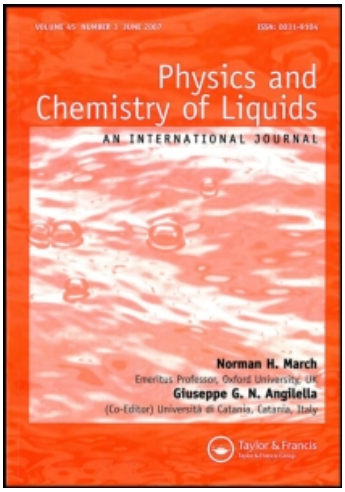

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Correlation of mean ionic activity coefficient using a two-parameters model

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Correlation of mean ionic activity coefficient using a two-parameters model

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In this study, a two-parameters model is presented based on the solvation phenomena. Using this model, the mean ionic activity coefficients of 146 salts and activity coefficients of individual ions of some 1 : 1 and 1 : 2 salts have been correlated successfully. The results of the present model have been compared with the Khoshkbarchi–Vera model and three-characteristic parameter correlation model of Lin and Lee model. These comparisons show that the present model predicts the mean ionic activity coefficient better than others.

Keywords: Aqueous electrolytes; Mean ionic activity coefficient; Individual activity coefficient

1. Introduction

Electrolyte solutions are ubiquitous in numerous industrial processes and natural environments such as oil recovery, separation, wastewater treatment, seawater desalination, gas scrubbing, and extractive distillation process. Design and scale-up of unit operations in industrial chemical process requires a thorough understanding of the chemical and phase behavior of process fluids. Therefore, thermodynamic properties and the phase equilibrium computations of aqueous electrolyte solutions were very important [1,2]. However, development of rigorous thermodynamic models for electrolytes, due to the complex nature of their behavior in solutions, is a cumbersome task. So, in the past decades, many attempts have been made to develop models with simpler expressions for the thermodynamic properties of electrolyte solutions. Bates *et al.* [3] developed the hydration model. Stokes and Robinson [4] proposed a new model for the estimation of the mean activity coefficient of electrolytes and the activity coefficient of individual ions. A two-parameters model based on the hydration theory has been proposed for estimation of the activity coefficients of individual ions by Rabie *et al.* [5]. Khoshkbarchi and Vera [6] proposed a

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two-parameters model based on the Pitzer model. Recently, Pazuki [7], Pazuki and Arabgol [8] and Pazuki and Rohani [9] modeled mean activity of individual ions, osmotic coefficient and activity of water in aqueous solution based on a new two-parameter model.

In this study, based on Lin and Lee model [10], a two-parameters model is suggested. The adjustable parameters of this model were obtained by nonlinear fitting of the model equations to the experimental data for mean ionic activity coefficients. The comparison of the SDs in the mean ionic activity coefficients obtained by this model with the results obtained by Khoshkbarchi–Vera (KV) and three-characteristic parameter correlation (TCPC) [11] (three characteristic parameter correlation) models show that the present model works much better than the others.

2. Thermodynamic model

Here, we assume that, the excess Gibbs energy of an electrolyte solution and consequently the activity coefficient of the species in the solution is the combination of long-range (LR) and short-range (SR) contributions:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{LR}} + \ln_i^{\mathrm{SR}}. \tag{1}$$

In the aforementioned equation, the LR interaction term accounts for the electrostatic interactions between ions and the SR interaction term considers the non-electrostatic interactions between all species (ion, solvent, and segment). We used here the Pitzer–Debye–Huckel equation (PDH) [11] as the LR contribution. This equation has the following form:

$$\ln \gamma_i^{\mathrm{LR}} = -A_\phi Z_i^2 \left[\frac{I^{1/2}}{1 + b_i I^{1/2}} + \frac{2}{b_i} \ln\left(1 + b_i I^{1/2}\right) \right] \tag{2}$$

in which A_ϕ is the Debye–Huckel constant for osmotic coefficients, b_i is the closest distance parameter of ion and I is the ion strength of the solution. However, in the electrolyte solutions, because of the attraction between ions and solvent molecules, solvation occurs. The electrostatic potential, Γ_{is}, between ion i and a solvent molecule, s, can be described by the Coulomb's law as the following equation:

