Use of Hydration and Dissociation Chemistries with the Electrolyte–NRTL Model

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Sound theoretical understanding and accurate mathematical representation of electrolyte solution nonideality were the subject of extensive research efforts for decades. It is demonstrated that these goals can be achieved by incorporation of hydration and partial dissociation chemistries with the semi-empirical electrolyte NRTL model. The resulting model provides a comprehensive thermodynamic framework for accurate correlation and reliable extrapolation of electrolyte solution nonideality over the entire concentration range.

Introduction

Reliable design and operation of industrial processes involving electrolytes require sound theoretical understanding and accurate mathematical representation of the solution nonideality of aqueous electrolyte systems. Many theories and engineering models have been proposed, and they are well summarized by Zemaitis et al. (1986), Loehe and Donohue (1997), and others. Among the successful engineering correlations are the models of Meissner and Tester (1972), Pitzer (1973), Bromley (1973), and the electrolyte nonrandom two-liquid (NRTL) model of Chen et al. (1982) and Chen and Evans (1986).

While existing engineering models are found to describe well the nonideality of aqueous electrolytes at relatively low concentrations, they often inaccurately represent the solution nonideality at high concentrations. For example, both the Pitzer and the Bromley models cover electrolyte concentrations only up to 6 molal. Much empiricism and data fitting are needed to extend their applicability to higher concentrations, especially beyond about 10 molal. This often results in poor extrapolation to concentrated electrolyte systems, multi-electrolyte systems, or mixed-solvent electrolyte systems.

The electrolyte NRTL model is capable of quantitatively accurate correlation over the entire concentration range for many electrolytes, through combination of the Pitzer-Debye-Hückel model for long-range ion–ion electrostatic interactions with the NRTL theory for short-range energetic interactions among various species in electrolyte solutions. Consequently, the model has been widely applied to correlate electrolyte systems encountered in the chemical industry (Aspen Technology, Inc., 1998). For some aqueous electrolyte systems, however, such as HCl, LiCl, $MgCl_2$, and $CaCl_2$, for which the nonideality in the high-concentration range is particularly large, the extrapolations from the NRTL model for mean ionic activity coefficients of electrolytes are found to be much lower than experimental values (Abovsky et al., 1998). There have been a number of attempts to improve the performance of the NRTL model (Haghtalab and Vera, 1988, 1991; Liu and Gren, 1991). Most recently, Abovsky et al. (1998) proposed the inclusion of concentration dependence of interaction parameters ‘‘in order to enhance the capability of the model in representing the nonideality of concentrated electrolyte solutions.’’

Thermodynamically rigorous modeling of electrolyte solutions requires proper accounting of prominent solution chemistries—hydration and partial dissociation—in addition to energetic interactions among the species (Robinson and Stokes, 1959; Conway, 1983). For example, cations of transition elements such as chromium and cobalt exhibit a marked tendency to form hydrated ions. These ions carry with them water molecules sufficiently permanently bound to be regarded as part of the ion (Robinson and Stokes, 1959). As for partial dissociation, strong acids like hydrogen chloride go through a smooth transition from effectively complete dissociation at low electrolyte concentrations, to partial dissociation at medium electrolyte concentrations, to insignificant dissociation at high electrolyte concentrations where the acids

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exist mainly as molecular species. Solution chemistries are inherent parts of electrolyte solution nonideality, and they should be properly accounted for in first-principle engineering models for electrolyte solutions.

Indeed, phase behavior of many highly nonideal electrolyte solutions has been satisfactorily described through the simultaneous account of the solution chemistries and the physical interactions (Cruz and Renon, 1978; Chen et al., 1979; Chen and Evans, 1986; Chen, 1987; Austgen et al., 1989, 1991; Aspen Technology, 1998). A particularly insightful study is that of Pinsky and Gruber (1992), who considered aqueous systems containing Na^+, K^+, Mg^{+2}; Cl^-, and SO_4^{-2} ions. They reported successful representation of $MgCl_2$ data by assuming a single thermodynamic entity of Mg^{+2} ion with six waters of hydration. They also cited independent experimental evidence for the hydrated ion ($Mg(H_2O)_6^{+2}$) from neutron diffraction and proton NMR studies of solutions and X-ray diffraction of solids; the hydrate water associated with Mg^{+2} has a relatively long lifetime, measured in microseconds. Pinsky and Gruber demonstrated that the combination of hydration with the NRTL model results in a successful engineering correlation with strong theoretical and analytical support.

Other related areas of research have identified the need to include the hydration of ions. Paritosh and Murad (1996) have shown through molecular-dynamics simulations that the reason ions do not penetrate semipermeable membranes is that water molecules strongly cluster around the ions, increasing their size considerably, and thus preventing them from permeating. Koneshan et al. (1998) have shown that the low mobility of small ions such as Li^+ is that their effective size is increased due to a cage of water molecules with a long residence time (that is, "hydrated ion").

In this work we demonstrate a thermodynamically consistent way to accurately represent the solution nonideality of aqueous electrolytes over the entire concentration range by unifying the solution chemistries just mentioned with the electrolyte NRTL model. Specifically, we propose that the perceived discrepancies of the NRTL model for highly nonideal electrolyte systems at high electrolyte concentrations are the result of failure to recognize the solution chemistries and the true species that exist in solutions. For example, for electrolytes with hydrated ions, theoretical considerations regarding the long range ion–ion interaction, and local interaction of the species, should be based on concentrations of the hydrated rather than the nonhydrated ions. Similarly, when some electrolytes only partially dissociate into ions at high electrolyte concentrations, true ion concentrations (as opposed to apparent ion concentrations based on complete dissociation) should be considered.

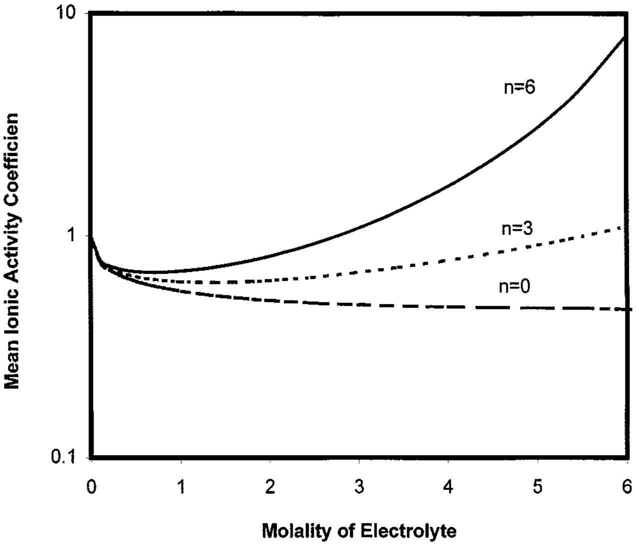


Figure 1. Mean ionic activity coefficient of a generic 1-1 electrolyte vs. apparent molality of the electrolyte in solution.

The dashed line represents results with hydration number, $n = 0$, the dotted line represents results with $n = 3$, and the solid line represents results with $n = 6$.

The focus of this article is on aqueous single electrolyte systems at room temperature. The original NRTL model correlates temperature effects accurately with parameters that are relatively independent of temperature (Chen et al., 1982). In addition, the NRTL model has been shown to be an effective model for mixed electrolyte systems (Chen and Evans, 1986). These highly advantageous characteristics of the NRTL model remain as we couple the solution chemistries with the model. On the other hand, we should note that solution compressibility effect is not accounted for in the NRTL model.

