Correlation and Prediction of Thermodynamic Properties of Nonaqueous Electrolytes by the Modified TCPC Model

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In this work, the modified three-characteristic-parameter correlation model was introduced to correlate and predict the thermodynamic properties, such as the mean activity coefficient, the osmotic coefficient, and the solvent activity, of different kinds of nonaqueous electrolyte solutions. Two sets of parameters, (*b*, *S*) and (*b*, *S*, *n*), for 46 single salts in methanol, ethanol, and 2-propanol, etc., were regressed from literature data at 298.15 K. Results of standard deviations showed the good applicability of our model. The calculated results of the mean activity coefficient by our model and the Pitzer model have been compared with each other with good agreement. Smoothed experimental data of osmotic coefficients and solvent activities were calculated with the present model with three or two parameters, and the one with three parameters showed a better performance. We also extended this model for some nonaqueous systems at elevated temperatures, and we also found good consistency between the results calculated from our model and experimental data. Moreover, we further developed this model for calculating those in the mixed-solvent electrolyte systems. The results showed our modified model could adequately describe these complicated electrolyte solutions.

Introduction

The design and operation of industrial processes involving electrolyte solutions are of essential need for thermodynamic properties, such as the mean activity coefficient, osmotic coefficient, and solvent activity, to represent the nonideality of the mixtures. In the past decades, various models have been developed to solve these problems, for instance, the Pitzer equations,[1–3] the Bromley model,[4–6] NRTL models,[7,8] and MSA-based models,[9,10] etc. Another noticeable model is the three-characteristic-parameter correlation (TCPC) model proposed by Lin et al.[11] for prediction of thermodynamic data in some strong electrolytes. This model introduced the PDH (Pitzer−Debye–Huckel) term in consideration of the long-range interaction between ions and the solvation effect to represent the short-range ion–molecule interaction. All three parameters have definite physical significance. These TCPC-based models are showing up as a very powerful tool, and the research based on it has been widely extended to the calculation of vapor pressure,[12] vapor–liquid equilibrium[13–15] of electrolyte solutions, medical chemistry,[16] biology and biochemistry,[17,18] etc.

In our previous work,[19] we have modified and extended this model for the correlation and prediction of many single salts in aqueous solutions at 298.15 K covering a wide range of concentrations (usually up to saturation). However, in contrast to aqueous systems, correlation of experimental data of nonaqueous electrolyte systems is scarce. To the knowledge of the authors, no systematic study about nonaqueous electrolyte solutions has been carried out using this model. Thus, as a continuation, the present work extended the modified model for the correlation and prediction of thermodynamic properties of different kinds of nonaqueous solutions at $T = 298.15$ K or other temperatures. Moreover, we also developed it to describe the complicated mixed-solvent electrolyte systems, which are often encountered in practical applications.

Table 1. Physical Properties of the Pure Solvents at 298.15 K

solvent	methanol	ethanol	2-proponal	*N*-methylformamide	acetonitrile
D	32.63	24.34	19.39	182.4	35.95
ρ	786.36	784.95	780.98	998.6	776.75
refs	20	21	21	22	21

General Equations. In our previous work,[19] we have modified the TCPC model based on the equations proposed by Lin et al.[11] The general equations for calculating the mean activity coefficient, osmotic coefficient, and the solvent activity for single electrolyte solutions can be written as follows

$$\ln \gamma\pm = -|z_+z_-|A_\varphi\left[\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b}\ln(1+bI^{1/2})\right] + \frac{S}{T}\cdot\frac{I^{2n}}{v_+ + v_-} \quad (1)$$

$$\varphi = 1 - |z_+z_-|A_\varphi\frac{I^{1/2}}{1+bI^{1/2}} + \frac{S}{T(v_+ + v_-)}\frac{2n}{2n+1}I^{2n} \quad (2)$$

$$\ln a_s = -(vmM_s/1000)\cdot\varphi \quad (3)$$

$$A_\varphi = \frac{1}{3}(2\pi L d_s)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2} \quad (4)$$

In the above equations, A_φ is the Debye–Huckel constant with a value of 0.392 $kg^{1/2}\cdot mol^{-1/2}$ at 298.15 K and D is the static dielectric constant of the solvent at temperature T. L is Avogadro's number; d_s is the density of solvent; k is Boltzmann's constant; and e is the electronic charge. z_+ and z_- are the charge numbers of the cation and anion, respectively, $I = 1/2\sum_i m_i z_i^2$ is the ionic strength; and m is the molality ($mol\cdot kg^{-1}$). v_+ and v_- are the stoichiometric coefficients of the cation and anion, respectively. $v = v_+ + v_-$, and M_s is the molecular weight of the solvent ($g\cdot mol^{-1}$).

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Table 2. Calculated Parameters for Nonaqueous Electrolyte Solutions at $T = 298.15$ K

electrolytes	mmax / mol·kg^{-1}	b	S ($n = 0.645$)	$10^2\,\delta$	b_0	S_0	n	$10^2\,\delta$	refs
				Methanol					
Am_4NBr	1.4000	3.3689	−10.7679	4.72	5.1571	−194.8582	0.19950	4.24	23
Bu_4NBr	1.6000	3.5995	−0.4847	4.95	5.3380	−169.1235	0.19150	4.63	23
Bu_4NClO_4	2.4000	0.7731	−16.1520	8.86	4.3052	−840.0172	0.18300	5.00	23
Bu_4NI	0.9000	1.8901	−157.7802	4.07	7.4185	−697.7628	0.21045	2.29	23
CsI	0.1000	3.7511	−1246.917	0.37	25.1079	−946.5040	0.23070	0.17	23
Et_4NBr	1.8000	4.7848	−89.6075	9.31	159.0368	−754.7582	0.16390	6.30	23
KBr	0.1000	4.4235	−626.8289	0.27	14.7605	−587.5910	0.22305	0.23	23
KI	0.7000	4.6970	−0.1740	1.79	5.8683	−90.2423	0.18565	1.73	23
NaCl	0.2000	5.0008	−186.0346	0.55	9.2452	−295.2606	0.22025	0.43	23
$NaClO_4$	1.2000	4.3829	71.9431	1.85	4.5797	55.0547	1.31915	1.22	23
NaI	0.7000	4.8428	167.2052	1.59	5.0626	206.9776	1.03010	1.35	23
RbI	0.4000	4.0895	−204.6471	1.45	8.8244	−395.7089	0.22555	0.96	23
NaBr	1.0000	4.9272	135.5361	1.64	5.2125	129.1934	1.1137	0.95	23
LiCl	4.4102	3.1135	198.0042	1.71	2.9755	219.1176	0.6179	1.52	24
$ZnCl_2$	6.2266	2.4927	13.3610	7.38	2.5859	0.0676	1.5327	5.00	25
$CaCl_2$	2.5916	4.8149	87.3584	3.68	5.0689	42.0765	0.80935	1.89	26
$LiClO_4$[a]	5.0585	6.5191	214.0429	2.66	7.3141	163.4196	0.71855	2.12	27
LiAc[a]	3.0102	4.1049	52.4216	1.50	4.6088	16.1277	1.09515	0.88	28
$LiNO_3$[a]	3.8049	5.2516	101.3416	2.32	4.0549	203.0365	0.46105	0.99	29
NaSCN[a]	3.4260	7.1129	117.6724	2.23	4.4505	265.0552	0.43230	0.53	30
TMGP[a]	7.6266	2.0555	−11.2521	7.69	16.1361	−214.9394	0.06630	5.46	31
$CoCl_2$[a]	2.0886	4.5133	8.1011	1.90	4.5980	0.1656	1.70915	1.45	32
$MnCl_2$[a]	4.5640	4.4136	30.1243	0.89	4.3152	41.3106	0.59195	0.48	32
$NiCl_2$[a]	1.3352	4.6829	43.0890	0.26	4.7694	29.9712	0.74455	0.18	32
				Ethanol					
LiBr	2.8135	5.0006	271.555	8.02	6.3721	107.9748	1.03835	1.13	33
LiCl	3.2979	3.7300	285.666	8.32	4.7243	119.9855	0.9595	2.11	33
NaI	1.8000	5.493	135.505	7.00	5.9665	53.7595	1.46605	4.65	21
$LiNO_3$	2.2155	5.3864	135.536	6.59	6.0385	37.0773	1.39265	3.77	34
$LiClO_4$[a]	1.4560	6.3666	170.7280	3.36	6.9536	97.7842	1.30295	2.11	27
$Ca(NO_3)_2$[a]	3.1852	5.4589	10.657	1.73	5.6193	0.5900	1.25020	1.24	35
$CaCl_2$[a]	2.3717	5.9025	33.3433	0.97	6.1241	12.0000	0.86635	0.57	35
$CoCl_2$[a]	2.9453	4.6343	21.9562	2.13	4.9373	0.6182	1.40915	0.74	32
$CuCl_2$[a]	3.4260	4.9571	10.9001	1.47	5.0729	0.5767	1.24040	0.75	36
$NiCl_2$[a]	1.2101	8.9982	186.823	2.06	10.1902	90.6512	0.88015	0.72	32
				2-Propanol					
LiBr	1.4924	2.4808	264.1535	0.66	2.4729	268.0328	0.63565	0.65	37
LiCl	1.4730	2.3681	239.1148	1.46	2.1433	350.0108	0.46685	0.82	37
$LiClO_4$	1.4884	2.8363	188.2963	2.71	2.9215	150.0250	0.87825	2.10	27
$LiNO_3$	1.8840	2.4858	129.9262	1.38	2.3040	220.0270	0.44465	0.95	37
NaI	1.2000	2.6188	287.3353	1.1	2.4581	349.1303	0.49705	0.53	21
				N-Methylformamide					
CsCl	0.0700	2.8238	−576.2044	0.14	92.8168	−205.774	0.27770	0.028	22
KCl	0.0700	1.5846	−1075.144	0.21	9.9463	−501.134	0.42845	0.14	22
NaBr	0.0800	3.3429	−332.3969	0.15	5.2495	−199.669	0.47995	0.11	22
LiCl	0.0900	−0.6105	−2058.375	0.46	23.2590	−1040.545	0.4254	0.058	22
NaCl	0.1000	−1.5114	−113.9985	1.28	55.3873	−204.194	0.22040	1.02	22
				Acetonitrile					
LiBr	0.8298	0.5725	−66.5016	6.37	7.6241	−970.288	0.3935	4.31	38
NaI	1.4000	3.2386	−56.0348	3.44	7.5426	−348.007	0.20295	2.35	21
average				2.93				1.76	

[a] Calculated from φ data: $\delta = [\sum_i (\varphi^{\text{exptl}} - \varphi^{\text{calcd}})^2/n_p]^{1/2}$.

