

Estimations of activity coefficients of constituent ions in aqueous electrolyte solutions with the two-ionic-parameter approach

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Abstract

The electrolyte-specific solvation parameter regarding the ionic solvation, and approaching parameter regarding the closest distance of approach between ions, in a electrolyte solution were defined by Lin and Lee [Fluid Phase Equil. 205 (2003) 69–83]. In this study, these two electrolyte-specific parameters of individual ions were correlated with the activity coefficients of ions in different aqueous single-electrolyte solutions from literature. With these two parameters and the two-ionic-parameter approach of Lin and Lee, the individual activity coefficients of the ions in the solutions of fourteen 1:1 type, two 1:2 type, and six 2:1 type electrolytes were calculated and compared to the literature values. Also the comparisons of the predicted and literature osmotic coefficients of aqueous multi-electrolyte solutions were reported. The results showed the estimated values fairly agree to the literature data.

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1. Introduction

The thermodynamic properties and phase equilibria of electrolyte solutions are so important to the chemical process development, waste treatment, water desalination, absorption heat pump development, and other processes involving electrolytes. A model describing the thermodynamic behavior of electrolyte solutions is obviously needed. For the study of behavior of electrolyte solutions, the Debye–Hückel theory [1] is the primary model that takes into consideration the electrostatic force (long-range interaction) between ions and is suitable for dilute solution. Based on the Debye–Hückel theory, many methods accounting for the interaction between ion and solvent molecule (short range interaction) were proposed by Pitzer [2], Pitzer and Mayorga [3], Pitzer and Kim [4], Hamer and Wu [5], and Bromley [6]. Later on, different approaches such as by Cruz and Renon [7] and Chen et al. [8] were developed by applying the Pitzer equation for the long-range interaction and the NRTL equation for

the short-range interaction along with the local composition consideration for multi-electrolyte solutions. Triolo et al. [9], Planche and Renon [10], Ball et al. [11] discussed the mean spherical approximation (MSA) approach considering a physical significant parameter other than the particle interaction parameter. Other researchers worked on the subject of electrolyte solutions included Kondo and Eckert [12], and Patwardhan and Kumar [13]. Lin et al. [14] proposed a different approach relating the parameters of the equivalent dielectric, the closest distance of approaching ions, and the solvation parameter.

It is well recognized that in a strong electrolyte solution, electrolytes dissolve and dissociate into ions that are surrounded by water molecules and counter ions. The non-ideal behavior of electrolyte solutions is dominantly caused by the particle interactions of water–ion and ion–ion but not the interaction between molecular electrolyte and water molecules. Thus, the fundamental species in electrolyte solutions are ions and water molecules, and it should be more significant if the thermodynamic properties are characterized by the ionic activity coefficients rather than by the mean activity coefficient of electrolytes. For example, in a multi-

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electrolyte solution of KBr and NaBr with common Br^- , there exists neither KBr nor NaBr molecules and no one can recognize from which electrolyte the Br^- was dissociated. Thus, the consideration of individual ion as the fundamental species is more significant and practical to describe the real behavior of an electrolyte solution. There have been reports considering individual ions, such as Shatkay and Lerman [15] used a Na^+ glass electrode and an Ag/AgCl electrode and determined the activity coefficients of Na^+ and Cl^- . Khoshkbarchi and Vera [16] used ion-selective electrode to measure the activity coefficients of individual ions in the aqueous solutions of NaCl, NaBr, and KCl. But Vera's research group reported the revised data and claimed in the latter paper [17] that the work of Khoshkbarchi and Vera [16] were erroneous because mistakes were observed while handling liquid junction. Lin and Lee [18] proposed the two-ionic-parameter approach and defined the electrolyte-specific approaching parameter and solvation parameter for each constituent ion in an electrolyte solution. The advantages of this approach: (1) applicability to multi-electrolyte solutions and only two parameters are needed for each existing ion in a multi-electrolyte solution. For instance, eight parameters are required for a two-electrolyte solution without a common ion, (2) estimations of thermodynamic properties are predictive. For instance, the predictions of vapor pressures of NaCl + KBr and KCl + NaBr solutions with 0.40% of AARD compared to experimental values [19], that of CaCl_2 , MgCl_2 , and BaCl_2 solutions with a largest 1.43% of AARD compared to experimental values [20], and osmotic coefficients reported in the later part of this study. The disadvantage of this approach is the necessity of experimental individual ion activity coefficient for correlating the electrolyte-specific approaching and solvation parameters.