Hydration Chemistry

As stated by Robinson and Stokes (1959), it is of utmost importance to our understanding and description of electrolyte solutions that we clearly identify the kinetic entity that we call an ion. It can be considered as a bare ion or as a single entity of an ion bound to a certain number of water molecules; the choice profoundly affects the predicted solution behavior. Robinson and Stokes further developed the underlying relation between the mean molal stoichiometric activity coefficient ($\gamma^{\pm}$; mean ionic activity coefficient in the molality scale), and the corresponding "rational" or true mole-fraction-based activity coefficient in a hydrated solution ($f'_{\pm}$) (Stokes and Robinson, 1948; Conway, 1981; Conway et al., 1983, also see the Appendix):

$$\ln \gamma^{\pm} = \ln f'_{\pm} - \frac{n}{\nu} \ln a_w - \ln\left(1 + \frac{\nu - n}{S}\right). \tag{1}$$

In Eq. 1, ν represents the summation of stoichiometric numbers of the cation and the anion in the electrolyte, ν_+ and ν_-, respectively; n is the total hydration number for the electrolyte (that is, sum of solvation numbers of cation and anion), a_w ($= f'_w x_w$) is the rational activity of the solvent (here water), with x_w being the true mole fraction of water in the solution; and S is the number of moles of solvent per mole of electrolyte, taken as anhydrous, in the solution. In this work, the NRTL model is used to compute the rational activity coefficients of water and the ion pairs in the hydrated solution for which the total hydration number is known, and then Eq. 1 is used to obtain $\gamma^{\pm}$. In parameter optimization, the parameters of the electrolyte NRTL model were regressed to obtain best fit to the $\gamma^{\pm}$ data.

To illustrate the general effect of the hydration of ions in an aqueous environment, Figure 1 presents values of $\gamma^{\pm}$ vs.

apparent molality (up to 6 molal) computed by the NRTL model (Chen and Evans, 1986) for a "generic" 1-1 electrolyte where the model parameters between the electrolyte and water, $\tau_{m,ca}$ and $\tau_{ca,m}$, are set to typical values of 8 and -4, respectively. As the total hydration number increases, the predicted $\gamma^{\pm}$ at higher concentrations also increases dramatically, indicating increased "effective" nonideality of the electrolyte solution.

With the trend shown in Figure 1 in mind, in data reduction we used $\gamma^{\pm}$ vs. apparent molality (up to 6 molal) data at 25°C presented by Robinson and Stokes (1959) for electrolytes. For each hydration number from zero to six, we fitted the binary interaction parameters of the NRTL model between electrolyte and water, $\tau_{m,ca}$ and $\tau_{ca,m}$, that result in the minimum sum of squares error in calculated $\gamma^{\pm}$. The NRTL nonrandomness factor was set to 0.2 in all calcula-

Table 1. Percent Average Absolute Deviations AAD%* in Mean Ionic Activity Coefficient Calculations

Electrolyte	Total Hydration Number	$\tau_{m,ca}$	$\tau_{ca,m}$	% $\text{AAD}_{\text{nonhydrated}}$	% $\text{AAD}_{\text{hydrated}}$	Max., m
			1-1 Electrolytes			
$AgNO_3$	0	7.4176	-3.2836	0.77	—	6
CsAc	0	8.6067	-4.6303	0.79	—	3.5
CsBr	0	8.5100	-4.1880	0.52	—	5
CsCl	0	8.5304	-4.2105	0.52	—	6
CsI	0	8.3317	-4.0481	0.52	—	3
$CsNO_3$	0	8.9873	-4.1480	0.24	—	1.4
HBr	3	8.2457	-4.4507	1.14	0.75	3
HCl	3	8.0549	-4.2984	2.64	0.53	6
$HClO_4$	3	8.7324	-4.5851	1.40	1.19	6
HI	3	7.2351	-4.1667	0.66	0.62	3
HNO_3	3	5.8851	-3.2654	0.66	0.80	3
KAc	0	8.6007	-4.6055	0.66	—	3.5
$KBrO_3$	0	7.0001	-3.0924	0.14	—	0.5
KCl	0	8.0679	-4.1083	0.23	—	4.5
$KClO_3$	0	7.5487	-3.5001	0.24	—	0.7
KCNS	0	7.4926	-3.8351	0.13	—	5
KF	0	8.7961	-4.5019	0.36	—	4
KH Adipate	0	5.5170	-2.9766	0.12	—	1
KH Malonate	0	7.4958	-3.6636	0.36	—	5
KH Succinate	0	8.1113	-4.0233	0.21	—	4.5
KTol	0	7.0001	-3.2735	2.47	—	3.5
KH_2PO_4	0	8.9275	-4.1130	0.22	—	1.8
KI	0	7.8046	-4.0709	0.38	—	4.5
KNO_3	0	7.6555	-3.4688	0.58	—	3.5
KOH	3 (0+3)**	7.964	-4.1700	1.62	0.48	6
LiAc	3	6.2763	-3.3516	0.37	0.22	4
LiBr	3	8.5631	-4.4980	3.72	0.95	6
LiCl	3	8.1202	-4.2751	2.99	0.88	6
$LiClO_4$	3	7.3557	-4.1193	1.84	1.32	4
LiI	3	6.7147	-3.9111	1.86	1.78	3
$LiNO_3$	3	6.5116	-3.5617	1.00	0.35	6
LiOH	6 (3+3)**	7.4520	-3.3977	1.89	3.0	4
LiTol	3	6.0748	-3.0359	1.03	0.97	4.5
NaAc	3	5.6153	-3.2177	0.55	0.79	3.5
NaBr	3	7.1304	-3.7213	0.68	0.36	4
$NaBrO_3$	3	7.2506	-3.3964	0.10	0.10	2.5
NaCl	3	7.1415	-3.6601	1.37	0.44	6
$NaClO_3$	3	5.9348	-2.8987	0.34	0.30	3.5
$NaClO_4$	3	6.2220	-3.1624	0.76	0.46	6
NaCNS	3	5.3935	-3.0004	0.82	1.22	4
NaF	3	7.0989	-3.4468	0.02	0.02	1
Na Formate	3	6.1636	-2.7578	0.30	0.71	3.5
NaH Malonate	3	6.6465	-3.1902	0.14	0.36	5
Na Propionate	3	5.8072	-3.4033	0.49	1.01	3
NaH Succinate	3	7.0333	-3.4352	0.16	0.35	5
NaTol	3	4.0085	-1.5735	1.08	0.99	4
NaI	3	6.9743	-3.7422	0.79	0.57	3.5
$NaNO_3$	3	6.3872	-3.0011	0.12	0.33	6

*$\text{AAD}\% = \sum_{1}^{n} \frac{|\gamma_{\text{exp}} - \gamma_{\text{cal}}|}{\gamma_{\text{exp}}} \times 100$ $n =$ number of data points.

