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Volume Properties of Aqueous Electrolytes. 1. Examination of Apparent Molal Volume Data by the Pitzer Model

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Literature data on the densities of aqueous single electrolyte solutions are analyzed by the virial coefficients model of Pitzer. The Pitzer coefficients obtained for apparent molal volumes are treated with temperature- and pressure-dependent equations. The density data used in this work cover the temperature range to about 200 °C and pressure to about 400 bar. The Pitzer equations represent the apparent molal volumes of these solutions with excellent accuracy.

Introduction

Recently, there has been a growing interest in the thermodynamic properties of aqueous electrolyte solutions, particularly since the development of the Pitzer specific interaction model (*1*). The pitzer model has proved to be very useful tool in estimating various thermodynamic properties of these solutions (*2*, *3*). Equations for apparent molal volume ϕ_V of a single electrolyte solution derived from the Pitzer equations for the activity coefficients (*1*) were successfully extended to very concentrated electrolyte mixtures by us (*4*–*8*).

In order to use the Pitzer equations for estimating densities and mean apparent molal volumes of mixtures, it is essential to determine virial coefficients of single electrolyte solutions. In this paper an attempt has been made to collect the density data on aqueous single electrolyte solutions; ϕ_V obtained therefrom are analyzed by the Pitzer equations and the Pitzer coefficients for several electrolytes are reported. This may help us better understand the utility of the Pitzer model in estimating ϕ_V of such electrolyte solutions.

Table I. Pitzer Coefficients for ϕ_v of Aqueous Electrolytes at 25 °C and 1 bar pressure

electrode	m_{max}, mol kg^{-1}	$(\partial\beta^{(0)}/\partial p)_T \times 10^5$	$(\partial C^{\phi}/\partial p)_T$, $\times 10^6$	$\sigma(\phi_v)$, cm^3 mol^{-1}
RbCl (*18*)[a]	6.1	1.307	−1.440	0.01
CsCl (18)	9.3	1.127	−1.056	0.01
CsBr (*18*)	4.7	1.390	−3.898	0.01
CsI (*18*)	2.2	1.302	−4.413	0.02
$NiCl_2$ (*19*)	5.4	1.919	−2.011	0.01
$MnCl_2$ (*20*)	6.0	0.906	−0.906	0.06
$CdCl_2$ (*20*)	6.4	1.121	−0.923	0.21
$ZnCl_2$ (*20*)	7.3	7.168	−8.975	0.37
$CdSO_4$ (*21*)	2.7	7.106	−9.586	0.07
$MnSO_4$ (*21*)	1.1	14.27	−116.1	0.06
$CoSO_4$ (*21*)	1.0	14.11	−105.9	0.06
$NiSO_4$ (*21*)	1.0	15.44	−116.1	0.04
$ZnSO_4$ (*21*)	1.0	14.89	−116.2	0.04
CuSO (*21*)	0.6	28.99	−542.6	0.20
$EuCl_3$ (*22*)	3.6	−0.443	4.800	0.03
$TbCl_3$ (*22*)	3.6	1.331	13.30	0.04
$HoCl_3$ (*22*)	3.7	1.304	0.330	0.04
$TmCl_3$ (*22*)	3.9	1.329	0.374	0.07
$LuCl_3$ (*22*)	4.1	1.129	0.883	0.12
YCl_3 (*22*)	3.9	1.340	0.005	0.08
$La(ClO_4)_3$ (*23*)	4.8	2.149	−1.456	0.03
$Pr(ClO_4)_3$ (*23*)	4.7	2.124	−1.133	0.08
$Nd(ClO_4)_3$ (*23*)	4.7	2.179	−1.381	0.04
$Sm(ClO_4)_3$ (*23*)	4.6	−0.259	3.234	0.03
$Eu(ClO_4)_3$ (*23*)	4.6	−0.398	5.045	0.05
$Gd(ClO_4)_3$ (*23*)	4.6	0.104	1.729	0.03
$Tb(ClO_4)_3$ (*23*)	4.6	0.186	1.277	0.02
$Dy(ClO_4)_3$ (*23*)	4.6	0.728	0.030	0.01
$Ho(ClO_4)_3$ (*23*)	4.6	1.622	−1.244	0.02
$Er(ClO_4)_3$ (*23*)	4.6	1.531	−1.030	0.01
$Tm(ClO_4)_3$ (*23*)	4.6	1.706	−1.330	0.01
$Yb(ClO_4)_3$ (*23*)	4.6	1.277	−0.376	0.06
$Lu(ClO_4)_3$ (*23*)	4.6	0.785	0.613	0.09

[a] Numbers in parentheses indicate the reference source of data.

