Modification and application of the mean spherical approximation method

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ABSTRACT

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The mean spherical approximation (MSA) method is improved by the introduction of the
effective diameter of the cation. The dependence of the ionic strength on the effective
diameters is mainly attributed to the solvation effect. This modified model has been used to
correlate the mean ionic activity coefficients for 85 single-electrolyte solutions. The results
show that the modified MSA gives smaller deviations than the original MSA and Pitzer
models. The modified MSA was also applied to calculate 32 mixed-electrolyte solutions
without any mixing parameters. The calculated results indicate that the modified MSA can
be used to calculate the mixture properties in terms of the parameters of single-electrolyte
solutions. Furthermore, the mean ionic activity coefficients of some single-electrolyte solu-
tions can be calculated for other temperatures by using the parameters obtained at 298.15 K.

INTRODUCTION

In recent years, increasing attention has been paid to the thermodynamics
of aqueous electrolyte solutions. For calculation of activity coefficients and
osmotic coefficients in single-electrolyte solutions, the Pitzer model (1973) is
used most widely because it has mathematical flexibility and high accuracy,
and many parameters have been given in the literature. But because of the
complex relationship between the parameters and temperature, it is difficult
to use this model to predict the properties over a wide temperature range.
For mixed-electrolyte solutions, the Pitzer model requires some additional
mixing parameters and such parameters are rarely available in the literature.

Based on statistical mechanics, the Ornstein–Zernicke (O–Z) integral
equation can be solved under some simplified conditions. Although it is not
as accurate as the hypernetted chain or even the Perkus–Yevick approxima-

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tion, the mean spherical approximation (MSA) is the method used to obtain the analytical solution of the radial distribution function of particles in fluids and fluid mixtures. The thermodynamic properties obtained from the MSA are in good agreement with results obtained from the Monte Carlo simulation. Many papers have been published in this field. Waisman and Lebowitz (1972) obtained an energy expression for an ionic fluid of equal sized 1:1 ions in the primitive model. Blum and Hoye (Blum and Hoye, 1977; Hoye and Blum, 1978) reported an expression for the excess free energy and activity coefficients of ionic mixtures. They applied this expression to electrolyte solutions of concentration less than 2 m (Triolo et al., 1978). Planche and co-workers (Planche and Renon, 1981; Ball et al., 1985) applied the MSA with a non-primitive model to calculate the osmotic coefficients of single- and mixed-electrolyte solutions, the ion strengths of which were below 6 m; however, the results are not as good as those obtained using the Pitzer equation. Landis (1985) and Gering et al. (1989) used the EXP-MSA to calculate the osmotic coefficients of electrolyte solutions of high concentration for some electrolyte systems. In order to apply the MSA to electrolyte solutions at high concentrations and to predict the thermodynamic properties of mixed-electrolyte solutions, both at 298.15 K and at other temperatures, using the parameters of single-electrolyte solutions obtained at 298.15 K, the authors have improved the MSA method and applied the modified MSA to the electrolyte solutions.

MSA AND ITS MODIFICATION

The basic assumption of the primitive model of the MSA method for electrolyte solutions is

$$
\begin{cases}
g_{ij}(r) = 0 & r < \sigma_{ij} \\
C_{ij}(r) = -Z_i Z_j e^2 / DkTr & r > \sigma_{ij}
\end{cases}
\tag{1}
$$

where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. From this equation, we can solve the O–Z equation by using the Fourier transformation and obtain the radial distribution function and the expression for the other thermodynamic properties. The expression for the activity coefficients is the sum of an electrostatic term and a hard-sphere term:

$$
\ln \gamma = \ln \gamma^{\text{elec}} + \ln \gamma^{\text{hs}}
\tag{2}
$$

The first term in eqn. (2) is the electrostatic contribution to the activity coefficient (Blum and Hoye, 1977)

$$
\ln \gamma_i^{\text{elec}} = \frac{Z_i e^2 M_i}{DkT} - \frac{P_n \sigma_i}{4\Delta} \left(\Gamma a_i + \frac{\pi}{12\Delta} \alpha^2 P_n \sigma_i^2 \right)
\tag{3}
$$

where

$$\alpha^2 = 4\pi_e^2 / DkT$$

$$\xi_n = \frac{\pi}{6} \sum_{k=1}^{N} \rho_k \sigma_k^n \quad (n = 0, 1, 2, 3)$$

$$\Delta = 1 - \xi_3$$

$$P_n = \frac{1}{\Omega} \sum_{k=1}^{N} \frac{\rho_k \sigma_k Z_k}{1 + \Gamma \sigma_k}$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_{k=1}^{N} \frac{\rho_k \sigma_k^3}{1 + \Gamma \sigma_k}$$

$$a_i = \frac{\alpha^2 \left[Z_i - \left(\frac{\pi}{2\Delta} \right) \sigma_i^2 P_n \right]}{2\Gamma(1 + \Gamma \sigma_i)}$$

$$M_i = \left(\frac{2\Gamma a_i}{\alpha^2} - Z_i \right) / \sigma_i$$

The shielding parameter Γ can be obtained from

$$4\Gamma^2 = \alpha^2 \sum_{k=1}^{N} \rho_k \left[\frac{Z_k - (\pi/2\Delta)\sigma_i^2 P_n}{1 + \Gamma \sigma_k} \right]^2 \tag{4}$$

