyte hydration, Stokes and Robinson (1973) derived equations for concentrated solutions; a similar model was recently proposed by Nesbitt (1982). More versatile models can also be obtained by introducing equations designed to represent the nonideality of nonelectrolyte solutions. This was early recognized by Scatchard (1936) in his study of concentrated electrolyte solutions.

More recently, Pitzer (1980) treated data for electrolyte systems extending from a dilute solution to a pure fused salt with a simple model using, in addition to a Debye-Hückel term, a contribution which is similar to the Van Laar equation.

This idea was also investigated by Cruz (1978) whose model is based on an expression for the excess Gibbs energy which includes three contributions: a Debye-Hückel term, a "salt effect" term produced, according to Debye and McAulay (Harned and Owen, 1958) by the change in dielectric constant with ionic concentration, and a short-range attractive contribution derived from the NRTL equation. A modified Cruz model is presented hereafter together with the first results obtained for strong electrolyte systems.

MODIFICATION AND EXTENSION OF THE CRUZ MODEL

Following the approach proposed by Cruz, we assume that the excess Gibbs energy, G^{Ex}, is the sum of three terms:

$$G^{Ex} = G^{Ex}_{\text{DEBYE-HÜCKEL}} + G^{Ex}_{\text{DEBYE-MCAULAY}} + G^{Ex}_{\text{NRTL}}$$

The first and second terms account for long-range coulombic interactions between ions; the Debye-McAulay term is introduced to attenuate the effect in the Debye-Hückel treatment of neglecting the variation of the dielectric constant with ionic concentration. The NRTL term accounts for short-range forces between all species. Within this framework, the Cruz model was modified in view of two main considerations:

1. It includes at least four adjustable parameters for the representation of binary solvent-salt systems.
2. The extension of this treatment to mixtures introduces new adjustable parameters.

This is mainly due to the way in which the dielectric constant is calculated, as we shall see in a later section. Therefore, in order to derive equations including fewer adjustable parameters and allowing the prediction of mixtures properties, we used a different expression for the Debye-McAulay contribution. In addition, it was preferred to use expressions in terms of molality rather than concentration.

Debye-Hückel (DH) Contribution

This contribution is similar to the term used by Cruz except for the introduction of ionic modalities m_i. It is the familiar Debye-Hückel expression including a, the distance of closest approach of the ions.

$$G^{Ex}_{DH} = -\frac{e^2 N}{4\pi\epsilon_o D_s}\left(\sum_i N_i Z_i^2\right) K' f(K'a) \qquad (1)$$

with

$$K' = \left(\frac{2e^2 N I'}{\epsilon_o D_s k T}\right)^{1/2} = 1.59146 \times 10^{10} (I'/D_s T)^{1/2} \qquad (2)$$

and

$$f(x) = \left(\frac{x^2}{2} - x + \ln(1+x)\right) \Big/ x^3 \qquad (3)$$

The ionic strength I' is given by:

$$I' = \frac{1}{2}\left(\sum_i m_i Z_i^2\right) \Big/ \left(\frac{1}{\rho_S} + \sum_i m_i \bar{v}_i\right) \qquad (4)$$

where $\bar{v}_i$ is the ionic partial molar volume at infinite dilution.

A value of $4.10^{-10}\ m$ is assumed for the closest approach parameter a, so that:

$$K'a = 6.3658\ (I'/D_S T)^{1/2}$$

Debye-McAulay (DM) Contribution

The high dielectric constant of water is related to the orientational polarizability of water molecules. The electrical field near a small ion is strong enough to orient the surrounding water molecules; this dielectric saturation results in a reduction in the macroscopic dielectric constant D of the solution.

One of the limitations of the Debye-Hückel primitive model is that the variation of D with ionic concentration is ignored. As coulombic forces are inversely proportional to D, this variation is of no little importance to the departure from limiting law behavior.

The approximation can be attenuated to some extent by incorporating in G^E the net electrical work necessary to transfer the ions from a solvent of dielectric constant D_S to a solution of dielectric constant D.

According to Debye and McAulay, this leads to the following expression:

$$G_{\mathrm{DM}}^{Ex} = \frac{1}{4\pi\epsilon_o}\left(\frac{1}{D} - \frac{1}{D_s}\right)\frac{Ne^2}{2}\Sigma_i\frac{N_i z_i^2}{r_i} \tag{5}$$

As few dielectric constant data are available for intermediate and high concentrations, Cruz developed an empirical expression for D. Although this expression is appropriate to the treatment of very concentrated binary electrolyte solution data, it uses two adjustable parameters; moreover, an extension of the equation to mixtures would introduce one new adjustable parameter for each new species in solution.

We therefore chose to estimate the dielectric constant in a different way, after Pottel's (1973) expression:

$$D = D_S\frac{1 - w_c}{1 + w_{c/2}} \tag{6}$$

The term w_c is the volumetric fraction of dielectrically saturated cavities. In the present work, w_c is replaced by the variable Y, given by:

$$Y = \frac{4\pi}{3}N\Sigma_i m_i r_i^3/V_i \tag{7}$$

where V_i is the volume of solution per kg of solvent:

$$V_i = \frac{1}{\rho_S} + \Sigma_i m_i \bar{v}_i \tag{8}$$

We turn now to the determination of the values of the ionic radii r_i. In view of the empirical character of the Debye-McAulay contribution and of the lack of extensive data related to dielectric effects, there is some uncertainty as to which value is most appropriate for the effective ionic radius. Several trial calculations were made for that purpose.