System of the Pitzer Equations

Details of the Pitzer equations for ϕ_V are given elsewhere (*5*). We only summarize them for immediate use. The Pitzer equations for ϕ_V as a function of molality m of an electrolyte of the type $M_{\nu_M}X_{\nu_X}$ are written as

$$\phi_V = \phi_V{}^0 + \nu|Z_M Z_X|(A_V/2b)\ln(1 + bI^{1/2}) + 2\nu_M\nu_X RT[mB_{MX}{}^V + m^2(\nu_M\nu_X)^{1/2}C_{MX}{}^V] \quad (1)$$

where

$$B_{MX}{}^V = (\partial\beta^{(0)}/\partial P)_T + (\partial\beta^{(1)}/\partial P)_T(2/\alpha^2 I) \times [1 - (1 + I^{1/2})\exp(-\alpha I^{1/2})] \quad (2)$$

and

$$C_{MX}{}^V = (\partial C^{\phi}/\partial P)_T/2 \quad (3)$$

$\phi_V{}^0$ is partial molal volume of an electrolyte at infinite dilution. A_V is the Pitzer–Debye–Hückel slope, values of which are taken from the tabulation and methods of Bradley and Pitzer (*9*), Rogers and Pitzer (*10*), and Ananthaswamy and Atkinson (*11*). R is the gas constant with a value of 83.1441 cm^3 mol^{-1} bar^{-1} K^{-1} and T is in kelvin. The stoichiometry of an electrolyte is

$$\nu = \nu_M + \nu_X$$

Z_M and Z_X are the ionic charges. I, the ionic strength on molal basis, is given by

$$I = \tfrac{1}{2}\sum_i m_i Z_i{}^2$$

α and b are 2.0 and 1.2 kg$^{1/2}$ mol$^{1/2}$, respectively.

The Pitzer coefficients $(\partial\beta^{(0)}/\partial P)_T$, $(\partial\beta^{(1)}/\partial P)_T$, and $(\partial C^{\phi}/\partial P)_T$ can be treated with temperature- and pressure-dependent equations of the form

$$Y = A + BT + CT^2 \quad (4)$$

where Y represents any of these Pitzer coefficients. A, B, and C are pressure-dependent terms as

$$A = a_0 + a_1 P + a_2 P^2 \quad (5)$$

with analogous terms for B and C.

Literature data on the solution density (d) may be converted to ϕ_v by using the relation

$$\phi_v = \frac{1000(d_0 - d)}{mdd_0} + \frac{M}{d} \quad (6)$$

where d_0 is the density of pure water, taken from Haar et al.

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Table II. Temperature Dependence of Pitzer Coefficients at 1 bar Pressure As Calculated by Eq 4 ($F = (\partial\beta^{(0)}/\partial P)_T$, $S = (\partial C^{\phi}/\partial P)_T$)