In the above equations, (b, S, n) are the adjustable parameters of this modified model. Herein, b is treated as an adjustable parameter to represent the closest distance between the cation and anion. S is an electrolyte-specific parameter that describes the incorporate solvation effects of the cation and anion. n is the parameter which is related to the distance between the ion and solvent molecule. In the earlier model,[11] n was regarded as a constant, 0.645, in all cases to simplify the process of optimization. In that case, this model becomes the one with two parameters (b, S). In our study, the two sets of parameters (b, S) and (b, S, n) were both obtained for comparison with each other.

Evaluation of Parameters. The parameters b, S, and n could be evaluated by the multiple regression analysis. The objective function is given below, and the optimization was performed by the least-squares method by the application of the MATLAB software:

$$\delta = \left[\sum_i (\ln \gamma_{\pm}^{\text{exptl}} - \ln \gamma_{\pm}^{\text{calcd}})^2/n_p\right]^{1/2} \quad \text{or} \quad \delta = \left[\sum_i (\varphi^{\text{exptl}} - \varphi^{\text{calcd}})^2/n_p\right]^{1/2} \quad (5)$$

Here, δ is defined as the standard deviation (%); n_p is the number of experimental data points; and the subscripts exptl

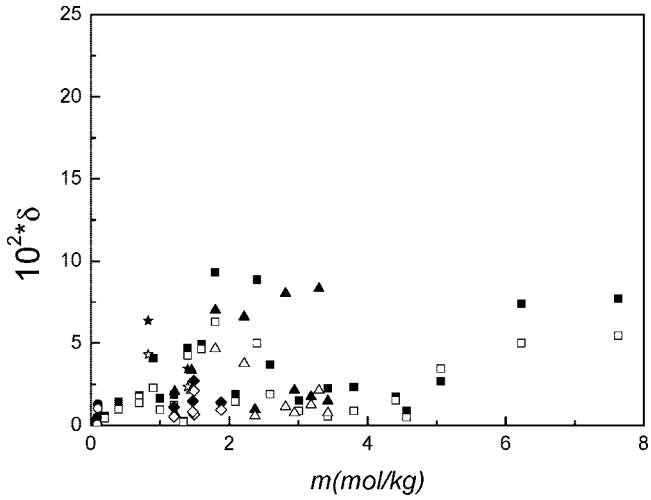

Figure 1. Standard deviations of different kinds of nonaqueous electrolyte solutions at 298.15 K. The solid and hollow symbols represent the calculated results by the present model with two parameters or three parameters, respectively. ■ and □, results in methanol; ▲ and Δ, results in ethanol; ♦ and ◊, results in 2-proponal; • and ○, results in *N*-methylformamide; and ★ and ☆, results in acetonitrile.

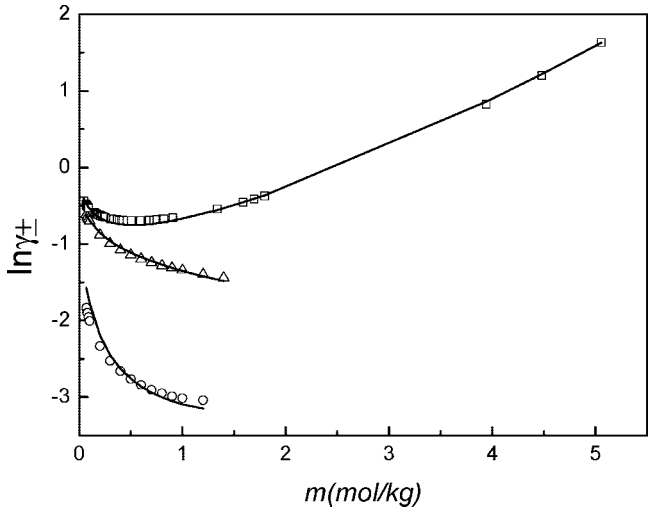

Figure 2. Calculated results of the mean activity coefficients of some nonaqueous electrolyte solutions. The solid lines and symbols are calculated from the present model with three parameters and the Pitzer model, respectively. □, $LiClO_4$ in methanol;[27] Δ, NaI in acetonitrile;[21] ○, NaI in 2-proponal.[21]

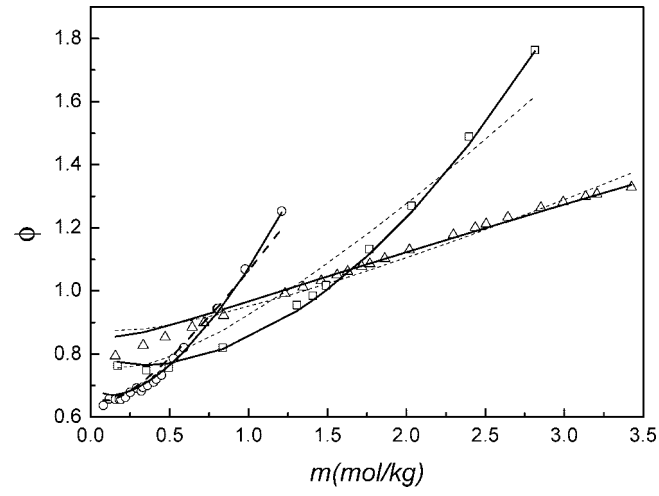

Figure 3. Calculated results of the osmotic coefficients of some nonaqueous electrolyte solutions. The solid lines and dotted lines are calculated from the present model with three parameters and two parameters, respectively. □, experimental data for LiBr in ethanol;[33] Δ, NaSCN in methanol;[30] ○, $NiCl_2$ in ethanol.[32]

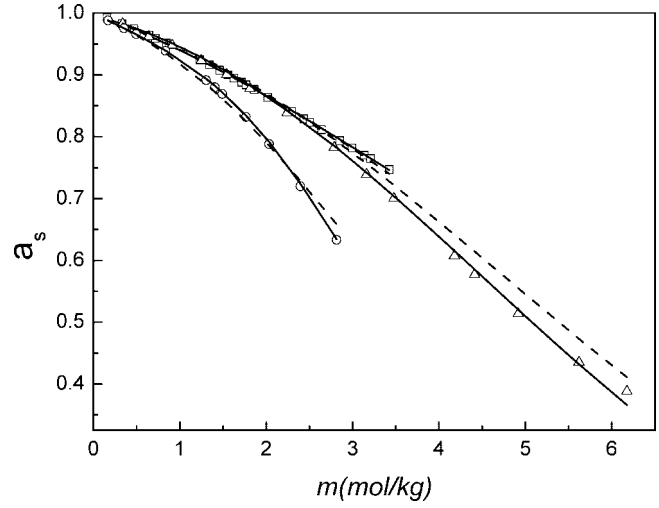

Figure 4. Calculated results of the solvent activities of some nonaqueous electrolyte solutions. The solid lines and dashed lines are calculated from the present model with three parameters and two parameters, respectively. □, experimental data for NaSCN in methanol;[30] Δ, LiCl in methanol; [24] ○, LiBr in ethanol.[33]

and calcd refer to the experimental and calculated data, respectively. Most of the parameters were obtained from the mean activity coefficients reported in the literature; a few sets of parameters were regressed from experimental osmotic coefficients. If experimental data for the same electrolyte solutions were found in different publications, we chose the latest one or the one covering a wider range of concentrations.

Nonaqueous Electrolyte Solutions at 298.15 K. According to eqs 1, 2, and 5, the adjustable parameters for every single nonaqueous electrolyte solution can be regressed from literature data. The dielectric constant and density of various pure solvents used in this section are listed in Table 1. The adjustable parameters for every single nonaqueous electrolyte solution are tabulated in Table 2. Results of standard deviations in this table show that our model with two or three parameters can be fitted to the experimental data very well for most of the studied systems, but the model with three parameters (*b*, *S*, *n*) (overall average 1.76 %) is better than the one with two parameters (*b*, *S*) (overall average 2.93 %), which indicates it is rational and beneficial to regard *n* as an adjustable parameter. Figure 1 shows the distribution of standard deviations calculated by our model with two or three parameters, respectively. One can find out that with an increase of molality the present model with two parameters shows a large discrepancy for some nonaqueous solutions, such as Bu_4NClO_4, TMGP in methanol and LiCl, and LiBr in ethanol, but the present model with three parameters can be fitted for all the systems fairly well across a wide range of concentrations. This phenomenon further proves that it is more important to treat *n* as an adjustable parameter, especially in the case of high ionic strength.