Taking the ionic radii as adjustable parameters raises a problem of consistency between the values determined in different systems with a common ion. We finally preferred to use the Pauling (1940) radii, which are known for a large number of ions. Within the framework of the Born model for ionic hydration these values have been shown to compare favorably with more sophisticated sets of radii (Friedman and Krishnan, 1973). They were used by Scatchard (1936) in the Debye-McAulay term incorporated in his model for concentrated electrolyte solutions. In addition the adjusted radii that we obtained in a first attempt are closer to the Pauling values than to the cavity radii correlated by Cruz.

In the case of ions for which the Pauling radii are not available, we used the values $r_{\mathrm{NO_3}} = 2$ A and $r_{\mathrm{SO_4^{2-}}} = 2.4$ A calculated by Marcus (1983) from data of the average distances between the ions and the nearest water molecules. Average adjusted radii were used only for a few cations. In this way, the "electrostatic" contribution does not generally include any adjustable parameter for pure electrolytes as well as mixtures.

NRTL Contribution

In the NRTL model, the local mole fraction of species j in the immediate neighborhood of species i is defined by:

$$x_{ji} = \frac{x_j G_{ji}}{\Sigma_k x_k G_{ki}} \tag{9}$$

with

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{10}$$

$$\text{and } \tau_{ji} = g_{ji} - g_{ii} \tag{11}$$

The parameters g_{ji} are related to the energies of interaction between the species i and j; α_{ij} is a characteristic of the nonrandomness of the mixture, which throughout this work is taken equal to 0.2.

From this model (according to Cruz) a short-range contribution is developed on the basis of two assumptions:

1) Free ions are supposed to be mainly surrounded by solvent molecules, so that the local mole fractions of solvent around free ions are close to 1.

2) Ion pairs are counted as if they were undissociated molecules.

In the case of a mixture of ions and undissociated species in a solvent S, the corresponding expression for the excess Gibbs energy, with pure components as reference states, is given by:

$$\begin{aligned} G_{\mathrm{NRTL}}^{Ex}/RT = {} & \Sigma_a N_a \tau_{Sa} + \Sigma_c N_c \tau_{Sc} \\ & + \Sigma_n N_n \frac{N_S G_{S,n}\tau_{S,n} + \Sigma_{n'}, N_n, G_{n',n}\tau_{n',n}}{N_n + N_S G_{S,n} + \Sigma_{n'} N_{n'} G_{n',n}} \\ & + N_S(\Sigma_j N_j G_{jS}\tau_{jS}/\Sigma_k N_k G_{kS}) \end{aligned} \tag{12}$$

Where j and k include all the species in solution and n stands for the undissociated solutes.

Two binary parameters, A_{ca} and B_{ca}, are defined for each salt ca:

$$A_{ca} = G_{cS}\tau_{cS} + \frac{Z_c}{Z_a}G_{aS}\tau a_S \tag{13}$$

$$B_{ca} = G_{cS} + \frac{Z_c}{Z_a}G_{aS}$$

Other parameters, G_{ij} and τ_{ij}, are needed for the undissociated species. As an asymmetrical convention is assumed for the electrostatic contribution, the NRTL term must be normalized to the infinite dilution reference state for the ions:

$$\begin{aligned} G_{\mathrm{NRTL}}^{Ex*} = {} & G_{\mathrm{NRTL}}^{Ex} - RT\Sigma_a N_a \lim_{x_a \to 0}(\ln f_a^{\mathrm{NRTL}}) \\ & - RT\Sigma_c N_c \lim_{x_c \to 0}(\ln f_c^{\mathrm{NRTL}}) \end{aligned} \tag{14}$$

Combination of Eqs. 12, 13, and 14 yields:

$$\begin{aligned} G_{\mathrm{NRTL}}^{ex*}/RT = {} & \Sigma_n N_n \frac{(N_S G_{S,n}\tau_{S,n} + \Sigma_{n'} N_{n'} G_{n',n}\tau_{n',n})}{N_n + N_S G_{S,n} + \Sigma_{n'} G_{n',n} N_{n'}} \\ & + N_S \frac{[\Sigma_c N_c \Sigma_a N_a Z_a A_{ca} + (\Sigma_n N_n G_{n,S}\tau_{n,S})(\Sigma_a N_a Z_a)]}{[\Sigma_c N_c \Sigma_a N_a Z_a B_{ca} + (\Sigma_n N_n G_{n,S} + N_S)(\Sigma_a N_a Z_a)]} \\ & - \frac{\Sigma_c N_c(\Sigma_a N_a Z_a A_{ca})}{\Sigma_a N_a Z_a} \end{aligned} \tag{15}$$

In the case of strong electrolyte solutions, Eq. 15 reduces to an expression involving two binary parameters A_{ca} and B_{ca} for single-salt systems, and no additional adjustable parameter for mixed salts solutions.