electrolyte, temp range, °C, m_{max}, mol kg^{-1}	term	10^4A	10^6B	10^9C	$\sigma(\phi_v)$, cm^3 mol^{-1}
HCl (*14*, *27*, *28*),[d] 0–75, 3.0	F	1.20	−0.073	1.61	0.003
	S	0.373	−0.227	0.318	
HBr (*14*), 25–75, 3.0	F	0.011	0.004	−0.130	0.004
	S	0.026	−0.026	0.089	
HI (*14*), 25–75, 3.0	F	−0.937	0.238	−0.365	0.008
	S	0.625	−0.328	0.545	
$HClO_4$ (*14*), 25–75, 3.0	F	61.84	−39.68	63.40	0.005
	S	1.59	−1.02	1.68	
NaBr (*26*, *31*), 15–55, 8.0	F	5.11	−3.04	4.55	0.01
	S	−0.535	0.316	−0.469	
NaOH (*28*, *34*), 0–70, 25.0	F	21.19	−13.99	23.38	0.04
	S	−0.070	0.041	−0.062	
$NaNO_3$ (*31*), 15–55, 8.0	F	9.50	−5.65	8.45	0.08
	S	−1.23	0.747	−1.13	
Na_2SO_4 (*36*), 0–50, 1.5	F	63.36	−39.73	62.77	0.01
	S	−41.65	26.71	−42.91	
KCl (*25*, *29*), 5,45, 4.5	S	0.083	−0.066	0.114	
KBr (*31*), 15–55, 4.0	F	7.34	−4.42	6.69	0.01
	S	−1.72	1.05	−1.60	
KNO_2 (*24*), 20–80, 35.0	F	1.66	−0.927	1.31	0.09
	S	−0.065	0.037	−0.053	
KNO_3 (*31*), 15–55, 4.0	F	5.11	−3.04	4.56	0.03
	S	−1.91	1.17	−1.79	
KOH (*35*), 60–100, 26.0	F	0.315	0.346	−1.10	0.04
	S	0.322	−0.215	0.344	
$CaCl_2$ (*4*, *5*, *19*, *25*, *26*, *31*), 5–55, 7.4	F	7.45	−4.58	7.108	0.10
	S	−0.38	0.010	0.014	
$CaCl_2$[a,b] (*32*), 75–200, 6.4	F	77.24	−119.8	−1.22	0.21
	S	2.53	−20.39	5.45	
$MgCl_2$ (*25*, *26*, *31*, *36*), 0–55, 5.2	F	7.19	−4.29	6.49	0.11
	S	−1.14	0.692	−1.05	
$SrCl_2$ (*31*), 15–55, 2.5	S	−1.20	0.878	−1.33	
$SrCl_2$[a,c] (*33*), 75–200, 2.7	F	80.56	−63.03	164.5	0.09
	S	26.07	−20.27	50.8	
$BaCl_2$ (*31*), 15–55, 1.5	F	18.72	−11.32	16.87	0.18
	S	−10.87	6.80	−10.35	
$MgSO_4$ (*36*), 0–50, 2.2	F	36.52	−21.65	32.38	0.05
	S	40.46	−32.07	62.57	
$Cd(NO_3)_2$ (*24*, *31*), 15–85, 13.0	F	0.080	−4.82	7.23	0.12
	S	−1.06	0.661	−1.10	
$Co(NO_3)_2$ (*24*), 25–80, 8.3	F	0.706	−0.254	0.079	0.10
	S	−0.025	0.006	0.015	
$SmCl_3$ (*41*), 0–80, 3.5	F	5.44	−3.06	4.32	0.04
	S	−0.575	0.320	−0.427	
$GdCl_3$ (*41*), 0–80, 3.5	F	8.08	−4.82	7.17	0.05
	S	−1.80	1.12	−1.71	
$DyCl_3$ (*41*), 0–80, 3.5	F	5.67	−3.18	4.44	0.04
	S	−0.596	0.329	−0.435	
$ErCl_3$ (*41*), 0–80, 3.5	F	5.80	−3.24	4.51	0.05
	S	−0.618	0.340	−0.449	
$YbCl_3$ (*41*), 0–80, 3.5	F	3.07	−1.60	2.08	0.04
	S	−0.029	0.013	−0.013	
$LaCl_3$ (*31*, *42*), 15–80, 3.5	F	4.14	−2.21	2.92	0.04
	S	−0.426	0.220	−0.261	
$PrCl_3$ (*42*), 0–80, 3.9	F	4.08	−2.17	2.86	0.04
	S	−0.359	0.182	−0.203	
$NdCl_3$ (*42*), 0–80, 3.9	F	4.21	−2.25	3.01	0.04
	S	−0.434	0.226	−0.276	
Bu_4PBr (*43*), 5–55, 10.5	F	−4.22	2.46	−3.65	0.28
	S	1.35	−0.775	1.13	
Bu_3PhPCl (*43*), 5–55, 5.3	F	−17.05	10.48	−16.42	0.32
	S	9.42	−5.80	9.0	
Bu_2Ph_2PCl (*43*), 5–55, 4.7	F	62.64	−43.64	75.34	0.17
	S	2.40	−1.42	2.21	
$BuPh_3PCl$ (*43*), 5–55, 1.8	F	−5.94	4.18	−8.10	0.02
	S	3.84	−2.65	4.89	
Ph_4PCl (*43*), 5–55, 1.1	F	−70.96	47.78	−81.14	0.04
	S	4.44	−2.89	5.67	
Bu_4PBr (*44*), 15–35, 0.14	F	−40.20	12.73		0.02
	S	267.3	−88.95		

[a] Data fitted were at a constant pressure of 20.27 bar. [b] F has additional term in eq 4 aq $D = -0.142 \times 10^{-9}$. [c] Additional term in eq 4 for F, $D = 0.183 \times 10^{-1}$, and for S, $D = -0.478 \times 10^{-11}$. [d] Numbers in parentheses indicate the reference source of data.