Equation (4) can be solved by a simple iterative procedure. The initial value of Γ is $\Gamma = K/2$ or $\Gamma = K/6$, where

$$K = \alpha \left(\sum_{k=1}^{N} \rho_k^2 Z_k \right)^{1/2}$$

The hard-sphere contribution to eqn. (2) can be obtained from the equation of state for a mixture of hard spheres, reported by Boublik (1970) and Mansoori et al. (1971). The expression for $\ln \gamma_i^{hs}$ is

$$\ln \gamma_i^{hs} = -\ln \Delta + \frac{\pi P^{hs} \sigma_i^3}{6kT} + E + 3F^2 G - F^3 H \tag{5}$$

where

$$E = \frac{3\xi_2 \sigma_i + 3\xi_i \sigma_i^2}{\Delta} + \frac{9\xi_2^2 \sigma_i^2}{2\Delta^2}$$

$$F = \frac{\xi_2 \sigma_i}{\xi_3}$$

$$G = \ln \Delta + \frac{\xi_3}{\Delta} - \frac{\xi_3^2}{2\Delta^2}$$

$$H = 2\ln \Delta + \frac{\xi_3(2 - \xi_3)}{\Delta}$$

$$P^{hs} = \frac{6kT}{\pi} \left[\frac{\xi_0}{\Delta} + \frac{3\xi_1 \xi_2}{\Delta^2} + \frac{\xi_2^3(3 - \xi_3)}{\Delta^3} \right] \tag{6}$$

Equations (2)–(6) can be used to calculate the activity coefficients. In the primitive MSA, the anion diameters are kept constant, and only the cation diameters are adjustable. The agreement between the calculated and experimental results is good only at low concentration. The difference between the calculated and experimental results becomes apparent when the salt concentration is high. In fact, the cation diameter as used in the primitive MSA was not the diameter of a lone ion but the diameter of a hydrated ion. The hydration of anions is weak and can therefore be neglected; however, the hydration of cations is strong and the hydration layer must be included in the effective diameter of the cation used in the calculation. Because the thickness of the hydration layer decreases as the ion strength increases, the diameter of cations in the MSA should decrease with increasing ionic strength.

Triolo et al. (1978) obtained an expression in which two parameters are included. This expression shows that the hard-core diameter decreases with increasing concentration. Their expression gives good results in the concentration range 0.2–2.0 M, Gering et al. (1989) and Corti (1987) gave the curves of the best-fit diameters of Li^+, Na^+, H^+ and Ca^{2+} as functions of concentration.

If we assume that the hydration of the cation is proportional to the electrostatic potential ψ in the solution, and λ is twice the thickness of the hydration layer of a cation, we have

$$\frac{\lambda}{\lambda_1} = \frac{\psi(a)}{\psi_0(a)} \qquad (7)$$

where λ_1 is twice the thickness of the hydration layer of the cation at infinite dilution. The electrostatic potential in the solution can be calculated by the Debye–Hückel theory using the ionic atmosphere approach.

The diameter of the hydrated cation in solution is

$$\sigma_+ = \sigma_{P+} + \lambda$$

$$= \sigma_{P+} + \lambda_1/(1 + Ka) \qquad (8)$$

where σ_{P+} is Pauling's diameter. If we take a, the distance between cation centres, as approximately equal to unity, and $I^{1/2}$ is substituted for K, eqn. (8) becomes

$$\sigma_+ = \sigma_{P+} + \lambda_1/(1 + I^{1/2}) \qquad (9)$$

Assuming $\sigma_0 = \sigma_{P+} + \lambda_1$, then

$$\sigma_+ = \sigma_0 - \frac{\lambda_1 I^{1/2}}{1 + I^{1/2}} \qquad (10)$$

where σ_0 is the hydration diameter of the cation at infinite dilution. Considering the polarization of the ions and the soft-sphere effect, we obtain the equation for the effective diameter of the cation:

$$\sigma_+ = \sigma_0 - \lambda_1 \frac{I^{1/2}}{1 + I^{1/2}} - \lambda_2 I^2 \tag{11}$$

where λ_2 is the empirical parameter for the ion polarization and the soft-sphere effect, which is only present at high concentrations.

To calculate the mean ionic activity coefficients in mixed-electrolyte solutions, we make the following assumptions. (1) The effective diameter of a cation depends only on the species of anions and the concentration of the cation itself. Here the interaction between the cations is neglected. (2) When there is more than one kind of anion in the solution, the effect of each species of anion on the effective diameter of the cation is proportional to the concentration of the anions. Here the interaction between anions is neglected.

If only one kind of anion exists in the mixed-electrolyte solution, according to assumptions (1), the effective diameter of a cation can be calculated from the equation

$$\sigma_M = \sigma_0 - \lambda_1 \left(\frac{I_{MA}^{1/2}}{1 + I_{MA}^{1/2}} \right) - \lambda_2 I_{MA}^2 \tag{12}$$

where σ_0, λ_1 and λ_2 are the same as the effective diameter parameters of the cations and I_{MA} is the total ionic strength of electrolyte MA in the mixed-electrolyte solution

$$I_{MA} = \frac{1}{2} (m_M Z_M^2 + m_A Z_A^2) \tag{13}$$

where m_M and m_A are the total molalities of ions M and A in the solution respectively.

If there are many different anions in the solution, according to assumption (2) the effective diameter of cation M can be obtained from a linear mixing rule

$$\sigma_{M(mix)} = \sum_{j=1} \sigma_{M(A_j)} X_{A_j} \tag{14}$$

where

$$X_{A_j} = m_{A_j} / \sum_j m_{A_j} \tag{15}$$

Applying eqns. (12)–(15), the effective diameter of any cation in any mixed-electrolyte solution can be calculated.

CALCULATION

In the calculation, the dielectric constant of water is calculated from the Malmberg and Maryott equation (1956):

$$D_{H_2O} = 87.74 - 4.0008 \times 10^{-1}t + 9.398 \times 10^{-4}t^2 - 1.41 \times 10^{-6}t^3 \qquad (16)$$

where $t = T - 298.15$.