Table Continued

***Second number in parenthesis indicates contribution to hydration from* OH^-.

Table 1. (Continued) Percent Average Absolute Deviations AAD%* in Mean Ionic Activity Coefficient Calculations

Electrolyte	Total Hydration Number	$\tau_{m,ca}$	$\tau_{ca,m}$	% $AAD_{nonhydrated}$	% $AAD_{hydrated}$	Max., m
			1-1 Electrolytes			
NaOH	6 (3 + 3)**	5.7292	−2.8600	2.16	0.63	6
NH_4Cl	0	7.8446	−4.0062	0.06	—	6
NH_4NO_3	0	7.3576	−3.5255	0.93	—	6
RbAc	0	8.7383	−4.6701	0.70	—	3.5
RbBr	0	8.0797	−4.0639	0.16	—	5
RbCl	0	8.2406	−4.1485	0.15	—	5
RbI	0	8.2050	−4.1153	0.18	—	5
$RbNO_3$	0	7.7096	−3.4591	0.85	—	4.5
TlAc	0	7.8613	−3.8202	0.92	—	6
$TlNO_3$	0	9.0000	−3.7700	0.55	—	0.4
$TlClO_4$	0	9.0000	−4.1300	0.22	—	0.5
			1-2 Electrolytes			
Cs_2SO_4	0	7.2106	−3.6412	0.47	—	1.8
K_2CrO_4	0	7.7302	−3.8775	1.37	—	3.5
Li_2SO_4	6 (3 × 2)	6.6178	−3.3703	1.06	0.81	3
Na_2CrO_4	6 (3 × 2)	7.0252	−3.4986	3.89	2.23	4
Na_2SO_4	6 (3 × 2)	6.9485	−3.3147	1.43	0.26	4
$Na_2S_2O_3$	6 (3 × 2)	6.9677	−3.4239	1.88	0.89	3.5
$(NH_4)_2SO_4$	0	7.9734	−3.8492	0.92	—	4
Rb_2SO_4	0	7.1983	−3.8492	0.47	—	1.8
			2-1 Electrolytes			
$BaBr_2$	3	7.0649	−3.9239	1.72	1.63	2
$BaCl_2$	3	5.7515	−3.3108	1.27	1.33	1.8
$Ba(ClO_4)_2$	3	7.9460	−4.2872	4.95	3.22	5
BaI_2	3	7.9991	−4.4169	2.28	2.02	2
$Ba(NO_3)_2$	3	8.9073	−4.2453	0.07	0.07	0.4
$CaBr_2$	6	8.6186	−4.5347	22.08	5.72	6
$CaCl_2$	6	7.8986	−4.2031	14.00	3.06	6
$Ca(ClO_4)_2$	6	8.3153	−4.5178	17.11	3.67	6
CaI_2	6	7.1392	−4.0960	2.96	2.46	2
$Ca(NO_3)_2$	6	6.1802	−3.2804	3.98	1.84	6
$CoBr_2$	6	8.0163	−4.3834	9.11	2.45	5
$CoCl_2$	6	7.1109	−3.9304	3.66	1.94	4
CoI_2	6	8.4410	−4.6377	14.78	5.83	6
$Co(NO_3)_2$	6	7.3352	−3.9734	7.34	2.39	5
$Cu(NO_3)_2$	6	6.9465	−3.7799	7.91	2.62	6
$FeCl_2$	6	6.4970	−3.6736	1.93	1.64	2
$MgAc_2$	6	6.8271	−3.5271	0.66	1.08	4
MgBr2	6	8.6597	−4.6248	14.51	4.16	5
$MgCl_2$	6	8.3786	−4.4386	12.96	3.65	5
$Mg(NO_3)_2$	6	7.4778	−4.0642	8.45	2.88	5

$$^{*}AAD\% = \sum_{1}^{n} \frac{|\gamma_{exp} - \gamma_{cal}|}{\gamma_{exp}} \times 100 \quad n = \text{number of data points.}$$

Table Continued

***Second number in parenthesis indicates contribution to hydration from OH^-.*

tions. Studying the results of this data fit, we then selected an optimum hydration number for each ion, applicable to any electrolyte containing that ion. Note that the Stokes-Robinson equation (Eq. 1) accounts for the total hydration number (anion plus cation), thus for a given electrolyte the selection of hydration number for individual ions depends on other factors that we discuss below in more detail. We should note that in general we considered only cations as hydrating, with OH^- being the only hydrating anion. The choice of the optimum hydration number was further influenced by phenomenological considerations based on ionic radius and charge. The selected hydration numbers and corresponding NRTL binary interaction parameters between electrolytes and water are given in Table 1. We also report percent average absolute deviations (%AAD) in $\gamma^{\pm}$ for the case of no hydration and that with ''optimum'' hydration.

The use of hydration slightly increases the average absolute deviation for a small number of electrolytes in Table 1. This is because a single, optimum hydration number is used for all electrolytes of a particular cation. For example, in the case of Mg^{+2}, considering hydration chemistry with a hydration number of 6 improves the results significantly for $MgBr_2$, $MgCl_2$ and $Mg(NO_3)_2$, whereas it results in a slightly increased average error for $MgAc_2$, which we consider statistically insignificant.

For many of the electrolytes the NRTL model performs very well without any hydration. This is reflected by low %AAD numbers for many electrolytes with a hydration num-

Table 1. (Continued) Percent Average Absolute Deviations AAD%* in Mean Ionic Activity Coefficient Calculations

Electrolyte	Total Hydration Number	$\tau_{m,ca}$	$\tau_{ca,m}$	% $AAD_{nonhydrated}$	% $AAD_{hydrated}$	Max., m
2-1 Electrolytes						
$MnCl_2$	6	5.8219	−3.3775	2.86	1.90	6
$NiCl_2$	6	7.4266	−4.0646	5.80	2.85	5
$Pb(ClO_4)_2$	6	7.3046	−3.9935	10.03	2.95	6
$Pb(NO_3)_2$	6	8.1172	−3.7016	0.96	1.45	2
$SrBr_2$	6	6.8324	−3.8298	2.69	2.35	2
$SrCl_2$	6	7.5774	−4.0434	6.00	2.73	4
$Sr(ClO_4)_2$	6	7.6769	−4.2292	11.20	2.76	6
SrI_2	6	6.9023	−3.9752	3.01	2.57	2
$Sr(NO_3)_2$	6	5.6940	−2.9049	1.90	2.00	4
UO_2Cl_2	6	5.7792	−3.4941	2.62	3.45	3
$UO_2(ClO_4)_2$	6	9.6994	−5.1858	30.16	7.26	5.5
$ZnCl_2$	6	5.9272	−3.1179	8.70	7.31	6
$Zn(ClO_4)_2$	6	9.0795	−4.8644	11.64	4.54	4
$Zn(NO_3)_2$	6	7.2097	−3.9602	10.24	2.94	6
2-2 Electrolytes						
$BeSO_4$	3	8.7629	−4.3553	2.49	1.83	4
$MgSO_4$	6	8.2066	−4.0737	1.52	1.45	3.5
$MnSO_4$	6	8.0811	−3.9882	2.15	1.50	4
$NiSO_4$	6	8.3234	−4.0849	0.99	1.26	2.5
$CuSO_4$	6	8.6811	−4.2443	1.11	1.33	1.4
$ZnSO_4$	6	8.2842	−4.0743	1.54	1.50	3.5
$CdSO_4$	6	8.0844	−3.9311	1.32	1.94	3.5
3-1 Electrolytes						
$AlCl_3$	6	8.7092	−4.7328	5.74	4.57	1.8
$CeCl_3$	6	7.8884	−4.3258	4.85	3.97	2
$CrCl_3$	3	7.0324	−4.1622	2.73	2.69	1.2
$Cr(NO_3)_3$	3	7.3447	−4.2208	2.95	2.88	1.4
$EuCl_3$	6	7.9988	−4.3885	5.12	4.18	2
$LaCl_3$	6	7.8000	−4.2950	4.76	3.96	2
$NdCl_3$	6	7.9816	−4.3612	4.81	3.87	2
$PrCl_3$	6	7.9052	−4.3288	4.72	3.82	2
$ScCl_3$	6	8.0963	−4.4679	4.28	3.46	1.8
$SmCl_3$	6	7.9792	−4.3737	4.91	3.97	2
YCl_3	6	8.2656	−4.4929	5.21	4.07	2