The set of parameters presented here can be used directly for the prediction of the mean activity coefficients, osmotic coefficients, and solvent activities. Figure 2 shows some results of calculating the mean activity coefficient. The calculated results based on the same experimental data by the Pitzer model, which are reported in the literature, are also drawn in, and one can see they are in good agreement.

Table 3. Calculated Parameters for Electrolytes in Nonaqueous Solvents at $T = 298.15$ K to 343.15 K

T	mmax	A_φ		S					
K	mol·kg^{-1}	kg$^{1/2}$·mol$^{-1/2}$	b	($n = 0.645$)	$10^2\ \delta$	b_0	S_0	n	$10^2\ \delta$
				LiCl in Methanol[24]					
298.15	4.4102	1.2943	3.1135	198.0042	1.71	2.9755	219.1176	0.6179	1.52
303.15	4.4102	1.31502	3.0851	200.2534	1.71	2.9357	224.0424	0.61505	1.47
308.15	4.4102	1.33639	3.0777	201.9588	1.76	2.9147	229.0048	0.6115	1.5
313.15	4.4102	1.35832	3.1208	202.8754	1.7	2.936	234.0373	0.60705	1.44
318.15	4.4102	1.38074	3.2062	202.8957	1.62	2.9913	238.9925	0.6018	1.40
323.15	4.4102	1.40356	3.175	204.7301	1.75	2.9531	243.9983	0.59865	1.46
				$CaCl_2$ in Methanol[26]					
298.15	2.59163	1.2943	4.7664	87.5683	3.64	5.0689	42.0765	0.80935	1.89
303.15	2.59163	1.31502	4.6481	89.0103	4.1	4.9125	39.009	0.83095	2.11
308.15	2.59163	1.33639	4.6017	92.2676	5.16	4.9029	34.0066	0.8716	2.67
313.15	2.59163	1.35832	4.4979	92.0455	5.88	4.8244	27.0196	0.9249	2.99
318.15	2.59163	1.38074	4.4269	92.306	6.51	4.9637	25.9747	0.93635	3.05
323.15	2.59163	1.40356	4.3524	92.7526	7.1	4.6893	20.3912	0.99375	3.66
				$ZnCl_2$ in Methanol[25]					
298.15	6.22669	1.2943	2.4927	13.3610	7.3800	2.5859	0.0676	1.5327	3.68
303.15	6.22669	1.31502	2.5178	13.1345	7.4	2.6076	0.0658	1.5346	3.89
308.15	6.22669	1.33639	2.5416	12.7461	7.27	2.6268	0.0633	1.53665	3.95
313.15	6.22669	1.35832	2.5655	12.2167	7.25	2.6467	0.0469	1.5815	4.03
318.15	6.22669	1.38074	2.5921	11.6348	7.22	2.6676	0.0401	1.60125	4.07
323.15	6.22669	1.40356	2.6182	11.1422	7.19	2.6899	0.0301	1.64395	4.14
				LiCl in Ethanol[33]					
298.15	3.29787	2.00527	3.73	285.6659	8.32	4.7243	119.9855	0.9595	2.11
303.15	3.29787	2.04555	3.8174	284.6763	8.15	4.7895	120.7895	0.95555	2.17
308.15	3.29787	2.0872	3.7477	287.426	7.43	4.612	130.0092	0.9305	2.06
313.15	3.29787	2.13077	3.818	287.0641	7.36	4.6588	130.9741	0.9276	1.97
318.15	3.29787	2.17629	3.9556	285.8748	7.41	4.825	126.4881	0.9397	1.92
323.15	3.29787	2.22424	4.1379	282.0808	7.42	5.0095	124.9313	0.94005	2.24
				LiBr in Ethanol[33]					
298.15	2.8135	2.00527	4.9461	271.9309	8	6.3097	107.998	1.0386	1.12
303.15	2.8135	2.04555	4.8083	275.5807	7.61	6.0482	113.0668	1.0228	1
308.15	2.8135	2.0872	4.8811	274.8289	7.54	6.0799	113.9109	1.0186	1.16
313.15	2.8135	2.13077	4.8324	276.8737	7.27	5.9577	117.0035	1.0094	1.16
318.15	2.8135	2.17629	4.9008	276.4585	7.17	5.9793	118.8693	1.0021	1.31
323.15	2.8135	2.22424	4.9559	277.1252	7.11	6.012	118.7312	1.0038	1.36
				$CaCl_2$ in Ethanol[26]					
298.15	2.12091	2.00527	4.7713	57.7545	0.69	5.0524	36.8267	0.73095	0.16
303.15	2.12091	2.04555	5.0475	53.3189	0.85	5.1069	35.1372	0.7455	0.15
308.15	2.12091	2.0872	5.1007	57.0304	1.05	5.1731	34.6202	0.76595	0.25
313.15	2.12091	2.13077	5.1763	57.2389	1.05	5.2498	34.2352	0.76945	0.19
318.15	2.12091	2.17629	5.3597	56.7267	1.24	5.306	34.1792	0.7776	0.22
323.15	2.12091	2.22424	5.2916	60.9769	1.32	5.3769	33.4048	0.79155	0.27
				$LiNO_3$ in Ethanol[34]					
298.15	2.21552	2.00527	5.3864	135.5363	6.59	6.0385	37.0773	1.39265	3.77
303.15	2.21552	2.04555	5.5002	129.8291	6.61	6.1396	31.9067	1.4618	3.78
308.15	2.21552	2.0872	5.582	125.0805	6.64	6.2035	27.6739	1.5291	3.88
313.15	2.21552	2.13077	5.8052	115.476	6.73	6.3976	22.3218	1.6224	4.01
318.15	2.21552	2.17629	5.7979	112.4775	6.59	6.3649	19.472	1.6939	3.87
323.15	2.21552	2.22424	5.9226	106.4655	6.62	6.4508	17.5604	1.7288	4.01
				LiBr in Acetonitrile[38]					
298.15	0.8298	1.11163	0.5467	−62.8134	6.38	5.2211	−857.0388	0.2044	4.31
303.15	0.8298	1.11627	0.4283	−41.8417	6.55	4.8264	−889.9921	0.2023	4.42
308.15	0.8298	1.12141	0.2628	25.2637	6.61	4.4996	−925.1259	0.1932	4.51
313.15	0.8298	1.12704	0.2046	61.7174	6.69	4.5819	−960.0271	0.18745	4.66
318.15	0.8298	1.13319	0.2185	56.2456	6.88	4.8062	−994.9274	0.18795	4.83
323.15	0.8298	1.13984	0.1983	62.2904	7.53	4.8456	−1030.618	0.1879	4.95
328.15	0.8298	1.14708	−0.0326	220.4216	7.63	4.2724	−1065.346	0.1722	5.67
333.15	0.8298	1.15485	−0.0315	217.0623	7.24	4.3385	−1099.681	0.1728	5.22
338.15	0.8298	1.16324	−0.1327	316.7922	7.57	4.1744	−1135.338	0.165	5.62
343.15	0.8298	1.17226	−0.3407	535.2842	7.17	3.4711	−1169.294	0.15235	5.02

It implies that our model is reliable to predict the mean activity coefficient. Figure 3 shows the experimental and calculated osmotic coefficients of some systems. From this figure, one can see that the model with three parameters performs better than the one with two parameters. Thus, one can use different sets of parameters in terms of different demands. Meanwhile, Figure 4 gives some predicted results of the solvent activities, and there is very good consistency between the calculated results and experimental ones. Also, the model with two parameters still shows a bit of a shortage

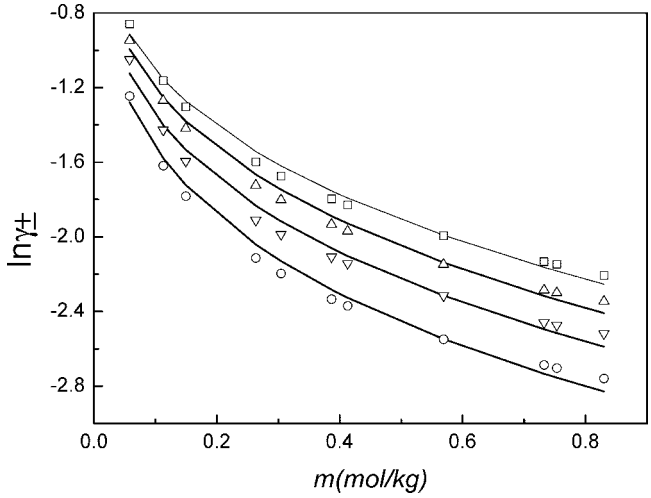

Figure 5. Calculated results of the mean activity coefficients of LiBr in acetonitrile. The solid lines are calculated from the present model with three parameters. Literature data:[38] □, 298.15 K; Δ, 308.15 K; ▽, 328.15 K; ○, 343.15 K.