DERIVED THERMODYNAMIC PROPERTIES

From Eqs. 1, 5, and 15, the activity coefficients on the mole fraction scale and the osmotic coefficient can be calculated according to:

$$\ln f_i = \frac{1}{RT}\left(\frac{\partial G^{Ex}}{\partial N_i}\right) T, P, N_j \neq i \tag{16}$$

$$\varphi = -\frac{1}{M_S \Sigma_i m_i}\ln(a_S) \tag{17}$$

TABLE 1. DATA TREATMENT USING PITZER'S MODEL

Results of fit for osmotic coefficients data of pure aqueous electrolytes.*

Aqueous Solutions of Salts at 25°C	Maximum Molality	$\beta^{(0)}$	$\beta^{(1)}$	Root Mean Square Deviation 100 $\sigma\varphi$
NaCl	6	0.08305	0.21900	0.3
NaBr	4	0.10164	0.25274	0.1
NaI	3.5	0.12549	0.31106	0.2
NaF	1	0.02147	0.20690	0.03
$NaNO_3$	6	0.00351	0.18642	0.15
KCl	4.8	0.04453	0.22839	0.1
KBr	5.5	0.04792	0.27445	0.3
KI	4.5	0.05708	0.34662	0.5
LiCl	6	0.16832	0.17721	0.8
LiBr	3	0.20243	0.06713	1.2
LiI	3	0.21024	0.36981	0.9
$LiNO_3$	3.5	0.12274	0.36821	0.4
RbCl	5	0.03934	0.17280	0.2
RbBr	5	0.03297	0.18897	0.2
RbI	5	0.03461	0.15964	0.2
KNO_3	3.5	−0.05771	−0.05759	0.4
C_SCl	6	0.03178	0.02762	0.2
NH_4Cl	6	0.03603	0.29619	0.7
NH_4NO_3	6	−0.01561	0.10898	0.1
$AgNO_3$	6	−0.05431	−0.21042	1.3
HCl	6	0.18029	0.27837	0.2
HBr	3	0.22156	0.23087	0.4
HI	3	0.23777	0.39920	0.2
HNO_3	3	0.11477	0.30437	0.1
$HClO_4$	6	0.21795	−0.00041	1.9
NaOH	6	0.10691	0.17653	1.3
KOH	6	0.14982	0.22070	0.3
$CaCl_2$	2.5	0.31231	1.64585	0.2
$CaBr_2$	6	0.40950	0.84275	6
CaI_2	2	0.43524	1.81137	0.1
$MgCl_2$	5	0.38110	1.21197	2
$MgBr_2$	5	0.45016	1.44995	1.4
MgI_2	5	0.53450	1.08454	3
$SrCl_2$	4	0.27967	1.72429	0.4
$BaCl_2$	1.8	0.21638	1.84591	0.8
$Pb(ClO_4)_2$	6	0.27386	2.71678	5
Na_2SO_4	4	0.04210	0.77712	1.4
$(NH_4)_2SO_4$	5.5	0.03369	0.74799	0.5
$AlCl_3$	1.8	0.70632	5.63756	1
$CrCl_3$	1.2	0.65169	6.14389	1.5

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* From Robinson and Stokes (1970).

For strong electrolytes in aqueous solution, the osmotic coefficient is then given by:

$$\varphi = -\frac{1}{M_S\Sigma_i m_i}\left[\frac{e^2M_SI'}{(4\pi\epsilon_oD_S)\rho_SkT}\frac{K'}{(aK')^3}\left[aK' + \frac{aK'}{1+aK'} - 2\ln(1+aK')\right] - \frac{3e^2M_S}{4kTV_i\rho_S}\frac{Y}{(1-Y)^2}\Sigma_i\frac{(m_iZ_i^2/r_i)}{4\pi\epsilon_oD_S} + \frac{S_1S_2}{(S_2+x_SS_3)^2} + \ln x_S\right] \quad (18)$$

with:

$$S_1 = \Sigma_c x_c \Sigma_a x_a Z_a A_{ca}$$
$$S_2 = \Sigma_c x_c \Sigma_a X_a Z_a B_{ca} \quad (19)$$
$$S_3 = \Sigma_a x_a Z_a$$

Molar fractions are calculated from the molalities by:

$$x_S = 1/(1 + M_S\Sigma_i m_i) \quad (20)$$

$$x_i = M_S m_i/(1 + M_S\Sigma_i m_i) \quad (21)$$

Equations for the activity coefficients and for the thermodynamic properties derived from the other models are given in appendices A and B, respectively.

REPRESENTATION OF OSMOTIC COEFFICIENTS

The best values of the parameters of the Pitzer model and of the modified Cruz model were evaluated by least-squares analysis of the same sets of data. The minimization was performed by using a Marquardt (1963) algorithm, which derives increments of parameters from derivatives of the objective function with respect to parameters. The following results were obtained for strong aqueous electrolytes at 25°C.

Single Electrolytes

Osmotic coefficients (Robinson and Stokes, 1970) were represented up to a maximum molality of 6 M (6 gmol/kg). For each model, the values of the adjusted parameters are given in Tables 1 to 3, together with the corresponding root mean square deviations between calculated and experimental values.