$$^{*}\mathrm{AAD\%} = \sum_{1}^{n} \frac{|\gamma_{\mathrm{exp}} - \gamma_{\mathrm{cal}}|}{\gamma_{\mathrm{exp}}} \times 100 \quad n = \text{number of data points.}$$

**Second number in parenthesis indicates contribution to hydration from OH^-.

ber of zero. For these systems, only marginal improvements, if any, were obtained by invoking hydration. The NRTL model not only gives an excellent fit to the mean ionic activity coefficient data up to 6 molal but also gives accurate predictions far beyond that concentration. Figure 2 shows the predictions of the NRTL model for three electrolytes without hydration: CsCl, NH_4NO_3, and $AgNO_3$. Using the interaction parameters obtained from fitting data only up to 6 molal, the model gives excellent extrapolations up to 20 molal.

For electrolytes containing ions such as lithium, magnesium, calcium, cobalt, and zinc, the improvement due to assuming hydration is substantial and beyond the uncertainty of the ‘‘smoothed’’ literature data used in data reduction. Our analysis indicates that uncertainty of the ‘‘smoothed’’ activity coefficients (for example, Goldberg, 1981) is typically 1−2% and essentially always within 5−10%. Figure 3 presents results for $MgCl_2$. As we consider larger hydration numbers, progressively better results are obtained. This electrolyte is only soluble in water up to about 5 molal at 25°C, and at $n = 6$, the entire concentration range up to saturation can be represented very well. Pinsky and Gruber (1992) have previously reported similar success for $MgCl_2$.

The absolute values of the interaction parameters for the NRTL model with hydration are always smaller than those of the NRTL model without hydration (compare Table 1 with the analogous table reported by Chen et al., 1982). This is consistent with the physical argument of the NRTL interaction parameters and the rationale that hydrated ions, while maintaining the same charge number, become larger in size and consequently weaker in interaction energetics. The values of the interaction parameters also fall in a narrower band than previously reported by Chen et al. (1982), suggesting better predictability of the model parameters.

Hydration Numbers

The results in Table 1 suggest that hydration is an ion-specific phenomenon, independent of the other ions in solution. The consideration of hydration chemistry significantly improves the description of mean ionic activity coefficients

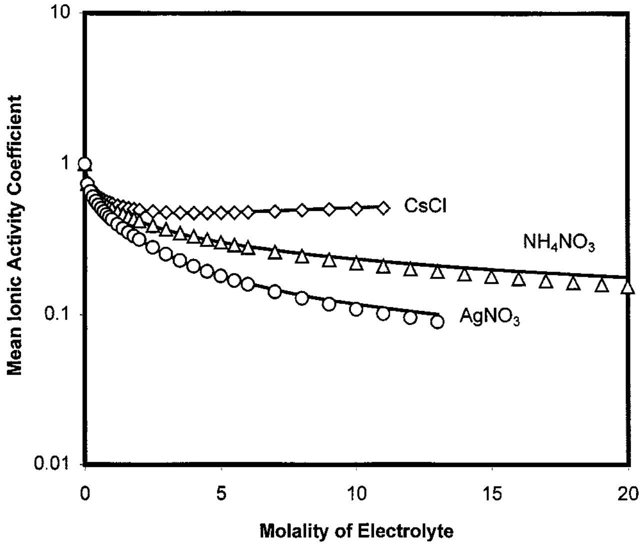


Figure 2. Mean ionic activity coefficient of electrolytes requiring no hydration vs. apparent molality of electrolyte in solution.

The points are data from Robinson and Stokes (1959). The model parameters were obtained by fitting data up to 6 molal. The solid lines represent results computed by the model.

for electrolytes with some smaller cations such as H^+ and Li^+. The benefits of inclusion of hydration chemistry diminish for electrolytes with cations of larger size, such as K^+, Cs^+, and Rb^+. In addition, the notion that hydration chemistry is primarily associated with cations appears justified. Note that there is evidence in independent investigations that cations are more likely to hydrate than anions. For example, Paritosh and Murad (1996) have reported in computer simulations of reverse osmosis that (hydrated) cations do not "leak" through membranes, while anions sometimes do. Koneshan et al. (1998) have shown that the residence time of the water molecules associated with small cations like Li^+ is significantly longer than the residence times of the water molecules associated with small anions like F^-. While our specific assumptions concerning hydration are clearly an approximation, they are broadly supported by empirical and theoretical observations.

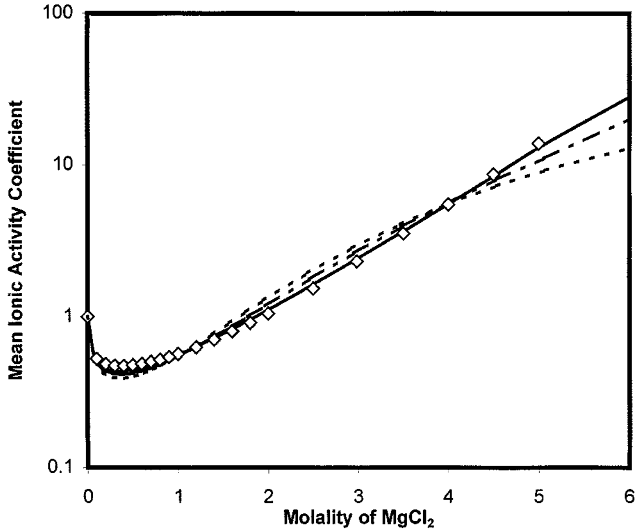


Figure 3. Mean ionic activity coefficient of $MgCl_2$ vs. apparent molality of electrolyte in solution.

The points are data from Robinson and Stokes (1959). The dotted line represents results with hydration number, $n = 0$, the dashed line represents results with $n = 3$, and the solid line represents results with $n = 6$.