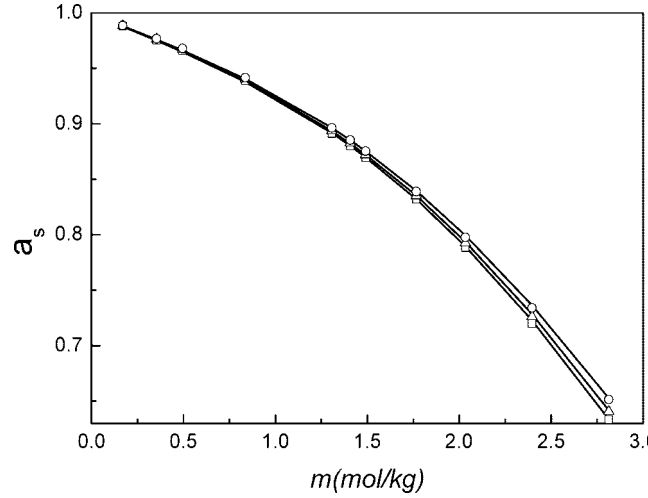

Figure 7. Calculated results of the solvent activity of LiBr in ethanol at elevated temperatures. The solid lines are calculated from the present model with three parameters. Literature data:[33] □, 298.15 K; Δ, 308.15 K; ○, 323.15 K.

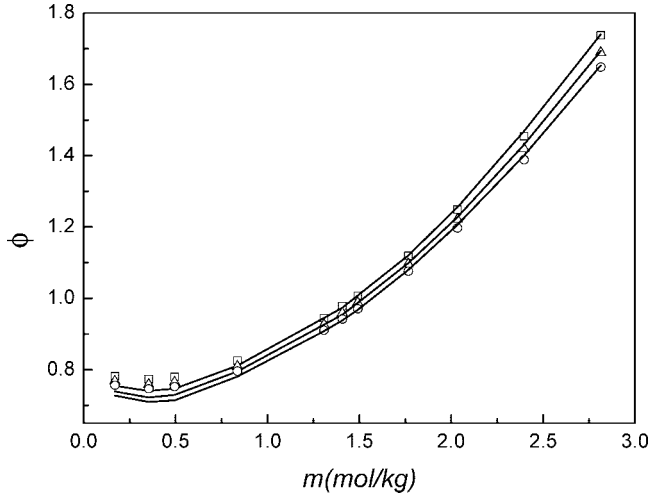

Figure 6. Calculated results of the osmotic coefficients of LiBr in ethanol at elevated temperatures. The solid lines are calculated from the present model with three parameters. Literature data:[33] □, 303.15 K; Δ, 313.15 K; ○, 323.15 K.

in the case of high concentration as it does in calculations of osmotic coefficients.

Nonaqueous Electrolyte Solutions at Elevated Temperatures. Considering the variations of dielectric constants and density of solvents, it is easy to extend the modified model for nonaqueous electrolyte solutions at elevated temperatures by using the new parameters regressed from the related experimental data. The adjustable parameters for some nonaqueous solutions are listed in Table 3. All these parameters were regressed from the experimental mean activity coefficient data reported in recent publications.

When the temperature range was not very wide (298.15 K to 343.15 K), it could be seen that if n was fixed at 0.645 the other two parameters (b, S) would represent a small fluctuation (seen in Table 3), such as LiCl, $CaCl_2$, and LiBr in ethanol. This indicates that the temperature dependence of our modified model is small. One of the possible reasons is that the temperature is regarded as one of the variables in our model; namely, the solvation parameter, S, is independent of temperature (seen in eqs 1 and 2). However, to accurately predict the thermodynamic properties, the set of parameters (b, S, n) at different temperatures was also listed in Table 3 (columns 7 to 9). It should be noted that the parameters show a significant change across a wide range of temperatures (for LiBr in acetonitrile[38]). In these cases, the newly obtained parameters are very essential for predicting those electrolyte properties.

Figures 5 to 7 show some calculated results by using these parameters. The calculated mean activity coefficients of LiBr in acetonitrile at different temperatures are presented in Figure 5, and the literature data were calculated from the Pitzer−Archer model. Good consistency between them proves that our model is available for predicting the mean activity coefficients at elevated temperatures. Similar results can also be observed in the calculations of osmotic coefficients and solvent activities for LiBr in ethanol.

Mixed Solvent Systems. As is well-known, mixed solvent electrolyte systems are very common in practical applications. Properties of electrolytes in mixed solvent systems are of particular interest in many environmental applications and industrial processes. For example, many petroleum problems would be more easily solved if a reliable and accurate model representative of phase equilibria of systems including, along with hydrocarbon elements, salts and water and even further additives such as alcohols was available.[59] Nevertheless, both the Pitzer model and TCPC model were initially designed to describe aqueous electrolyte solutions. In this work, the modified model is adapted for solutions with a mixed solvent of water and other kinds of solvents systematically.

The parameters for some electrolytes in mixed solvent systems with different mass fractions (w) of nonaqueous solvents are summarized in Table 4. Results of the standard deviation in this table show that the modified model is also suitable in the case of the mixed solvent systems. It should be noted that the results for 1–2 or 2–1 electrolytes are not as well as described as those of 1–1 electrolytes. One possible reason is that some electrolytes, for example, $SrCl_2$, will form several complex ions in water, which is not consistent with the assumption of the model. With the increase of concentration, this effect will bring about a large deviation. The consideration of the degree of association is promising to improve the predictive accuracy, which is the subject of future work.

Some examples for predicting the mean activity coefficients and osmotic coefficients by using this modified model are shown in Figures 8 to 10. These figures clearly prove the reliability of

Table 4. Calculated Parameters for Electrolytes in Mixed Solvent Systems at $T = 298.15$ K (w: Mass Fraction)

electrolytes	w	mmax / mol·kg^{-1}	b	S ($n = 0.645$)	10^2* δ	b	S	$2n$	10^2* δ	refs
KCl				Ethylene Glycol (w) + Water ($1-w$)						
	0.2	3.5	2.6517	−2.6715	5.41	9.5434	−179.5131	0.1693	4.06	39
	0.4	2	3.1331	−20.797	5.16	13.3726	−232.5467	0.17845	3.45	39
	0.6	1.5	3.4590	−37.6997	5.54	16.6014	−291.0959	0.1808	3.6	39
	0.8	0.7	3.9741	−190.067	5.48	33.3740	−480.9777	0.1947	2.94	39
KCl				Acetonitrile (w) + Water ($1-w$)						
	0.1	3.5	2.5480	−8.3701	5.31	10.7464	−195.1210	0.17625	3.57	39
	0.2	2.5	2.5678	−18.0131	5.66	13.3647	−240.3545	0.17855	3.71	39
	0.3	0.7	3.2269	−181.1125	4.3	33.2138	−384.9783	0.20755	2.03	39
	0.4	0.4	3.3328	−388.0826	3.82	37.4690	−488.6078	0.2265	1.64	39
KCl				1,4-Dioxane (w) + Water ($1-w$)						
	0.1	3	2.8073	−7.4948	5.27	10.9194	−198.6186	0.17335	3.74	39
	0.2	2.5	2.9953	−22.9692	6.01	15.5979	−285.0320	0.1765	3.8	39
	0.3	2	3.4890	−34.086	6.43	15.4220	−321.6418	0.1783	4.07	39
	0.4	1.5	3.6054	−64.3621	8.1	20.4542	−469.3038	0.1783	5.07	39
KCl				Ethanol (w) + Water ($1-w$)						
	0.2	2	2.8374	−28.466	3.65	10.3717	−225.4885	0.19605	2.25	40
	0.4	1	3.1602	−117.7926	3.72	24.9353	−422.3246	0.19895	1.81	40
HCl				*N*,*N*-Dimethylformamide (w) + Water ($1-w$)						
	0.1	4.1328	3.1906	111.4894	1.31	2.6946	138.9362	0.582	0.84	41
	0.2	4.31	3.1825	106.714	1.42	2.6558	137.0510	0.5758	0.83	41
	0.3	4.0188	3.1166	103.5372	1.15	2.8429	120.0290	0.60165	0.86	41
	0.4	4.2396	3.2786	98.5481	1.27	2.8450	124.9893	0.57795	0.89	41
NaCl				*N*,*N*-Dimethylformamide (w) + Water ($1-w$)						
	0.05	0.1	24.6903	−3.3335	0.96	92.5928	−39.5446	0.2467	0.37	42
	0.075	1.9035	12.5518	−0.0668	4.97	357.9511	−86.2089	0.1078	3.43	42
	0.1	0.1	24.3068	−3.5272	1.12	124.3186	−46.3199	0.23285	0.41	42
	0.15	1.9373	13.6052	−0.0862	5.26	365.0838	−81.2366	0.11605	3.32	42
	0.3	1.6671	12.3506	−0.1121	5.06	369.9018	−95.7058	0.1147	3.28	42
	0.45	1.308	14.3804	−0.2892	5.59	417.4210	−90.3826	0.1408	2.57	42
NaCl				Fructose (w) + Water ($1-w$)						
	0.1	3.5844	2.9667	41.7722	2.13	3.1591	29.0117	0.77545	2	43
	0.2	3.3396	3.0230	50.8272	2.42	3.2748	33.9575	0.79435	2.24	43
	0.3	3.4592	3.3312	52.9097	2.99	3.6075	35.0536	0.79565	2.78	43
	0.4	3.7493	3.2441	59.2705	2.95	3.4996	39.0077	0.7895	2.75	43
NaCl				Maltose (w) + Water ($1-w$)						
	0.1	3.0676	3.6334	37.3204	1.96	3.4715	45.0005	0.5849	1.95	44
	0.2	3.082	2.9956	32.8545	0.78	3.1592	22.7933	0.77965	0.65	44
	0.3	2.8636	3.3345	29.2953	1.51	3.5918	13.0797	0.99385	1.23	44
	0.4	2.797	4.2588	35.8917	0.79	4.4705	24.9083	0.7947	0.65	44
NaCl				Trehalose (w) + Water ($1-w$)						
	0.1	2.51	3.3758	32.8252	1.76	3.6388	17.4158	0.96955	1.51	44
	0.2	2.9998	2.6287	48.4441	1.47	2.8806	29.9570	0.83395	1.16	44
	0.3	3.0002	2.3211	55.8592	1.19	2.5354	36.7468	0.7987	0.94	44
	0.4	2.9373	2.8856	61.6978	2.14	3.1059	41.9917	0.8041	1.92	44
NaCl				Methanol (w) + Water ($1-w$) at 298.15 K						
	0.2	4	2.8443	31.3282	5.56	3.1046	7.0099	1.20005	4.98	45
	0.4	2	3.4165	13.7886	5.18	8.8258	−149.7113	0.16175	4.7	45
	0.6	1	3.1641	−37.8001	6.27	16.4795	−354.5917	0.1845	4.51	45
	0.8	0.5	3.4267	−258.6396	6.87	27.5428	−625.9335	0.1979	4.19	45
NaCl				Methanol (w) + Water ($1-w$) at 308.15 K						
	0.1	2.0651	3.5241	34.948	1.39	3.8452	15.1480	1.19745	0.98	46
	0.3	1.4833	3.4991	26.6096	2.19	3.6275	14.7079	1.62665	1.89	46
	0.5	0.9169	3.3209	−11.6232	2.36	8.0180	−184.7606	0.1811	2.02	46
	0.7	0.3507	3.5044	−234.506	3.57	19.8169	−470.2333	0.1991	2.5	46
	0.9	0.0751	2.4402	−1860.134	2.51	29.7723	−1013.396	0.231	1.66	46
NaCl				Methanol (w) + Water ($1-w$) at 318.15 K						
	0.1	2.0909	2.8583	46.9377	1.67	3.1155	24.9700	1.0527	1.28	46
	0.3	1.6602	2.9929	39.0536	2.07	3.1639	20.0316	1.3479	1.71	46
	0.5	0.8262	3.1361	6.0509	2.68	6.9883	−171.1892	0.1763	2.42	46
	0.7	0.2928	1.9577	67.9888	1.95	1.9688	498.4413	1.32055	1.84	46
	0.9	0.0747	0.9274	−1305.917	2.56	34.3501	−1100.059	0.2185	1.73	46
NaF				Glucose (w) + Water ($1-w$)						
	0.1	0.8467	2.3643	−28.9102	4.83	2.2985	−39.7490	1.4374	4.78	47
	0.2	0.701	2.4540	−30.973	4.43	4.5330	−116.9830	0.2275	4.33	47