2. The two-ionic-parameter approach of Lin and Lee

The two-ionic-parameter approach of Lin and Lee [18] was developed on the basis of considerations of Pitzer–Debye–Hückel long-range interaction and short-range solvation effects. Here, only the related equations were briefly introduced. Lin and Lee [18] expressed the activity coefficient of an ion in an aqueous electrolyte solution as a combination of two parts

$$\ln \gamma_i = \ln \gamma_i^{\text{pdh}} + \ln \gamma_i^{\text{sv}} \quad (1)$$

The term $\ln \gamma_i^{\text{pdh}}$ is part of the ionic activity coefficient attributed to long-range interaction and $\ln \gamma_i^{\text{sv}}$ is that attributed to short-range interaction. The final expressions of $\ln \gamma_i^{\text{pdh}}$ applied by Lin and Lee [18] for cation and anion are

$$\ln \gamma_+^{\text{pdh}} = -A_\phi z_+^2 \left[\frac{I^{1/2}}{1 + b_+ I^{1/2}} + \frac{2}{b_+} \ln(1 + b_+ I^{1/2}) \right] \quad (2)$$

and

$$\ln \gamma_-^{\text{pdh}} = -A_\phi z_-^2 \left[\frac{I^{1/2}}{1 + b_- I^{1/2}} + \frac{2}{b_-} \ln(1 + b_- I^{1/2}) \right] \quad (3)$$

In the above equations, z_i is the charge number of ion, I is the ionic strength of electrolyte, b_i is the approaching parameter of ion i , and A_ϕ is the Debye–Hückel constant given as

$$A_\phi = \frac{1}{3} (2\pi L d_w)^{1/2} \left(\frac{e^2}{4\pi\epsilon_0\epsilon_r kT} \right)^{3/2} \quad (4)$$

Both cation and anion share the identical value of A_ϕ . The parameter ϵ_r is the electric permittivity of solution and represented by a temperature function of

$$\epsilon_r = 0.0007(T - 273.15)^2 - 0.3918(T - 273.15) + 87.663 \quad (5)$$

Other physical properties involved in A_ϕ were explained in the List of symbols. The “approaching parameters”, b_+ and b_- , were defined by Lin and Lee [18] based on the consideration that a strong electrolyte will dissociate into anion and cation. Consequently, the fundamental individual species in an aqueous electrolyte solution is an ion, always surrounded by the opposite-sign ions and water molecules (the interaction effect by water molecules was considered in the short-range interaction), rather than an electrolyte being considered as the fundamental individual species. Lin and Lee [18] considered approaching parameter separately for cations and anions since the atmosphere of cation-in-center is different from the atmosphere of anion-in-center in solutions. These two approaching parameters are dependent on the distance between the closest-approaching ions, size and configuration of ion, and the magnitude of the interaction force between ions.

The term $\ln \gamma_i^{\text{sv}}$ was related to the electric potential generated between an ion and a solvent molecule by the Coulomb's law and the consideration that an ion surrounded by solvent molecules is due to the polarity of solvent. This specific interaction is called “solvation effect”. Applying the similar consideration for defining the approaching parameter, the solvation parameters were considered individually for cation and anion, i.e. the surrounding effect on the solution property by the water molecules around a cation would be different from that around an anion. The final expressions of the solvation parameters of cation and anion given by Lin and Lee [18] are

$$S_+ = \frac{h_{\text{cs}} e^2 \mu}{2\beta_{\text{cs}}^2 k} \quad (6)$$

and

$$S_- = \frac{h_{\text{as}} e^2 \mu}{2\beta_{\text{as}}^2 k} \quad (7)$$

where μ is the dipole moment of solvent (here is water), h_{is} and β_{is} are the proportional factors for estimating elec-

tric potential and distance between particles, respectively. The final ionic activity coefficients for cations and anions attributed to the solvation effect are expressed as

$$\ln \gamma_+^{\text{sv}} = \frac{S_+ z_+^2 I^\alpha}{T} \quad (8)$$

and

$$\ln \gamma_-^{\text{sv}} = \frac{S_- z_-^2 I^\alpha}{T} \quad (9)$$

where the parameter α in the above equations is a constant value of 1.29 obtained in [18].

Substituting the equations of $\ln \gamma_i^{\text{pdh}}$ and $\ln \gamma_i^{\text{sv}}$ described in the previous paragraph into Eq. (1), the final equations of activity coefficients of cation and anion are

$$\ln \gamma_+ = -A_\phi z_+^2 \left[\frac{I^{1/2}}{1 + b_+ I^{1/2}} + \frac{2}{b_+} \ln(1 + b_+ I^{1/2}) \right] + \frac{S_+ z_+^2 I^\alpha}{T} \quad (10)$$

and

$$\ln \gamma_- = -A_\phi z_-^2 \left[\frac{I^{1/2}}{1 + b_- I^{1/2}} + \frac{2}{b_-} \ln(1 + b_- I^{1/2}) \right] + \frac{S_- z_-^2 I^\alpha}{T} \quad (11)$$