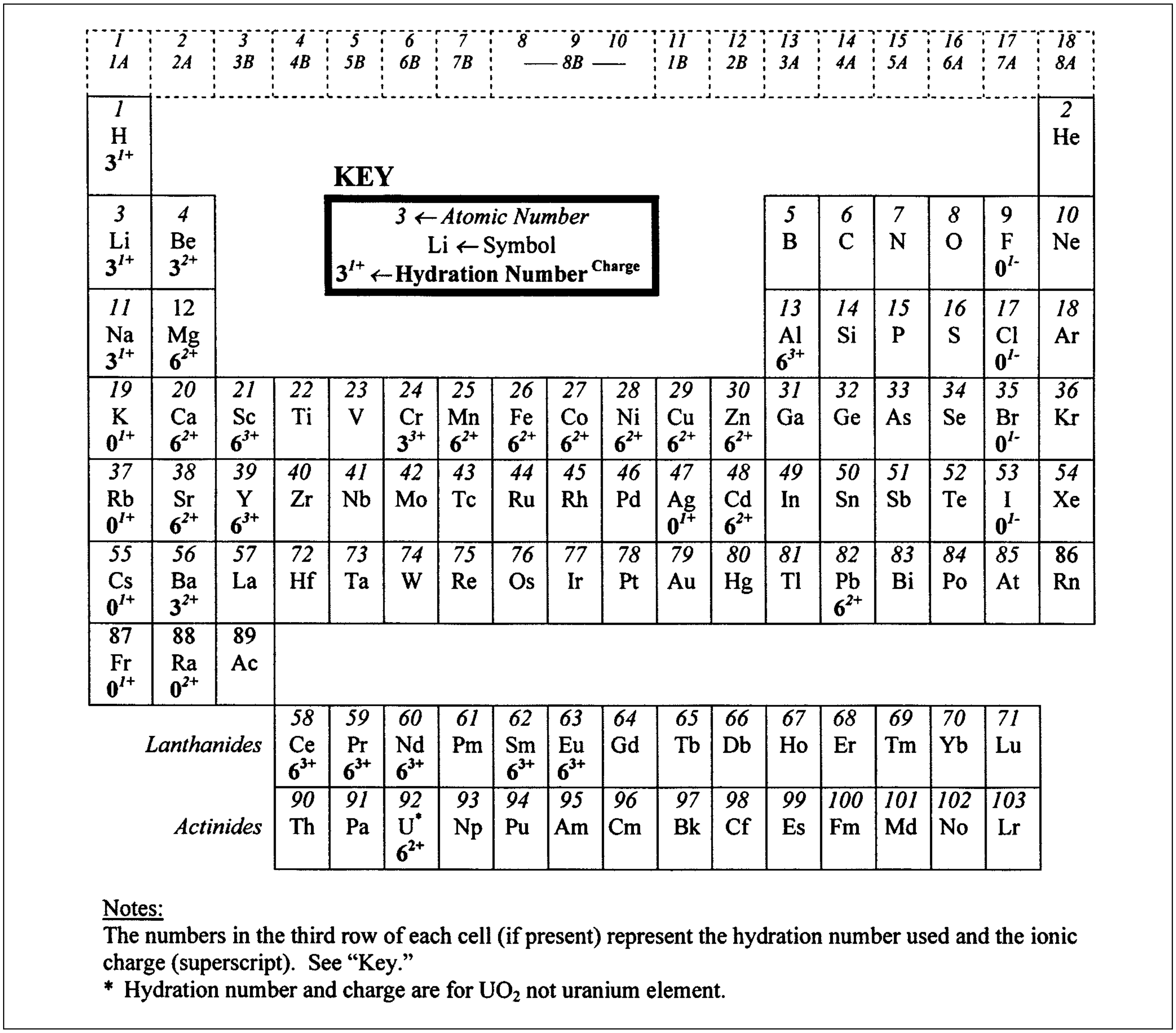
Our analysis of the hydration numbers for elemental cations in Table 1 suggests a relatively simple correlation in terms of the charge and the radius (Pauling radius) of the ion. A larger positive ionic charge increases the hydration number; increased ionic size decreases the hydration number. Figure 4, which has mapped the hydration numbers onto the periodic table, illustrates these trends. For the 1A group of elements, H^+, Li^+, and Na^+ each have a hydration number of 3, while the larger ions have a hydration number of zero. Similarly, for the 2A group of elements, Be^{+2} has a hydration number of 3; Mg^{+2}, Ca^{+2}, and Sr^{+2} each have hydration numbers of 6; Ba^{+2} has a hydration number of 3; and Ra^{+2} has a hydration number of zero. The explanation is that a small 2+ ion like Be^{+2} has a strong coulombic force, but is too small to accommodate more than three water molecules. The remainder of the 2A ions follows the trend that larger ions have fewer waters of hydration. The 2+ transition-metal ions also follow the same simple pattern. All the 3+ elemental cations we considered in this work have a hydration number of 6, except for Cr^{+3}, which has a hydration number of 3, due to its small radius.

Figure 5 further illustrates the trends presented in the periodic table (see Figure 4). The pattern of hydration number vs. charge and Pauling radius of ions (see Table 2) is simple and clear. For example, Ag^+ (1.26 Å) falls in line with the pattern of the 1A ions. The 3+ metal cations we have studied indicate a pattern that the large ions have a hydration number of 6, while the small ions have a hydration number of 3; there may not be any 3+ metal cations large enough to show a drop in hydration number. The simple pattern of hydration number with charge and size suggests a potential predictive method.

The results in Figure 5 may also explain why the hydration numbers of the 7A group ions (halogen anions) are zero: they are too large—in addition to the weaker intrinsic tendency of anions to hold water. F^-, Cl^-, Br^-, and I^- have Pauling radii of 1.36 Å, 1.81 Å, 1.96 Å, and 2.16 Å, respectively. These radii are all larger than the values at which the 1+ cations begin to have hydration numbers of zero. Finally, the trends in Figure 5 suggest that (large) compound ions will generally have a hydration number of zero.

The trends presented in Figures 4 and 5 provide phenomenological supports for our hydration chemistry model, and a methodology to estimate the hydration numbers of other ions.

The combination of the NRTL model with hydration chemistry not only gives an excellent fit to the mean ionic activity coefficient data up to 6 molal but also gives accurate predictions beyond 6 molal. To examine the extrapolation behavior of the NRTL model for electrolytes with hydration, we report the results of mean ionic activity coefficient calculations for LiCl and HCl in Figures 6a and 6b, respectively.



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 3^{1+}																	2 He
3 Li 3^{1+}	4 Be 3^{2+}											5 B	6 C	7 N	8 O	9 F 0^{1-}	10 Ne
11 Na 3^{1+}	12 Mg 6^{2+}											13 Al 6^{3+}	14 Si	15 P	16 S	17 Cl 0^{1-}	18 Ar
19 K 0^{1+}	20 Ca 6^{2+}	21 Sc 6^{3+}	22 Ti	23 V	24 Cr 3^{3+}	25 Mn 6^{2+}	26 Fe 6^{2+}	27 Co 6^{2+}	28 Ni 6^{2+}	29 Cu 6^{2+}	30 Zn 6^{2+}	31 Ga	32 Ge	33 As	34 Se	35 Br 0^{1-}	36 Kr
37 Rb 0^{1+}	38 Sr 6^{2+}	39 Y 6^{3+}	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag 0^{1+}	48 Cd 6^{2+}	49 In	50 Sn	51 Sb	52 Te	53 I 0^{1-}	54 Xe
55 Cs 0^{1+}	56 Ba 3^{2+}	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb 6^{2+}	83 Bi	84 Po	85 At	86 Rn
87 Fr 0^{1+}	88 Ra 0^{2+}	89 Ac															
Lanthanides			58 Ce 6^{3+}	59 Pr 6^{3+}	60 Nd 6^{3+}	61 Pm	62 Sm 6^{3+}	63 Eu 6^{3+}	64 Gd	65 Tb	66 Db	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
Actinides			90 Th	91 Pa	92 U* 6^{2+}	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

KEY

3 ← Atomic Number
Li ← Symbol
3^{1+} ← Hydration Number $^{\text{Charge}}$

Notes:
The numbers in the third row of each cell (if present) represent the hydration number used and the ionic charge (superscript). See "Key."
* Hydration number and charge are for UO_2 not uranium element.