Table 4. (continued)

electrolytes	w	mmax / mol·kg^{-1}	b	S (n = 0.645)	10^2* δ	b	S	$2n$	10^2* δ	refs
NaF					Glucose (w) + Water (1−w)					
	0.3	0.6075	3.5500	−79.5818	2	15.0888	−242.7554	0.20065	1.23	47
	0.4	0.4859	2.9887	−73.7342	0.87	6.4629	−177.7788	0.2316	0.62	47
NaF					Sucrose (w) + Water (1−w)					
	0.1	0.799	2.7418	−52.9804	0.89	8.7261	−191.4084	0.216	0.54	47
	0.2	0.7353	3.0733	−63.6933	1.54	10.9769	−214.3363	0.20905	0.96	47
	0.3	0.6086	3.2494	−59.2789	1.15	8.2827	−178.6587	0.21795	0.79	47
	0.4	0.4804	4.4444	−95.2982	0.73	31.2858	−276.9981	0.1809	0.38	47
NaF					Methanol (w) + Water (1−w)					
	0.1	0.5423	3.4605	−83.114	0.36	18.2873	−233.1482	0.2025	0.12	48
	0.2	0.3761	2.9739	−232.8636	1.66	35.4503	−373.0312	0.2102	0.81	48
	0.3	0.1854	1.7019	−343.157	1.27	31.6664	−470.6598	0.21035	0.77	48
	0.4	0.122	2.2807	−795.706	1.47	35.5650	−553.8078	0.22675	0.81	48
	0.5	0.0744	0.5569	−116.9402	2.32	0.5569	−116.9402	0.645	2.32	48
	0.6	0.03996	1.9057	−2895.435	1.03	47.0676	−881.9690	0.249	0.59	48
	0.7	0.02374	3.1558	−6707.311	0.88	56.7316	−1232.867	0.2708	0.55	48
	0.8	0.01305	4.8532	−19356.4	1.03	172.0239	−1975.374	0.27985	0.33	48
NaF					Ethanol (w) + Water (1−w)					
	0.1	0.5867	1.7984	−44.2176	1.36	5.6761	−190.3737	0.2303	1.03	48
	0.2	0.1849	3.0678	−538.9213	1.48	72.4732	−466.9323	0.2122	0.73	48
	0.3	0.1757	1.5397	−686.7878	2.43	91.5404	−657.8800	0.2145	1.42	48
	0.4	0.085	1.0587	−1299.348	1.93	106.0943	−818.4110	0.21725	1.08	48
	0.5	0.05346	1.6378	−2954.805	1.09	70.9390	−1088.711	0.2459	0.51	48
	0.6	0.02591	3.3317	−10762.2	1.37	133.9845	−1818.868	0.2739	0.5	48
NH_4Cl					1-Proponal (w) + Water (1−w)					
	0.1	3.8012	2.7712	−8.823	5.42	11.1738	−199.9271	0.16815	3.58	49
	0.2	3.4467	2.7021	−26.0966	6.54	27.3671	−337.4809	0.17235	3.29	49
	0.3	3.4482	2.6048	−41.4606	7.94	32.8055	−438.2103	0.18005	3.25	49
	0.4	1.62	2.8542	−144.1083	8.71	47.9281	−606.1554	0.19845	2.95	49
	0.5	2.3403	2.7297	−135.9157	11.7	57.4904	−776.2224	0.169	3.34	49
NH_4Cl					2-Proponal (w) + Water (1−w)					
	0.1	3.1743	2.6191	−13.2309	6.68	13.3918	−234.6573	0.16185	5.45	50
	0.2	3.0218	2.7534	−38.3034	6.55	28.1298	−357.1625	0.1818	2.8	50
	0.3	2.3195	2.7374	−71.449	7.9	37.6780	−469.5585	0.189	3.02	50
NH_4Cl					Ethanol (w) + Water (1−w)					
	0.1	3.6928	2.8401	−4.2322	5.08	7.9161	−148.3907	0.1678	3.76	51
	0.2	3.2922	2.8431	−12.7474	5.83	13.0755	−234.8283	0.1685	3.73	51
	0.3	3.0055	2.7850	−23.7185	6.77	13.5707	−289.5466	0.17855	3.94	51
	0.4	2.4213	2.7684	−53.9223	7.8	36.1643	−460.0858	0.17715	3.65	51
	0.5	1.9779	2.8910	−98.2876	8.87	39.0979	−568.6499	0.1874	3.45	51
RbCl					Acetonitrile (w) + Water (1−w)					
	0.25	1.5	2.8273	−50.0699	5.14	37.4214	−331.7996	0.1839	2.92	52
	0.5	1.5	4.9431	−80.8217	5.71	64.7904	−372.0469	0.18865	3.01	52
RbCl					Methanol (w) + Water (1−w)					
	0.1	3.4008	1.4427	−39.0193	5.47	63.2879	−439.8088	0.1889	2	53
	0.2	2.5849	1.2742	−132.5814	7.42	77.8732	−606.8831	0.2385	0.63	53
	0.3	2.7985	0.5221	−121.6882	8.07	80.8295	−808.0725	0.23565	2.31	53
	0.4	1.872	0.1573	−234.1043	17.5	85.5665	−1094.225	0.2351	6.09	53
CsCl					Ethanol (w) + Water (1−w)					
	0.2	7	2.2876	−3.1086	6.1	4.8822	−140.3437	0.18	4.96	40
	0.4	4	2.5659	−22.222	6.29	33.8410	−434.0280	0.1631	3.76	40
	0.6	2	2.8279	−71.5605	7	36.1202	−611.8978	0.1761	3.77	40
	0.7	1	3.2892	−225.1714	6	59.9888	−810.7718	0.1877	2.42	40
CsCl					Acetonitrile (w) + Water (1−w)					
	0.25	1.5	2.5169	−60.8981	5.56	59.5700	−379.7290	0.1827	2.92	52
	0.5	1.5	0.3941	3.2644	7.55	63.0617	−546.6217	0.1825	3.84	52
CsCl					Methanol (w) + Water (1−w)					
	0.1	1.6631	2.9586	−54.2946	3.19	62.5299	−317.3860	0.1805	1.28	54
	0.2	0.4531	2.9734	−254.5504	2.64	79.8456	−420.7363	0.2047	0.95	54
	0.25	0.7	1.7592	−166.7646	3.73	48.1896	−490.9439	0.20395	1.83	55
	0.3	0.9437	3.5840	−198.8448	3.29	81.6965	−445.5364	0.21555	0.46	54
	0.4	0.8027	1.2890	−295.1649	5.75	95.0587	−722.5826	0.2217	1.61	54
	0.5	0.7	1.6689	−289.6736	4.97	102.7072	−722.9672	0.20925	1.88	55
	0.75	0.7	1.7577	−291.6834	6.53	101.6721	−895.9370	0.19515	3.12	55