(*12*). *M* is the molecular weight of an electrolyte.

Results and Discussion

In literature, there are numerous experimental data on some solutions. In such cases, selection of data was made on the basis of the experimental accuracy quoted in original papers and data with poor accuracy and less extensive concentrations were discarded.

Least-squares program was used to generate the Pitzer coefficients from eq 1 to 3. ϕ_V^0 needed in eq 1 was taken from the available compilations (*13*). In those cases where the desired ϕ_V^0 values were not available in ref *13*, such values quoted in the original papers were used. Initially we fitted ϕ_V vs. m data with and without the $(\partial\beta^{(1)}/\partial P)_T$ term. But since the use of this term did not significantly improve the overall fit of most of the electrolytes, we opted to drop this term for all the electrolytes. Rogers and Pitzer (*10*) also found that in preliminary isothermal and isobaric calculations, this term could not be determined from volumetric data.

For the convenience of the readers, we have divided the evaluated Pitzer coefficients into three tables. Table I lists the Pitzer coefficients of many electrolytes together with the standard deviations of fits σ at 25 °C and 1 bar pressure. In Table II are given the temperature dependence of the Pitzer coefficients as evaluated by using eq 4 for those electrolytes whose densities were known at more than three temperatures and at 1 bar pressure. For electrolyte solutions whose densities were known at varying temperatures and pressures, Pitzer

Table III. (A) Pressure Dependence and (B) Temperature and Pressure Dependence of Pitzer Coefficients at 25 °C[a]

A

electrolyte, press. range, bar, m_{max}, mol kg^{-1}	term	10^5a_0	10^9a_1	$10^{10}a_2$	$\sigma(\phi_v)$, cm^3 mol^{-1}
LiCl (*26*, *30*),[b] 1–400, 5.0	F	0.57	−7.36	−0.049	0.02
	S	−0.02	0.665	−0.006	
KCl (*26*), 1–400, 3.0	F	1.65	−3.02	0.447	0.02
	S	−0.310	−4.80	0.345	
NaBr (*26*), 1–400, 5.0	F	1.33	−3.67	−0.195	0.07
	S	0.185	−5.77	0.18	
$CaCl_2$ (*26*), 1–400, 5.0	F	1.48	−23.77	0.205	0.09
	S	−0.09	4.49	−0.538	
$MgCl_2$ (*26*), 1–400, 5.0	F	1.16	5.41	−0.541	0.08
	S	−0.050	−7.51	0.246	

B

	Na_2CO_3		K_2CO_3		Na_2SO_4	
term	*F*	*S*	*F*	*S*	*F*	*S*
10^5a_0	23.1	−4.04	18.2	−3.2	24.3	−1.34
10^9a_1	14.2	−3.25	14.2	16.2	13.3	0.85
$10^{10}a_2$	10.3	−2.85	16.3	0.85	42.2	−0.65
10^6b_0	6.4	0.58	−7.36	11.50	40.0	−0.20
10^7b_1	0.9	0.39	2.85	9.54	13.01	−0.10
10^9b_2	0.18	−0.02	3.89	2.89	17.80	−0.36
10^7c_0	0.82	−0.29	2.83	1.85	0.18	−0.85
10^8c_1	0.45	23.8	1.80	2.80	0.05	0.87
$10{\cdot}c_2$	0.90	24.2	0.08	1.00	0.02	−0.85
$\sigma(\phi_v)$	0.12		0.14		0.21	
m_{max}	1.7		2.5		1.5	
temp. range, °C	0–90		20–90		20–90	
press. range, bar	1–300		1–300		1–300	
ref	*37*, *38*		*37*		*39*, *40*	

[a] $F = (\partial\beta^{(0)}/\partial P)_T$, $S = (\partial C/\partial P)_T$. [b] Numbers in parentheses indicate reference source of data.

coefficients were treated with both temperature- and pressure-dependent equations (4) and (5). These are reported in Table III along with the standard deviation of the fits. There are very few electrolytes which are common in Tables II and III, but since the experimental conditions were not identical, we chose to give them separately.