Figure 4. Hydration numbers and charges of ions mapped on to the Periodic Table.

With a hydration number of 3, the model was very successfully fit to data up to 6 molal. The model was found to give very good extrapolation up to 10 molal, displaying a much improved extrapolation capability compared to the nonhydration case. Above 10 molal, the hydration model predictions begin to deviate from the data. This is because the hydration ion consumes most of the water present in the system. Above 18 molal, no free water would exist if hydration were to remain the only chemistry in the solution.

Partial Dissociation

At high concentrations, partial dissociation cannot be ignored for many electrolytes. For example, at high concentrations HCl is only partially dissociating (Cruz and Renon, 1978). The NRTL model with hydration predicts positive deviations, as observed in the cases of LiCl $\gamma^{\pm}$ and HCl $\gamma^{\pm}$ (Figures 6a and 6b) that can be explained by the partial dissociation mechanism. Partial dissociation yields "molecular" electrolytes in the solution. To account for this fact in modeling, first the relation between the mean molal stoichiometric activity coefficient ($\gamma^{\pm}$) and the corresponding "rational" or true mole-fraction-based activity coefficient in a hydrated solution ($f'_{\pm}$) given in Eq. 1 needs to be modified as follows (see the Appendix for details):

$$\ln\gamma^{\pm} = \xi\ln f'_{\pm} - \frac{n}{\nu}\ln a_w - \frac{\nu_+}{\nu}\ln\left(\frac{\nu_+}{\nu+S}\right) - \frac{\nu_-}{\nu}\ln\left(\frac{\nu_-}{\nu+S}\right) + \xi\left(\frac{\nu_+}{\nu}\ln\frac{\xi\nu_+}{S-n+\xi\nu+1-\xi} + \frac{\nu_-}{\nu}\ln\frac{\xi\nu_-}{S-n+\xi\nu+1-\xi}\right) + \frac{1-\xi}{\nu}\left(\ln\frac{1-\xi}{S-n+\xi\nu+1-\xi} + \ln f_i\right). \quad (2)$$

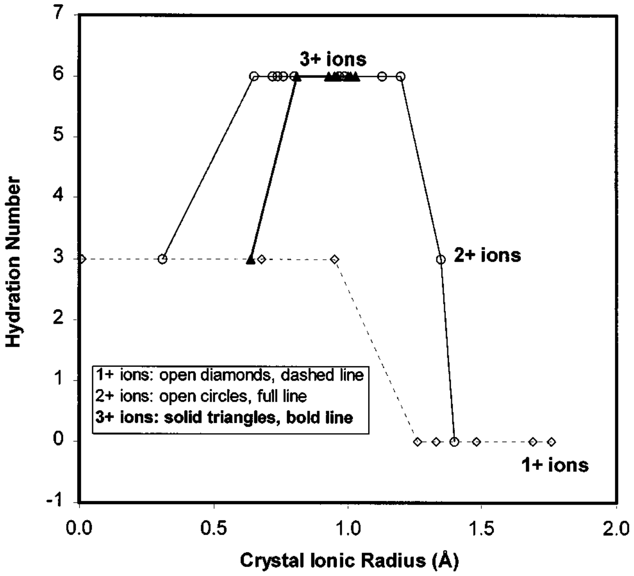


Figure 5. Hydration numbers of elemental, metal cations as a function of charge number and size.

Table 2. Pauling Radius for Various Ions

Name	Symbol	Charge	R, Å	Total Hydration Number
Fluorine	F	−1	1.36	0
Chlorine	Cl	−1	1.81	0
Bromine	Br	−1	1.96	0
Iodine	I	−1	2.16	0
Hydrogen	H	1	0.01	3
Lithium	Li	1	0.68	3
Sodium	Na	1	0.95	3
Silver	Ag	1	1.26	0
Potassium	K	1	1.33	0
Rubidium	Rb	1	1.48	0
Cesium	Cs	1	1.69	0
Francium	Fr	1	1.76	0
Beryllium	Be	2	0.31	3
Magnesium	Mg	2	0.65	6
Nickel	Ni	2	0.72	6
Copper	Cu	2	0.72	6
Cobalt	Co	2	0.74	6
Zinc	Zn	2	0.74	6
Iron	Fe	2	0.76	6
Manganese	Mn	2	0.80	6
Cadmium	Cd	2	0.97	6
Calcium	Ca	2	0.99	6
Strontium	Sr	2	1.13	6
Lead	Pb	2	1.20	6
Barium	Ba	2	1.35	3
Radium	Ra	2	1.40	0
Chromium	Cr	3	0.64	3
Scandium	Sc	3	0.81	6
Yttrium	Y	3	0.93	6
Europium	Eu	3	0.95	6
Samarium	Sm	3	0.96	6
Neodymium	Nd	3	1.00	6
Praseodymium	Pr	3	1.01	6
Cesium	Ce	3	1.03	6

Source: Dean (1985).

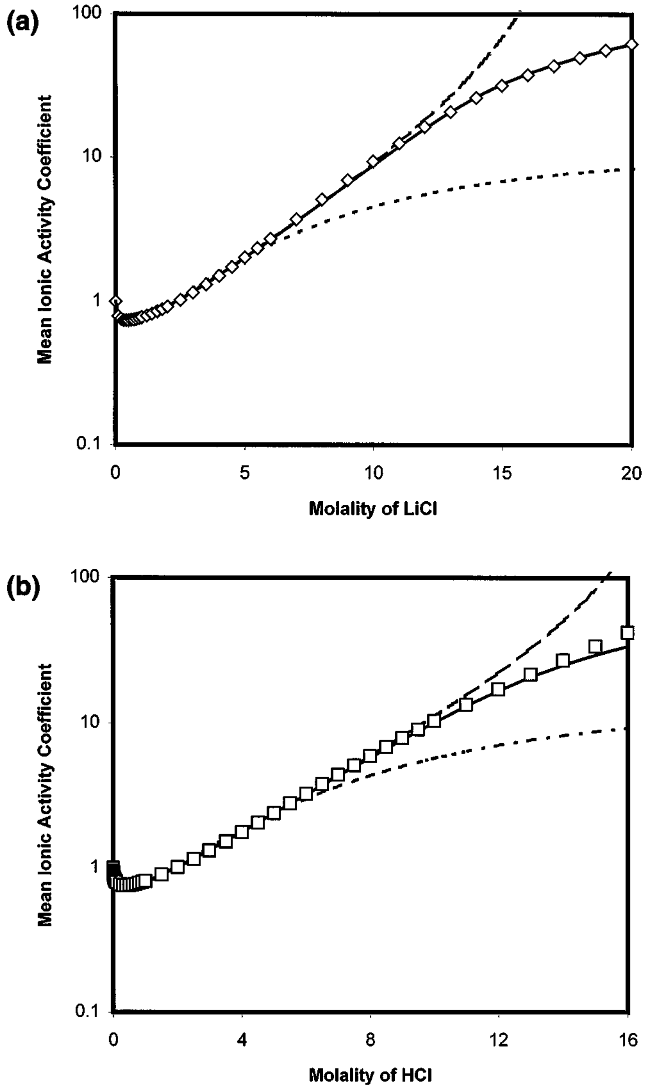


Figure 6. (a) Mean ionic activity coefficient of strong electrolyte LiCl vs. apparent molality of electrolyte in solution; (b) mean ionic activity coefficient of strong electrolyte HCl vs. apparent molality of electrolyte in solution.