Table 4. (continued)

electrolytes	w	mmax / mol·kg^{-1}	b	S ($n = 0.645$)	$10^2 * \delta$	b	S	$2n$	$10^2 * \delta$	refs
CsCl				Acetonitrile (w) + Water ($1-w$)						
	0.25	0.7	1.7297	−181.3244	3.72	49.3997	−498.2379	0.2068	1.72	55
	0.5	0.7	1.8972	−111.1014	4.64	42.1389	−541.9049	0.18395	3.03	55
	0.75	0.7	0.8925	−1506.738	9.86	28.9324	−1974.691	0.3253	0.35	55
CsCl				1,4-Dioxane (w) + Water ($1-w$)						
	0.25	0.7	1.8271	−116.2	3.5	26.4039	−405.6858	0.2007	2.05	55
	0.5	0.7	1.9236	−90.7334	5.11	22.4829	−530.8260	0.1865	3.61	55
	0.75	0.7	2.0250	13.037	8.88	8.9101	−595.5280	0.18035	7.61	55
CsBr				Methanol (w) + Water ($1-w$)						
	0.25	0.7	1.8500	−103.7465	3.59	42.5936	−431.9077	0.18875	2.2	55
	0.5	0.7	1.9336	−68.3777	4.42	12.5726	−392.3756	0.19575	3.19	55
	0.75	0.7	1.5447	−549.8478	7.19	89.1711	−112.0352	0.22935	1.9	55
CsBr				Acetonitrile (w) + Water ($1-w$)						
	0.25	0.7	1.8101	−128.9192	3.61	32.1256	−434.3790	0.2001	2.04	55
	0.5	0.7	1.8475	−136.407	4.67	28.0421	−535.8358	0.1953	2.87	55
	0.75	0.7	1.8067	−240.0419	6.49	86.1007	−854.3863	0.18905	3.51	55
CsBr				1,4-Dioxane (w) + Water ($1-w$)						
	0.25	0.7	1.7954	−134.7851	3.54	28.1150	−424.8872	0.2047	1.94	55
	0.5	0.7	1.9388	−72.3627	5.07	8.7930	−389.3061	0.20375	3.72	55
	0.75	0.7	2.0570	49.6713	8.75	7.2522	−497.2083	0.17785	7.81	55
CsI				Methanol (w) + Water						
	0.25	0.7	1.8828	−88.3787	3.55	42.7895	−418.6790	0.18455	2.3	55
	0.5	0.7	2.0933	55.1893	4.13	6.8779	−205.3827	0.1649	3.96	55
	0.75	0.7	5.7356	2287.481	1.56	5.7356	2287.4810	0.645	1.56	55
CsI				Acetonitrile (w) + Water ($1-w$)						
	0.25	0.7	2.0477	14.3872	3.24	7.8551	−196.4857	0.1782	2.85	55
	0.5	0.7	1.7833	−193.8332	4.82	59.6293	−628.3399	0.1962	2.52	55
	0.75	0.7	1.1855	−1058.697	8.58	87.1228	−1596.851	0.27605	0.3	55
CsI				1,4-Dioxane (w) + Water ($1-w$)						
	0.25	0.7	2.0781	30.9287	3.15	2.0820	220.8685	2.4043	2.77	55
	0.5	0.7	2.1772	137.261	4.58	2.4008	380.4863	1.8916	3.63	55
	0.75	0.7	2.2427	338.1521	8.09	2.5858	759.1462	1.73405	6.1	55
NaBr				Maltose (w) + Water ($1-w$)						
	0.1	2.117	3.2839	52.4608	1.91	3.6042	28.5512	1.01925	1.55	56
	0.2	2.1003	3.5383	59.4944	1.73	3.9060	36.1938	0.9443	1.3	56
	0.3	2.1005	3.6412	70.7718	1.88	4.0426	45.2700	0.90275	1.52	56
	0.4	2.0999	3.8460	82.5685	1.88	4.1700	60.0834	0.83055	1.63	56
Li_2SO_4				Methanol (w) + Water ($1-w$)						
	0.15	1.4	2.7823	−21.0336	10.0	8.6738	−508.0954	0.17765	7.26	57
	0.3	0.8	2.6818	−40.6083	14.4	10.8532	−695.8838	0.16735	13.2	57
Li_2SO_4				Acetonitrile (w) + Water ($1-w$)						
	0.1	1.4	2.6490	−21.27	9.92	8.3385	−490.2726	0.18	7.1	57
	0.2	0.5	2.6035	−161.129	8.78	28.8332	−961.4980	0.1913	4.76	57
$SrCl_2$				Methanol (w) + Water ($1-w$)						
	0.25	1.5	3.2468	68.7525	8.47	3.4911	17.8256	1.0962	7.7	58
	0.5	1.5	2.7927	102.138	12.8	3.0504	21.5133	1.1664	11.5	58
$SrCl_2$				Ethanol (w) + Water ($1-w$)						
	0.25	1.5	2.0210	91.2555	10.0	2.2216	27.1088	1.0435	9.12	58
	0.5	1.5	1.4152	181.4869	11.7	1.5777	101.7358	0.8237	11.1	58
$SrCl_2$				Acetonitrile (w) + Water ($1-w$)						
	0.2	1	2.9731	59.6809	8.51	3.1453	9.6728	1.5334	7.67	52
	0.4	1	2.4659	194.3199	12.6	2.8368	58.5582	1.19325	10.6	52
$BaCl_2$				Methanol (w) + Water ($1-w$)						
	0.15	1.5	4.7564	27.1871	7.82	4.9095	2.4052	1.5034	7.28	58
	0.3	1.5	6.9966	25.1772	9.81	7.1507	1.1754	1.75585	9.16	58
$BaCl_2$				Ethanol (w) + Water ($1-w$)						
	0.15	1.5	3.0557	51.6942	8.82	3.2501	8.3946	1.26385	8.07	58
	0.3	1.5	2.6812	101.586	12.4	2.9440	22.3303	1.15175	11.0	58
$BaCl_2$				Acetonitrile (w) + Water ($1-w$)						
	0.15	1	3.1902	25.925	7.58	3.2441	3.0026	1.79815	7.09	52
	0.3	1	2.9384	35.6569	9.56	3.0051	3.6554	1.84245	8.88	52

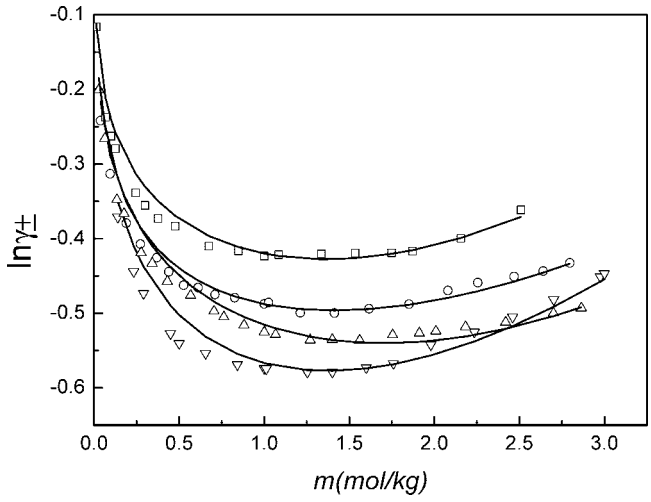

Figure 8. Calculated results of the mean activity coefficients of NaCl in fructose + water or maltose + water at $T = 298.15$ K. The solid lines are calculated from the present model with three parameters. Literature data[44] for different mass fractions (w) of nonaqueous solvent: □, trehalose ($w = 0.1$); ▽; trehalose ($w = 0.3$); Δ, maltose ($w = 0.3$); ○, maltose ($w = 0.4$).

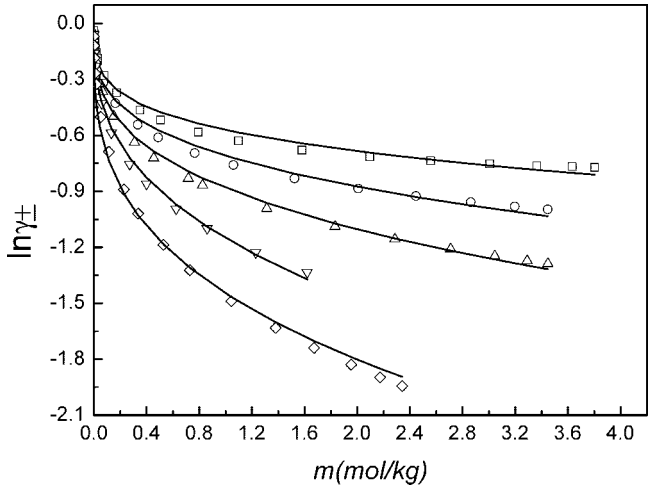

Figure 9. Calculated results of the mean activity coefficients of NH_4Cl in 1-proponal + water solutions at $T = 298.15$ K. The solid lines are calculated from the present model with three parameters. Literature data[49] for different mass fractions (w) of 1-proponal: □, $w = 0.1$; ○, $w = 0.2$; Δ, $w = 0.3$; ▽, $w = 0.4$; ◇, $w = 0.5$.

our model, whereas a large deviation was found in calculations for the low concentration range (seen in Figure 8), which indicates the modified model is more compatible to predict the thermodynamic properties of electrolytes in the high concentration region.