The results, as summarized in Table 4, show only slight differences in accuracy for the representation of the osmotic coefficients of 1-1 salts. As could be expected, for the other types of salts the departure of the calculated values from the experimental ones is

TABLE 2. DATA TREATMENT USING CHEN'S MODEL (ASPEN TECHNOLOGY, 1983)

Results of fit for osmotic coefficients data of pure aqueous electrolytes.*

Aqueous Solutions of Salts at 25°C	Maximum Molality	$\tau_{ca,S}$	$\tau_{s,ca}$	Root Mean Square Deviation 100 $\sigma\varphi$
NaCl	6	−4.5916	9.0234	1.2
NaBr	4	−4.6070	8.9288	0.6
NaI	3.5	−4.6920	8.9820	0.7
NaF	1	−3.7493	7.4322	0.02
$NaNO_3$	6	−3.6151	7.2886	0.2
KCl	4.8	−4.1341	8.1354	0.2
KBr	5.5	−4.1707	8.1699	0.3
KI	4.5	−4.1217	7.9408	0.2
LiCl	6	−5.1737	10.1242	2.4
$LiNO_3$	3.5	−4.6136	8.7565	0.4
$AgNO_3$	6	−3.1090	7.0619	0.7
KNO_3	3.5	−3.2747	7.2728	0.6
RbCl	5	−4.1358	8.2053	0.2
RbBr	5	−4.0399	8.0151	0.2
RbI	5	−4.0916	8.1419	0.1
C_sCl	6	−4.3726	8.4238	0.4
NH_4Cl	6	−4.0121	7.8599	0.07
NH_4NO_3	6	−3.3162	6.8739	0.5
HCl	6	−5.2286	10.1728	1.9
HBr	3	−5.2194	9.9746	0.8
HI	3	−5.2039	9.7714	1.0
HNO_3	3	−4.3663	8.7223	0.5
LiBr	6	−5.3628	10.5393	2.8
LiI	3	−5.0883	9.5925	1.5
$HClO_4$	6	−5.4365	10.7078	3.3
NaOH	6	−4.7893	9.4200	2.3
KOH	6	−5.0644	9.2928	1.5
$CaCl_2$	6	−5.2549	10.5126	9
$CaCl_2$	2.5	−4.8618	9.3732	2.5
$CaBr_2$	6	−5.4801	11.0038	13
CaI_2	2	−5.1151	9.7214	2.4
$MgCl_2$	5	−5.3583	10.6681	9
$MgBr_2$	5	−5.5307	10.9725	9
MgI_2	5	−5.7064	11.3459	11
$SrCl_2$	4	−4.9537	9.7230	5
$BaCl_2$	1.8	−4.2068	7.9145	1.2
$Pb(ClO_4)_2$	6	−5.1308	10.1330	7
Na_2SO_4	4	−3.8760	7.9756	2.2
$(NH_4)_2SO_4$	5.5	−3.7871	7.7870	0.8
$MgSO_4$	3	−4.1796	8.2533	5
$AlCl_3$	1.8	−5.2306	10.0495	6
$LaCl_3$	2	−4.8883	9.3370	5
$CrCl_3$	1.2	−4.7759	8.7991	3.5

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* From Robinson and Stokes (1970).

TABLE 3. DATA TREATMENT USING THE MODIFIED CRUZ MODEL

Results of fit for osmotic coefficients data of pure aqueous electrolytes.*

Aqueous Solutions of Salts at 25°C	Maximum Molality	A_{ca}	B_{ca}	Root Mean Square Deviation 100 $\sigma\varphi$
NaCl	6	0.23016	3.05076	1.3
NaBr	4	0.07797	2.96247	0.7
NaI	3.5	0.02438	0.07738	0.6
NaF	1	1.1255	5.4868	0.02
KCl	4.8	2.03016	3.26647	0.1
KBr	5.5	2.79278	2.34475	0.1
KI	4.5	6.08256	1.02254	0.1
RbCl	5	2.16878	4.01938	0.3
RbBr	5	3.25119	3.10891	0.3
RbI	5	3.59893	3.50919	0.4
CsCl	6	2.63938	4.95717	0.8
NH_4Cl	6	3.39937	1.91302	0.3
NH_4NO_3	6	7.13255	2.39371	0.6
$AgNO_3$	6	9.84835	2.69254	0.9
$NaNO_3$	6	7.42037	1.95750	0.7
KNO_3	3.5	7.12825	3.72880	0.6
LiCl	6	8.97235	2.18011	1.2**
LiBr	6	11.1051	2.16733	0.6**
LiI	3	34.5059	0.92233	1.2**
$LiNO_3$	3.5	111.34334	0.26675	0.2**
NaOH	6	−0.70824	1.04936	0.9
KOH	6	−7.72454	0.88336	0.9
HCl	6	4.80594	1.75371	0.2**
HBr	3	3.45188	3.30909	0.4**
HI	3	2.8658	0.58823	0.7**
HNO_3	3	31.22398	0.75900	0.3**
$HClO_4$	6	11.0948	3.23198	0.8**
$CaCl_2$	6	0.04106	261.36	5
	2.5	0.26690	29.9753	1.2
$CaBr_2$	6	−49.98650	0.29960	11.0
CaI_2	2	0.30039	19.5218	1.3
$MgCl_2$	5	0.79893	30.7017	1.8
$MgBr_2$	5	0.43744	57.6517	3
MgI_2	5	1.3067	42.5219	5
$MgCl_2$	5	7.48032	3.55276	1.4**
$MgBr_2$	5	7.17076	3.97271	1.1**
MgI_2	5	7.53911	7.44982	1.8**
$SrCl_2$	4	0.69452	18.5596	1
$BaCl_2$	1.8	5.05276	4.15855	1.2
$Pb(ClO_4)_2$	6	18.7132	1.68744	1.8
Na_2SO_4	4	18.11182	0.98301	1.2
$(NH_4)_2SO_4$	5	14.54094	1.22292	2.8
$MgSO_4$	3	689.0170	0.14052	1.4
$AlCl_3$	1.8	76.8883	1.71422	2.5
$LaCl_3$	2	738.447	0.00552	2
$CrCl_3$	1.2	2566.46	0.02783	2.5