The electrolyte-specific approaching and solvation parameters, b_+ , b_- , S_+ , and S_- , for cation and anion of an electrolyte were determined by correlating the experimental ionic activity coefficients of an aqueous single-electrolyte solution. These parameters are called “primary parameters” and denoted as b_+^0 , b_-^0 , S_+^0 , and S_-^0 in the later sections. The objective function for correlating these parameters is given below and the optimization was performed by the Simplex technique

$$\frac{\text{Min} \sum_i |\ln \gamma_i^{\text{cal}} - \ln \gamma_i^{\text{exp}}|}{n_p} \quad (12)$$

After the primary parameters were determined, the individual activity coefficients of the constituent ions, the mean activity coefficients, and the osmotic coefficients of aqueous single-electrolyte solutions were estimated and compared to the literature data. It should be mentioned that the accuracy of the approaching and solvation parameters is dependent on the accuracy of experimental activity coefficients of individual ions since these parameters are somewhat semi-empirical even they have physical significance. Thus, accurate ionic activity coefficients are essential to the application of the model of Lin and Lee.

3. Estimations of activity coefficients of ions in single-electrolyte aqueous solutions

As mentioned in the previous paragraph, the experimental activity coefficients of individual ions in single-electrolyte

solutions are required for correlating the individual solvation and approaching parameters, then the Lin and Lee’s method is applied to estimate the thermodynamic properties of aqueous electrolyte solutions. In this study, the experimental data for determining the primary solvation and approaching parameters were obtained by Vera et al. [17]. These data include 1:1 type electrolytes of KF, KCl, KBr, NaF, NaCl, NaBr, LiCl, LiBr, CsCl, HCl, NaOH, NaNO₃, and KNO₃, of 1:2 type electrolytes, Na₂SO₄ and K₂SO₄, and of 2:1 electrolytes, BaCl₂, MgCl₂, CaCl₂, BaBr₂, MgBr₂, and CaBr₂. The correlated approaching parameters and solvation parameters and the values of AARD% of individual ion in the above aqueous electrolyte solutions were listed in Table 1. It is observed that most AARD% values of ions dissociated from 1-1 electrolytes are smaller than 2.0% except the acid and basic groups from electrolytes KNO₃, NaNO₃, and KOH with AARD% larger than 2.0%. For 2:1 electrolytes, the AARD% values of anions are reasonable but that of Mg²⁺ in MgBr₂ solution is the worst, 9.0%, among all estimated ionic activity coefficients. For the brevity reason, the extensive data of the literature and the estimated activity coefficients of all ions were not given here. For 1:2 type electrolyte solutions, the available literature activity coefficients were only the constituent ions of Na₂SO₄ and K₂SO₄ solutions. The correlated approaching and solvation parameters and the values of AARD% of each ion in these two solutions were also listed in Table 1. It showed that the values of AARD% of the calculated activity coefficients are reasonable for cations, Na⁺ and K⁺, but that of SO₄²⁻ anion are larger than 6.0%. If comparisons were made between the results of uni-valence and bi-valence ions one might observe that the values of AARD% of the bi-valence ions are larger than that of the uni-valence ions. These results might be attributed to (1) the larger ion sizes of bi-valence ions that cause more complicated interaction with opposite-sign ions and water molecules, (2) the possible existence of HSO₄⁻ group in this electrolyte solution. All the values of AARD% of the activity coefficients of individual ions discussed in this section were plotted in Fig. 1

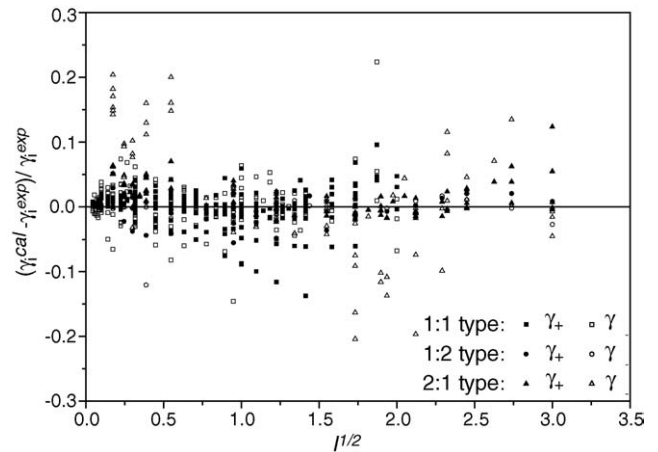


Fig. 1. Average absolute relative deviation percentages of individual ion activity coefficients of single-electrolyte solutions.

