Model for Describing Activity Coefficients in Mixed Electrolyte Aqueous Solutions

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Most models for describing activity coefficients in ionic solutions are only appropriate for single aqueous electrolyte solutions. Extensions to mixed electrolyte solutions are rarely found and are often unreliable, especially at higher electrolyte concentrations. A new model is developed by combining ionic solvation equilibria and physical interaction forces. It is shown that by using the parameters correlated from single electrolyte aqueous systems, the activity coefficients in mixed electrolyte aqueous solutions can be accurately predicted up to the solubility limit, for example, at very high ionic strength.

Introduction

Electrolyte solutions play an important role in the chemical industry and are also relevant in other fields of science and technology. For example, there is a growing interest in the thermodynamic properties of mixed electrolyte aqueous solutions due to their importance in the understanding of various natural and industrial processes such as wastewater treatment, seawater desalination, manufacture of inorganic chemicals, and hydrometallurgical processes. Maurer (1983) and Renon (1986) have reviewed recent developments. The existing models to describe and correlate activity coefficients in aqueous electrolyte solutions can roughly be assigned to physical or chemical models.

Most physical models start from the Debye-Hückel limiting law and assume that all necessary corrections are due to physical interactions between the ionic species. The virial-type of ionic-interaction model of Pitzer (1973) is the most commonly applied example. Local composition models, for example, the electrolyte NRTL and electrolyte UNIQUAC model of Cruz and Renon (1978), Ball et al. (1985), Chen and Evans (1982, 1986), Christensen et al. (1983), Haghtalab and Vera (1988, 1991), and Liu et al. (1989, 1991) are among those models. They are able to provide a continuous transition from electrolyte to nonelectrolyte systems.

There are also physical models which do not start from the Debye-Hückel limiting law, but from a statistical thermodynamics expression for the free energy, which again is based on interparticle potentials. The mean spherical approximation method of Ball et al. (1985) and the equation of state method of Jin and Donohue (1988a,b; 1991) are typical examples for such models.

Chemical models describe deviations from the ideal mixture as a result of chemical reaction leading to solvated ions. The solvation models of Stokes and Robinson (1948) and some later modifications (Glueckauf, 1955; Stokes and Robinson, 1973; Nesbitt, 1981; Kawaguchi et al., 1981, 1982; Ghosh and Patwardhan, 1990) are typical examples for such models.

While most of the above models are appropriate for single electrolyte solutions, their extensions to mixed electrolyte aqueous solutions are often unreliable, particularly at high ionic strength near the solubility limit.

Here a new model is presented which combines chemical reaction (solvation equilibria) with physical interactions (local composition equation). The model parameters are reduced from experimental results on single electrolyte aqueous systems. The model is tested by comparing predicted and measured activities and solubilities of salts in concentrated mixed electrolyte aqueous solutions at 298.15 K. The results are mainly compared with experimental data and with predictions by the standard method of Pitzer (1973) and some of its modifications.

Model Development

The physical chemical model is to describe the Gibbs excess energy, especially osmotic coefficient ϕ and mean activity coefficients $\gamma_{\pm}$ of dissolved electrolytes in a mixed electrolyte aqueous solution. Dissolving strong electrolytes in water results

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in a mixture of water molecules, unsolvated, and solvated ions. Incomplete dissociation as well as ion pairing are both neglected here. Solvation equilibria are applied to calculate the true concentrations of solvated and unsolvated ions from the overall concentration of the dissolved electrolyte. Deviation from ideal mixing behavior is taken into account by combining the Debye-Hückel law with the UNIQUAC model.

Solvation equilibria

When an electrolyte $M_{\upsilon_c}X_{\upsilon_a}$ is dissolved in water, it completely dissociates and attains ionic solvation equilibria in the solution:

$$M^{Z_c}+h_cH_2O \rightleftharpoons M^{Z_c}\cdot h_cH_2O \tag{1}$$

$$X^{Z_a}+h_aH_2O \rightleftharpoons X^{Z_a}\cdot h_aH_2O \tag{2}$$

where h_c and h_a are the numbers of water molecules in a solvation complex with cation M and anion X respectively. The thermodynamical equilibrium condition for these solvation reactions is:

$$K_c=\frac{a_{hc}}{a_c\cdot a_w^{h_c}}=\frac{z_{hc}}{z_c\cdot z_w^{h_c}}\cdot\frac{\overset{*}{\gamma}_{hc}}{\overset{*}{\gamma}_c\cdot\gamma_w^{h_c}} \tag{3}$$

$$K_a=\frac{a_{ha}}{a_a\cdot a_w^{h_a}}=\frac{z_{ha}}{z_a\cdot z_w^{h_a}}\cdot\frac{\overset{*}{\gamma}_{ha}}{\overset{*}{\gamma}_a\cdot\gamma_w^{h_a}}. \tag{4}$$

K_c and K_a are equilibrium constants (depending on temperature and pressure only); a_c, a_a are the true activities of unsolvated ions; a_{hc}, a_{ha} are those of the solvated ions; a_w is the activity of water which is normalized according to Raoult's law:

$$a_w=z_w\cdot\gamma_w \tag{5}$$

where z_w and γ_w are the true mole fraction and the true activity coefficient of water.

The activity of any dissolved species k (unsolvated and solvated ion) is normalized according to Henry's law:

$$a_k=z_k\cdot\overset{*}{\gamma}_k \tag{6}$$

where z_k and γ_k^* are the true mole fraction and the true activity coefficient of specie k.

When $\overline{m}_s$ moles of a single electrolyte are dissolved in one kilogram of water, mass balance can be expressed by n_{hc} and n_{ha}, the numbers of moles of solvated cation and anion respectively. The total number of moles n_t in the solution is:

$$n_t=\frac{1{,}000}{M_w}+(\upsilon_c+\upsilon_a)\cdot\overline{m}_s-h_c\cdot n_{hc}-h_a\cdot n_{ha}. \tag{7}$$

The true mole fractions of all species are:

$$z_{hc}=\frac{n_{hc}}{n_t} \tag{8}$$

$$z_{ha}=\frac{n_{ha}}{n_t} \tag{9}$$

$$z_c=\frac{\upsilon_c\cdot\overline{m}_s-n_{hc}}{n_t} \tag{10}$$

$$z_a=\frac{\upsilon_a\cdot\overline{m}_s-n_{ha}}{n_t} \tag{11}$$

$$z_w=1-z_{hc}-z_{ha}-z_c-z_a \tag{12}$$

Substituting Eqs. 8 to 12 back into Eqs. 3 and 4 allows the calculation of the true concentration of solvated cations (n_{hc}) and anions (n_{ha}) as well as the total composition of the aqueous solution, provided the equilibrium constants K_c and K_a, the solvation number h_c, h_a and an appropriate expression for calculating true activity coefficients is available. The extension to multicomponent mixtures is given in Appendix A.

N electrolytes $M_{\upsilon_{c,s}}X_{\upsilon_{a,s}}$ (s = 1, . . . , N) dissociate completely when being dissolved in water. Using the theory discussed by Prigogine and Defay (1954), the mean ionic activity coefficient $\gamma_\pm$ on molality scale and the osmotic coefficient ϕ are related to the true activities of solvated ions and water and to the overall molalities of the dissolved ions by:

$$\begin{aligned}(\upsilon_{c,s}+\upsilon_{a,s})\ \ln\gamma_{\pm,s}&=\upsilon_{c,s}\ln a_{hc}+\upsilon_{a,s}\ln a_{ha}\\&-(\upsilon_{c,s}\cdot h_c+\upsilon_{a,s}\cdot h_a)\ln a_w-\ln(\overline{m}_c^{\upsilon_{c,s}}\cdot\overline{m}_a^{\upsilon_{a,s}})\\&-(\upsilon_{c,s}+\upsilon_{a,s})\ln\frac{M_w}{1{,}000}\end{aligned} \tag{13}$$

$$\phi=\frac{-1{,}000}{M_w\sum_{k=1}^{I+J}\overline{m}_k}\ln(\gamma_w\cdot z_w) \tag{14}$$

where $\overline{m}_k$ is the overall molality of ion k (solvated and unsolvated) and I and J are the number of different cations and anions in all dissolved electrolytes. Details of the derivations are given in Appendix B.