* From Robinson and Stokes (1970).

** Results obtained by using weighted means of adjusted cationic radii (r^+_{Li} = 0.15 A; r^+_H = 0.19 A; r^{++}_{Mg} = 0.52 A).

larger, especially in the case of Chen's model. On the whole, the best fit is achieved with Pitzer's model.

Figures 1 and 2 illustrate, for the H_2O–HCl system, the various contributions to the osmotic coefficient derived from the two local composition models.

Especially noteworthy are the opposite trends of the NRTL contributions. The NRTL contribution derived from Chen's model is a short-range repulsive term. This is consistent with the cellular structure pictured by the model (Chen et al., 1982), where ions can be in the immediate neighborhood of ions of the opposite sign, so that in addition to ion solvent interactions, ionic repulsion is also taken into account. In contrast, the NRTL term used in the Cruz model is based on the assumption that the ions are mainly surrounded by solvent molecules. Although all short-range interactions are underlying this contribution, major importance is given to the ionic hydration, through ion solvent parameters, and the resulting term is an attractive one.

TABLE 4. SUMMARY OF RESULTS OF REPRESENTATION OF OSMOTIC COEFFICIENTS FOR SINGLE-SALT AQUEOUS SOLUTIONS AT 25°C

100 × Avg. Root Mean Square Deviation in φ.

Solutions		Pitzer's Model	Modified Cruz Model	Chen's Model
1-1 Salts	27 systems	0.5	0.6	0.9
Other salts	13 systems	1.8	2.4	5.5

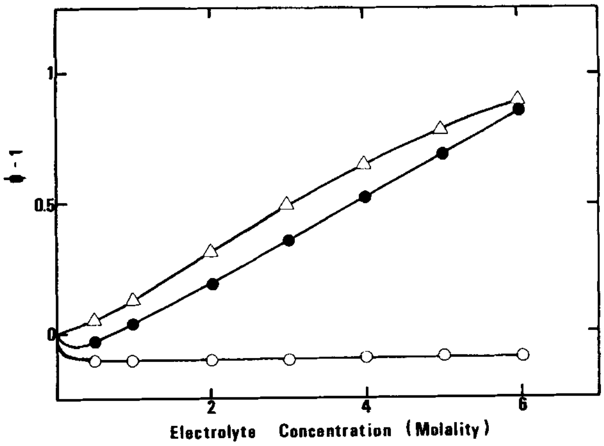

Figure 1. Contributions given by Chen's model to the osmotic coefficient for the system H_2O-HCl at 25°C.

- ● Experimental points
- ○ Debye-Hückel contribution
- △ NRTL contribution

Mixed Electrolytes

In order to test the predictivity of the models, the parameters fitted on pure electrolyte data were used to calculate the osmotic coefficients of 21 aqueous mixtures of two salts. The root mean square deviations between calculated and experimental values are given in Table 5. The osmotic coefficients of mixtures are best predicted by Pitzer's model. Both local composition models give reasonably good results showing an average accuracy of less than 2%. This further supports the idea discussed by Covington et al.

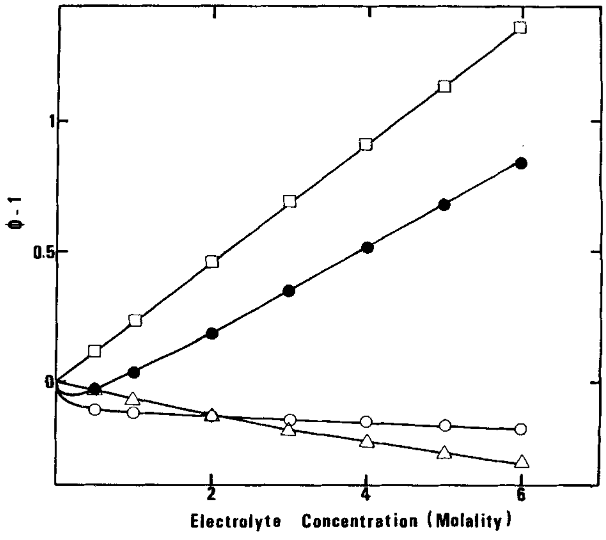

Figure 2. Contribution given by the modified Cruz model to the osmotic coefficient for the system H_2O-HCl at 25°C.