The activity coefficient obtained from eqns. (2)–(6) is in the McMillan–Mayer (MM) reference state. It can be changed to that in the Lewis–Randall (LR) reference state using the equation of Pailthorpe et al. (1984):

$$\ln \gamma_{\pm}^{LR} = \ln \gamma_{\pm}^{MM} - \Pi V_{\pm}/RT \qquad (17)$$

where Π is the osmotic pressure, $\Pi = RTvmM_a\phi^{MM}/1000V_a$. The osmotic coefficient can be calculated from

$$\phi = 1 + \frac{1}{m} \int_0^m m \, \mathrm{d} \ln \gamma_{\pm} \qquad (18)$$

The mean partial molar volume of the ions $V_{\pm}$, and the molar volume of water, V_a, are calculated from the density of the electrolyte solution. The density of the electrolyte solution can be expressed by the equation of Novotuy and Sohnel (1988):

$$d(c, T) = d_{H_2O}(T) + (A + B + CT^2)c + (D + ET + FT^2)c^{3/2} \qquad (19)$$

For a given electrolyte, A, B, C, D, E and F in eqn. (19) are constants. The density of water is

$$d_{H_2O} = 999.65 + 2.0438 \times 10^{-1}t - 6.174 \times 10^{-2}t^{3/2} \qquad (20)$$

The osmotic pressure of the mixed-electrolyte solutions can be solved from the mean ionic activity coefficients of electrolytes using the Gibbs–Duhem equation. An integral is needed in this method and the calculation is complicated. Therefore we propose a simple approach to the calculation of the osmotic coefficients in mixed-electrolyte solutions according to the ionic strength fraction y_i:

$$\phi_{mix}(I, T) = \sum_{i=1} \phi_i(I, T)y_i \qquad (21)$$

where $\phi_i(I, T)$ is the osmotic coefficient of the single-electrolyte solution at temperature T and ionic strength I. Using eqn. (21) to calculate the osmotic coefficient for the transformation of the reference state, the mean ionic activity coefficients obtained are close to those obtained from the Gibbs–Duhem equation: the deviation is less than 0.5%.

Because literature data for the density of mixed-electrolyte solutions are scarce, we use an ionic strength average from the densities of the corresponding single-electrolyte solutions:

$$d_{mix}(I, T) = \sum_{i=1} d_i(I, T)y_i \qquad (22)$$

TABLE 1

Diameters of some anions

Ion	σ (nm)	Ion	σ (nm)	Ion	σ (nm)
F^-	0.272	NO_3^-	0.230	BrO_3^-	0.342
Cl^-	0.362	ClO_4^-	0.352	NO_2^-	0.215
Br^-	0.390	SO_4^{2-}	0.285	OH^-	0.360
I^-	0.432	ClO_3^-	0.323	CH_3COO^-	0.502

where $d_i(I, T)$ is the density of the single electrolyte i at ionic strength I and temperature T.

The partial molar volume of electrolyte i in the mixed-electrolyte solution is

$$V_i = \left(\frac{\partial V}{\partial m_i}\right)_{P,T,m_l=j} \tag{23}$$

where

$$V = \left(\sum_i m_i M_i + 1000\right)/d_{mix} \tag{24}$$

and the partial volume of the solvent is

$$V_a = \frac{M_a}{1000}\left(V - \sum_{i=A,B} m_i V_i\right) \tag{25}$$

In the calculation, the anion diameters are kept constant. The diameters of some anions are listed in Table 1. The diameters of the halide anions are Pauling diameters; the others are regressed by the authors because there are no uniform diameter values for these ions in the literature. The effective diameters of the cations are calculated using eqn. (11). There are three adjustable parameters for a single electrolyte. They can be obtained by regression of the mean ionic activity coefficient data.

RESULTS AND DISCUSSION

Figure 1 shows the ionic strength dependence of σ_{Na^+} in NaCl, NaNO$_3$ and NaCl + NaNO$_3$ solutions (in which the mole ratio of each salt is 1:1) and of σ_{Li^+} in LiCl solution. It shows that the effective cationic diameters decrease sharply with ionic strength when the latter is below 1 m. When the ionic strength is high, the effective cationic diameters may decrease continuously or increase slightly depending on the value of λ_2. Figure 1 also shows that σ_{Na^+} in NaCl + NaNO$_3$ solutions falls between the diameters of Na$^+$ in the corresponding single-electrolyte solutions.
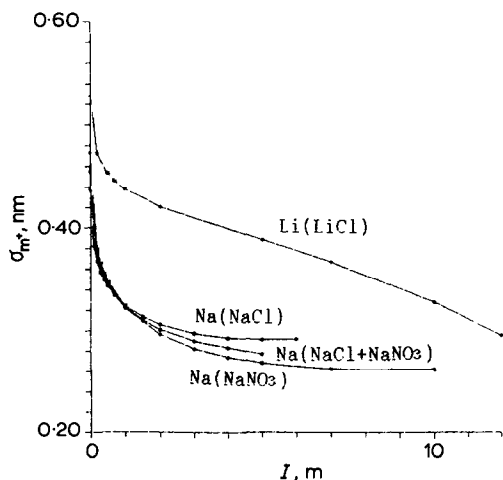
Fig. 1. Effective diameters of Na^+ in NaCl, $NaNO_3$, $NaCl + NaNO_3$ and of Li^+ in LiCl aqueous solutions.

Assuming the electrolytes are completely ionized, we have correlated the data of 85 single-electrolyte solutions, including 1:1, 1:2, 2:1, 3:1 and 2:2 types of electrolyte. The data source of the mean ionic activity coefficients of electrolytes is the same as in the paper of Kim and Frederick (1988).

The parameters of the effective diameters of cations, the average relative deviations of the correlated mean activity coefficients of ions and the maximum molal concentrations are listed in Tables 2–4. These tables show that the average relative deviation of the mean ionic activity coefficients calculated from the modified MSA model are mostly less than 1%. For electrolytes in high concentrations, the average relative deviations are less than 2%, except for LiCl.