The points are data from Robinson and Stokes (1959). The dotted line represents results with hydration number $n = 0$, the dashed line represents results with hydration, with $n = 3$, and the solid line represents results with hydration and partial dissociation, with $n = 3$. The model parameters are as given in Table 3.

In Eq. 2, ξ is the fraction of electrolyte dissociated per mole of electrolyte added to S moles of solvent; ν_+ and ν_- are the stoichiometric numbers of the cation and the anion in the electrolyte, respectively; and f_i is the rational activity coefficient of the "molecular" electrolyte, computed from the NRTL model.

In addition, the presence of molecular electrolytes in solution results in additional pairs of interacting species for which the NRTL model parameters must be considered. Anticipating that there is little free water left in the solution at high electrolyte concentrations for hydrating electrolytes such as

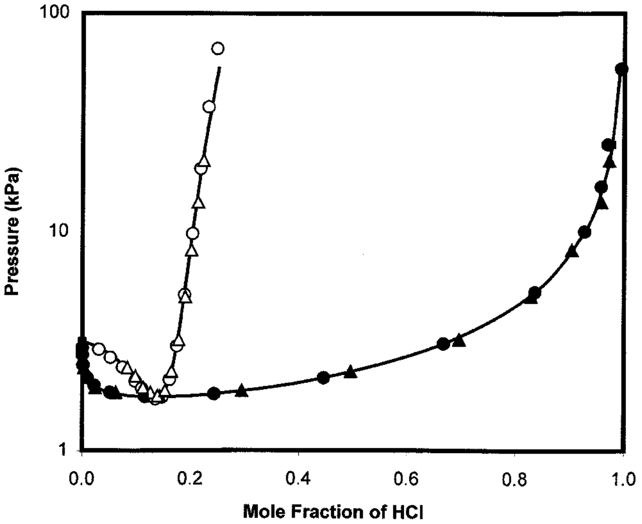


Figure 7. Pressure vs. apparent mole fraction of HCl in liquid and in vapor for HCl + water binary mixture.

The dots are experimental data from Vega and Vera (1976); the triangles are experimental data from Haase et al. (1963), the solid lines represent results calculated considering both hydration and partial dissociation chemistries, with parameters given in Table 3.

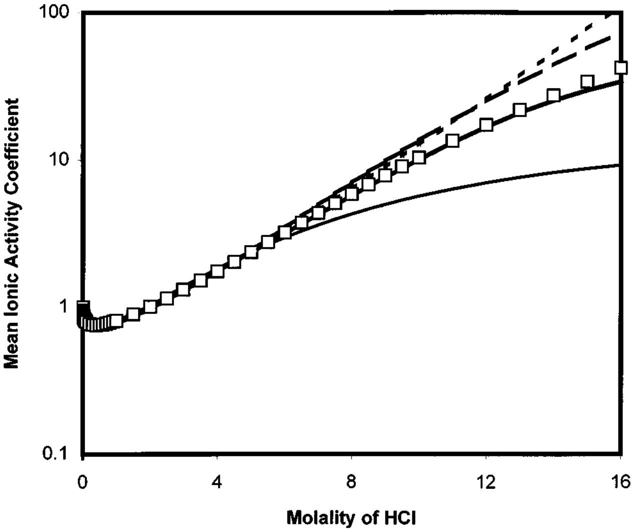


Figure 8. Mean ionic activity coefficient of HCl as predicted by the NRTL model (solid lines, with and without hydration and partial dissociation chemistries), the Pitzer model (dotted line), and the Meissner model (dashed line).

HCl, we assumed that accounting for only the electrolyte–molecular HCl parameters in addition to the electrolyte–water parameters reported in Table 1 would suffice. These additional NRTL model parameters were regressed together with the equilibrium constant of the electrolyte dissociation reaction. The results of such a parameter-fitting exercise are shown in Figures 6a and 6b for LiCl and HCl for $\gamma^{\pm}$. For the HCl case, we also considered the vapor–liquid equilibrium (VLE) at 25°C of HCl + water mixture, with results displayed in Figure 7. These results show that accounting for the partial dissociation at high concentrations enables the NRTL model to correlate and extrapolate the mean ionic activity coefficients (and VLE in the case of HCl) with high accuracy over the entire concentration range.

Figure 8 further shows the improved results of the NRTL model for the mean ionic activity coefficient of HCl in comparison with those of the Pitzer model and the Meissner model as reported by Zemaitis et al. (1986). As we have noted before, the uncertainty in the smoothed experimental data is less than 10%, and thus the NRTL model gives statistically significantly improved results for both the absolute values and the general trend of the mean ionic activity coefficient over the Pitzer model and the Meissner model.

The model can also be used to correlate mean ionic activity coefficients of some relatively weaker electrolytes for which the $\gamma^{\pm}$ vs. molality data show unusual trends. Two examples are shown in Figure 9 for Na-caproate and $ZnBr_2$. With the NRTL model parameters and the dissociation constant (K_{diss}) for electrolyte dissociation reported in Table 3, the model is capable of accurately describing the inflections observed in the data. For these cases, since the electrolytes are weakly dissociating, there may be sufficient free water and molecular electrolyte in the solution so that the binary interactions between this pair need to be accounted for. However, we have arbitrarily assumed that we can set the binary interaction parameters for this pair to zero.

The NRTL model was successfully applied to essentially all the systems we investigated. The only exception is cadmium electrolytes ($CdCl_2$, $CdBr_2$, CdI_2, and $Cd(NO_3)_2$), for which it was not possible to capture the correct trend in the data

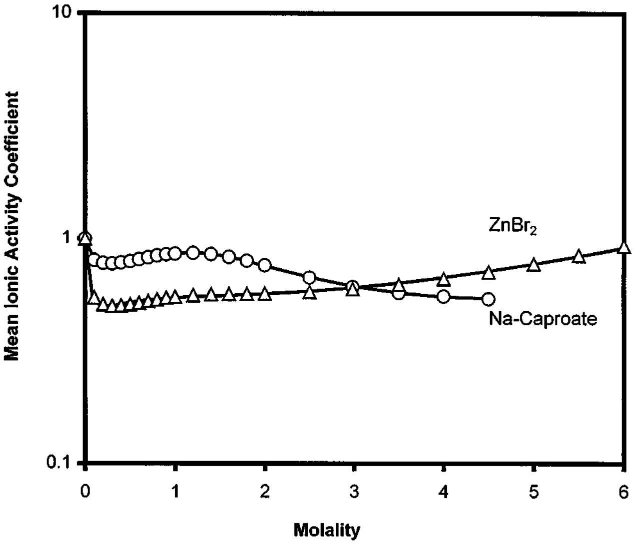


Figure 9. Mean ionic activity coefficient of electrolytes Na-caproate and $ZnBr_2$ vs. apparent molality of electrolyte in solution.