- ● Experimental points
- ○ Debye-Hückel contribution
- △ NRTL contribution
- □ Debye-McAulay contribution.

TABLE 5. RESULTS OF THE PREDICTION OF OSMOTIC COEFFICIENTS FOR MIXED ELECTROLYTES

Aqueous Solutions of Two Salts at 25°C	100 × Root Mean Square Deviation in φ			
	Pitzer	Chen	New Model	Ref.*
NaCl-KCl	1.8	0.8	1.6	a
NaCl-CsCl	2	1.1	3.4	b
NaBr-KBr	1.2	1.0	0.8	c
NaCl-NaBr	0.2	1.1	1.1	c
KCl-KBr	0.3	0.4	0.3	c
KCl-CsCl	0.4	0.3	0.3	d
NaCl-$MgCl_2$	1.5	4.4	1.2	e
KCl-$MgCl_2$	3	4.8	3.6	f
NaCl-$CaCl_2$	0.9	2.1	2.1	g
$CaCl_2$-$MgCl_2$	1	1.5	1.5	h
NaCl-$SrCl_2$	0.4	1.1	0.7	i
KCl-$SrCl_2$	5	4.3	4.2	j
NaCl-$BaCl_2$	0.5	0.8	0.7	k
KCl-$BaCl_2$	2	1.8	1.8	l
CsCl-$BaCl_2$	2.5	2.2	2.2	m
LiCl-$BaCl_2$	1.2	2.2	2.3	m
LiCl-NaCl	0.5	1.7	0.8	n
KCl-KNO_3	0.5	1.5	1.3	o
$NaNO_3$-KNO_3	1	1.2	0.4	o
NaCl-$NaNO_3$	0.8	2.0	2.0	o
KCl-$CaCl_2$	3	2.0	1.8	o
Mean Values of $\sigma\varphi$	1.4	1.8	1.9	

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

(1968) and Pitzer (Pitzer and Kim, 1974) that the main effects on mixing electrolytes arise from pure electrolyte properties.

DISCUSSION

Concerning the modified Cruz model, we must point out that the data treatment raises some difficulties. The parameters are generally strongly correlated; this often results in some uncertainty as to the best values of the parameters, and sometimes in the existence of multiple roots. This may be a typical feature of local composition models, but from a more general point of view, we may notice that in many models devoted to electrolyte solutions and using two adjustable parameters, the parameters are not independent. Pitzer has shown that such a trend existed between the parameters involved in the second virial coefficient of his equation and that it could be used to get rough estimates of activity coefficients, at least for 1-1 electrolytes.

In fact, the three models we have studied succeed in representing excess properties by using several contributions which somewhat compensate one another. This provides some flexibility, but on the other hand, as we are dealing with simple equations the effects of the various contributions overlap in an empirical manner.

So we feel that further studies on electrolyte solutions might succeed in developing a one-parameter model, valid up to a 6 M (6 gmol/kg) molality, provided that a more detailed picture of the physical interactions is used. This could be achieved by using a good representation of repulsive forces and a nonprimitive model, as proposed by Planche (1981).

APPENDIX A

Equations for Ionic Activity Coefficients Deduced from Modified Cruz Model

In the case of strong aqueous electrolytes, Eq. 16 leads to the following expressions of the ionic activity coefficients in mole fraction scale:

$$\begin{aligned}\ln f_a = \frac{e^2}{4\pi\epsilon_o D_s kT}\Bigg\{ & -\frac{Za^2}{2}\frac{K'}{(1+aK')} \\ & + \frac{\pi N}{V_i^2(1-Y)^2}(r_a^3 V_i - \bar{v}_a \Sigma_j m_j r_j^3) \ \sum_i (m_i Z_i^2/r_i) \\ & + \frac{Za^2}{2r_a}\left(\frac{D_S}{D}-1\right)\Bigg\} + \frac{\bar{v}_a}{8\pi N a^3}\Bigg\{aK' + \frac{aK'}{1+aK'} \\ & - 2\ln(1+aK')\Bigg\} + Z_a\{S_1[S_2^2 + 2X_S S_2 S_3 \\ & - X_s S_3^2(\Sigma_c X_c B_{ca})]/S_3/(S_2 + X_S S_3) \\ & - S_2 \Sigma_c X_c A_{ca}\}/S_3/(S_2 + X_S S_3) \qquad \text{(A1)}\end{aligned}$$

$$\begin{aligned}\ln f_c = \frac{e^2}{4\pi\epsilon_o D_S kT}\Bigg[& -\frac{Zc^2 K'}{2(1+aK')} \\ & + \frac{\pi N}{V_i^2(1-Y)^2}(r_c^3 V_i - \bar{v}_c \Sigma_j m_j r_j^3) \Big/ \sum_i (m_i Z_i^2/Z_i) \\ & + \frac{Zc^2}{2r_c}\left(\frac{D_S}{D}-1\right)\Bigg] + \frac{v_c}{8\pi N a^3} \\ & \times\left[aK' + \frac{aK'}{1+aK'} - 2\ln(1+aK')\right] \\ & - [X_S S_1(\Sigma_a X_a Z_a B_{ca})/(S_2 + X_S S_3) \\ & + S_2(\Sigma_a X_a Z_a A_{ca})/S_3]/(S_2 + X_S S_3) \qquad \text{(A2)}\end{aligned}$$

