Nonrandom Factor Model for Electrolyte Solutions

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In the previous work (Haghtalab and Vera, 1988, 1989), we presented a two-parameter nonrandom factor (NRF) model for the excess Gibbs energy of electrolyte solutions that consistently produced better results than any other similar model. For any salt other than those of the type bi-bivalent, tri-trivalent, and so on, $\nu_A = Z_C$, $\nu_C = Z_A$, and $\nu = \nu_A + \nu_C = Z_A + Z_C$, which is not the case of bi-bivalent electrolytes, for example, for which $Z_C = Z_A = 2$ and $\nu_C = \nu_A = 1$. Although trivial, this fact was ignored in our previous work and in an oversimplification we considered $\nu_A = Z_C$ and $\nu_C = Z_A$ in the phenomenological derivation of our model. In our previous work we wanted to keep the treatment simple and we did not foresee any advantage in keeping both ν_i's and Z_i's in the treatment. In this note we show that at the price of a minor increase in the complexity of the equations, the results for 2:2 electrolytes can definitely be improved. On the other hand, the final equations and thus the results are unchanged for all other types of electrolytes considered in our previous work.

Modified NRF Model

As in our previous work, (Haghtalab and Vera, 1988, 1989) we assume that the excess Gibbs energy of an aqueous electrolyte solution can be expressed as the sum of a contribution due to long-range coulombic interactions and a contribution of short-range interactions due to local composition. For the first contribution we use the Debye-Hückel expression (Debye and Hückel, 1923). For the short-range interactions we use the same version as before of the nonrandom two-liquid (NRTL) model (Renon and Prausnitz, 1968) modified in terms of nonrandom factors (NRF). The modification introduced in this work concerns only the NRTL-NRF term.

Following Chen and Evans (1986) we use the effective mole fractions of the ions.
This time, however, we write,

$$X_A = Z_A x_A = Z_A \nu_A x_S \qquad (1)$$

$$X_C = Z_C x_C = Z_C \nu_C x_S \qquad (2)$$

In these equations, which correspond to Eqs. 6a and 6b of the previous treatment, we have used the consistent forms $x_A = \nu_A x_S$ and $x_C = \nu_C x_S$. Moreover, by the condition of electroneutrality the following relation can be written.

$$Z_A \nu_A = Z_C \nu_C = Z_E \nu_E \qquad (3)$$

Following step by step our previous phenomenological reasoning, with necessary changes made, we obtain the modified excess Gibbs energy function as

$$\left(\frac{g^{ex}}{RT}\right)_{NRTL\text{-}NRF} = \nu_A \nu_C (Z_A + Z_C) x_S^2 (\Gamma_E - 1)\lambda_E - x_W^2 (\Gamma_W - 1)\lambda_W \qquad (4)$$

and in unsymmetrical form as

$$\left(\frac{g^{ex}}{RT}\right)^*_{NRTL\text{-}NRF} = \nu_A \nu_C (Z_A + Z_C) x_S^2 (\Gamma_E - 1)\lambda_E - x_W^2 (\Gamma_W - 1)\lambda_W + x_S(\nu - 2Z_E \nu_E \beta_W)\lambda_W \qquad (5)$$

which correspond to Eqs. 22b and 28 of our previous work. Thus, our previous Eqs. 29 and 30 for activity coefficients take the following forms:

$$(\ln\gamma^*_\pm)_{NRTL\text{-}NRF} = Z_E \nu_E x_S \lambda_E \left[(1 + x_W)(\Gamma_E - 1) + x_S x_W \left(\frac{\nu - Z_E \nu_E \beta_E}{\beta_E}\right)\Gamma_E^2\right] + x_W^2 \lambda_W (\Gamma_W - 1) - \lambda_W (x_W^3 \Gamma_W^2 - 1)\left(1 - \frac{2 Z_E \nu_E}{\nu}\beta_W\right) \qquad (6)$$

and

$$(\ln\gamma^*_W)_{NRTL\text{-}NRF} = \nu_A \nu_C (Z_A + Z_C) x_S^2 \lambda_E \left[1 - \Gamma_E + x_S \left(\frac{Z_E \nu_E \beta_E - \nu}{\beta_E}\right)\Gamma_E^2\right] - x_W \lambda_W (2 - x_W)(\Gamma_W - 1) - x_S x_W^2 \Gamma_W^2 \lambda_W (2 Z_E \nu_E \beta_W - \nu) \qquad (7)$$

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In the expressions above, the nonrandom factors take the form

$$\Gamma_E = \frac{\beta_E}{Z_E \nu_E x_S \beta_E + x_W} \tag{8}$$

and

$$\Gamma_W = \frac{1}{2\nu_E Z_E x_S \beta_W + x_W} \tag{9}$$

where β_E and β_W are related to the adjustable parameters λ_E and λ_W by

$$\beta_E = \exp\left(\frac{-\lambda_E}{8}\right) \tag{10}$$

$$\beta_W = \exp\left(\frac{-\lambda_W}{8}\right) \tag{11}$$

For completeness, we remark that, as in our previous work, we use here

$$x_W + \nu x_S = 1 \tag{12}$$

with

$$x_S = \frac{m}{\nu m + 50.5083} \tag{13}$$

As explained elsewhere (Haghtalab, 1990), under well-defined assumptions the expressions for the activity coefficients of the ions become