Gibbs excess energy

To take into account the real behavior of the mixture (consisting of water, unsolvated and solvated ions) an expression for the Gibbs excess energy in such a solution is needed. Here the Debye-Hückel equation is combined with the UNIQUAC equation (Abrams and Prausnitz, 1975):

$$G^E=G^E_{\mathrm{DH}}+G^E_{\mathrm{UNIQUAC}} \tag{15}$$

Thus the activity coefficient of a charged specie k (for example, unsolvated or solvated ion) is:

$$\ln\gamma_k^*=\ln\overset{*}{\gamma}_{k,\mathrm{DH}}+\ln\overset{*}{\gamma}_{k,\mathrm{UNIQUAC}} \tag{16}$$

For each ionic specie k, the individual ion size parameter d_k, the charge number Z_k, the ionic strength:

$$I_m=\frac{1}{2}\sum_{l=1}^{I+J}\overline{m}_l\cdot Z_l^2 \tag{17}$$

and the Debye-Hückel constant A (298.15 K) = 0.5115 and B(298.15 K) = 0.3291 (Robinson and Stokes, 1959) are needed to calculate the Debye-Hückel contribution to the activity coefficient:

$$\ln \gamma^{*}_{k,\mathrm{DH}} = \frac{-Z_k^2 A \sqrt{I_m}}{1 + B d_k \sqrt{I_m}}. \tag{18}$$

The contribution of the UNIQUAC equation to the activity coefficient of an ionic species is:

$$\ln \gamma^{*}_{k,\mathrm{UNIQUAC}} = \ln \gamma_{k,\mathrm{UNIQUAC}} - \ln \gamma^{\infty}_{k,\mathrm{UNIQUAC}} \tag{19}$$

where $\gamma_{k,\,\mathrm{UNIQUAC}}$ is the activity coefficient according to the UNIQUAC model and $\gamma^{\infty}_{k,\,\mathrm{UNIQUAC}}$ is the infinite dilution UNIQUAC activity coefficient of compound k in pure water.

$$\begin{aligned}\ln \gamma^{*}_{k,\mathrm{UNIQUAC}} &= \ln \frac{q_k}{r_k} + \ln \frac{\sum_{l=1}^{2(I+J)+1} z_l \cdot r_l}{\sum_{l=1}^{2(I+J)+1} z_l \cdot q_l} \\ &+ \frac{z}{2} q_k \left(\ln \frac{q_w}{r_w} + \ln \frac{\sum_{l=1}^{2(I+J)+1} z_l \cdot r_l}{\sum_{l=1}^{2(I+J)+1} z_l \cdot q_l} \right) \\ &- \frac{r_k}{\sum_{l=1}^{2(I+J)+1} z_l r_l} \cdot \sum_{l=1}^{2(I+J)+1} z_l l_l + \frac{r_k}{r_w} \cdot l_w \\ &- q_k \left(\ln \sum_{l=1}^{2(I+J)+1} \theta_l \frac{\tau_{l,k}}{\tau_{w,k}} - \tau_{k,w} + \sum_{l=1}^{2(I+J)+1} \frac{\theta_l \cdot \tau_{l,k}}{\sum_{m=1}^{2(I+J)+1} \theta_m \cdot \tau_{m,l}} \right)\end{aligned} \tag{20}$$

where q_k and r_k are surface and volume parameters of specie k, $l_k = z/2(r_k - q_k) - (r_k - 1)$, z is the coordination parameter and $\tau_{l,k}$ and $\tau_{k,l}$ are parameters for physical interactions between species k and l.

The activity coefficient of water is given by:

$$\ln \gamma_w = \ln \gamma_{w,\mathrm{DH}} + \ln \gamma_{w,\mathrm{UNIQUAC}} \tag{21}$$

Employing the Gibbs-Duhem equation, the contribution of the Debye-Hückel term to the activity coefficient of water is as follows:

$$\ln \gamma_{w,\mathrm{DH}} = \frac{M_w}{1{,}000} \cdot \frac{2A}{B^3 \cdot I_m} \sum_{k}^{2(I+J)} \left[\frac{m_k \cdot Z_k^2}{d_k^3} \left(1 + B d_k \sqrt{I_m} - 2 \ln(1 + B d_k \sqrt{I_m}) - \frac{1}{1 + B d_k \sqrt{I_m}} \right) \right] \tag{22}$$

where m_k is the true molality of ionic compound k (solvated and unsolvated species), which is related to true mole fractions by:

$$m_k = \frac{z_k}{z_w} \cdot \frac{1{,}000}{M_w} \tag{23}$$

The details of the derivations are given in Appendix C.

Determination of Model Parameter

Reduction of the number of adjustable parameters

The model requires a large number of parameters. For example, when an aqueous solution of a single 1:1 electrolyte is considered, there are 12 "pure component" parameters (four ionic radii of unsolvated and solvated ions, four size and surface parameters for the UNIQUAC expression and four solvation constants) and 20 UNIQUAC interaction parameters. To limit the number of adjustable parameters, some reasonable assumptions were necessary:

- in the Debye-Hückel expression the difference between the ion size parameter d of a solvated and an unsolvated ion is neglected. Furthermore, the ion size parameter is approximately the sum of the radius of solvated central ion r^{*}_{hci} or r^{*}_{haj} and the average radius of the solvated oppositely charged ions:

$$d_{hci} = d_{ci} = r^{*}_{hci} + \sum_{j=1}^{J} \lambda_{ci,aj} \cdot r^{*}_{haj} \cdot \left(\frac{\overline{m}_{aj}}{\sum_{k=1}^{J} \overline{m}_{ak}} \right)^{b_{aj}} \tag{24}$$

$$d_{haj} = d_{aj} = r^{*}_{haj} + \sum_{i=1}^{I} \lambda_{ci,aj} \cdot r^{*}_{hci} \cdot \left(\frac{\overline{m}_{ci}}{\sum_{k=1}^{I} \overline{m}_{ck}} \right)^{b_{ci}} \tag{25}$$

where $\lambda_{ci,aj} = \lambda_{aj,ci}$ is a binary size correction parameter. Parameter b is to correct the effect of some special ions. Generally, $b_{ci} = b_{aj} = 1$ except for $b_{\mathrm{H}^+} = 0.5$ and $b_{\mathrm{OH}^-} = 1.5$. Since the effective volume of a solvated ion can be approximated by the sum of the volume of water in the solvation shell and the volume of the ion, the radius of a solvated ion r^{*}_{hk} relates to the radius r^{*}_{k} of an unsolvated one by:

$$\frac{3}{4} \pi (r^{*}_{hk})^3 = \tilde{v}_w \cdot h_k + \frac{3}{4} \pi (r^{*}_{k})^3 \tag{26}$$

where $\tilde{v}_w = 2.9910 \times 10^{-28} m^3$ is the volume occupied by a water molecule in liquid water at 298 K.

Following these assumptions the only remaining adjustable "pure component" parameter is the radius r^{*}_{k} of an unsolvated ion.

- In the UNIQUAC contribution the coordination number z is fixed at the value of 6 as discussed by Liu and Gren (1991).

The UNIQUAC size parameters of charged species were approximated by the corresponding ionic radii of ions, that is, $r_k = r^{*}_{k}/\text{Å}$. Furthermore, all ionic species k are considered showing no distinction between UNIQUAC size and surface parameters, that is, $r_k = q_k$. Those parameters for water ($r_w = 0.92$, $q_k = 1.40$) were taken from the literature (Prausnitz et al., 1986).