From these equations, the ionic activity coefficients in the molality scale, γ_i, can be calculated according to

$$\gamma_i = f_i/(1 + M_S \Sigma_i m_i) \qquad \text{(A3)}$$

APPENDIX B

Equations of Pitzer's Model

The excess Gibbs energy of a multicomponent system is given by:

$$\begin{aligned}\frac{G^{Em}}{m_S RT} = f^\varphi & + 2\Sigma_c\Sigma_a m_c m_a[B_{ca}^\varphi + (\Sigma mZ)C_{ca}^\varphi] \\ & + \Sigma_c\Sigma_{c'} m_c m_{c'}[\theta_{cc'} + \Sigma_a m_a \psi_{cc'a}/2] \\ & + \Sigma_a\Sigma_{a'} m_a m_{a'}[\theta_{aa'} + \Sigma_c m_c \psi_{caa'}/2] \qquad \text{(B1)}\end{aligned}$$

and the osmotic coefficient by:

$$\begin{aligned}\varphi - 1 = (\Sigma_i m_i)^{-1}\Bigg\{ & 2If^\varphi + 2\Sigma_c\Sigma_a m_c m_a\left[B_{ca}^\varphi + \frac{\Sigma mZ}{(Z_c Z_a)^{1/2}}C_{ca}^\varphi\right] \\ & + \Sigma_c\Sigma_{c'} m_c m_{c'}[\theta_{cc'} + I\theta_{cc'} + \Sigma_a m_a \psi_{cc'a}] \\ & + \Sigma_a\Sigma_{a'} m_a m_{a'}[\theta_{aa'} + I\theta_{aa'} + \Sigma_c m_c \psi_{caa'}]\Bigg\} \qquad \text{(B2)}\end{aligned}$$

with:

$$f^\varphi = -A^\varphi I^{1/2}/(1 + 1,2I^{1/2}) \qquad \text{(B3)}$$

$$A^\varphi = \tfrac{1}{3}(2\pi N \rho_S/1000)^{1/2}(e^2/DkT)^{3/2} \qquad \text{(B4)}$$

$$B_{ca}^\varphi = \beta_{ca}^{(0)} + \beta^{(1)}\exp(-\alpha I^{1/2}) \qquad \text{(B5)}$$

or, in the case of 2–2 electrolytes:

$$B_{ca}^\varphi = \beta_{ca}^{(0)} + \beta^{(1)}\exp(-\alpha_1 I^{1/2}) + \beta^{(2)}\exp(-\alpha_2 I^{1/2}) \qquad \text{(B6)}$$

In this work only the parameters $\beta^{(0)}$ and $\beta^{(1)}$ were used.

Equations of Chen's Model

Assuming specific ion interaction and local electroneutrality around solvent molecules, the following expression is obtained by Chen for the molar excess Gibbs energy:

$$\begin{aligned} G^{Ex}/RT = &-(\Sigma_k X_k)(1/M_S)^{1/2}(4A\phi I_x/\rho)\ln(1+\rho I_x^{1/2}) \\ &+ x_S(\Sigma_j x_{jS}\tau_{jS}) + \Sigma_c X_c Z_c[\Sigma_{a'}X_{a'}Z_{a'}(\Sigma_j X_{jc}\tau_{jc,a'c})/\Sigma_{a''}X_{a''}Z_{a''}] \\ &+ \Sigma_a X_a Z_a[\Sigma_{c'}X_{c'}Z_{c'}(\Sigma_j X_{ja}\tau_{ja,c'a})/\Sigma_{c''}X_{c''}Z_{c''}] \\ &- \Sigma_a X_a Z_a \Sigma_{c'}X_{c'}Z_{c'}\tau_{Sa,c'a}/\Sigma_{c''}X_{c''}Z_{c''} \\ &- \Sigma_a X_a Z_a G_{As}\tau_{aS} - \Sigma_c X_c Z_c \Sigma_{a'}X_{a'}Z_{a'}\tau_{Sc,ac'}/\Sigma_{a''}X_{a''}Z_{a''} \\ &- \Sigma_c X_c Z_c G_{cS}\tau_{cS} \end{aligned} \quad \text{(B7)}$$

where $$I_x = (\tfrac{1}{2})\Sigma_i x_i Z_i^2 \quad \text{(B8)}$$

ρ is here the closest approach parameter, set equal to 14.9.

The local mole fraction of the species surrounding the species i is assumed to satisfy the relation:

$$X_{ji}/X_{ii} = (X_j Z_j/X_i Z_i)G_{ji}$$

There are two adjustable parameters, $\tau_{Ca,S}$ and $\tau_{S,Ca}$, for binary systems related to the basic NRTL parameters by:

$$\tau_{ca,S} = \tau_{aS} = \tau_{cS}$$

$$\tau_{S,ca} = \tau_{Sc} - \tau_{ac} = \tau_{sa} - \tau_{ca} \quad \text{(B9)}$$