Table 1

The approaching and solvation parameters of aqueous single-electrolyte solutions and the average absolute relative deviation percentages of estimated and literature values at 25 °C

Electrolyte	m_{\max}	Cation	b_+	S_+	Anion	b_-	S_-	AARD%			
								γ_+ ^a	γ_- ^a	γ_{\pm} ^a	ϕ ^b
1-1 type											
KF	3.0	K ⁺	1.316	22.634	F ⁻	2.763	27.917	0.9	2.0	4.0	1.7
KCl	4.0	K ⁺	1.243	13.296	Cl ⁻	3.235	11.158	1.9	1.0	1.0	0.6
KBr	2.0	K ⁺	0.720	0.022	Br ⁻	3.837	19.292	1.4	1.5	5.2	3.5
NaF	1.0	Na ⁺	2.393	18.792	F ⁻	1.647	18.176	1.6	0.7	2.9	1.8
NaCl	4.0	Na ⁺	4.352	26.448	Cl ⁻	1.827	19.245	1.3	1.0	2.2	0.6
NaBr	4.0	Na ⁺	2.935	43.406	Br ⁻	2.554	17.469	1.7	1.4	0.4	0.5
LiCl	3.0	Li ⁺	6.768	82.778	Cl ⁻	1.887	20.090	2.0	0.6	1.2	0.8
LiBr	3.0	Li ⁺	2.559	101.776	Br ⁻	4.747	21.461	1.7	2.0	0.9	0.6
CsCl	3.0	Cs ⁺	1.174	11.153	Cl ⁻	1.880	7.311	1.2	0.4	0.4	0.2
NaOH	2.0	Na ⁺	0.971	59.306	OH ⁻	6.052	15.685	1.0	0.7	1.0	1.1
KOH	1.9	K ⁺	0.002	36.479	OH ⁻	22.347	159.038	2.0	3.5	1.6	1.6
HCl	2.0	H ⁺	5.161	65.860	Cl ⁻	2.552	55.666	2.6	1.7	0.7	0.6
NaNO ₃	3.5	Na ⁺	4.080	13.053	NO ₃ ⁻	0.556	0.176	2.1	2.9	0.9	1.0
KNO ₃	3.5	K ⁺	0.955	0.011	NO ₃ ⁻	0.372	1.003	5.3	3.0	2.8	3.5
1-2 type											
Na ₂ SO ₄	3.0	Na ⁺	1.552	3.464	SO ₄ ²⁻	1.662	0.022	0.9	6.8	2.7	3.6
K ₂ SO ₄	0.69	K ⁺	1.655	0.017	SO ₄ ²⁻	1.570	2.273	1.7	6.2	1.8	0.8
2-1 type											
BaCl ₂	1.4	Ba ²⁺	2.985	14.899	Cl ⁻	2.203	3.092	4.3	0.6	1.8	1.2
MgCl ₂	3.0	Mg ²⁺	4.785	22.914	Cl ⁻	1.860	12.942	5.7	1.2	2.6	0.7
CaCl ₂	3.0	Ca ²⁺	3.908	18.321	Cl ⁻	2.085	10.745	4.9	1.4	1.4	0.8
BaBr ₂	2.3	Ba ²⁺	4.606	13.665	Br ⁻	1.960	9.861	6.9	1.0	2.6	1.5
MgBr ₂	3.0	Mg ²⁺	5.645	28.311	Br ⁻	1.859	17.401	9.0	1.6	3.5	1.8
CaBr ₂	3.0	Ca ²⁺	6.855	25.315	Br ⁻	1.260	9.085	6.9	0.8	2.6	1.7

AARD% = $\sum_i (|\phi_i^{\text{cal}} - \phi_i^{\text{exp}}| / \phi_i^{\text{exp}} / N) \times 100\%$, AARD γ % = $\sum_i (|\gamma_i^{\text{cal}} - \gamma_i^{\text{exp}}| / \gamma_i^{\text{exp}} / N) \times 100\%$.

^a From literature [17].

^b From literature [21].

and the values of AARD% of the mean activity coefficient of electrolyte and those of osmotic coefficients of solutions were plotted in Fig. 2. These two figures showed the values of AARD% of individual ion activity coefficients, mean activity coefficients, and osmotic coefficients distribute randomly.

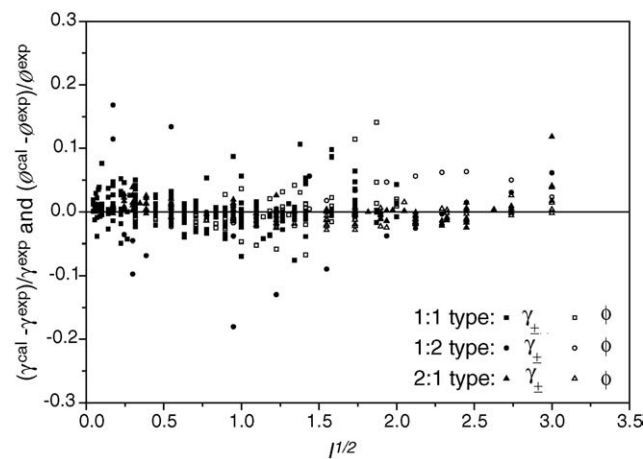


Fig. 2. Average absolute relative deviation percentages of mean activity coefficients of electrolytes and osmotic coefficients of single-electrolyte solutions.