$$\Gamma_{\mathrm{is}} = h_{\mathrm{is}} \frac{Z_i e \mu}{r^2} \tag{3}$$

in which Z_i, r, μ and h_{is} are, respectively, the charge number of ion i, the distance between the ion i and the solvent molecule, the dipole moment of the solvent molecule and the relative parameter. Here, we assumed that, the separation between the solvent molecule and the ion i is inversely proportional to the ionic strength via the adjustable parameters α and n:

$$r = \alpha I^{-n}. \tag{4}$$

The parameters α and n can be evaluated using the correlation of the activity coefficient data. With the substitution of equation (4) into equation (3), the electrical potential is expressed in terms of ionic strength as:

$$\Gamma_{\text{is}} = h_{\text{is}} Z_i \left(\frac{e\mu}{\alpha^2}\right) I^n. \tag{5}$$

A dimensionless potential, φ_{is}, is defined for an ion and a surrounding molecule as follows:

$$\varphi_{\text{is}} = \frac{e\Gamma_{\text{is}}}{kT}. \tag{6}$$

With the substitution of this dimensionless potential into equation (6) we have:

$$\varphi_{\text{is}} = h_{\text{is}} Z_i \left(\frac{e^2\mu}{\alpha^2 kT}\right) I^n. \tag{7}$$

The ionic activity coefficient due to the solvation effect can be calculated following the charging process:

$$\ln \gamma_i^{\text{SR}} = \int_0^Z \varphi_{\text{is}} \cdot \mathrm{d}Z. \tag{8}$$

Therefore, the activity coefficient of the ionic species i due to the solvation effect can be obtained from equations (8) and (9) as:

$$\ln \gamma_i^{\text{SR}} = h_{\text{is}} \left(\frac{e^2\mu}{\alpha^2 kT}\right) I^n \cdot \frac{Z_i^2}{2}. \tag{9}$$

Finally, we obtain the SR contribution in activity coefficient of ion i as the following equation:

$$\ln \gamma_i^{\text{SR}} = c_i I^n Z_i^2 \tag{10}$$

in which the parameter c_i has been defined as:

$$h_{\text{is}} \left(\frac{e^2\mu}{2\alpha^2 kT}\right) = c_i. \tag{11}$$

Here, we assume that the c_i parameter is dependent on the composition as:

$$c_i = c_{0i} + c_{1i} I \tag{12}$$

where c_{0i} and c_{1i} are adjustable parameters. Combination of the PDH equation, equation (2), as the LR contribution and equation (10) as the SR contribution according to equation (1) gives us the follwing equation as the activity

coefficient of ion i:

$$\ln \gamma_i^{\mathrm{LR}} = -A_\phi Z_i^2 \left[\frac{I^{1/2}}{1 + b_i I^{1/2}} + \frac{2}{b_i} \ln\left(1 + b_i I^{1/2}\right) \right] + \left(c_{0j} + c_{1j} I\right) I^n Z_i^2 \tag{13}$$

in which the parameters b_i, c_{0i}, and c_{1i} are the ion-specific adjustable parameters of the model. The mean activity coefficient of an electrolyte, $\ln \gamma_\pm$, could be obtained easily from the activity coefficient of cation, $\ln \gamma_+$, and the activity coefficient of anion, $\ln \gamma_-$, following the equation:

$$\ln \gamma_\pm = \frac{\nu_+ \ln \gamma_+ + \nu_- \ln \gamma_-}{\nu_+ + \nu_-}. \tag{14}$$

in which ν_+ and ν_- are the numbers of cation and anion in one molecule of the electrolyte, respectively. The $\ln \gamma_\pm$ obtained in this manner contains eight adjustable parameters. In order to decrease the number of parameters, we assume that the b and c parameters for cation and anion are equal. Hence, the number of parameters are reduced to four.

3. Results and discussion

In this study, 146 sets of experimental mean ionic activity coefficients at 298.15 K from [12] were used to fit the adjustable parameters of the modified model.

The model parameters including b, c_{0i}, c_{1i} and n were determined using the following objective function

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N} \left[\ln\left(\gamma_\pm^{\mathrm{exp}}\right) - \ln\left(\gamma_\pm^{\mathrm{cal}}\right)\right]^2}{N}} \tag{15}$$

In the used objective function, N is the number of experimental data. For simplification of the calculations of individual activity coefficients, the parameters c_{0i} and n are set to constant values of -0.07 and 0.2. This reduces the number of model parameters to two parameters for each salt. The model parameters and the SD in $\ln(\gamma_\pm)$ have been collected in table 1. This table also contains SDs obtained by KV model [6] and TCPC model [11]. It is evident that the present model is better than the KV and TCPC models.