The modified MSA model has been compared with the original MSA and Pitzer models. The results of the original MSA were calculated by the authors using adjusted cationic diameters that did not vary with concentration. The results of the Pitzer model were calculated by the authors, but the parameters for this model were obtained from Kim and Frederick (1988). The calculated results are also listed in Tables 2–4. From these tables it can be seen that the precision of our model is the best. The deviation of the original MSA model is 11 times larger than that of the modified MSA model. This indicates that our improvement is successful. The deviation of the Pitzer model is larger than that of our model by a factor of 4 for 1:1 electrolytes, by a factor of 2 for 3:1 and 2:2 electrolytes and by a factor of 1 for 1:2 and 2:1 electrolytes.

Figures 2 and 3 give the correlated results of these three models for LiBr and $CaCl_2$ solutions; the deviations between the original MSA model and the experimental data are very large. When the concentration of electrolyte

TABLE 2

The effective diameter parameters of the cations and the relative deviations in $\gamma_\pm$ calculated from the original MSA, the Pitzer model and the present work for 1:1 electrolytes at 298.15 K

Salt	Parameter (nm)			m_{max}	Average relative deviation (%)		
	$\sigma_0 \times 10$	$\lambda_1 \times 10$	$\lambda_2 \times 10^4$		Original MSA	Pitzer	Present work
LiCl	5.281	1.789	1.547	19.2	28.34	10.08	2.12
LiBr	4.710	0.702	1.216	20.0	29.50	9.63	0.94
LiI	6.570	3.740	−17.738	3.0	3.45	3.80	0.29
LiNO$_3$	7.029	3.388	0.498	20.0	22.77	10.76	1.04
LiClO$_3$	5.396	1.104	7.122	4.2	3.67	0.32	0.20
LiClO$_4$	6.561	2.388	0.239	4.5	4.94	2.28	0.15
NaF	4.528	3.603	–	1.0	0.82	0.26	0.09
NaCl	4.371	2.266	−4.189	6.1	2.11	0.68	0.16
NaBr	4.008	1.297	0.058	9.0	3.14	3.14	0.48
NaI	4.069	1.184	0.472	12.0	4.73	2.46	0.84
NaNO$_3$	4.732	3.030	−1.929	10.8	2.96	0.35	0.20
NaNO$_2$	4.788	1.754	7.320	12.3	4.14	1.67	0.80
NaClO$_3$	4.601	3.066	−2.497	3.0	1.92	0.28	0.15
NaClO$_4$	4.665	2.468	−5.038	6.0	2.22	3.00	0.07
NaBrO$_3$	3.678	3.076	–	2.6	1.61	0.66	0.22
NaOH	3.899	1.564	−1.720	10.0	1.72	1.50	0.50
CH$_3$COONa	4.212	2.510	14.709	3.5	1.54	0.45	0.37
KF	3.835	0.235	0.585	17.5	5.97	4.40	1.30
KCl	3.657	1.907	–	5.0	2.00	0.56	0.27
KBr	3.692	2.022	–	5.5	2.25	0.45	0.21
KI	4.042	2.579	2.980	4.5	2.83	0.22	0.14
KNO$_3$	3.292	4.226	−4.742	3.5	2.60	0.46	0.13
KNO$_2$	3.596	1.039	0.055	34.1	3.38	1.46	0.37
KClO$_3$	3.801	5.674	–	0.7	0.86	0.15	0.10
KBrO$_3$	3.537	5.885	–	0.5	0.64	0.24	0.09
KOH	4.883	1.716	0.842	20.0	19.86	2.54	1.41
RbCl	2.915	0.905	–	7.8	0.61	0.52	0.28
RbBr	2.956	1.520	–	5.0	1.47	0.27	0.12
RbNO$_3$	2.743	3.542	−6.003	4.5	2.65	1.44	0.14
CsF	5.933	2.314	2.772	3.5	2.92	3.64	0.16
CsCl	1.809	–	–	5.0	0.33	0.75	0.33
CsBr	1.718	–	–	5.0	0.52	0.82	0.52
CsNO$_3$	2.495	3.206	–	1.5	1.07	0.53	0.22
HCl	5.555	1.928	2.788	9.0	9.83	2.38	0.13
HBr	5.524	1.537	2.685	9.0	10.54	5.23	0.25
HI	6.427	2.902	1.966	10.0	17.02	4.36	0.64
HNO$_3$	6.95	3.559	0.257	15.0	14.26	4.71	0.31
HClO$_4$	5.306	0.575	0.807	16.0	16.25	11.89	1.01
NH$_4$Cl	3.857	2.038	1.347	7.4	3.09	0.90	0.13
NH$_4$NO$_3$	3.428	1.704	−0.535	26.0	2.61	3.37	0.84
NH$_4$I	4.162	3.035	0.485	7.5	5.14	1.27	0.14
Total averge relative deviation					6.06	2.46	0.44

TABLE 3

The effective diameter parameters of the cations and the relative deviations in $\gamma_{\pm}$ calculated from the original MSA, the Pitzer model and the present work for 1:2 and 2:1 electrolytes at 298.15 K