- UNIQUAC parameters $\tau_{i,j}$ are related to binary interaction energies $u_{i,j}$ by:

$$\tau_{i,j} = \exp\left[-\frac{u_{i,j}-u_{j,j}}{RT}\right] = \exp\left[-\frac{\overset{*}{u}_{i,j}-\overset{*}{u}_{j,j}}{T}\right] \qquad (27)$$

Some of the reduced energies $\overset{*}{u}_{i,j}$ were preset:

$\overset{*}{u}_{i,j} = 2{,}000$ K whenever i and j represent ions carrying charges of the same sign.

$\overset{*}{u}_{i,j} = \overset{*}{u}_{j,i}$ whenever i and j represent ions carrying charges of a different sign.

$\overset{*}{u}_{i,w} = \overset{*}{u}_{w,i} = 0$ for interactions between any ion and a water molecule since these interactions are taken into account by the solvation reaction.

$\overset{*}{u}_{w,w} = 0$ the parameter for interactions between water molecules is arbitrarily set to zero.

No distinction is made between solvated and unsolvated ions as far as the binary interaction energies are concerned.

Thus for any ion k of a strong electrolyte, there remain only 3 "pure component" parameters, that is, the unsolvated ionic radius r_k^*, solvation number h_k and solvation equilibrium constant K_k. Furthermore there are two binary parameters for interactions between a cation and an anion, that is, one size correction parameter $\lambda_{ci,aj} = \lambda_{aj,ci}$ and one energy parameter $\overset{*}{u}_{c,a} = \overset{*}{u}_{a,c}$.

Determination of parameters for 48 systems including 16 ions

In order to apply the model to mixed electrolyte aqueous systems, parameters have to be known for a large number of ions. In the present work, "pure component" parameters as well as binary parameters of 10 cations (H^+, Li^+, Na^+, K^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and 6 anions (Cl^-, Br^-, I^-, OH^-, NO_3^-, SO_4^{2-}) were simultaneously fitted to experimental results for the mean ionic activity coefficients of 48 single electrolytes at 298.15 K as tabulated by Robinson and Stokes (1959), Hamer and Wu (1972) and Goldberg and Nuttall (1978). In the correlation the total number of adjustable parameters was 144.

Table 1 gives the "pure component" parameters. Table 2 gives the binary parameters, a comparison of correlated mean ionic activity coefficients with the underlying experimental data, as well as a comparison of calculated osmotic coefficients with experimental data. The new model gives both properties very accurately even for very soluble electrolytes near the solubility limit ($\overline{m}_{\max} = 29$). Some of the results up to high molalities are shown in Figures 1 and 2. Table 3 presents a comparison between the new model and some other models suitable for extremely concentrated electrolyte solutions, for example, the model of Stokes and Robinson (1973), Kim and Frederick's modification (1988) of Pitzer's model, and the models of Liu et al. (1991) and Haghtalab and Vera (1988). The comparison is restricted to those single systems which, following Stokes and Robinson (1973), are difficult to correlate. In most cases the new model works at least as well as the older ones. In representing the osmotic coefficient the new model generally yields no improvement over the model of Stokes and Robinson and some minor improvement over Pitzer's model and its modifications. In representing mean ionic activity coefficients, the new model gives some minor improvement over the models of Haghtalab and Vera (1988) and Liu et al. (1991). Such slight improvements are no surprise, as it is well known that the models mentioned previously provide reliable correlations of thermodynamic properties for aqueous solutions of single electrolytes at 298.15 K. New models have to be developed especially to predict the properties of mixed electrolyte solutions from data for single electrolyte solutions. As far as the literature methods discussed here are concerned, extensions to mixed electrolyte systems are straightforward only for the Pitzer and the new model. Therefore, predictions from these two models are compared to experimental results for mixed electrolyte solutions.

Table 1. "Pure Component" Parameters of the New Model at 298.15 K

ion k	r_k^*/Å	h_k	K_k
H^+	0.208	1.840	4.367
Li^+	0.348	1.840	4.643
Na^+	0.080	0.810	5.281
K^+	2.520	0.530	10.00
Cs^+	2.950	0.025	16.00
NH_4^+	2.750	0.110	7.630
Ca^{2+}	0.150	5.050	4.680
Mg^{2+}	2.530	4.120	5.720
Sr^{2+}	3.470	5.600	4.260
Ba^{2+}	0.020	1.030	16.50
Cl^-	1.721	1.547	5.708
Br^-	2.675	1.835	8.123
I^-	4.113	2.215	4.483
OH^-	0.009	2.067	7.111
NO_3^-	1.610	0.019	7.960
SO_4^{2-}	0.010	0.074	14.80

Prediction in Multicomponent Electrolyte Systems at 298.15 K

Mean ionic activity coefficient and osmotic coefficient

Experimental results for the mean ionic activity coefficient and the osmotic coefficient of aqueous solutions of 22 mixed electrolytes with a common ion are compared with predictions in Table 4. For the Pitzer model two different sets of parameters were used: one set (Pitzer-6; Pitzer, 1973) was determined from experimental data of single electrolyte solutions at concentrations up to 6 molal, whereas the other set (Kim and Frederick, 1988) is based on data at higher concentrations up to the solubility limit. In general at molalities up to about 6, the new model gives results which are very similar to those using the Pitzer-6 model. When higher concentrations are included the quality of the prediction by the new model is not reduced significantly (cf. also Table 3), but an essential improvement over both Pitzer models is observed.

In Table 5 experimental results for the trace mean ionic activity coefficient

$$\ln \gamma_{\pm,1}^{tr} = \lim_{\overline{m}_1 \to 0} \ln \gamma_{\pm,1} \qquad (28)$$

of NaCl or NaBr in aqueous solutions of mixed electrolytes of different charge type with a common ion are compared with predictions. Again the new model compares favorably with the Pitzer model. The comparison for the aqueous solution of $NaBr + Ca(NO_3)_2$ (cf. Tables 5 and Figure 3) shows that the improvement over Pitzer's model also holds for mixed electrolytes without a common ion.

Table 6 gives an example for the prediction of properties of multicomponent electrolyte aqueous solutions. Mean ionic ac-

Table 2. Binary Parameters for Electrolytes in Aqueous Solutions and Comparison with Experimental Data at 298.15 K