Conclusions

The modified TCPC model initially designed for aqueous solutions was introduced for predicting the thermodynamic properties of nonaqueous electrolyte solutions at 298.15 K or other temperatures. Two sets of parameters (b, S) and (b, S, n) were obtained from the regression of the literature data. The results have showed the good applicability of the modified model, and the one with three parameters was better than the one with two parameters. Our model showed a small temperature dependence for predicting the thermodynamic properties of electrolytes across a narrow temperature range. Furthermore, we developed our model for mixed solvent

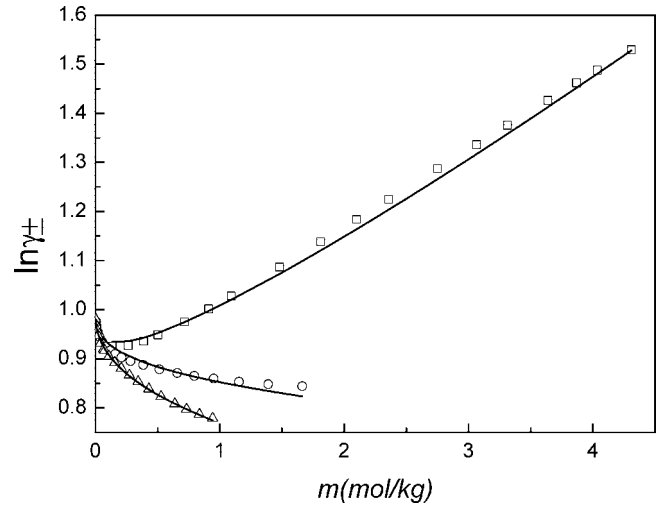

Figure 10. Calculated results of the osmotic coefficients of electrolytes in mixed solvent solutions at $T = 298.15$ K. The solid lines are calculated from the present model with three parameters. Literature data for different mass fractions (w) of nonaqueous solven: □, HCl in *N*,*N*-dimethylformamide ($w = 0.2$) + water;[41] ○, CsCl in methanol ($w = 0.1$) + water;[54] Δ, CsCl in methanol ($w = 0.3$) + water.[54]

systems. For all of the different compositions of solvents, this model performed fairly well in being fitted to the experimental data. Some typical calculated results indicate that the model with three parameters is more compatible to predict the thermodynamic properties of electrolytes in high concentration regions, whereas the one with two parameters is suitable in the case of very low concentrations.

Literature Cited

(1) Pitzer, K. S.; Mayogra, G. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268–277.
(2) Kim, H. T.; Frederick, W. J., Jr. Evalution of Pitzer Ion Interaction parameters of Aqueous Electrolytes at 25°C. 1. Single Salt Parameters. *J. Chem. Eng. Data* **1988**, *33*, 177–184.
(3) Kim, H. T.; Frederick, W. J., Jr. Evalution of Pitzer Ion Interaction parameters of Aqueous Electrolytes at 25°C. 2. Ternary Mixing Parameters. *J. Chem. Eng. Data* **1988**, *33*, 278–283.
(4) Bromley, L. A. Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions. *AIChE J.* **1973**, *19*, 313–320.
(5) Borge, G.; Castano, R.; Carril, M. P.; Corbillon, M. S.; Madariaga, J. M. Development of a Modified Bromley's Mathodology(MBM) for the Estimation of Ionic Media Effects on Solution Equilibria. Part 1. Calculation of the Interaction Parameters in the Molar and Molal Scales at 25°C. *Fluid Phase Equilib.* **1996**, *121*, 85–98.
(6) Borge, G.; Luis, A. N. E.; Maria, A. F.; Carril, M. P.; Olazabal; Madariaga, J. M. Development of a Modified Bromley's Mathodology(MBM) for the Estimation of Ionic Media Effects on Solution Equilibria. Part 2. Correlation of the Molar and Molal Interaction Parameters with the Charge and Crystal Radii of the Ions. *Fluid Phase Equilib.* **1996**, *121*, 99–109.
(7) Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Local Composition Model for Excess Gibbs Energy of Electrolyte Systems. *AIChE J.* **1982**, *28*, 588–596.
(8) Chen, C. C.; Evans, L. B. A Local Composition Model for Excess Gibbs Energy of Electrolyte Systems. *AIChE J.* **1986**, *32*, 444–454.
(9) Lu, J. F.; Yu, Y. X.; Li, Y. G. Modification and Application of the Mean Spherical Approximation Method. *Fluid Phase Equilib.* **1996**, *85*, 81–100.
(10) Salimi, H. R.; Taghikhani, V.; Ghotbi, C. Application of the GV-MSA Model to the Electrolyte Solutions Containing Mixed Salts and Mixed solvents. *Fluid Phase Equilib.* **2005**, *231*, 67–76.
(11) Lin, C. L.; Lee, L. S.; Tseng, H. C. Thermodynamic Behavior of Electrolyte Solutions. Part I. Activity and Osmotic Coefficients of Binary Systems. *Fluid Phase Equilib.* **1993**, *90*, 57–79.
(12) Zuo, Y. X.; Furst, W. Use of an Electrolyte Equation of State for the Calculation of Vapor-liquid Equilibria and Mean Activity Coefficients in Mixed Solvent Electrolyte systems. *Fluid Phase Equilib.* **1998**, *150–151*, 267–275.

(13) Chou, T. J.; Tanioka, A. A Vapor Pressure Model for Aqueous and Non-aqueous Solutions of Single and Mixed Electrolyte Systems. *Fluid Phase Equilib.* **1997**, *137*, 17–32.

(14) Sun, T. F.; Bullock, K. R.; Teja, A. S. Correlation and Prediction of Salt Effects on Vapor-liquid Equilibrium in Alcohol-water-salt Systems. *Fluid Phase Equilib.* **2004**, *219*, 257–264.

(15) Shiah, I. M.; Weng, W. L.; Wang, M. C. An Activity Coefficient model for Predicting Salt effects on Vapor-liquid Equilibria of Mixed Solvent Systems. *Fluid Phase Equilib.* **2004**, *170*, 297–308.

(16) Shiah, I. M.; Tseng, H. C. Prediction of Vapor-liquid Equilibria for Acetic Acid Aqueous Solutions Containing Salt. *Fluid Phase Equilib.* **1996**, *124*, 1–13.

(17) Nasirzadeh, K.; Salabat, A. The Modified Three-characteristic-parameter Correlation Model for Non-aqueous Electrolyte Solutions. *J. Mol. Liq.* **2004**, *113*, 9–11.

(18) Detty, M. R.; Gibson, S. L.; Hilf, R. Comparison of the Dark and Light-induced Toxicity of Thio and Seleno Analogues of the Thiopyrylium Dye AA1. *Bioorg. Med. Chem.* **2004**, *12*, 2589–2596.

(19) Ge, X. L.; Wang, X. D.; Zhang, M.; Seetharaman, S. Correlation and Prediction of Activity and Osmotic Coefficients of Aqueous Electrolytes at 298.15 K by the Modified TCPC Model. *J. Chem. Eng. Data* **2007**, *52*, 538–547.

(20) Barthel, J.; Neueder, R.; Lauermann, G. Vapor Pressure of Non-aqueous Electrolyte Solutions. Part 1. Alkali Metal Salts in Methanol. *J. Solution Chem.* **1985**, *14*, 621–633.

(21) Barthel, J.; Lauermann, G. Vapor Pressure of Non-aqueous Electrolyte Solutions. Part 3. Solutions of Sodium Iodide in Ethanol, 2-propanol, and Acetonitrile. *J. Solution Chem.* **1986**, *15*, 869–877.

(22) Luksha, E.; Criss, C. M. Thermodynamic Properties of Nonaqueous Solutions. II Free Energies, Entropies, and Activity Coefficients of Selected Alkali Metal Halides in Anhydrous N-Methylformamide. *J. Phys. Chem.* **1966**, *70*, 1496–1502.

(23) Barthel, J.; Lauermann, G.; Neueder, R. Vapor Pressure of Non-aqueous Electrolyte Solutions. Part 2. Tetraalkylammonium Salts in Methanol. Activity Coefficients of Various 1–1 Electrolytes at High Concentrations. *J. Solution Chem.* **1986**, *15*, 851–867.

(24) Safarov, J. T. Study of Thermodynamic Properties of Binary Solutions of Lithium Bromide or Lithium Chloride with Methanol. *Fluid Phase Equilib.* **2005**, *236*, 87–95.

(25) Safarov, J. T. Investigation of the Vapor Pressure *p* of Zinc Bromide or Zinc Chloride Solutions with Methanol by Static Method. *J. Chem. Thermodyn.* **2006**, *38*, 304–311.

(26) Safarov, J. T. Vapor Pressure Measurements of Binary Solutions of $CaCl_2$ with Methanol and Ethanol at T=(298.15 to 323.15) K Using a Static Method. *J. Chem. Eng. Data* **2006**, *51*, 360–365.

(27) Barthel, J.; Neueder, R.; Poepke, H.; Wittmann, H. Osmotic and Activity Coefficients of Nonaqueous Electrolyte Solutions. 1. Lithium Perchlorate in the Protic Solvents Methanol, Ethanol, and 2-Propanol. *J. Solution Chem.* **1998**, *27*, 1055–1066.

(28) Zafarani-Moattar, M. T.; Nasirzade, K. Osmotic Coefficient of Methanol + LiCl, + LiBr, and + $LiCH_3COO$ at 25 °C. *J. Chem. Eng. Data* **1998**, *43*, 215–219.