4. The predictions of mean activity coefficients and osmotic coefficients of aqueous single-electrolyte solutions

The definition of mean activity coefficients of an electrolyte

$$\ln \gamma_{\pm} = \frac{\nu_+ \ln \gamma_+ + \nu_- \ln \gamma_-}{\nu_+ + \nu_-} \quad (13)$$

The activity coefficients of ions on the right-hand side of above equation can be expressed in terms of electrolyte-specific approaching and solvation parameters as [18]

$$\ln \gamma_{\pm} = \frac{\sum \nu_i \{ -A_{\phi} z_i^2 [I^{1/2} / (1 + b_i I^{1/2}) + (2/b_i) \ln(1 + b_i I^{1/2})] + (S_i z_i^2 I^{\alpha} / T) \}}{\nu_+ + \nu_-} \quad (14)$$

It is obvious that the mean activity coefficients of the electrolytes discussed in the previous paragraph can be estimated by the approaching and solvation parameters of ions.

The osmotic coefficient of a solution, ϕ , is related to the activity of solvent (here is water) by

$$\phi = \frac{-1000}{m_T M_w} \ln a_w \quad (15)$$

In the above equation, the solvent activity, a_w , was expressed in terms of electrolyte-specific approaching and solvation parameters by Lin and Lee [18]. Then the final formula for osmotic coefficient is

$$\phi = 1 - A_\phi \sum_i x_i z_i^2 \frac{I^{1/2}}{1 + b_i I^{1/2}} + \frac{\alpha I^\alpha}{(\alpha + 1)T} \sum_i x_i z_i^2 S_i \quad (16)$$

The mean activity coefficients of the previous 1:1, 2:1, and 1:2 type single-electrolytes and osmotic coefficient of these electrolyte solutions were listed in Table 1. From this table, it is observed that the largest AARD% of mean activity coefficient is 5.2% for KBr and the smallest is 0.5% for NaBr. The largest AARD% of osmotic coefficient is about 3.5% for KBr, KNO₃, and Na₂SO₄ and the smallest are 0.5% and 0.2% for NaBr and CsCl, respectively.

From Table 1 one could also observe that the values of AARD% of the activity coefficients of SO₄²⁻ ions in K₂SO₄ and Na₂SO₄ solutions and those of cations in all 2:1 type electrolyte solutions are larger than those of the mean activity coefficients of these electrolytes. It seems that the approach of Lin and Lee provides more accurate estimations for univalence ions than for bi-valence ions. Is this the weakness of Lin and Lee's approach? At present, one cannot visualize merely from the AARD% of the mean activity coefficients of present electrolytes, we think more estimations are to be performed in the future. However, this observation might imply that in an electrolyte solution, the consideration of individual ions as fundamental species should be more significant than considering electrolyte as mentioned earlier. In other words, the good estimations for mean activity coefficients of electrolytes do not ensure good estimations for individual ion activity coefficients, but good estimations for individual ion activity coefficients will lead to good estimations for mean activity coefficients of electrolytes.

5. Multi-electrolyte aqueous solutions

In a chemical, water treatment, and other processes, it is very common that multi-electrolyte aqueous solutions are involved. The method of Lin and Lee is very convenient to be applied to handle these types of electrolyte solutions.

In a multi-electrolyte solution, the approaching and solvation parameters of constituent ions were calculated by a mixing rule and the electrolyte-specific primary parameters as mentioned before. Here, the mixing rule proposed by Lin and Lee [18] is introduced. The approaching parameter of an ion in a multi-electrolyte solution was estimated by equation and the corresponding primary parameters of that ion

$$b_i = \sum_l y_l b_{i,l}^0 \quad (17)$$

and the corresponding solvation parameter was estimated by

$$S_i = \sum_l y_l S_{i,l}^0 \quad (18)$$

where l under summation represents all the opposite-sign ions in solution and $b_{i,l}^0$ and $S_{i,l}^0$ are the other constituent electrolyte-specific primary approaching parameters and the solvation parameters of ion i . Note that the fraction y_l in the above equation was calculated by

$$y_l = \frac{x_l}{\sum_k x_k} \quad (19)$$

where $\sum_k x_k$ is the sum of the mole fractions of all the opposite-sign ions in the solution and

$$x_l = \frac{m_l}{m_T} \quad (20)$$

Care must be taken whether the solution we are concerned contains the common ions or not. Two examples were given in Appendix A to illustrate how the present mixing rule was formulated. When the method of Lin and Lee is applied to multi-electrolyte solutions, the estimation of the thermodynamic property of solutions is predictive rather than correlative. In our previous report [19], the vapor pressures of NaBr + KCl and NaCl + KBr aqueous solutions were predicted by Lin and Lee's method and compared to the experimental values. The results showed the AARD% between the predicted and experimental data is only 0.40%.