Electrolyte	$\overline{m}_{\max}$	u^{*}_{ca}/K	λ_{ca}	$\sigma_{\ln\gamma\pm}$*	SD_{ϕ}**
HCl	16.0	64.19	1.194	0.0210	0.0200
HBr	11.0	109.2	0.635	0.0120	0.0111
HI	10.0	−81.60	0.846	0.0093	0.0076
HNO_3	28.0	0.280	2.170	0.0310	0.0268
LiCl	19.0	40.26	0.831	0.0129	0.0126
LiBr	20.0	1.410	0.555	0.0100	0.0098
LiI	3.0	−130.0	0.866	0.0086	0.0075
LiOH	4.0	−252.6	0.064	0.0149	0.0113
$LiNO_3$	20.0	196.1	1.850	0.0217	0.0146
NaCl	6.0	−75.80	0.800	0.0075	0.0067
NaBr	9.0	−121.0	0.705	0.0124	0.0123
NaI	12.0	−209.0	0.606	0.0144	0.0141
NaOH	29.0	−0.780	0.614	0.0133	0.0117
$NaNO_3$	10.0	−87.19	0.528	0.0593	0.0570
KCl	5.0	−198.0	0.442	0.0027	0.0024
KBr	5.5	−220.0	0.390	0.0021	0.0021
KI	4.5	−265.0	0.467	0.0075	0.0071
KOH	20.0	46.90	0.481	0.0172	0.0163
KNO_3	3.5	−424.5	0.577	0.0059	0.0045
CsCl	11.0	−190.0	0.001	0.0067	0.0060
CsBr	5.0	−235.0	0.010	0.0088	0.0066
CsI	3.0	−289.0	0.015	0.0051	0.0043
CsOH	1.2	−11.00	0.861	0.0031	0.0021
$CsNO_3$	1.6	−416.0	0.285	0.0039	0.0036
NH_4Cl	7.0	−200.0	0.500	0.0051	0.0048
NH_4NO_3	26.0	−287.2	0.452	0.0051	0.0044
$MgCl_2$	5.0	21.10	0.578	0.0150	0.0148
$MgBr_2$	5.0	−42.01	0.602	0.0313	0.0305
MgI_2	5.0	−134.3	0.359	0.0356	0.0363
$Mg(NO_3)_2$	5.0	2,580.0	0.887	0.0102	0.0076
$CaCl_2$	10.0	−72.20	0.523	0.0337	0.0337
$CaBr_2$	9.0	−147.5	0.678	0.0338	0.0340
CaI_2	1.8	−219.4	0.493	0.0049	0.0031
$Ca(NO_3)_2$	6.0	−157.9	0.704	0.0049	0.0049
$SrCl_2$	4.0	−165.4	0.284	0.0051	0.0044
$SrBr_2$	2.0	−179.0	0.326	0.0067	0.0058
SrI_2	2.0	−230.1	0.345	0.0065	0.0036
$Sr(NO_3)_2$	4.0	−312.5	0.393	0.0034	0.0034
$BaCl_2$	2.5	−71.10	0.944	0.0043	0.0036
$BaBr_2$	2.0	−96.16	0.800	0.0019	0.0017
BaI_2	2.0	−197.9	0.724	0.0079	0.0069
$Ba(NO_3)_2$	0.4	−560.3	0.987	0.0013	0.0018
Li_2SO_4	3.0	−347.0	1.309	0.0113	0.0104
Na_2SO_4	4.5	−349.0	1.215	0.0400	0.0377
K_2SO_4	0.7	−495.7	0.725	0.0007	0.0006
Cs_2SO_4	1.6	−475.5	0.855	0.0021	0.0019
$(NH_4)_2SO_4$	4.0	−499.3	0.673	0.0111	0.0101
$MgSO_4$	3.0	95.50	0.399	0.0268	0.0446

* $$\sigma_{\ln\gamma\pm} = \left(\frac{1}{N}\cdot\sum_{i=1}^{N}(\ln\gamma_{\pm,\mathrm{cal}} - \ln\gamma_{\pm,\mathrm{exp}})_i^2\right)^{0.5}$$

** $$SD_{\phi} = \left(\frac{1}{N-1}\cdot\sum_{i=1}^{N}(\phi_{\mathrm{cal}} - \phi_{\mathrm{exp}})_i^2\right)^{0.5}$$

tivity coefficients of salts in Dead Sea brine of 7.878 total molal ionic strength as reported by Marcus (1981) are compared to predictions, showing again some improvements of the new model over Pitzer's equation.

Solubilities of salts in mixed electrolyte solutions

In Table 7 and Figures 4 to 6 predicted solubilities of a strong electrolyte in an aqueous solution of another strong electrolyte at 298.15 K are compared with experimental results. The experimental solubilities in the mixed electrolyte solutions were taken from Linke and Seidell (1965). The solubility product was calculated using either tabulated values of the Gibbs energy as reported by Zemaitis et al. (1986) or the solubility of a single electrolyte in water as reported by Linke and Seidell (1965). The new model represents the experimental results sat-

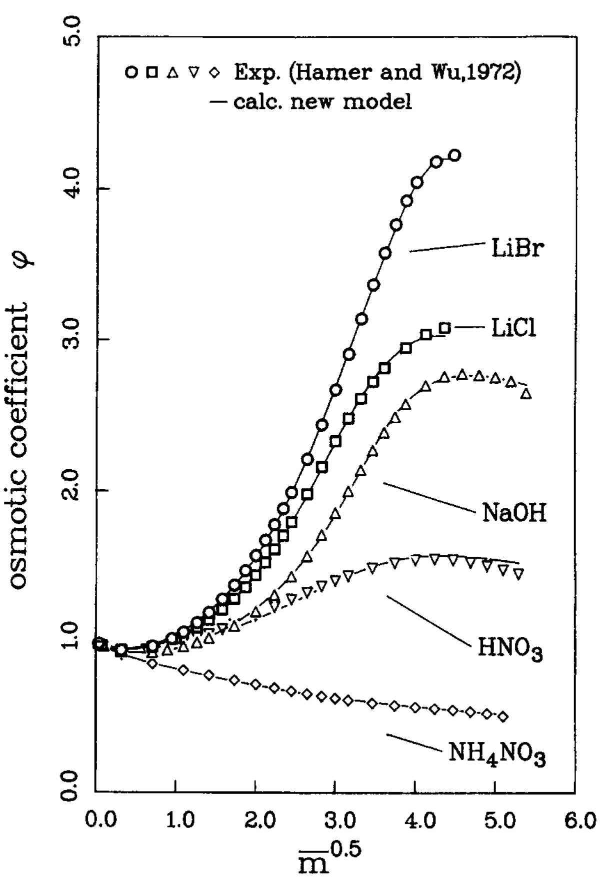

Figure 1. Comparison between measured and calculated osmotic coefficients of some uni-univalent single electrolyte aqueous solutions at 298.15 K.

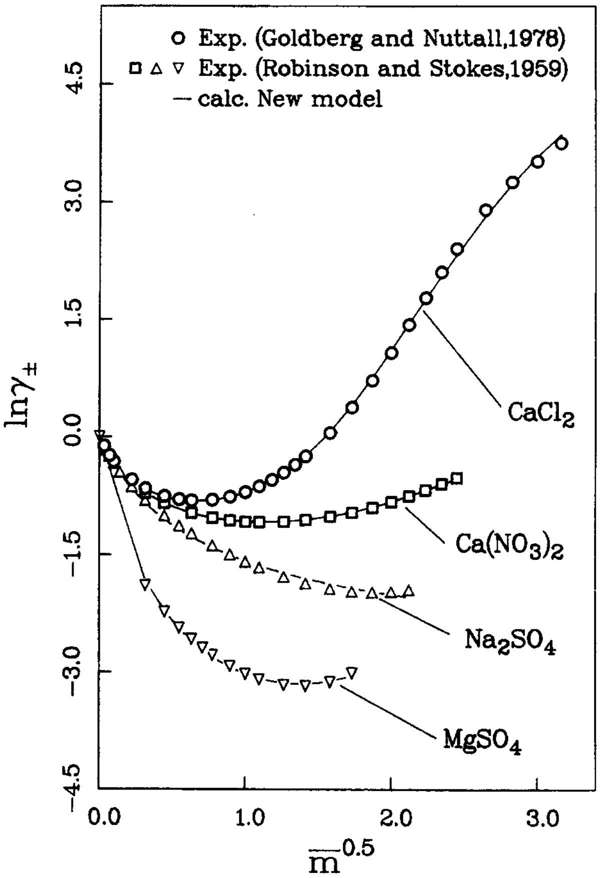

Figure 2. Comparison between measured and calculated mean ionic activity coefficients of some single electrolyte aqueous solutions at 298.15 K.

isfactory although no model parameter was adjusted to any ternary data. The Pitzer-6 model whose parameters were also determined from experimental data of single electrolyte aqueous solutions yields larger deviations. The deviation observed with Pitzer's equation can be reduced when the interaction parameters are adjusted using experimental data of mixed electrolyte aqueous solutions—that modification is here called the Pitzer-corr model. But the deviations are still larger than those observed using the new model. The solubilities of the salt in Table

Table 3. Comparison of Models for Extremely Concentrated Electrolyte Solutions at 298.15 K