Salt	Parameter (nm)			m_{max}	Average relative deviation (%)		
	$\sigma_0 \times 10$	$\lambda_1 \times 10$	$\lambda_2 \times 10^4$		Original MSA	Pitzer	Present work
LiSO$_4$	6.738	4.254	−1.458	3.2	5.95	1.65	0.49
Na$_2$SO$_4$	5.780	4.584	−0.795	2.0	4.07	0.37	0.38
K$_2$SO$_4$	3.181	0.445	–	0.7	0.23	0.53	0.20
Rb$_2$SO$_4$	5.615	3.154	1.266	1.7	2.84	0.31	0.34
Cs$_2$SO$_4$	5.319	2.059	7.596	1.6	2.67	0.45	0.31
BaCl$_2$	5.096	0.372	6.437	1.8	1.32	0.26	0.39
BaBr$_2$	6.246	1.897	5.002	2.3	4.40	0.59	0.70
Cd(NO$_3$)$_2$	8.382	3.018	3.903	2.6	6.25	1.21	0.99
CaCl$_2$	6.228	1.422	1.210	7.5	22.33	4.59	0.76
CaBr$_2$	7.002	2.124	0.671	7.7	25.67	8.94	1.55
Ca(NO$_3$)$_2$	7.505	3.060	−1.845	6.0	6.78	2.14	0.49
CoCl$_2$	7.039	2.374	3.779	4.1	12.69	3.64	0.31
Co(NO$_3$)$_2$	8.567	2.925	0.686	5.6	12.55	2.08	1.16
MgCl$_2$	7.552	2.770	1.124	5.9	18.52	1.83	0.91
MgBr$_2$	8.191	3.265	1.295	5.6	21.50	0.49	1.67
Cu(NO$_3$)$_2$	8.628	3.328	0.424	7.8	17.60	0.81	1.17
MnCl$_2$	7.203	3.168	3.196	5.0	15.23	3.39	1.57
NiCl$_2$	6.966	2.297	2.683	5.0	3.09	5.52	0.55
Ni(NO$_3$)$_2$	9.279	3.803	0.584	4.6	11.50	3.52	1.56
SrCl$_2$	6.148	1.782	2.211	4.0	4.29	1.22	0.42
SrBr$_2$	7.134	2.694	–	2.1	3.77	1.04	0.38
UO$_2$Cl$_2$	7.591	2.365	5.163	3.2	9.30	1.56	1.51
Total average relative deviation					9.66	2.10	0.81

is low, both the Pitzer model and our model give good results, but when the concentration is high, the Pitzer model yields lower and then higher results compared with the experimental data. Only our model gives good results from low concentrations up to saturation.

The mean ionic activity coefficients of 32 mixed-electrolyte solutions have been predicted. These systems include both symmetric and asymmetric electrolytes. In these systems the electrolytes are considered to be completely ionized. The experimental data of the mean ionic activity coefficients were measured by the e.m.f. method, using the most recent data available. The maximum ionic strength was 6 m.

The standard deviations between the predicted and experimental data of the mean ionic activity coefficients in 32 mixed-electrolyte systems are listed

TABLE 4

The effective diameter parameters of the cations and the relative deviations in $\gamma_{\pm}$ calculated from the original MSA, the Pitzer model and the present work for 3:1 and 2:2 electrolytes at 298.15 K

Salt	Parameter (nm)			m_{max}	Average relative deviation (%)		
	$\sigma_0 \times 10$	$\lambda_1 \times 10$	$\lambda_2 \times 10^4$		Original MSA	Pitzer	Present work
LaCl$_3$	8.401	2.954	1.194	3.9	28.68	3.02	0.80
La(ClO$_4$)$_3$	9.510	1.892	0.942	3.5	28.76	19.22	1.26
CeCl$_3$	6.992	1.120	1.565	2.0	5.97	2.56	0.76
PrCl$_3$	8.408	2.974	1.133	3.9	28.32	1.40	0.55
NdCl$_3$	8.035	2.508	1.130	3.9	27.35	3.45	0.67
SmCl$_3$	8.155	2.576	1.229	3.6	25.55	1.96	0.45
EuCl$_3$	8.102	2.425	1.321	3.6	24.80	1.94	0.54
GdCl$_3$	8.133	2.393	1.335	3.6	25.28	2.49	0.59
TbCl$_3$	8.392	2.638	1.357	3.6	26.51	1.72	0.50
DyCl$_3$	8.677	2.978	1.280	3.6	28.64	1.24	0.55
HoCl$_3$	8.961	3.322	1.222	3.7	29.73	1.92	0.55
ErCl$_3$	8.665	2.966	1.203	3.8	29.38	1.02	0.68
TmCl$_3$	8.526	2.813	1.172	3.9	30.48	2.74	1.06
YbCl$_3$	8.441	2.703	1.186	3.8	28.63	2.70	0.84
LuCl$_3$	8.725	3.094	1.101	4.0	31.55	1.42	1.27
YCl$_3$	8.811	3.140	1.132	4.0	31.53	1.06	1.00
AlCl$_3$	7.560	0.691	2.133	1.8	6.00	2.49	0.35
MgSO$_4$	4.836	0.357	-1.688	3.6	5.35	2.12	1.59
NiSO$_4$	3.332	-1.048	-1.257	2.5	3.17	7.10	1.75
CuSO$_4$	2.235	-2.995	9.395	1.4	2.22	3.55	1.18
ZnSO$_4$	3.332	-1.083	-1.979	3.5	7.47	5.04	1.69
BeSO$_4$	2.667	-2.998	0.011	4.0	9.13	1.94	1.43
Total average relative deviation					21.11	3.28	0.91

in Table 5. Table 5 also contains the calculated results of the Pitzer equation (Pitzer, 1979) both with and without the mixing parameters θ and ψ. The data sources are listed in the last column of this table. The parameters of the Pitzer model for single electrolytes were obtained from Pitzer and Mayerga (1973). Although Pitzer (1975) has pointed out that the higher order electrostatic effects may be ignored for several mixed systems, we include these effects for all mixtures of asymmetrical electrolytes with common ions. The mixing parameters θ and ψ were obtained by using multiple regression.