The aqueous multi-electrolyte solutions in this study include two-electrolyte solutions of 1:1 + 1:1, 1:1 + 1:2, 1:1 + 2:1, 1:2 + 1:2, and 2:1 + 1:2 type and three-electrolyte solutions of 1:1 + 1:1 + 1:1 and 1:1 + 1:1 + 2:1 type as given in Table 2. The individual activity coefficients of the constituent ions in these multi-electrolyte solutions can also be predicted with the Lin and Lee approach based on the primary electrolyte-specific approaching and solvation parameters. The predicted activity coefficients of all individual ions in multi-electrolyte solutions are not reported here since literature data could not be obtained to make comparison.

6. Predictions of osmotic coefficients of multi-electrolyte aqueous solutions

The aqueous multi-electrolyte solutions considered for osmotic coefficient prediction are the same as discussed in the previous section. The two-electrolyte include seven 1:1 + 1:1 type, four 1:1 + 1:2 type, six 1:1 + 2:1 type, one 1:2 + 1:2 type, and one 2:1 + 2:1 type and the three-electrolyte include two 1:1 + 1:1 + 1:1 type and two 1:1 + 1:1 + 2:1 type. In this study, only the osmotic coefficients of the above electrolyte solutions were estimated to show the usability of Lin and Lee's method since only these osmotic coefficient data were available from literature as given in Table 2. The mean activity coefficients of electrolytes were not considered since it is meaningless to consider as mentioned earlier. Ions in a multi-

Table 2

The average absolute relative deviation percentages of the osmotic coefficients of aqueous multi-electrolyte solutions of the predicted and literature values at 25 °C

Electrolyte	<i>m</i> (mixed)	AARD%	<i>N</i> ^a	Literature
1:1 + 1:1 type				
LiCl + KCl	0.300–6.000	4.6	48	[22,23]
NaBr + LiBr	0.100–2.500	1.3	66	[24]
NaCl + KCl	0.200–6.000	2.0	58	[25,26]
NaCl + LiCl	0.510–5.841	1.6	36	[27]
NaCl + NaBr	2.829–2.962	1.1	6	[28]
KCl + NaBr	1.041–4.249	9.3	6	[28]
NaCl + CsCl	3.000–3.062	4.5	3	[22]
1:1 + 1:2 type				
NaCl + Na ₂ SO ₄	0.262–7.629	8.9	51	[29,30,31]
KCl + K ₂ SO ₄	0.005–2.300	1.2	54	[30,32]
KCl + Na ₂ SO ₄	0.915–2.701	3.5	20	[30]
NaCl + K ₂ SO ₄	0.389–2.197	1.9	19	[30]
1:1 + 2:1 type				
KCl + BaCl ₂	0.583–3.000	1.5	96	[22,33]
KCl + MgCl ₂	0.430–4.670	1.8	153	[34,35]
KCl + CaCl ₂	0.495–4.252	1.8	66	[36]
NaCl + BaCl ₂	0.385–2.470	1.8	48	[22]
NaCl + MgCl ₂	0.216–5.894	1.2	326	[29,37,38]
NaCl + CaCl ₂	0.370–4.684	1.0	69	[39]
1:2 + 1:2 type				
Na ₂ SO ₄ + K ₂ SO ₄	0.311–1.187	1.8	18	[30]
2:1 + 2:1 type				
CaCl ₂ + MgCl ₂	0.306–4.076	1.1	104	[40]
1:1 + 1:1 + 1:1 type				
LiCl + NaCl + CsCl	2.975–5.233	8.8	5	[22]
LiCl + NaCl + KCl	2.895–3.096	3.0	4	[22]
1:1 + 1:1 + 2:1 type				
LiCl + NaCl + BaCl ₂	1.674–2.583	2.7	3	[22]
NaCl + KCl + BaCl ₂	0.798–2.675	2.6	8	[21]

^aNumber of data; $AARD\phi\% = \sum_i |\phi_i^{\text{cal}} - \phi_i^{\text{exp}}| / \phi_i^{\text{exp}} / N \times 100\%$.

electrolyte solution behave much more complicated than that in a single-electrolyte solution, particularly for the a solution containing one or more common ions since no one can tell how does/do the common ion/ions interact with the counter ions in a solution.

For the sake of brevity only the values of AARD% of the osmotic coefficients of these solutions were listed in Table 2. It is observed that the predicted data agree with literature data fairly well except KCl + NaBr and NaCl + Na₂SO₄ solutions with AARD% of 9.3 and 8.9%, respectively for two-electrolyte solutions.