4. Conclusion

In this study, a simple two-parameters model has been developed based on the solvation concept. The activity coefficients of individual ions and the mean activity coefficient of some 1 : 1 and 1 : 2 electrolytes as well as the osmotic coefficients are correlated by the model equations. The adjustable parameters of the model have been evaluated by fitting the model equations to the experimental data.

Table 1. Adjustable parameters for new model and SDs of this work, KV model and TCPC model.

Salt	b	n	$\sigma(\ln(\gamma_{\pm}))$	$\sigma(\ln(\gamma_{\pm}))_{KV}$	$\sigma(\ln(\gamma_{\pm}))_{TCPC}$
1 : 1 salts					
HCl	5.0198	0.2062	0.010	0.021	0.021
HBr	5.0891	0.2730	0.001	0.010	0.014
HI	5.6163	0.3570	0.006	0.008	0.028
$HClO_4$	4.2780	0.2523	0.012	0.048	0.020
HNO_3	4.3604	0.1214	0.003	0.005	0.080
LiOH	1.6602	0.0352	0.006	0.008	0.029
LiCl	4.2602	0.1899	0.003	0.029	0.015
LiBr	4.1895	0.2337	0.007	0.037	0.021
LiI	6.8770	0.2567	0.005	0.015	0.021
$LiClO_4$	6.7240	0.2377	0.007	0.012	0.018
$LiNO_3$	5.1297	0.1188	0.017	0.002	0.031
LiAC	4.0057	0.0923	0.002	0.002	0.049
LiTol	3.2675	0.0192	0.011	0.012	0.020
NaOH	3.2051	0.1135	0.012	0.028	0.039
NaF	3.2083	−0.0486	0.004	0.001	0.012
NaCl	3.0666	0.1028	0.016	0.017	0.006
NaBr	3.7294	0.1049	0.004	0.008	0.013
NaI	4.3053	0.1381	0.002	0.007	0.017
$NaClO_3$	3.0554	−0.0007	0.001	0.005	0.013
$NaClO_4$	3.4126	0.0373	0.005	0.008	0.047
$NaBrO_3$	2.4281	−0.0506	0.010	0.005	0.035
$NaNO_3$	2.3811	−0.0163	0.012	0.006	0.034
NaFormate	3.9265	0.0520	0.002	0.001	0.008
NaAc	5.0152	0.1325	0.007		0.012
NaPropionate	5.6867	0.1735	0.009	0.002	0.013
NaButyrate	7.7442	0.1780	0.034	0.023	0.049
NaValerate	14.664	0.0813	0.076		0.088
NaPelargonate	−0.1491	−0.0162	0.111	0.079	0.165
NaCaprate	−0.1762	−0.3617	0.149		0.207
NaHMalonate	2.5320	−0.0009	0.010	0.006	0.020
NaHSuccinate	2.5518	0.0246	0.010	0.008	0.017
NaSCN	4.6822	0.0863	0.004	0.004	0.013
NaH_2PO_4	1.2420	−0.0189	0.032	0.026	0.045
KOH	3.8128	0.1691	0.009	0.015	0.019
KF	3.1149	0.0831	0.006	0.007	0.022
KCl	2.9485	0.0309	0.007	0.005	0.013
KBr	3.1466	0.0365	0.005	0.005	0.008
KI	3.6921	0.0452	0.004	0.002	0.019
$KClO_3$	3.0745	−0.2791	0.004		0.025
$KBrO_3$	3.2401	−0.3787	0.003		0.022
KNO_3	1.4513	−0.0968	0.016	0.008	0.067
KAC	5.3748	0.1538	0.008	0.001	0.011
KHMalonate	2.1730	−0.0259	0.018	0.012	0.042
KHSuccinate	2.3025	0.0046	0.014	0.011	0.027
KHAdipate	3.5823	−0.0136	0.004	0.001	0.005
KTol	2.6465	−0.1181	0.019		0.089
KSCN	3.0570	0.0124	0.004	0.002	0.007
KH_2PO_4	1.4410	−0.1387	0.013	0.008	0.041
NH_4Cl	3.0474	0.0227	0.005	0.002	0.001
NH_4NO_3	1.8166	−0.0336	0.010		0.053
RbCl	2.5926	0.0277	0.007	0.001	0.001
RbBr	2.5876	0.0194	0.007	0.005	0.013
RbI	2.4957	0.0223	0.007	0.005	0.018
$RbNO_3$	1.1936	−0.0801	0.020	0.011	0.079
RbAc	5.4085	0.1636	0.008	0.002	0.012
CsOH	5.2563	0.1590	0.005		0.006