Table 5 shows that the average standard deviation of the mean ionic activity coefficients between the results predicted by our model and the experimental data is 0.0113. When the ionic strength of the solution is 0–6 m, the average deviation is less than 0.020, except for aqueous
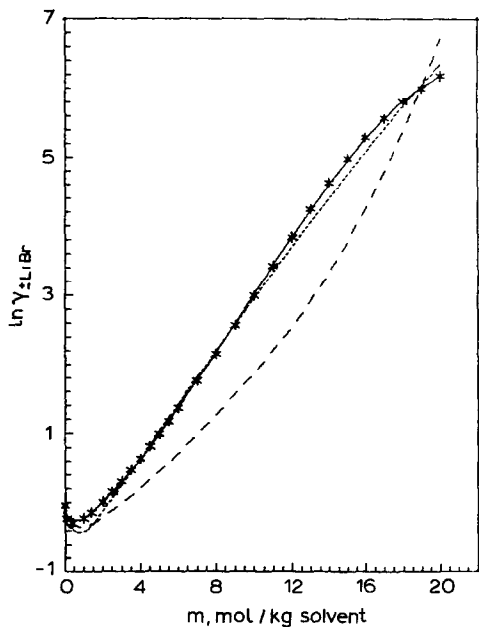
Fig. 2. Activity coefficients of aqueous LiBr solution at 298.15 K: $*$, experimental data; $\cdots$, Pitzer equation; ---, original MSA; ——, present work.
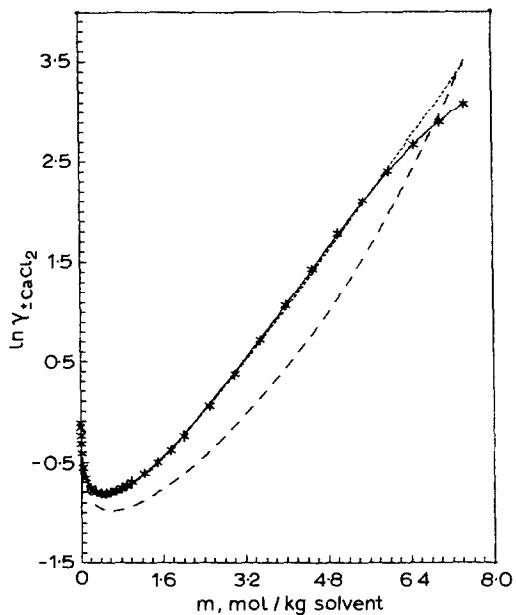

Fig. 3. Activity coefficients of aqueous CaCl$_2$ solution at 298.15 K: $*$, experimental data; $\cdots$, Pitzer equation; ---, original MSA; ——, present work.

TABLE 5

Comparison between the standard deviation in $\ln \gamma_{\pm}$ predicted from the Pitzer model and the present work at 298.15 K

System	Predicted	Standard deviation			I_{max}	Ref.[c]
		Present	Pitzer 1[a]	Pitzer 2[b]		
HCl + LiCl	$\ln \gamma_{\pm HCl}$	0.0136	0.0231	0.0072	5.01	1
HBr + LiBr	$\ln \gamma_{\pm HBr}$	0.0196	0.0272	0.0133	2.51	1
HCl + NaCl	$\ln \gamma_{\pm HCl}$	0.0063	0.0400	0.0022	3.01	1
HBr + NaBr	$\ln \gamma_{\pm HBr}$	0.0189	0.0281	0.0023	3.01	1
HCl + KCl	$\ln \gamma_{\pm HCl}$	0.0087	0.0341	0.0104	4.00	2
HCl + CsCl	$\ln \gamma_{\pm HCl}$	0.0286	0.0824	0.0053	3.00	1
HCl + NH₄Cl	$\ln \gamma_{+HCl}$	0.0142	0.0279	0.0101	3.00	3
HCl + CoCl₂	$\ln \gamma_{\pm HCl}$	0.0066	0.0285	0.0022	3.00	4
HCl + NiCl₂	$\ln \gamma_{\pm HCl}$	0.0064	0.0289	0.0028	3.00	5
HCl + CaCl₂	$\ln \gamma_{\pm HCl}$	0.0096	0.0356	0.0054	5.00	6
HBr + CaBr₂	$\ln \gamma_{+HBr}$	0.0071	0.0244	0.0037	2.00	7
HCl + MnCl₂	$\ln \gamma_{\pm HCl}$	0.0189	0.0332	0.0062	5.00	8
HCl + MgCl₂	$\ln \gamma_{\pm HCl}$	0.0144	0.0452	0.0066	5.00	9
HBr + MgBr₂	$\ln \gamma_{\pm HBr}$	0.0085	0.0262	0.0061	3.00	10
HCl + BaCl₂	$\ln \gamma_{\pm HCl}$	0.0035	0.0247	0.0046	3.00	11
HBr + BaBr₂	$\ln \gamma_{\pm HBr}$	0.0138	0.0426	0.0040	2.00	12
HCl + SrCl₂	$\ln \gamma_{\pm HCl}$	0.0116	0.0365	0.0065	5.00	13
HBr + SrBr₂	$\ln \gamma_{\pm HBr}$	0.0057	0.0235	0.0047	2.00	14
NaCl + MgCl₂	$\ln \gamma_{\pm NaCl}$	0.0145	0.0546	0.0064	6.00	15
NaCl + CaCl₂	$\ln \gamma_{\pm NaCl}$	0.0096	0.0506	0.0044	5.00	15
NaCl + SrCl₂	$\ln \gamma_{\pm NaCl}$	0.0092	0.0465	0.0053	6.00	15
KCl + KOH	$\ln \gamma_{\pm KOH}$	0.0135	0.0564	0.0050	1.00	16
NaCl + NaClO₄	$\ln \gamma_{\pm NaCl}$	0.0081	0.0504	0.0163	6.00	15
NaCl + NaNO₃	$\ln \gamma_{\pm NaCl}$	0.0090	0.0180	0.0146	3.00	15
NaCl + CH₃COONa	$\ln \gamma_{\pm NaCl}$	0.0160	0.0153	0.0084	3.00	15
HCl + AlCl₃	$\ln \gamma_{\pm HCl}$	0.0115	0.0685	0.0047	5.00	1
HCl + LaCl₃	$\ln \gamma_{\pm HCl}$	0.0096	0.0303	0.0037	3.00	17
HCl + CeCl₃	$\ln \gamma_{\pm HCl}$	0.0055	0.0226	0.0021	1.00	16
HCl + NaCl + KCl	$\ln \gamma_{\pm HCl}$	0.0096	0.0162	0.0017	1.00	18
HCl + NH₄Cl + KCl	$\ln \gamma_{\pm HCl}$	0.0084	0.0143	0.0075	1.00	18
HCl + CsCl + BaCl₂	$\ln \gamma_{\pm HCl}$	0.0174	0.0473	0.0328	1.00	19
HCl + NaCl + MgCl₂	$\ln \gamma_{\pm HCl}$	0.0073	0.0167	0.0122	1.00	20
Average standard deviation		0.0113	0.0350	0.0071		