Salt	$\bar{m}_{max}$	New Model	SD_ϕ* Stokes	Kim + Frederick	New Model	$\sigma_{\ln\gamma\pm}$** Liu (1991)	Haghtalab (1989)
KOH	20	0.016	0.018	0.027	0.017	0.013	0.039
NaOH	29	0.012	0.018	0.086	0.013	0.043	0.084
HCl	16	0.020	0.019	0.014	0.021	0.029	0.024
LiCl	19	0.013	0.015	0.053	0.013	0.027	0.052
LiBr	20	0.010	0.017	0.094	0.010	0.017	0.095
NaCl	6	0.007	0.008	0.001	0.008	0.016	0.011
$CaCl_2$	10	0.034	0.041	0.016	0.034	0.043	0.109
$CaBr_2$	9	0.034	0.014	0.088	0.034	0.034	0.072
av.	dev.†	0.018	0.018	0.044	0.019	0.028	0.061

[*] $SD_\phi = \left(\frac{1}{N-1} \cdot \sum_{i=1}^{N} (\phi_{cal} - \phi_{exp})_i^2\right)^{0.5}$

[**] $\sigma_{\ln\gamma\pm} = \left(\frac{1}{N} \cdot \sum_{i=1}^{N} (\ln \gamma_{\pm,cal} - \ln \gamma_{\pm,exp})_i^2\right)^{0.5}$

[†] $\text{av. dev.} = \sum_{s=1}^{N} \frac{|SD_{\phi,s}|}{N} \text{ or } \sum_{s=1}^{N} \frac{|\sigma_{\ln\gamma\pm,s}|}{N}$

Table 4. Mean Ionic Activity Coefficients ln $\gamma_{\pm}$ and Osmotic Coefficients ϕ for Mixed Electrolyte Aqueous Solutions with a Common Ion Predicted from Several Models Compared with Experimental Data at 298.15 K

System (1) + (2)	SD[*] between Predictions and Experimental Data Pitzer-Sat	Kim + Frederick	New Model	Experimental Data $I_{m,\max}$	Property	Ref[‡]
HCl + KCl	0.0171	0.0476	0.0210	3.5	ln $\gamma_{\pm,1}$	a
HCl + NaCl	0.0405	0.0805	0.0438	3.0	ln $\gamma_{\pm,1}$	a
HCl + LiCl	0.0276	0.0666	0.0189	4.0	ln $\gamma_{\pm,1}$	a
HCl + $CaCl_2$	0.0097	0.0570	0.0183	5.0	ln $\gamma_{\pm,1}$	b
HCl + $BaCl_2$	0.0169	0.0521	0.0153	3.0	ln $\gamma_{\pm,1}$	c
HCl + $SrCl_2$	0.0250	0.0289	0.0671	2.5	ln $\gamma_{\pm,1}$	a
HBr + KBr	0.0196	0.0540	0.0172	3.0	ln $\gamma_{\pm,1}$	a
HBr + NaBr	0.0409	0.1083	0.0360	3.0	ln $\gamma_{\pm,1}$	a
HBr + LiBr	0.0465	0.1125	0.0335	3.0	ln $\gamma_{\pm,1}$	a
HBr + $CaBr_2$	0.0078	0.0938	0.0126	2.0	ln $\gamma_{\pm,1}$	d
NaCl + KCl	0.0290	0.0258	0.0180	4.3	ln $\gamma_{\pm,1}$	e
NaBr + KBr	0.0078	0.0119	0.0049	4.4	ϕ	f
NaCl + LiCl	0.0139	0.0353	0.0109	6.0	ϕ	g
NaCl + $CaCl_2$	0.0094	0.0103	0.0096	6.0	ϕ	h
NaCl + $MgCl_2$	0.0073	0.0060	0.0100	6.0	ϕ	i
KCl + $CaCl_2$	0.0239	0.0256	0.0078	5.0	ϕ	j
$NaNO_3$ + $LiNO_3$	0.0521	0.0385	0.0446	7.0	ϕ	g
LiCl + $BaCl_2$	0.0219	0.0481	0.0086	4.0	ϕ	k
KCl + KBr	0.0044	0.0044	0.0077	4.4	ϕ	f
NaCl + NaBr	0.0013	0.0019	0.0065	4.4	ϕ	f
$CaCl_2$ + $Ca(NO_3)_2$	0.5905	0.1146	0.0490	18.3	ϕ	l
$MgCl_2$ + $Mg(NO_3)_2$	0.1276	0.0302	0.0281	13.7	ϕ	l
av. dev[**]	0.0519	0.0479	0.0222			
av. dev.[†]	0.0212	0.0455	0.0206			

[*] SD: standard deviation.

[**] av. dev. cf. Table 3.

[†] Restricted comparison ($\overline{m}_s < 6$).

[‡] a. Harned and Owen (1958); b. Roy et al. (1981); c. Khoo et al. (1978); d. Khoo et al. (1979); e. Huston and Butler (1969); f. Covington et al. (1968); g. Robinson et al. (1971); h. Robinson and Bower (1966); i. Platford (1968); j. Robinson and Covington (1968); k. Lindenbaum et al. (1972); l. Platford (1971).

7 are all less than 6 molal. For a salt whose saturated concentration is above 6 molal, such as NH_4NO_3, the predictions of Pitzer-6 model and its modification by Kim and Frederick are not as reliable as those from the new model (cf. Figure 6).

Table 5. Comparison of the Trace Mean Ionic Activity Coefficient ln $\gamma^{tr}_{\pm,1}$ of NaCl or NaBr in Mixed Salt Aqueous Solutions at 298.15 K

System (1) + (2)	I_m	ln $\gamma^{tr}_{\pm,1}$ exp	New Model	Pitzer-6
NaBr + $NaNO_3$[a]	0.3	−0.376	−0.388	−0.368
	0.5	−0.444	−0.445	−0.419
	1.0	−0.467	−0.516	−0.481
	2.0	−0.553	−0.567	−0.516
	3.0	−0.578	−0.576	−0.506
	4.0	−0.578	−0.568	−0.475
	5.0	−0.525	−0.550	−0.430
	6.0	−0.513	−0.526	−0.377
NaCl + Na_2SO_4[b]	1.0	−0.560	−0.569	−0.511
	3.0	−0.707	−0.714	−0.615
	6.0	−0.705	−0.787	−0.583
NaCl + $CaCl_2$[b]	1.0	−0.410	−0.419	−0.382
	3.0	−0.322	−0.334	−0.297
	6.0	−0.032	−0.044	−0.014
NaBr + $Ca(NO_3)_2$[c]	3.0	−0.475	−0.512	−1.059
	4.5	−0.423	−0.474	−1.185
	6.0	−0.412	−0.416	−1.274

Experimental data from: (a) Haghtalab and Vera (1991a); (b) Lanier (1965); (c) Haghtalab and Vera (1991b).

Conclusion

By combining ionic solvation equilibria with an appropriate expression for the excess Gibbs energy, a new model for describing activities in aqueous mixed electrolyte solutions has been developed. The new method is especially aimed to predicting properties in aqueous mixed electrolyte solutions from information on the properties of single electrolyte aqueous solutions alone. As solvation results in new species, solvated ions, the original model needs many parameters. By introducing some reasonable assumptions the number of parameters can be reduced drastically to three "pure component" parameters per ion and two binary parameters for interactions between a cation and an anion. Parameters were determined for 10 cations (H^+, Li^+, Na^+, K^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and 6 anions (Cl^-, Br^-, I^-, OH^-, NO_3^-, SO_4^{2-}) at 298.15 K. The capabilities of the new model in predicting properties of aqueous solutions of mixed electrolytes is shown by comparing predicted osmotic coefficients, mean ionic activity coefficients and solubilities with experimental results not only in diluted, but also in extremely concentrated mixed electrolyte aqueous solutions. Extensions of the model to include more ionic as well as nonionic species and investigations on the influence of temperature on the model parameters are in progress.