(*Continued*)

Table 1. Continued.

Salt	b	n	$\sigma(\ln(\gamma_\pm))$	$\sigma(\ln(\gamma_\pm))_{KV}$	$\sigma(\ln(\gamma_\pm))_{TCPC}$
CsCl	1.9844	0.0256	0.011	0.008	0.024
CsBr	1.9644	0.0187	0.012	0.008	0.026
CsI	2.1185	−0.0109	0.006	0.003	0.024
$CsNO_3$	1.6448	−0.1784	0.010	0.006	0.037
CsAc	5.7661	0.1641	0.009	0.002	0.012
$AgNO_3$	1.0733	−0.0681	0.028	0.016	0.098
$TlNO_3$	1.4508	−0.4794	0.005		0.017
$TlClO_4$	2.3472	−0.3549	0.004		0.019
TlAc	1.8586	−0.0126	0.011	0.005	0.024
2 : 1 salts					
$MgCl_2$	3.9680	0.0805	0.014	0.064	0.019
$MgBr_2$	4.6828	0.0968	0.006	0.070	0.005
MgI_2	5.1746	0.1170	0.005	0.0100	0.034
$Mg(ClO_4)_2$	5.5231	0.1198	0.008	0.064	0.024
$Mg(NO_3)_2$	4.7110	0.0578	0.020	0.031	0.039
$MgAc_2$	2.9930	0.0245	0.016		0.038
$CaCl_2$	4.0030	0.0632	0.027	0.055	0.043
$CaBr_2$	0.2235	0.0599	0.164	0.137	0.042
CaI_2	4.9478	0.0954	0.002	0.022	0.010
$Ca(ClO_4)_2$	6.1072	0.0866	0.068	0.043	0.096
$Ca(NO_3)_2$	3.6305	0.0181	0.009	0.042	0.017
$SrCl_2$	3.8709	0.0553	0.009	0.027	0.010
$SrBr_2$	4.1875	0.0678	0.006	0.024	0.014
SrI_2	4.8212	0.0874	0.004	0.022	0.013
$Sr(ClO_4)_2$	5.9066	0.0683	0.093	0.033	0.116
$Sr(NO3)_2$	3.1597	0.0028	0.013	0.042	0.026
$BaCl_2$	3.9065	0.0341	0.003		0.032
$BaBr_2$	4.1667	0.0507	0.003	0.048	0.018
BaI_2	4.7626	0.0802	0.007	0.031	0.013
$Ba(ClO_4)_2$	5.4326	0.0415	0.049	0.048	0.070
$Ba(NO_3)_2$	2.6313	−0.0695	0.005		0.050
$BaAc_2$	3.9144	0.0059	0.045		0.046
$MnCl_2$	5.7910	0.0327	0.094		0.104
$FeCl_2$	4.0832	0.0622	0.004	0.027	0.010
$CoCl_2$	4.7265	0.0570	0.044	0.043	0.057
$CoBr_2$	5.5632	0.0807	0.071	0.025	0.092
CoI_2	7.9071	0.0970	0.187	0.238	0.099
$Co(NO_3)_2$	4.4452	0.0520	0.021	0.026	0.035
$NiCl_2$	4.7632	0.0599	0.062	0.038	0.090
$CuCl_2$	5.3594	0.0160	0.060	0.079	0.072
$Cu(NO_3)_2$	4.4663	0.0415	0.038	0.031	0.043
$ZnCl_2$	3.8996	0.0095	0.058	0.123	0.101
$ZnBr_2$	8.7416	0.0141	0.055		0.090
ZnI_2	22.4568	0.0199	0.142		0.160
$Zn(ClO_4)_2$	4.9954	0.1250	0.010	0.064	0.023
$Zn(NO_3)_2$	5.1975	0.0515	0.044	0.027	0.061
$CdCl_2$	0.4938	0.0214	0.112	0.150	
$CdBr_2$	0.2235	0.0599	0.164	0.170	
CdI_2	−0.1067	0.1748	0.446	0.238	
$Cd(NO_3)_2$	4.4885	0.0330	0.011		0.018
$Pb(ClO_4)_2$	4.9785	0.0530	0.050	0.025	0.066
$Pb(NO_3)_2$	1.6689	−0.0162	0.019	0.033	0.059
UO_2Cl_2	5.7364	0.0586	0.035	0.048	0.043
$UO_2(ClO_4)_2$	83.1126	0.1488	0.100	0.086	
$UO_2(NO_3)_2$	10.8112	0.0421	0.187	0.155	0.142