[a] Pitzer equation without mixing parameters.
[b] Pitzer equation with two mixing parameters.
[c] Data sources: 1, Hand and Owen (1958); 2, Chan and Khoo (1979); 3, Downes (1975); 4, Khoo et al. (1978a); 5, Khoo et al. (1978b); 6, Roy et al. (1982); 7, Khoo et al. (1979a); 8, Roy et al. (1980b); 9, Roy et al. (1980a); 10, Roy et al. (1990); 11, Khoo et al. (1978c); 12, Khoo et al. (1979b); 13, Roy et al. (1986); 14, Lim et al. (1980); 15, Lander (1965); 16, Teng and Li (1983); 17, Khoo et al. (1981); 18, Chan et al. (1979); 19, Lietzke et al. (1969); 20, White et al. (1980).
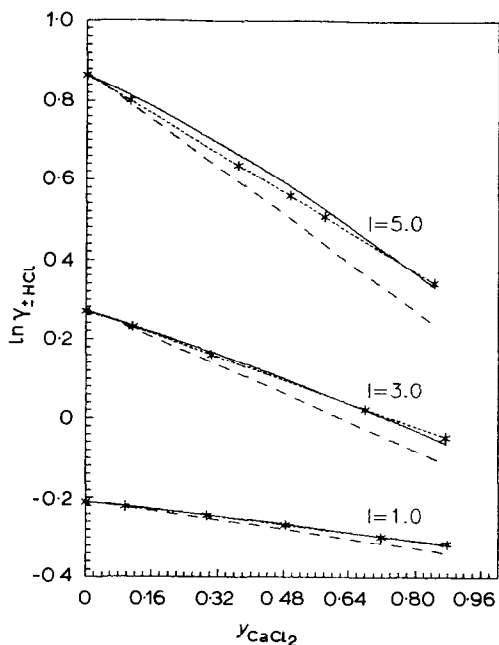
Fig. 4. Comparison of experimental $\ln \gamma_{\pm HCl}^{-}$ for aqueous $HCl + CaCl_2$ solution with calculated results from Pitzer equation and present work: $*$, Roy et al. (1982); ---, Pitzer equation ($\theta = 0$, $\psi = 0$); $\cdots$, Pitzer equation ($\theta \neq 0$, $\psi \neq 0$).

$HCl + CsCl$ solution. Table 5 also shows that the standard deviation of the Pitzer model without mixing parameters is larger than that of our model by a factor of 2. The Pitzer model with mixing parameters is a little better than our model.

The calculated and experimental mean ionic activity coefficients for aqueous $HCl + CaCl_2$, $NaCl + MgCl_2$, $NaCl + NaClO_4$ and $HCl + AlCl_3$ solutions at 298.15 K are plotted in Figs. 4, 5, 6 and 7 respectively. From these figures it can be seen that when $I = 1$ m, the calculated results from these three models are coincident with the experimental data. When the ionic strength increases, the results of the Pitzer equation without θ and φ are much lower than the experimental data. The Pitzer equation with θ and φ and our model give approximately the same deviation. Both are in good agreement with the experimental data.

In order to test the dependence of our model on temperature, five models were used to correlate the mean ionic activity coefficients at temperatures other than 298.15 K. The experimental data and the correlation method for the Pitzer, Bromley (1972), Meissner and Tester (1972) and Chen et al. (1982) models are taken from Zemaitis et al. (1986). The temperature dependence of the parameters in the above four models was considered. The parameters used in our model are those obtained at 298.15 K. Table 6 shows the results.
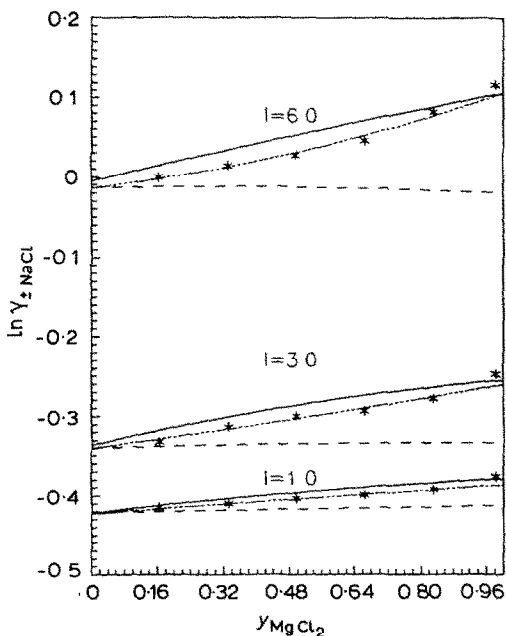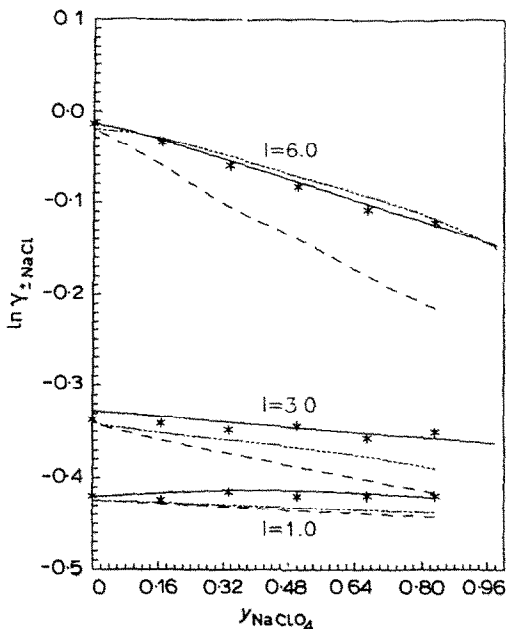
Fig. 5. Comparison of experimental $\ln \gamma_{\pm \text{NaCl}}$ for aqueous $\text{NaCl} + \text{MgCl}_2$ solution with calculated results from Pitzer equation and present work: $*$, Lander (1965); ---, Pitzer equation ($\theta = 0, \psi = 0$); $\cdots$, Pitzer equation ($\theta = 0, \psi = 0$); ——, present work.