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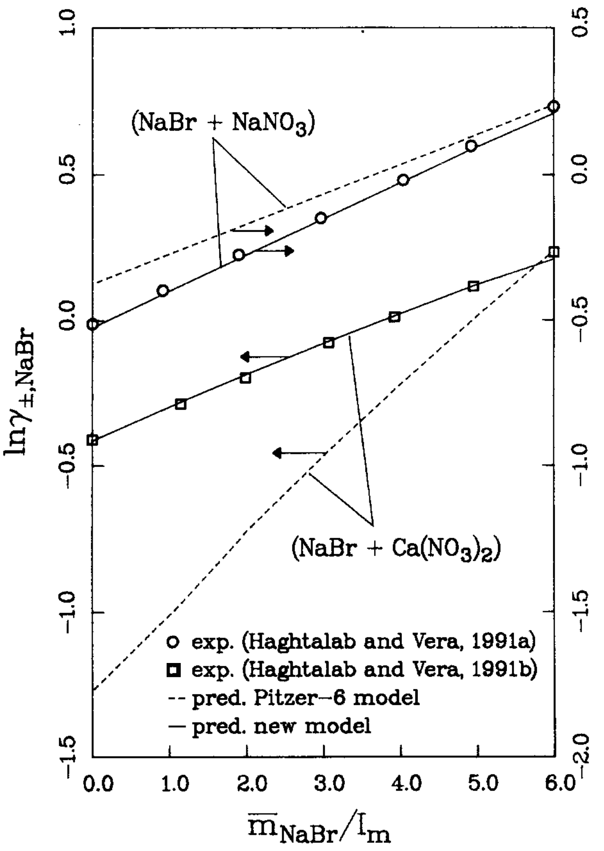

Figure 3. Mean ionic activity coefficient of NaBr in a aqueous solution of 6 molal total ionic strength with $NaNO_3$ or $Ca(NO_3)_2$ at 298.15 K.

Table 6. Comparison of the Mean Ionic Activity Coefficient of Components in Dead Sea Brine at 298.15 K

Electrolytes	Molality	Exp*	$\gamma_\pm$ New Model	Pitzer-6
NaCl	1.733	1.236	1.254	1.285
KCl	0.158	0.878	0.913	1.053
$MgCl_2$	1.549	1.589	1.619	1.651
$CaCl_2$	0.447	1.320	1.330	1.330

*Marcus (1981)

Notation

a = true activity
A = Debye-Hückel constant
A^{Z_a} = anion
b = correction parameter in Eqs. 24 and 25
B = Debye-Hückel constant
d = ionic size parameter
G^E = excess Gibbs energy
h = solvation number
I = number of cationic species
I_m = ionic strength
J = number of anionic species
i, j = species i, j
k, l = species k, l
K = solvation equilibrium constant
l = pure component parameter in UNIQUAC equation
m_k = true molality of charged specie k
$\overline{m}_k$ = overall (stoichiometric, apparent) molality of component k

Table 7. Mean Deviation Δ between Calculated and Experimental Results for the Solubility of NaCl, KCl and Na_2SO_4 in Mixed Electrolyte Solutions at 298.15 K*

Systems	max. I_m	Δ** New Model	Pitzer- Corr Model
NaCl + HCl	19	0.088	0.060
KCl + HCl	11	0.098	0.114
NaCl + $CaCl_2$	14	0.106	0.164
KCl + $CaCl_2$	18	0.185	0.199
NaCl + KCl	7.4	0.111	0.086
Na_2SO_4 + NaOH	18	0.096	0.443

*Experimental data from Linke and Seidell (1965).

** $\Delta = \sum_{i=1}^{N} \frac{|\overline{m}_{\text{solub.,cal}} - \overline{m}_{\text{solub.,exp}}|_i}{N}$

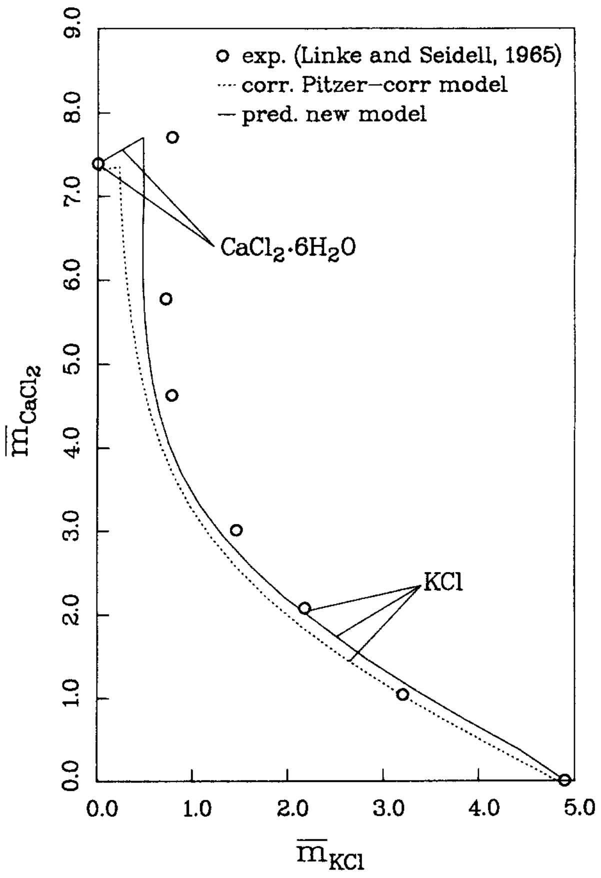

Figure 4. Measured and predicted solubilities for mixed electrolytes KCl + $CaCl_2$ in water at 298.15 K.

M_w = molecular weight of water
M^{Z_c} = cation
n_k = mole number of specie k
n_t = total number of moles in a solution
N = number of component
q = surface parameter in UNIQUAC equation
r = size parameter in UNIQUAC equation
r_k^* = ionic radius of specie k
R = gas constant
SD_ϕ = standard deviation of the osmotic coefficient (cf. Table 2)
T = temperature, K
u = interaction energy parameter in UNIQUAC equation

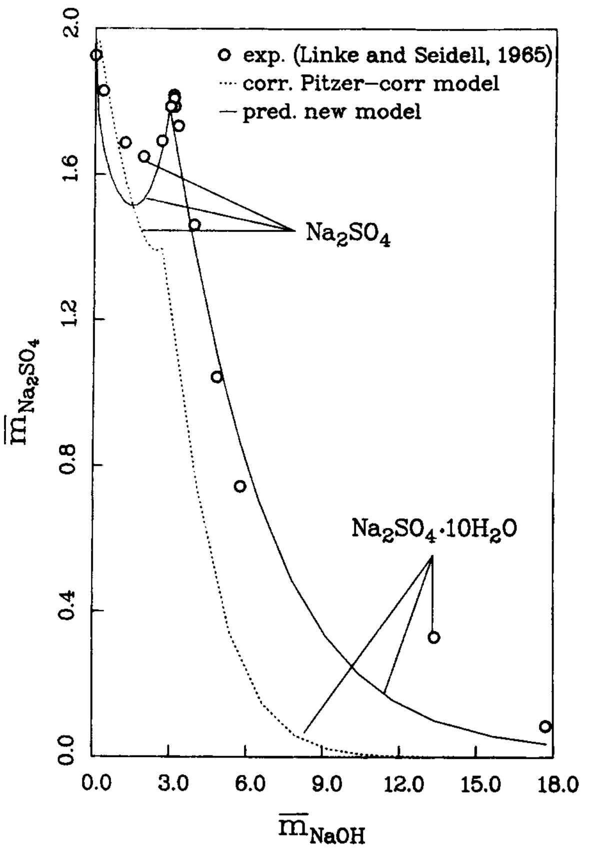

Figure 5. Measured and predicted solubilities for mixed electrolytes $Na_2SO_4 + NaOH$ in water at 298.15 K.