(29) Nasirzade, K.; Neueder, R. Measurement and Correlation of Osmotic Coefficients and Evaluation of Vapor Pressure for Electrolyte Solutions of $LiClO_4$ and $LiNO_3$ in Methanol at 25 °C. *J. Mol. Liq.* **2004**, *113*, 13–20.

(30) Nasirzade, K.; Salabat, A. Isopiestic Determination of Osmotic Coefficients and Evaluation of Vapor Pressures for Solutions of Sodium Bromide and Sodium Thiocyanate in Methanol at 25°C. *J. Mol. Liq.* **2003**, *106/1*, 1–14.

(31) Sardroodi, J. J.; Sadr, M. H.; Zafarani-Moattar, M. T. Correlation of the Osmotic Coefficients of the Solutions of 1:1 Salts in Methanol by Modified Local Composition Models at 298.15 K. *J. Chem. Thermodyn.* **2005**, *37*, 1177–1185.

(32) Sardroodi, J. J.; Seyedahmadian, S. M.; Sadr, M. H.; Kazemi, Y. Isopiestic Study of the Solutions of $MnCl_2$, $CoCl_2$ and $NiCl_2$ in Methanol and Ethanol at 298.15K. *Fluid Phase Equilib.* **2006**, *240*, 114–121.

(33) Safarov, J. T. Vapor Pressures of Lithium Bromide or Lithium Chloride and Ethanol Solutions. *Fluid Phase Equilib.* **2006**, *243*, 38–44.

(34) Verevkin, S.; Safarov, J. T.; Bich, E.; Hassel, E.; Heintz, A. Study of Vapour Pressure of Lithium Nitrate Solutions in Ethanol. *J. Chem. Thermodyn.* **2006**, *38*, 611–616.

(35) Zafarani-Moattar, M. T.; Sardroodi, J. J. Measurement and Correlation of Osmotic Coefficients and Evaluation of Vapor Pressures for Solutions of $CaCl_2$ and $Ca(NO_3)_2$ in Ethanol at 298 K. *Fluid Phase Equilib.* **2000**, *172*, 221–235.

(36) Zafarani-Moattar, M. T.; Sardroodi, J. J. Isopiestic and Volumetric Study of $CuCl_2$ + Ethanol at 25 °C. *J. Chem. Eng. Data* **2003**, *48*, 308–313.

(37) Zafarani-Moattar, M. T.; Aria, M. Isopiestic Determination of Osmotic and Activity Coefficients for Solutions of LiCl, LiBr, and $LiNO_3$ in 2-Propanol at 25°C. *J. Solution Chem.* **2001**, *30*, 351–363.

(38) Nasirzade, K.; Neueder, R.; Kunz, W. Vapor Pressures, Osmotic and Activity Coefficients for (LiBr + Acetonitrile between the Temperatures (298.15 and 343.15) K. *J. Chem. Thermodyn.* **2004**, *36*, 511–517.

(39) Manzoni, A.; Mussini, P. R.; Mussini, T. Thermodynamics of the Amalgam Cell {K_xHg_{1-x} KCl(m) AgCl Ag}and Primary Medium Effects upon KCl in{Ethylene Glycol + Water},{Acetonitrile + Water}, and{1,4-dioxane + Water} Solvent Mixtures. *J. Chem. Thermodyn.* **2000**, *32*, 107–122.

(40) Mussini, P. R.; Mussini, T.; Perelli, A.; Rondinimi, S.; Vertova, A. Thermodynamics of the Cell:{Me_xHg_{1-x} MeCl(m) AgCl Ag}(Me=Na, K, Cs) in (Ethanol + Water) Solvent Mixtures. *J. Chem. Thermodyn.* **1995**, *27*, 245–251.

(41) Dehyhimi, F.; Ebrahimi, A.; Roohi, H.; Koochaki, K. Determination of Activity Coefficients, Osmotic Coefficients, and Excess Gibbs Free Energies of HCl in N,N-Dimethylformamide-Water Mixed Solvent Systems by Potentiometric Measurements. *J. Chem. Eng. Data* **2004**, *49*, 1185–1188.

(42) Garcia-Paneda, E.; Masestre, A.; Yanes, C. Activity Coefficients for NaCl in (*w*) N-Dimethylformamide + (1-*w*)Water Mixtures at 25 °C. *J. Chem. Eng. Data* **1999**, *44*, 1055–1057.

(43) Hernandez-Luis, F.; Grandoso, D.; Lemus, M. Activity Coefficients of NaCl in Fructose + Water at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 668–674.

(44) Hernandez-Luis, F.; Amado-Gonzalez, E.; Esteso, M. A. Activity Coefficients of NaCl in Trehalose-Water and Maltose-Water Mixtures at 298.15 K. *Carbon Res.* **2003**, *338*, 1415–1424.

(45) Basili, A.; Mussini, P. R.; Mussini, T.; Rondinimi, S. Thermodynamics of the Cell:{Na_xHg_{1-x} NaCl(m) AgCl Ag} in (Methanol + Water) Solvent Mixtures. *J. Chem. Thermodyn.* **1996**, *28*, 923–933.

(46) Yao, J.; Yan, W. D.; Xu, Y. J.; Han, S. J. Activity Coefficients for NaCl in MeOH + H_2O by Electromotive Force Measurements at 308.15 and 318.15 K. *J. Chem. Eng. Data* **1999**, *44*, 497–500.

(47) Hernandez-Luis, F.; Galleguillos, H. R.; Vazquez, M. V. Activity Coefficients of NaF in (Glucose + Water) and (Sucrose + water) Mixtures at 298.15 K. *J. Chem. Thermodyn.* **2004**, *36*, 957–964.

(48) Hernandez-Luis, F.; Vazquez, M. V.; Esteso, M. A. Activity Coefficients for NaF in Methanol-Water and Ethanol-Water Mixtures at 25°C. *J. Mol. Liq.* **2003**, *108/1–3*, 283–301.

(49) Dehyhimi, F.; Ghalami-Choobar, B. Determination of Activity Coefficients for NH_4Cl in 1-propanol/Water Mixed Solvents by Potentiometric Measurements. *J. Mol. Liq.* **2005**, *122*, 116–120.

(50) Dehyhimi, F.; Ghalami-Choobar, B. Activity Coefficients for NH_4Cl in 2-propanol/Water Mixed Solvent and Some Thermodynamic Correlations for NH_4Cl in ROH/Water Mixed Solvents (R = Me, Et, 1-Pr and 2-Pr). *Fluid Phase Equilib.* **2006**, *246*, 185–190.

(51) Dehyhimi, F.; Ghalami-Choobar, B.; Salami-Ahangari, R. Activity Coefficients for NH_4Cl in ethanol/Water Mixed Solvents by Electromotive Force Measurements. *J. Mol. Liq.* **2005**, *116*, 93–97.

(52) Falciola, L.; Mussini, P. R.; Mussini, T.; Vimercati, A. Thermodynamics of the Amalgam Cells {M-Amalgam MCl or MCl_2. (m) AgCl Ag}(M=Rb, Cs, Sr, Ba) and Primary Medium Effects in{Acetonitrile + Water}. *J. Chem. Thermodyn.* **2004**, *36*, 465–471.

(53) Cui, R. F.; Hu, M. C.; Jin, L. H.; Li, S. N.; Jiang, Y. C.; Xia, S. P. Activity Coefficients of Rubidium Chloride and Cesium Chloride in Methanol-Water Mixtures and a Comparative Study of Pitzer and Pitzer-Simonson-Clegg Models (298.15 K). *Fluid Phase Equilib.* **2007**, *251*, 137–144.

(54) Hu, M. C.; Cui, R. F.; Li, S. H.; Jiang, Y. C.; Xia, S. P. Determination of Activity Coefficients for Cesium Chloride in Methanol-Water and Ethanol-Water Mixed Solvents by Electromotive Force Measurements at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 357–362.

(55) Falciola, L.; Longoni, G.; Mussini, P. R.; Mussini, T. Thermodynamics of the Amalgam Cells {Cs-Amalgam CsX(m) AgX Ag}(*X*=Cl, Br, I) and Primary Medium Effects in{Methanol + Water},{Acetonitrile + Water}, and{1,4-dioxane + Water} Solvent Mixtures. *J. Chem. Thermodyn.* **2006**, *38*, 788–798.

(56) Zhuo, K. L.; Zhang, H. H.; Wang, Y. P.; Liu, Q.; Wang, J. J. Activity Coefficients and Volumetric Properties for the NaBr + Maltose + Water System at 298.15 K. *J. Chem. Eng. Data* **2005**, *50*, 1589–1595.

(57) Faverio, C. L.; Mussini, P. R.; Mussini, T. Thermodynamics of the Amalgam Cells {Li_xHg_{1-x} Li_2SO_4. (m) Hg_2SO_4 Hg} in Water, (Methanol + Water), and (Acetonitrile + Water) Solvent Mixtures. *J. Chem. Thermodyn.* **1998**, *30*, 985–997.

(58) Falciola, L.; Mussini, P. R.; Mussini, T.; Vimercati, A. Thermodynamics of Amalgam Cells {M-Amalgam MCl_2. (m) AgCl Ag}(M=Sr, Ba. and Primary Medium Effects in{Methanol + Water} and {Ethanol + Water} Solvent Mixtures. *J. Chem. Thermodyn.* **2005**, *38*, 363–369.

(59) Boukhalfa, N.; Meniai, A. H. Activity Coefficients for Salts in Water-Methanol Mixed Solvent Solutions. *Desalination* **2007**, *206*, 380–393.

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