The prediction of the osmotic coefficients of three-electrolyte solutions is similar to that of two-electrolyte solutions. The values of AARD% of the predictions of the three-electrolyte solutions were also listed in Table 2. It was observed that the predicted values agree with literature data fairly well with the only exception of LiCl + NaCl + CsCl solution with 8.8% of AARD%.

The values of AARD% of the osmotic coefficients of aqueous multi-electrolyte solutions were plotted in Fig. 3. From this figure, one can observe that the predicted data by the

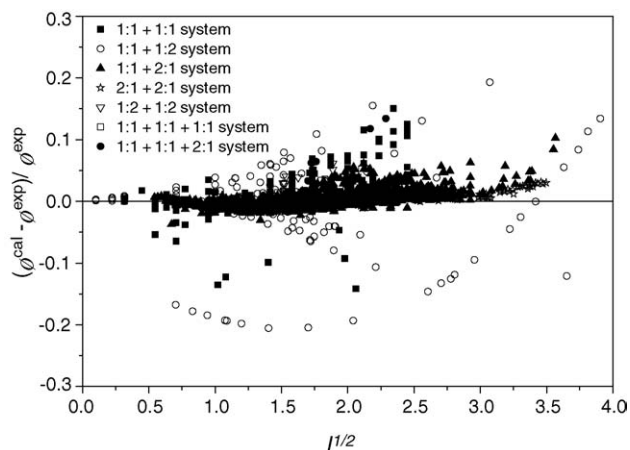


Fig. 3. Average absolute relative deviation percentages of the osmotic coefficients of aqueous multi-electrolyte solutions.

model of Lin and Lee [18] agree fairly well with literature data.

7. Conclusion

In this study, the individual activity coefficients of the constituent ions in aqueous single-electrolyte solutions and osmotic coefficients of these solutions were estimated with the primary solvation and approaching parameters correlated from literature electrolyte-specific ion activity coefficients. The values of AARD% showed the estimations with these two correlated parameters are reasonable for the single-electrolyte solutions except MgBr₂, Na₂SO₄, and K₂SO₄ solutions.

The primary electrolyte-specific solvation and approaching parameters were then used along with a mixing rule to predict the activity coefficients of individual ions in multi-electrolyte solutions and the osmotic coefficients of these electrolyte solutions. The values of AARD% showed the prediction is reasonable except KCl + NaBr, NaCl + Na₂SO₄, and LiCl + NaCl + CsCl solutions with larger deviations.

The estimations of osmotic coefficients of different types of electrolyte solutions, particularly the multi-electrolyte, showed that the advantage of predictive aspect of Lin and Lee's approach. In addition, this approach is able to estimate the individual activity coefficients of constituent ions in aqueous multi-electrolyte solutions. Unfortunately, this application has not been given at present since the lack of literature data makes the comparison to estimated values impossible.

List of symbols

a_w	activity of water
A_ϕ	Debye–Hückel constant
b_i	approaching parameter of ion <i>i</i> .
b_+	approaching parameter of cation
b_-	approaching parameter of anion

$b_{i,j}^0$	electrolyte-specific primary approaching parameter of ion i present in the solution containing ion i and counter-ion l alone
d_w	density of water (kg/m^3)
e	unit charge ($1.6021 \times 10^{-19} \text{ C}$)
h_{as}	interaction parameter between anion and solvent molecule
h_{cs}	interaction parameter between cation and solvent molecule
h_{is}	interaction parameter between ion i and solvent molecule
I	ionic strength (mol/kg)
k	Boltzmann constant ($1.3805 \times 10^{-23} \text{ J K}^{-1}$)
L	Avogadro number ($6.023 \times 10^{23} \text{ mol}^{-1}$)
m	molality of solution (mol/kg)
m_i	molality of ion i (mol/kg)
m_T	$\sum_i m_i$ (mol/kg)
M_w	molecular weight of water (g/mol)
n_i	moles of ion i (mol)
n_p	number of points
n_w	moles of water (mol)
R	universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
S_i	solvation parameter of ion i
S_+	solvation parameter of cation
S_-	solvation parameter of anion
$S_{i,l}^0$	electrolyte-specific primary solvation parameter of ion i present in the solution containing ion i and counter-ion l alone
T	temperature of solution (K)
x_i	mole fraction of ion i on water-free basis (m_i/m_T)
y_i	mole fraction of ion l on water and opposite-sign ion-free basis
z_i	absolute charge number of ion i
z_+	absolute charge number of cation
z_-	absolute charge number of anion