Fig. 6. Comparison of experimental $\ln \gamma_{\pm \text{NaCl}}$ for aqueous $\text{NaCl} + \text{NaClO}_4$ solution with calculated results from Pitzer equation and present work: $*$, Lander (1965); ---, Pitzer equation ($\theta = 0, \psi = 0$); $\cdots$, Pitzer equation ($\theta \neq 0, \psi \neq 0$); ——, present work.
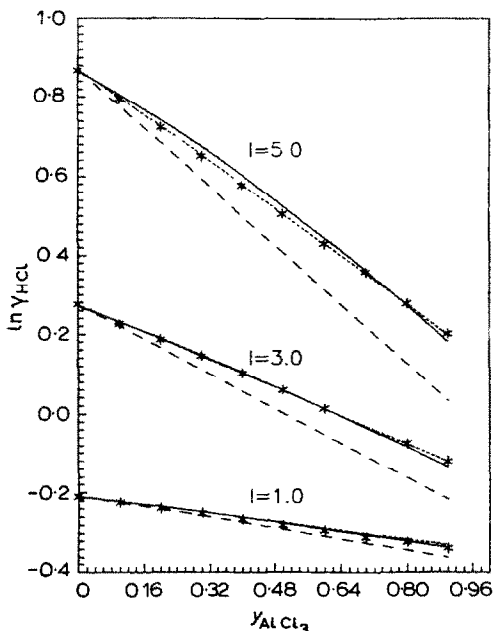
Fig. 7. Comparison of experimental $\ln \gamma_{\pm HCl}$ for aqueous $HCl + AlCl_3$ solution with cal-cualted results from Pitzer equation and present work: $*$, Hand et al. (1958); ---, Pitzer equation ($\theta = 0, \psi = 0$); $\cdots$, Pitzer equation ($\theta \neq 0, \psi \neq 0$); ——, present work.

TABLE 6

Comparison of the relative deviation in $\gamma_{\pm}$ calculated from five models at different temperatures

Salt	Average relative deviation in $\gamma_{\pm}$					m_{max}	T (K)
	Pitzer	Bromley	Meissner	Chen	Present work		
HCl	0.66	1.52	0.53	1.09	0.98	2.0	323.15
NaCl	3.66	4.73	2.63	2.22	2.53	6.0	373.15
KCl	6.98	5.28	1.13	4.91	5.43	4.0	353.15
NaOH	1.01	2.90	2.75	2.73	1.51	4.0	308.15
Na$_2$SO$_4$	12.57	28.50	4.94	10.51	10.53	1.6	353.15
MgSO$_4$	5.01	113.90	36.20	5.98	6.55	2.0	353.15
Total	4.98	26.14	8.03	4.57	4.59		

From Table 6 it can be seen that the temperature dependence of the parameters of our model is small. Because temperature is one of the variables in the activity coefficient equation of the MSA (eqns. (3)–(6)), the slight temperature dependence is understandable. When the parameters calculated at 298.15 K are used to predict the mean ionic activity coefficients

at other temperatures, the precision of the calculation is not as good as at 298.15 K, but it is acceptable.

CONCLUSION

The MSA is improved in calculations of the activity coefficients in single- and mixed-electrolyte solutions over a wide concentration range by the introduction of an expression for the effective cationic diameter. The modified MSA was also tested in calculations of the activity coefficients at temperatures other than 298.15 K. The results show that our improvement is effective.

LIST OF SYMBOLS

a	closest distance between cation and anion (nm)
c	molarity (mol dm^{-3})
C	direct correlation function
d	density of solution (kg m^{-3})
D	dielectric constant
e	unit electronic charge (C)
g	radial distribution function
I	ion strength (mol kg^{-1})
k	Boltzmann constant
m	molality (mol kg^{-1})
M	molecular weight (g mol^{-1})
N	number of ion species
p	pressure (Pa)
r	radial distance (nm)
T	absolute temperature (K)
V	partial molar volume (m^{3} mol^{-1}) or volume of solution (m^{3})
X	mole fraction of anion
y	ion strength fraction
Z	valence of ion

Greek letters

γ	activity coefficient
Γ	shielding parameter
θ, ψ	mixing parameters in Pitzer equation
K	Debye inverse length (nm^{-1})
λ	parameter of effective diameter of cation (nm)
Π	osmotic pressure (Pa)
ρ	number density (nm^{-3})
σ	hard-sphere diameter or effective diameter (nm)

ϕ osmotic coefficient
ψ electrostatic potential

Subscripts

A   anion
i, j, k components i, j, k
M   cation
mix   mixed electrolyte solution
a   solvent
0   infinite dilution
$\pm$ ionic average

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