These tables do not include the results on aqueous NaCl as they are reported in extensive calculations by Rogers and Pitzer (*10*). Herrington et al. (*14*) have recently reported densities of aqueous HCl, HBr, HI, and $HClO_4$ with a precision of 10 × 10^{-6} g cm^{-3}, and analyzed the ϕ_v obtained therefrom with the full form of the Pitzer equations. We have refitted their data without the $(\partial\beta^{(1)}/\partial P)_T$ term. Our fits show equally good standard deviations, as is apparent from Table II. Chen et al. (15) have reported ϕ_v of aqueous NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ at 0, 25, and 50 °C and up to 1000 bar pressure. Unfortunately, we could not use their data for the high-pressure fits as the number of the experimental data points were very less and also the concentration range was very low.

An examination of the tables shows that ϕ_v of the most of the electrolytes can accurately be fitted with the Pitzer equations with an average standard deviation of 0.04 cm^3 mol^{-1}. The fits were random throughout. There are however exceptions for a few systems, where association or some other structural changes are well-known, and the standard deviations in such cases are relatively higher. Nitrates and carbonates are examples of this kind. Association in these solutions are supported by the recent Raman spectroscopy (*16*, *17*).

We plot in Figure 1 the difference (Δ) in the experimental and calculated ϕ_v against m for four different electrolytes under different conditions. Except aqueous $ZnCl_2$, the fits are random throughout. We observe a systematic $\Delta\phi_v$ with high positive and negative values as a function of m. This is not a surprising situation as complexation in aqueous $ZnCl_2$ is known to occur. Similarly, in aqueous $CdCl_2$ and $Cd(NO_3)_2$ (not shown in the figure), such $\Delta\phi_v$ are observed. $CdCl_2$ is the most associated electrolyte among the transition-metal chlorides. Therefore, the standard deviation and the Pitzer coefficients reported for the aqueous $ZnCl_2$, $CdCl_2$, and $Cd(NO_3)_2$ may not have any physical significance. We also observe that inclusion of $(\partial\beta^{(1)}/\partial P)_T$ term for these solutions improves the fits only up to the concentration of 0.5 mol kg^{-1} but then the fits at higher concentration get worse. We feel that more accurate forms of the Pitzer equations are needed in future where the complexation should be explicitly considered. Our attempts in this direction are in progress.

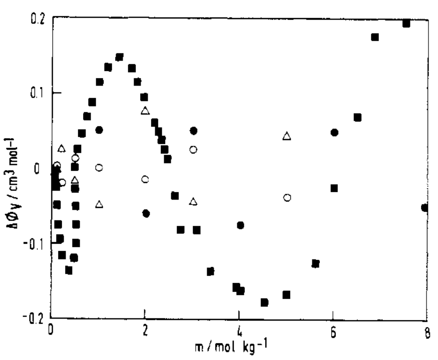

Figure 1. $\Delta\phi_v$ (experimental ϕ_v − calculated ϕ_v) vs. m. ○, $CaCl_2$, 25 °C, 171.3 bar, ref *26*. ■, $ZnCl_2$, 25 °C, 1 bar, ref *20*. ●, $NaNO_3$, 55 °C, 1 bar, ref *31*. Δ, NaBr, 25 °C, 103.8 bar, ref *26*.

In summary, we have successfully attempted to test a more general form of the Pitzer equations. A survey of the results quoted in the tables shows that these equations emerge as very powerful tool for predicting ϕ_v of the aqueous single electrolyte solutions under varying conditions of the temperature, pressure and concentration. The Pitzer coefficients obtained above may be used to estimate the mixture densities and the apparent molal volumes by the equations and methods outlined earlier (*5*).