Greek letters

α	$2n$
β_{as}	a parameter
β_{cs}	a parameter
β_i	a parameter
γ_i	activity coefficient of ion i
γ_+	activity coefficient of cation
γ_-	activity coefficient of anion
γ_{\pm}	mean ionic activity coefficient of electrolyte
ϵ_r	dielectric constant
ϵ_0	electrical permittivity in vacuum ($8.8538 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$)
μ	dipole moment
μ_i	chemical potential of ion i
μ_w	chemical potential of water
ν	$\nu_+ + \nu_-$
ν_+	stoichiometric number of cation
ν_-	stoichiometric number of anion
ϕ	osmotic coefficient

Superscripts

cal	calculated value
exp	experimental value
pdh	Pitzer–Debye–Hückel term
sv	solvation term

Subscripts

i, l	ions i and l , respectively
s	solvent
w	water
+	cation
–	anion

Appendix A

The mixing rule applied in this report for approaching parameter and solvation parameter are

$$b_i = \sum_l y_l b_{i,l}^0 \quad \text{and} \quad S_i = \sum_l y_l S_{i,l}^0$$

where the mole fraction is defined by

$$y_l = \frac{x_l}{\sum_k x_k}$$

For a multi-electrolyte solution without common ion, for instance in KCl + NaBr solution the approaching parameter for K^+ and Na^+

$$b_{\text{K}^+} = y_{\text{Cl}^-} b_{\text{K}^+, \text{Cl}^-}^0 + y_{\text{Br}^-} b_{\text{K}^+, \text{Br}^-}^0,$$

$$b_{\text{Na}^+} = y_{\text{Cl}^-} b_{\text{Na}^+, \text{Cl}^-}^0 + y_{\text{Br}^-} b_{\text{Na}^+, \text{Br}^-}^0$$

for Cl^- and Br^-

$$b_{\text{Cl}^-} = y_{\text{Na}^+} b_{\text{Cl}^-, \text{Na}^+}^0 + y_{\text{K}^+} b_{\text{Cl}^-, \text{K}^+}^0,$$

$$b_{\text{Br}^-} = y_{\text{Na}^+} b_{\text{Br}^-, \text{Na}^+}^0 + y_{\text{K}^+} b_{\text{Br}^-, \text{K}^+}^0$$

The solvation parameter for K^+ and Na^+

$$S_{\text{K}^+} = y_{\text{Cl}^-} S_{\text{K}^+, \text{Cl}^-}^0 + y_{\text{Br}^-} S_{\text{K}^+, \text{Br}^-}^0,$$

$$S_{\text{Na}^+} = y_{\text{Cl}^-} S_{\text{Na}^+, \text{Cl}^-}^0 + y_{\text{Br}^-} S_{\text{Na}^+, \text{Br}^-}^0$$

for Cl^- and Br^-

$$S_{\text{Cl}^-} = y_{\text{Na}^+} S_{\text{Cl}^-, \text{Na}^+}^0 + y_{\text{K}^+} S_{\text{Cl}^-, \text{K}^+}^0,$$

$$S_{\text{Br}^-} = y_{\text{Na}^+} S_{\text{Br}^-, \text{Na}^+}^0 + y_{\text{K}^+} S_{\text{Br}^-, \text{K}^+}^0$$

For multi-electrolyte solutions with common ion, for instance, LiCl + KCl solution, the approaching parameter for cations, Li^+ and K^+

$$b_{\text{Li}^+} = y_{\text{Cl}^-} b_{\text{Li}^+, \text{Cl}^-}^0 = b_{\text{Li}^+, \text{Cl}^-}^0,$$

$$b_{\text{K}^+} = y_{\text{Cl}^-} b_{\text{K}^+, \text{Cl}^-}^0 = b_{\text{K}^+, \text{Cl}^-}^0$$

For anion Cl^-

$$b_{\text{Cl}^-} = y_{\text{Li}^+} b_{\text{Cl}^-, \text{Li}^+}^0 + y_{\text{K}^+} b_{\text{Cl}^-, \text{K}^+}^0$$

The solvation parameters for cations, Li^+ and K^+

$$S_{\text{Li}^+} = y_{\text{Cl}^-} S_{\text{Li}^+, \text{Cl}^-}^0 = S_{\text{Li}^+, \text{Cl}^-}^0,$$

$$S_{\text{K}^+} = y_{\text{Cl}^-} S_{\text{K}^+, \text{Cl}^-}^0 = S_{\text{K}^+, \text{Cl}^-}^0$$

for common anion Cl^-

$$S_{\text{Cl}^-} = y_{\text{Li}^+} S_{\text{Cl}^-, \text{Li}^+}^0 + y_{\text{K}^+} S_{\text{Cl}^-, \text{K}^+}^0$$

It is obvious that the approaching parameters and solvation parameters of cations, Li^+ and K^+ , are equal to their corresponding primary parameters since they interact with the only one anion, Cl^- in solution.

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