For multicomponent systems, one additional type of adjustable parameter, $\tau_{ca,c'a}$, is needed. The other parameters, τ^*_{cS}, τ^*_{aS}, $\tau^*_{Sa,ca}$ and $\tau^*_{Sc,ca}$, calculated using

$$\exp(-0.2\tau^*_{cS}) = \Sigma_a X_a Z_a G_{ca,S}/\Sigma_{a'}X_{a'}Z_{a'}$$

$$\exp(-0.2\tau^*_{aS}) = \Sigma_c X_c Z_c G_{ca,S}/\Sigma_{c'}X_{c'}Z_{c'} \quad \text{(B10)}$$

$$\tau^*_{Sa,ca} = \tau^*_{aS} - \tau_{ca,S} + \tau_{S,ca}$$

$$\tau^*_{Sc,ca} = \tau^*_{cS} - \tau_{ca,S} + \tau_{S,ca} \quad \text{(B11)}$$

with: $$G_{ca,S} = \exp(-0.2\tau_{ca,S}) \quad \text{(B12)}$$

The osmotic coefficient is then given by:

$$\begin{aligned} \varphi = -\frac{1}{M_S \Sigma_i m_i}\Bigg\{ &\ln x_S + 2\left(\frac{1}{M_S}\right)^{1/2} A\phi I_x^{3/2}/(1+\rho I_x^{1/2}) \\ &+ \Sigma_j (G_{jS}X_j Z_j \tau_{jS})/\Sigma_j(G_{js}X_j Z_j) \\ &- X_S \Sigma_j (G_{jS}X_j Z_j \tau_{jS})/(\Sigma_j G_{jS}X_j Z_j)^2 \\ &+ \Sigma_c Z_c \Sigma_{a'}X_{a'}Z_{a'}[X_c G_{Sc,a'c}(\tau_{Sc,a'c} - \Sigma_k G_{kc,a'c}X_k \\ &\times Z_k \tau_{kc,a'c}/\Sigma_j G_{jc,a'c}X_j Z_j)/\Sigma_j G_{jc,a'c}X_j Z_j]/\Sigma_{a''}X_{a''}Z_{a''} \\ &+ \Sigma_a Z_a \Sigma_{c'}X_{c'}Z_{c'}[X_a G_{Sa,c'a}(\tau_{Sa,c'a} - \Sigma_k G_{ka,c'a}X_k \\ &\times Z_k \tau_{ka,c'a}/\Sigma_j G_{ja,c'a}X_j Z_j/\Sigma_j G_{ja,c'a}X_j Z_j]/\Sigma_{c''}X_{c''}Z_{c''}\Bigg\} \end{aligned} \quad \text{(B13)}$$

with $G_{ji,ki} = \exp(-\alpha\tau_{ji,ki})$.

NOTATION

a = distance of closest approach of opposite ions, m
a_S = activity of solvent
A_{ca}, B_{ca} = binary parameters for the modified Cruz equation
A^ϕ = Debye-Hückel constant for the osmotic coefficient
B^ϕ = second virial coefficient for pure electrolytes in Eq. B1
C^ϕ = third virial coefficient for pure electrolytes in Eq. B1
D = dielectric constant of the solution
D_S = dielectric constant of pure liquid solvent
e = electron charge, 1.6021×10^{-19}C
f = activity coefficient in mole fraction scale
G^{Ex} = excess Gibbs energy in mole fraction scale
G^{Em} = excess Gibbs energy in molality scale
G_{ij} = NRTL parameter ($= e^{-\alpha\tau ij}$)
I_x = ionic strength in mole fraction scale
I' = ionic strength used in modified Cruz model $[\tfrac{1}{2}(\Sigma_i m_i Z_i^2)/(1/\rho_S + \Sigma_i m_i \bar{v}_i)]$
k = Boltzmann constant, 1.38054×10^{-23} J·K^{-1}·mol^{-1}
K' = reciprocal Debye length, m^{-1}
m_i = molality of solute i, mol/kg of solvent
M_S = molecular weight of solvent, kg·mol^{-1}
N = Avogadro's number, 6.02252×10^{23} molecule·mol^{-1}
N_i = number of moles of species i
r_i = ionic radius, m
T = absolute temperature, K
$\bar{v}_i$ = ionic partial molar volume, L/mol
V_i = volume of solution per kg of solvent, m^3
w_c = volumetric fraction of dielectrically saturated cavities
x_i = liquid phase mole fraction of species i
Y = variable defined by Eq. 7
z_i = absolute value of ionic charge

Greek Letters

α = NRTL nonrandomness factor
β^0, β^1 = binary parameters of Pitzer's model
γ = activity coefficient in molality scale
ϵ_o = electric permittivity of free space, 8.854 10^{-12} F/m
θ = binary ion–ion difference parameter of the Pitzer equation
ρ = closest approach parameter in Eq. B7
ρ_S = density of pure solvent (kg/m^3)
σ = root mean square deviation
τ_{ij} = NRTL parameter
φ = osmotic coefficient
ψ = ternary ion–ion difference parameter of the Pitzer equation

Superscripts

$*$ = asymmetrical convention or parameters of Chen's equation for multicomponent systems
m = molality scale
x = mole fraction scale

Subscripts

a, a', a'' = anion
c, c', c'' = cation
i, j, k = solute
n = undissociated solute
S = solvent

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Manuscript received July 9, 1982; revision received Jan. 31, 1984, and accepted Feb. 4.