Data are as reported by Robinson and Stokes (1959). The solid lines represent results obtained considering both hydration and partial dissociation chemistries, with parameters reported in Table 3.

Table 3. Parameters Used in Various Modeling Modes and Model Performances

Electrolyte	Hydration No.	Water–Ion Pair Parameters $\tau_{m,ca}$	Water–Ion Pair Parameters $\tau_{ca,m}$	Electrolyte–Ion Pair Parameters $\tau_{m,ca}$	Electrolyte–Ion Pair Parameters $\tau_{ca,m}$	ln (K_{diss})	% AAD (Max. m)
No Hydration or Partial Dissociation							
LiCl	0	10.030	−5.1537	—	—	—	25.52 (20)
HCl	0	10.089	−5.2117	—	—	—	14.52 (16)
Hydration Only							
LiCl	3	8.1202	−4.2751	—	—	—	10.61 (20)
HCl	3	8.0549	−4.2984	—	—	—	9.72 (16)
Hydration and Partial Dissociation							
LiCl	3	8.1202	−4.2751	0.0140	−4.6158	13.45	1.35 (20)
HCl	3	8.0549	−4.2984	0.4970	−2.4751	9.91	1.76 (16)
Na-caproate	3	8.4408	−4.5716	−2.1121	−1.9411	2.22	0.26 (4.5)
ZnBr2	6	7.1107	−3.3524	−0.6085	3.7374	−10.67	1.27 (6)
$CdCl_2$	6	13.424	−6.0671	5.1932	−19.5852	1.93	1.60 (6)

with acceptable values for binary interaction parameters between water and ion pairs. In Figure 10 the results for $CdCl_2$ are shown. An accurate fit of the data was possible only with the exceptionally large binary interaction parameters reported in Table 3. It is worthwhile exploring to determine whether other mechanisms, such as complex formation, are playing a role for these electrolytes. This should be further investigated in the future.

Conclusions

The electrolyte NRTL model has been shown to successfully represent the solution nonideality for many aqueous electrolytes. For electrolytes that show no hydration, the model not only correlates accurately the solution nonideality at low to moderate electrolyte concentrations but also provides excellent extrapolation capability into the high-concentration region, with the parameters obtained at concentrations of 6 molal or less. For electrolytes that exhibit hydration and/or partial dissociation, it is essential that such chemistries should be taken into account properly and the hydrated ions and molecular electrolytes considered explicitly as the true species in the solution. The use of hydration and partial dissociation chemistries with the electrolyte NRTL model provides a comprehensive thermodynamic framework with strong correlative and extrapolative capability in representing aqueous electrolyte nonideality over the entire concentration range.

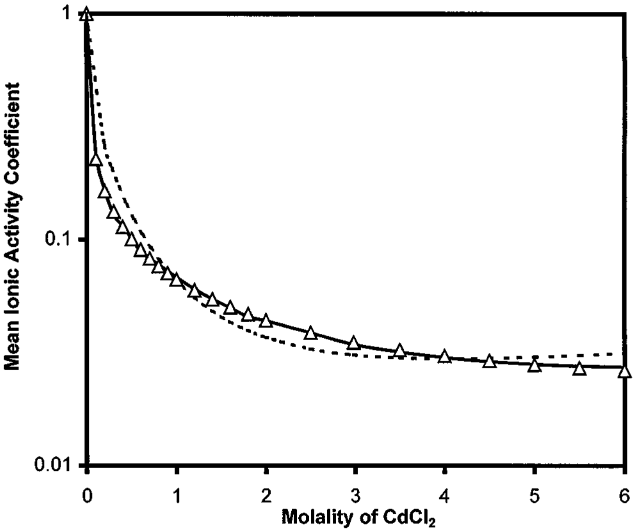


Figure 10. Mean ionic activity coefficient of $CdCl_2$ vs. apparent molality of electrolyte in solution.

The solid line represents results obtained considering both hydration and partial dissociation chemistries. The dashed lines represent results with no hydration or partial dissociation. All model parameters are given in Table 3.

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Appendix

Conway (1981) and Conway et al. (1983) present in detail the Stokes and Robinson treatment that results in Eq. 1 of this article. Below is a brief summary of this treatment.

Regardless of the model chosen to describe an electrolyte solution, the measured properties must remain the same. Thus, the free energy of the solution, G, can be written in terms of the apparent concentrations, or in terms of the true concentrations, considering ion hydration for a solution that contains ν_+ moles of cation and ν_- moles of ion in S moles of water:

$$G = S\mu_w + \nu_+ \mu_+ + \nu_- \mu_- = (S-n)\mu_w + \nu_+ \mu'_+ + \nu_- \mu'_- . \tag{A1}$$

The μ terms represent chemical potentials and n is the total hydration number. The terms with a prime represent the true solution properties in a hydrated solution. Replacing chemical potential terms with their counterparts in terms of rational activity coefficients and mole fractions,

$$\mu_i = \mu_i^0 + RT \ln a_i = \mu_i^0 + RT \ln(x_i f_i), \tag{A2}$$

and rearranging

$$\begin{aligned} \nu_+(\mu_+^0 - \mu_+^{0\prime})/RT + \nu_-(\mu_-^0 - \mu_-^{0\prime})/RT + n\mu_w^0/RT \\ + n\ln(a_w) + \nu \ln\left(\frac{S+\nu-n}{S+\nu}\right) + \nu_+ \ln f_+ + \nu_- \ln f_- \\ = \nu_+ \ln f'_+ + \nu_- \ln f'_- . \end{aligned} \tag{A3}$$

At the limit of infinite dilution, $S \to \infty$, all logarithmic terms in Eq. A3 become zero; hence, the sum of the first three terms on the lefthand side of Eq. A3 must also be zero.

Considering this, and also introducing mean activity coefficients $f_\pm = (f_+^{\nu_+}\ f_-^{\nu_-})^{1/\nu}$ and $f'_\pm = (f_+^{\nu_+\prime} f_-^{\nu_-\prime})^{1/\nu}$, Eq. A3 can be arranged as

$$\ln f'_\pm = \ln f_\pm + \frac{n}{\nu}\ln a_w + \ln\left(\frac{S+\nu-n}{S+\nu}\right). \tag{A4}$$

It is more practical to relate the rational activity coefficient $f'_\pm$ to mean molal activity coefficient $\gamma^\pm$, substituting the relations below in Eq. A4

$$\ln f_\pm = \ln \gamma^\pm (1 + \nu \times MW_w \times m/1{,}000)$$

and

$$S = 1{,}000/(MW_w \times m),$$

resulting in Eq. 1:

$$\ln \gamma^\pm = \ln f'_\pm - \frac{n}{\nu}\ln a_w - \ln\left(1 + \frac{\nu - n}{S}\right).$$

Here MW_w represents the molecular weight of water, and m is molality.

In writing Eq. 2 of the text, we follow the same treatment, but consider that for each mole of electrolyte added to S moles of water, the number of moles of cation in the solution is $\xi\nu+$, and the number of moles of anion is $\xi\nu_-$. In addition there is $(1-\xi)$ moles of molecular electrolyte left in the solution, contributing to the total Gibbs free energy of the solution.

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