(*Continued*)

Table 1. Continued.

Salt	b	n	$\sigma(\ln(\gamma_{\pm}))$	$\sigma(\ln(\gamma_{\pm}))_{KV}$	$\sigma(\ln(\gamma_{\pm}))_{TCPC}$
1 : 2 salts					
Li_2SO_4	2.9144	0.0153	0.017	0.031	0.020
Na_2SO_4	2.1736	0.0007	0.043	0.026	0.044
Na_2CrO_4	2.6272	0.0140	0.048	0.036	0.063
$Na_2S_2O_3$	2.5059	0.0078	0.034	0.026	0.051
K_2SO_4	2.4965	−0.0235	0.005	0.026	0.021
K_2CrO_4	2.5794	0.0051	0.023	0.039	0.033
$(NH_4)_2SO_4$	1.9525	0.0008	0.019	0.045	0.021
Sc_2SO_4	2.7537	−0.0018	0.015	0.029	0.016
Rb_2SO_4	2.6491	−0.0063	0.017	0.028	0.026
Na_2Fumarate	2.9349	0.0290	0.006	0.039	0.011
Na_2Maleate	2.1217	0.0173	0.005	0.049	0.021
2 : 2 salts					
$BeSO_4$	2.2593	0.0165	0.016	0.012	0.020
$MgSO_4$	2.2469	0.0133	0.019	0.115	0.036
$MnSO_4$	2.1637	0.0117	0.028	0.115	0.046
$NiSO_4$	2.1682	0.0105	0.019	0.101	0.035
$CuSO_4$	2.1982	0.0087	0.008	0.088	0.013
$ZnSO_4$	2.1147	0.0132	0.033	0.107	0.041
$CdSO_4$	2.1376	0.0101	0.019	0.119	0.042
UO_2SO_4	2.2109	0.0104	0.034	0.106	0.030
3 : 1 salts					
$AlCl_3$	4.2346	0.0507	0.022	0.041	0.023
$ScCl_3$	4.2534	0.0418	0.004	0.057	0.050
$CrCl_3$	4.4472	0.0430	0.006	0.054	0.028
YCl_3	4.0612	0.0387	0.007	0.054	0.016
$LaCl_3$	4.1429	0.0331	0.003	0.054	0.035
$CeCl_3$	4.0837	0.0337	0.006	0.060	0.031
$PrCl_3$	4.0581	0.0336	0.005	0.057	0.036
$NdCl_3$	4.0407	0.0345	0.004	0.057	0.034
$SmCl_3$	4.1340	0.0353	0.004	0.056	0.042
$EuCl_3$	4.1847	0.0359	0.006	0.054	0.014
$Cr(NO_3)_3$	4.3680	0.0367	0.007	0.065	0.021
3 : 2 salts					
$Al_2(SO_4)_3$	3.0114	0.0084	0.027	0.068	0.049
$Cr_2(SO_4)_3$	3.5130	0.0067	0.043	0.064	0.069
1 : 4 salts					
$K_4Fe(CN)_6$	3.4359	−0.0009	0.009		
1 : 3 salts					
$K_3Fe(CN)_6$	3.2968	0.0052	0.009		
4 : 1 salts					
$Th(NO_3)_4$	8.1315	0.0055	0.119		0.121
Average			0.0288	0.0396	0.0388

Comparison of the results with the results of KV, and TCPC models show that the new model correlates the experimental data better than the other methods.

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