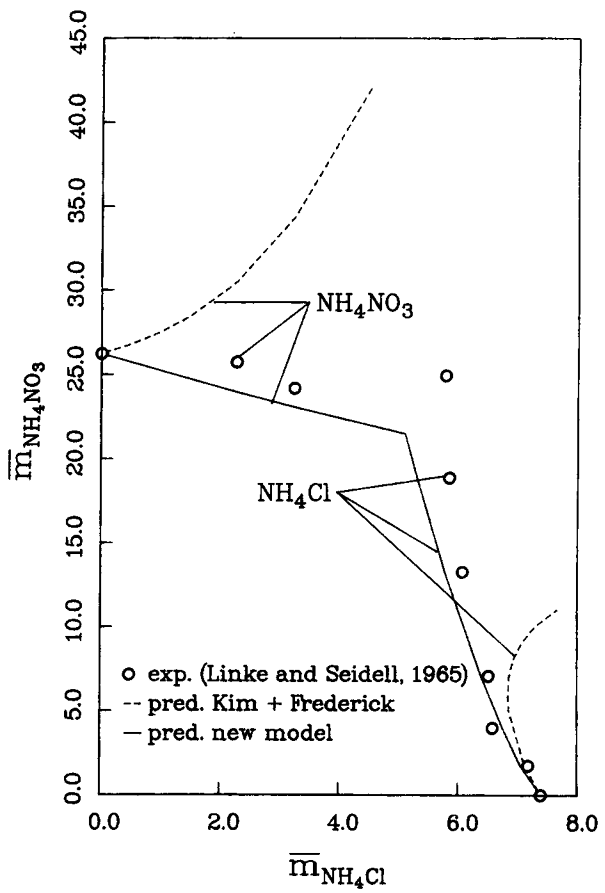

Figure 6. Measured and predicted solubilities for mixed electrolytes $NH_4NO_3 + NH_4Cl$ in water at 298.15 K.

u^* = u/R, interaction energy parameter in UNIQUAC equation
$\tilde{v}_w$ = volume of water molecule
y_k = ionic strength fraction of ion k
z = coordination number in UNIQUAC equation
z_k = true mole fraction of specie k
Z = charge number of ionic species

Greek letters

γ_k = true activity coefficient of specie k on mole fraction scale normalized according to Raoult's law
γ_k^* = true activity coefficient of specie k on mole fraction scale normalized according to Henry's law
$\gamma_\pm$ = mean ionic activity coefficient on molality scale
$\gamma_\pm^{tr}$ = trace mean ionic activity coefficient on molality scale
θ = area fraction in UNIQUAC equation
$\lambda_{ci,aj}$ = binary size correction parameter between cation c and anion a
μ = chemical potential
σ = root mean square deviation
τ = energy interaction parameter in UNIQUAC equation
ν = stoichiometric number of ion in an electrolyte
ϕ = osmotic coefficient

Subscripts

a = anion
aj, ak = anion j, anion k
c = cation
ci, ck = cation i, cation k
ca = strong electrolyte of cation c and anion a
cal = calculated
DH = contribution from Debye-Hückel law
exp = experimental
ha = solvated anion
haj = solvated anion j
hc = solvated cation
hci = solvated cation i
hk = solvated species k
k = species k
l = species l
(m) = on molality scale
max = maximum
s = strong electrolyte s
solub = at solubility limit
UNIQUAC = contribution from UNIQUAC equation
w = water
(z) = on true mole fraction scale

Superscripts

∞ = infinite dilution
o = reference state

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Appendix A: Solvation Equilibria in Multicomponent Electrolyte Aqueous Solutions

It is assumed that N electrolytes $M_{v_{c,s}}X_{v_{a,s}}$ $(s=1, \ldots, N)$ built from I different cations and J different anions are dissolved in water and thereby completely dissociated. The ionic solvation equilibrium in the solution is represented by:

$$M_i^{Z_c} + h_{ci}\mathrm{H_2O} \rightleftharpoons M_i^{Z_c} \cdot h_{ci}\mathrm{H_2O} \quad (i=1, \ldots, I) \qquad \text{(A1)}$$

$$X_j^{Z_a} + h_{aj}\mathrm{H_2O} \rightleftharpoons X_j^{Z_a} \cdot h_{aj}\mathrm{H_2O} \quad (j=1, \ldots, J) \qquad \text{(A2)}$$

where h is solvation number. Due to solvation, there are $2I+2J+1$ species in the solution. The thermodynamical equilibrium constants are given by

$$K_{ci}=\frac{a_{hci}}{a_{ci}\cdot a_w^{h_{ci}}}=\frac{z_{hci}}{z_{ci}\cdot z_w^{h_{ci}}}\cdot\frac{\overset{*}{\gamma}_{hci}}{\overset{*}{\gamma}_{ci}\cdot\gamma_w^{h_{ci}}}\quad(i=1,\ \ldots,\ I)\tag{A3}$$

$$K_{aj}=\frac{a_{haj}}{a_{aj}\cdot a_w^{h_{aj}}}=\frac{z_{haj}}{z_{aj}\cdot z_w^{h_{aj}}}\cdot\frac{\overset{*}{\gamma}_{haj}}{\overset{*}{\gamma}_{aj}\cdot\gamma_w^{h_{aj}}}\quad(j=1,\ \ldots,\ J)\tag{A4}$$

When $\overline{m}_s$ $(s=1,\ \ldots,\ N)$ moles of electrolytes are dissolved in one kilogram of water, mass balance can be expressed by n_{hci} $(i=1,\ \ldots,\ I)$ and n_{haj} $(j=1,\ \ldots,\ J)$, moles of solvated cations and anions respectively. The total number of moles n_t in the solution is:

$$n_t=\frac{1{,}000}{M_w}+\sum_{s=1}^{N}(v_{c,s}+v_{a,s})\cdot\overline{m}_s-\sum_{i=1}^{I}h_{ci}\cdot n_{hci}-\sum_{j=1}^{J}h_{aj}\cdot n_{haj}\tag{A5}$$

the true mole fractions of all species are:

$$z_{hci}=\frac{n_{hci}}{n_t}\quad(i=1,\ \ldots,\ I)\tag{A6}$$

$$z_{haj}=\frac{n_{haj}}{n_t}\quad(j=1,\ \ldots,\ J)\tag{A7}$$

$$z_{ci}=\frac{\sum_{s=1}^{N}v_{ci,s}\cdot\overline{m}_s-n_{hci}}{n_t}\quad(i=1,\ \ldots,\ I)\tag{A8}$$

$$z_{aj}=\frac{\sum_{s=1}^{N}v_{aj,s}\cdot\overline{m}_s-n_{haj}}{n_t}\quad(j=1,\ \ldots,\ J)\tag{A9}$$

$$z_w=1-\sum_{i=1}^{I}z_{hci}-\sum_{j=1}^{J}z_{haj}-\sum_{i=1}^{I}z_{ci}-\sum_{i=1}^{J}z_{aj}\tag{A10}$$

Appendix B: Relationship Between True Activities and Apparent Properties

When $\overline{m}_s$ $(s=1,\ \ldots,\ N)$ moles of electrolytes are dissolved in one kilogram of water, according to the theory of Prigogine and Defay (1954), the activity of water is:

$$a_w=a_{w,\text{true}}=\gamma_w\cdot z_w\tag{B1}$$

or

$$\phi=\frac{-1{,}000}{M_w\sum_{s=1}^{N}v_s\cdot\overline{m}_s}\ln a_w=\frac{-1{,}000}{M_w\sum_{s=1}^{N}v_s\cdot\overline{m}_s}\ln(\gamma_w\cdot z_w)\tag{B2}$$

where $v_s=v_{c,s}+v_{a,s}$.