$$\begin{aligned}(\ln\gamma_C^*)_{NRTL\text{-}NRF} = {} & (Z_A + Z_C)x_A(x_W + x_A)(\Gamma_E - 1)\lambda_E \\ & + (Z_A + Z_C)x_A x_C\left(x_W \frac{1 - Z_C\beta_E}{\beta_E} + Z_C x_A\right)\Gamma_E^2\lambda_E \\ & + x_W^2(\Gamma_W - 1)\lambda_W - (1 - Z_C\beta_W)(x_W^3\Gamma_W^2 - 1)\lambda_W \\ & - x_A x_W^2 \beta_W (Z_A - Z_C)\Gamma_W^2\lambda_W \end{aligned} \tag{14}$$

$$\begin{aligned}(\ln\gamma_A^*)_{NRTL\text{-}NRF} = {} & (Z_A + Z_C)x_C(x_W + x_C)(\Gamma_E - 1)\lambda_E \\ & + (Z_A + Z_C)x_A x_C\left(x_W \frac{x_W}{\beta_E} + Z_C x_C\right)\Gamma_E^2\lambda_E \\ & + x_W^2(\Gamma_W - 1)\lambda_W - (1 - Z_A\beta_W)(x_W^3\Gamma_W^2 - 1)\lambda_W \\ & - x_C x_W^2 \beta_W (Z_C - Z_A)\Gamma_W^2\lambda_W \end{aligned} \tag{15}$$

The present Eqs. 14 and 15 replace Eqs. 32 and 33 of our previous work.

Results

For the activity coefficients of electrolytes other than bi-bivalent, tri-trivalent, and so on, the equations derived here are identical to those presented before. Thus parameters determined and results presented previously remain unchanged for all electrolytes other than the bi-bivalent cases. For these bi-bivalent electrolytes, results change; they are compared in Table 1. Parameters λ_E and λ_W determined in this study are reported in Table 2 together with the maximum molality of the data. With the exception of UO_2SO_4, the standard deviations are improved by over 25% with respect to our previous work.

Table 1. Comparison of Fit for Bi-Bivalent Electrolytes

Electrolyte	Std. Dev. of ln Values Previous Work (1988)	 This Work
$BeSO_4$	0.078	0.059
$MgSO_4$	0.074	0.052
$MnSO_4$	0.084	0.051
$NiSO_4$	0.072	0.046
$CuSO_4$	0.067	0.046
$ZnSO_4$	0.083	0.049
$CdSO_4$	0.073	0.055
UO_2SO_4	0.054	0.096

Table 2. Fit of Molality Mean Ionic Activity Coefficient Data of Aqueous Bi-Bivalent Electrolytes at 298.15 K

Bi-Bivalent Electrolyte	Max. Molality*	λ_E	λ_W
$BeSO_4$	4	−9.645	17.730
$MgSO_4$	3	−9.870	17.529
$MnSO_4$	4	−9.675	15.622
$NiSO_4$	2.5	−10.404	18.320
$CuSO_4$	1.4	−11.415	24.001
$ZnSO_4$	3.5	−10.154	17.458
$CdSO_4$	3.5	−9.841	15.594
UO_2SO_4	6	−8.853	13.294

*Robinson and Stokes, 1959

Table 3. Activity Coefficients of Ionic Species in Aqueous Solutions of NaCl at 298.15 K

	γNa^+		γCl^-	
Molality	Hydration Model	NRTL-NRF Model	Hydration Model	NRTL-NRF Model
0.1	0.783	0.771	0.773	0.771
0.2	0.744	0.725	0.726	0.723
0.5	0.701	0.674	0.661	0.667
1.0	0.697	0.662	0.620	0.637
2.0	0.756	0.721	0.590	0.625
3.0	0.870	0.839	0.586	0.626
4.0	1.038	1.010	0.591	0.627
5.0	1.272	1.239	0.600	0.624
6.0	1.594	1.535	0.610	0.617

As a matter of curiosity, we have computed the values of the activity coefficients of the ions Na^+ and Cl^- in aqueous solution of NaCl; the results are presented in Table 3 and compared with the results obtained by the hydration model (Bates et al., 1970). The agreement obtained with both models is surprisingly good since both treatments are quite different in nature. Should a strong disagreement have been found it would have been difficult to decide which values were more realistic, because there are not any experimental data for activity coefficient of ions with which the predicted values can be compared. However, the agreement suggests that the NRTL-NRF model is, in some sense, representing well the physical phenomena.

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Notation

g^{ex} = molar excess Gibbs energy
m = molality
x = mole fraction
X = effective mole fraction
Z = charge number
Z_A = absolute charge number of anion
Z_C = absolute charge number of cation

Greek letters

β_E = electrolyte interaction energy parameter
β_W = solvent interaction energy parameter
γ_i = activity coefficient of species i
$\gamma_\pm$ = mean ionic activity coefficient
Γ_{ij} = nonrandom factor of species i around species j
λ = NRTL-NRF parameter
λ_E = electrolyte adjustable parameter
λ_W = solvent adjustable parameter
ν = stoichiometric number of electrolyte = $\nu_A + \nu_C$
ν_A = stoichiometric number of anion
ν_C = stoichiometric number of cation
σ_γ = root mean square deviation of logarithm values

Superscripts

ex = excess
$*$ = unsymmetrical convention

Subscripts

$\pm$ = mean
i, j, k = component or species
A = anion
C = cation
E = electrolyte
W = water
S = salt
DH = Debye-Hückel
$NRTL\text{-}NRF$ = nonrandom two-liquid–nonrandom factor

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