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Volume Properties of Aqueous Electrolytes. 2. Application of the Pitzer Model in Estimating Apparent Molal Compressibility and Expansibility

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The Pitzer model of virial coefficients is applied to the apparent molal compressibility and expansibility of aqueous single electrolyte solutions. Pitzer coefficients for several electrolyte solutions are given in the form of temperature-dependent equations. Also, these coefficients are applied for estimating the above properties in aqueous mixed electrolytes. The Pitzer equations can predict these properties with excellent accuracy.

Introduction

The Pitzer equations are proving to be very useful in estimating various thermodynamic properties of aqueous single and mixed electrolytes (*1*, *2*). In our attempts to understand better their utility in predicting volume properties of electrolytic solutions, we (*3*) recently successfully fitted the apparent molal volumes of several single electrolytes and presented the Pitzer coefficients. We now apply these equations for estimating apparent molal compressibility ϕ_K and expansibility ϕ_E of single electrolytes. The Pitzer coefficients obtained from the single-electrolyte analysis are used for calculating these properties in mixtures.

Pitzer Equations

The details of the Pitzer equations are given elsewhere (*4*). For immediate use, the system of Pitzer equations is given below. Since the equations used for ϕ_K and ϕ_E are analogous, we give them for general property ϕ. Apparent molal property of a single electrolyte $M_{\nu_M}X_{\nu_X}$ as a function of concentration m (mol kg^{-1}) is

$$\phi = \phi^0 + \nu|Z_M Z_X|(A/2b)\ln(1 + bI^{1/2}) + 2\nu_M\nu_X RT[mB_{MX} + m^2(\nu_M\nu_X)^{1/2}C_{MX}] \quad (1)$$

where

$$B_{MX} = \beta^{(0)}_{MX} + 2\beta^{(1)}_{MX}/\alpha^2 I[1 - (1 + \alpha I^{1/2})e^{-\alpha I^{1/2}}] \quad (2)$$

$$C_{MX} = C_{MX}{}^{\phi}/2 \quad (3)$$

Note that for ϕ_K, terms $\beta^{(0)}_{MX}$ and $\beta^{(1)}_{MX}$ are $(\partial^2\beta/\partial P^2)$ and $(\partial^2\beta/\partial P^2)$, respectively. For ϕ_E, they are $(\partial^2\beta^{(0)}/\partial P\partial T)$ and $(\partial^2\beta^{(1)}/\partial P\partial T)$, respectively. Similarly, in eq 3, $(\partial^2 C^{\phi}/\partial P^2)_T$ and $(\partial^2 C^{\phi}/\partial P\partial T)$ are for ϕ_K and ϕ_E, respectively. Terms $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and C^{ϕ}_{MX} are the Pitzer coefficients. A, the Pitzer–Debye–Hückel slope, can be taken from elsewhere (*5–7*). ϕ^0, apparent molal compressibility or expansibility at infinite dilution, is equal to the partial molal compressibility or expansibility at infinite dilution.

Any of the Pitzer coefficients may be fitted with the temperature-dependent equation of the form

$$Y = A + BT + CT^2 \quad (4)$$

where A, B, and C are the coefficients.

Apparent molal property of an ion in mixture, ϕ_i, is given by

$$\phi_i = \phi_i{}^0 + (Z_i A/2b)\ln(1 + bI^{1/2}) + RT\sum_i B_{iJ}m_J + (RT/2|Z_i|^{1/2})\sum_i C_{iJ}m_J{}^2|Z_J|^{1/2} + RT\sum_k \theta_{ik}m_k \quad (5)$$

in eq 5, the last term on the right-hand side expresses the mixing term recognizing explicitly the interactions among like-charged ions. θ_{ik} is the difference parameter and can be evaluated from the experimental ϕ and ϕ obtained from eq 5 minus last term. One notes that last term has the sum over k ions with the same charge ions and over i with the opposite charge ions. The equation for calculating θ_{ik} is

$$\theta_{ik} = \frac{\Delta\phi^*(m_1 + m_2)}{RTm_1m_2(\nu_i + \nu_k)} \quad (6)$$

where m_1 and m_2 are molalities of the electrolytes whose cations are under consideration for interactions and ν_i and ν_k are the moles of i and k in their respective electrolytes.

The calculated ϕ_i is converted to ϕ^* by using the relation

$$\phi^* = \frac{\sum_J m_J\phi_J}{\sum_J m_J} \quad (7)$$

where $\phi_J = \sum_i \nu_i\phi_i$.

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