To relate the true activities to the conventionally used mean ionic activity coefficient on molality scale of an electrolyte with any cation c and any anion a in a multicomponent electrolyte aqueous solution, the chemical potential is considered:

$$\mu_{ca}=\mu^o_{ca(m)}+\mathrm{RT}\ \ln\ [\overline{m}_c^{v_c}\cdot\overline{m}_a^{v_a}\cdot(\gamma_{\pm,ca})^{v_s}]\tag{B3}$$

$\overline{m}_c$ and $\overline{m}_a$ are the apparent (overall, stoichiometric) molalities of cation c and anion a. $\mu^o_{ca(m)}$ is the chemical potential of an electrolyte ca in the standard state on molality scale.

On the other hand, as μ_{ca} depend neither on the choice of standard state nor on the concentration scale:

$$\begin{aligned}\mu_{ca}&=v_c\cdot\mu_c+v_a\cdot\mu_a\\&=v_c\cdot[\mu^o_{c(z)}+RT\ln(z_c\cdot\overset{*}{\gamma}_c)]+v_c\cdot[(\mu^o_{a(z)}+RT\ln(z_a\cdot\overset{*}{\gamma}_a)]\end{aligned}\tag{B4}$$

Solvation reaction yields:

$$\mu_c+h_c\cdot\mu_w=\mu_{hc}\tag{B5}$$

$$\mu_a+h_a\cdot\mu_w=\mu_{ha}\tag{B6}$$

where the chemical potential of water is:

$$\mu_w=\mu^o_w+RT\ln(z_w\cdot\gamma_w)\tag{B7}$$

which is normalized according to Raoult's law on mole fraction scale. Hence, there is:

$$\begin{aligned}\mu_{ca}&=v_c\cdot\mu_c+v_a\cdot\mu_a\\&=v_c(\mu_{hc}-h_c\cdot\mu_w)+v_a(\mu_{ha}-h_a\cdot\mu_w)\\&=v_c\cdot\mu^o_{hc}+v_a\cdot\mu^o_{ha}-(v_c\cdot h_c+v_a\cdot h_a)\cdot\mu^o_w\\&\quad+RT[v_c\ln a_{hc}+v_a\ln a_{ha}-(v_c\cdot h_c+v_a\cdot h_a)\ln a_w]\end{aligned}\tag{B8}$$

Combining Eqs. B3 and B8, results in:

$$\begin{aligned}RT\ln(\gamma_{\pm,ca})^{v_s}&=RT\ln\left(\frac{z_{hc}^{v_c}\cdot z_{ha}^{v_a}}{z_w^{(v_c\cdot h_c+v_a\cdot h_a)}}\cdot\frac{1}{\overline{m}_c^{v_c}\cdot\overline{m}_a^{v_a}}\right)\\&\quad+RT\ \ln\left(\frac{\overset{*}{\gamma}_{hc}^{\,v_c}\cdot\overset{*}{\gamma}_{ha}^{\,v_a}}{\gamma_w^{(v_c\cdot h_c+v_a\cdot h_a)}}\right)-[\mu^o_{ca(m)}-v_c\cdot\mu^o_{hc}-v_a\cdot\mu^o_{ha}\\&\quad+(v_c\cdot h_c+v_a\cdot h_a)\mu^o_w]\end{aligned}\tag{B9}$$

As the standard states depend only on temperature and pressure, the sum of standard state chemical potentials can be determined by extrapolating Eq. B9 to infinitely diluted electrolyte solutions, that is, $\overline{m}_s\rightarrow 0$ $(s=1,\ \ldots,\ N)$. As all activity coefficients approach unity and as due to solvation, there are:

$$\lim_{\overline{m}_c\rightarrow 0}\frac{z_{hc}}{\overline{m}_c}=\lim_{\overline{m}_a\rightarrow 0}\frac{z_{ha}}{\overline{m}_a}=\frac{M_w}{1{,}000}$$

and

$$\mu^o_{ca(m)} - v_c \cdot \mu^o_{hc} - v_a \cdot \mu^o_{ha} + (v_c \cdot h_c \cdot v_a \cdot h_a)\mu^o_w$$

$$= \lim_{\overline{m}_s \to 0} RT \ln\left(\left(\frac{z_{hc}}{\overline{m}_c}\right)^{v_c} \cdot \left(\frac{z_{ha}}{\overline{m}_a}\right)^{v_a} \cdot \frac{1}{z_w^{(v_c \cdot h_c + v_a \cdot h_a)}}\right)$$

$$= v_s RT \ln \frac{M_w}{1,000} \qquad \text{(B10)}$$

The mean ionic activity coefficient of a dissolved electrolyte *ca* on molality scale can therefore be calculated from the overall molality of ions $\overline{m}_c$ and $\overline{m}_a$, the true mole fraction of solvated ions z_{hc} and z_{ha} and the true mole fraction of water by:

$$\ln (\gamma_{\pm,ca})^{v_s} = \ln\left(\left(\frac{z_{hc} \cdot \overset{*}{\gamma}_{hc}}{\overline{m}_c}\right)^{v_c} \cdot \left(\frac{z_{ha} \cdot \overset{*}{\gamma}_{ha}}{\overline{m}_a}\right)^{v_a} \cdot \frac{1}{(z_w \cdot \gamma_w)^{(v_c \cdot h_c + v_a \cdot h_a)}}\right)$$

$$- v_s \cdot \ln \frac{M_w}{1,000} \qquad \text{(B11)}$$

Appendix C: Activity of Water in Electrolyte Solutions According to the Debye-Hückel Theory

The activity of water in the Debye-Hückel theory is:

$$a_{w,DH} = \gamma_{w,DH} \cdot z_w \qquad \text{(C1)}$$

Employing the Gibbs-Duhem equation results in:

$$\frac{1,000}{M_w} \cdot d \ln \gamma_{w,DH} = - \sum_{k=1}^{2(I+J)} m_k d \ln \overset{*}{\gamma}_{k,DH} \qquad \text{(C2)}$$

where m_k is the true molality of ionic species (solvated and unsolvated), which is related to the true mole fraction of species k by:

$$m_k = \frac{z_k}{z_w} \cdot \frac{1,000}{M_w} \qquad \text{(C3)}$$

From the Debye-Hückel theory, the true activity coefficient for an *ionic species* k is:

$$\ln \overset{*}{\gamma}_{k,DH} = \frac{-Z_k^2 A \sqrt{I_m}}{1 + Bd_k \sqrt{I_m}} \qquad \text{(C4)}$$

Let $x_k = Bd_k \sqrt{I_m}$, then

$$d \ln \gamma_k = \frac{-Z_k^2 A}{Bd_k (1 + x_k)^2} dx_k \qquad \text{(C5)}$$

Defining an ionic strength fraction y_k of an ion k:

$$y_k = \frac{\frac{1}{2} Z_k^2 m_k}{I_m} \qquad \text{(C6)}$$

and combining Eqs. C2, C5 and C6, results in:

$$\frac{1,000}{M_w} \cdot d \ln \gamma_{w,DH} = \frac{2A}{B} \sum_k^{2(I+J)} \left[\frac{y_k I_m}{d_k (1 + x_k)^2} dx_k\right] \qquad \text{(C7)}$$

and replacing I_m by $I_m = (x_k / d_k B)^2$

$$\frac{1,000}{M_w} \cdot d \ln \gamma_{w,DH} = \frac{2A}{B^3} \sum_k^{2(I+J)} \left[\frac{y_k x_k^2}{d_k^3 (1 + x_k)^2} dx_k\right] \qquad \text{(C8)}$$

Integrating Eq. C8 at constant ionic strength fraction y_k yields the true activity coefficient of water:

$$\ln \gamma_{w,DH} = \frac{M_w}{1,000} \cdot \frac{2A}{B^3 \cdot I_m} \sum_k^{2(I+J)} \left[\frac{m_k \cdot Z_k^2}{d_k^3}\left(1 + Bd_k \sqrt{I_m}\right.\right.$$

$$\left.\left. - 2 \ln (1 + Bd_k \sqrt{I_m}) - \frac{1}{1 + Bd_k \sqrt{I_m}}\right)\right] \qquad \text{(C9)}$$

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