Correlation and Prediction of Thermodynamic Properties of Some Complex Aqueous Electrolytes by the Modified Three-Characteristic-Parameter Correlation Model

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In this paper, the thermodynamic properties, such as the mean activity coefficient, osmotic coefficient, and water activity, for 129 complex aqueous electrolyte solutions have been calculated by the modified three-characteristic-parameter correlation model. We also calculated the adjustable parameters of the Pitzer model and the Bromley model. Results of the standard deviations showed that our modified model is fairly suitable for predicting the mean activity coefficient, osmotic coefficient, and water activity of these electrolytes. This new model is much better than the Bromley model for all studied electrolyte solutions in this paper, and it is almost on par with the Pitzer model. Especially for 3–1 and 3–2 electrolytes, our model shows a better result than the Pitzer model.

Introduction

As is well-known, accurate prediction of the thermodynamic properties in aqueous solutions plays an important role in many fields, such as extraction, oil recovery, biological studies, etc. Also, a number of models have been developed to describe these electrolyte properties, such as Pitzer equations,[1] the Bromley model,[2,3] the NRTL model[4,5] and MSA-based models,[6,7] etc. The Pitzer model, which introduced the short-range interactions between ions, is admitted as the most widely used semiempirical model, especially after Kim and Frederick[8,9] published the Pitzer parameters for 304 single salts in aqueous solutions at 298.15 K. But it should be noted that many complex electrolytes including ones with organic anions or cations, which are very significant in some related fields, were not summarized in their paper. Also, much new research on some other electrolytes has been carried out after their publications. So, it is necessary to obtain the Pitzer parameters of these electrolytes. On the other hand, another noticeable model is the three-characteristic-parameter correlation (TCPC) approach proposed by Lin and Lee,[10] whose parameters possess clear physical significance, and it is also showing up as a powerful tool for calculating the thermodynamic properties of electrolytes in aqueous solution.

This model has been modified, and parameters for many strong aqueous electrolyte solutions have been obtained across a wide concentration range in our previous work.[11] We also have extended this model for nonaqueous electrolyte solutions including mixed solvent systems.[12] We proved that the modified TCPC model is on par with the Pitzer model and much better than the Bromley model in estimating the mean activity coefficient or osmotic coefficients. The model for calculating the thermodynamic properties of multicomponent systems is also under research in our group now. Since these kinds of models developed the concept of solvation for the short-range interaction term, it is also hopeful to predict thermodynamic properties of weak electrolyte aqueous solutions. Therefore, as a part of this series of work, the present study aims to extend this modified model for predictions of the thermodynamic properties of some complex electrolyte aqueous solutions and, additionally, to determine the sets of parameters for the Pitzer and Bromley models.

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Thermodynamic Models

Pitzer Model. Pitzer et al.[1] presented the short-range interactions by binary interaction parameters. The equations for calculating the mean activity coefficient and osmotic coefficient of an electrolyte solution were written as

$$\ln \gamma_{\pm} = -A_{\varphi}|Z_+Z_-|f^{\gamma} + m\frac{2\upsilon_+\upsilon_-}{\upsilon}B^{\gamma} + m^2\frac{2(\upsilon_+\upsilon_-)^{3/2}}{\upsilon}\cdot\frac{3}{2}C^{\varphi} \quad (1)$$

$$f^{\gamma} = -A_{\varphi}\left[\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b}\ln(1+bI^{1/2})\right] \quad (2)$$

$$B^{\gamma} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I}\left[1-\left(1+\alpha I^{1/2}-\frac{1}{2}\alpha^2 I\right)\exp(-\alpha I^{1/2})\right] \quad (3)$$

$$\varphi = 1 - A_{\varphi}|Z_+Z_-|f^{\varphi} + m\frac{2\upsilon_+\upsilon_-}{\upsilon}B^{\varphi} + m^2\frac{2(\upsilon_+\upsilon_-)^{3/2}}{\upsilon}C^{\varphi} \quad (4)$$

$$f^{\varphi} = -A_{\varphi}\frac{I^{1/2}}{1+bI^{1/2}} \quad (5)$$

$$B^{\varphi} = \beta^{(0)} + \beta^{(1)}\exp(-\alpha I^{1/2}) \quad (6)$$

For 2–2 electrolytes, it is necessary to add another parameter, $\beta^{(2)}$, and eqs 3 and 6 can be expressed as:

$$B^{\gamma} = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha_1 I}\left[1-\left(1+\alpha_1 I^{1/2}-\frac{1}{2}\alpha_1 I\right)\exp(-\alpha_1 I^{1/2})\right] + \frac{2\beta^{(2)}}{\alpha_2 I}\left[1-\left(1+\alpha_2 I^{1/2}-\frac{1}{2}\alpha_2 I\right)\exp(-\alpha_2 I^{1/2})\right] \quad (7)$$

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$$B^{\varphi} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta^{(2)} \exp(-\alpha_2 I^{1/2}) \quad (8)$$

Here, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^{(\varphi)}$ are the Pitzer parameters. A_φ is the Pitzer−Debye–Huckel (PDH) constant with a value of 0.391 $kg^{1/2}\ mol^{-1/2}$ at 298.15 K. Z_i is the charge number of ion i, and $I = \Sigma m_i Z_i^2$ is the ionic strength of the electrolyte. m is the molality of solution ($mol \cdot kg^{-1}$). b was regarded as a constant with a value of 1.2. υ_i is the stoichiometric number of ion i, and α was a constant with a value of 2.0 $kg^{1/2}\ mol^{1/2}$ in eqs 3 and 6. For 2–2 electrolytes, $\alpha_1 = 1.4\ kg^{1/2}\ mol^{1/2}$ and $\alpha_2 = 12\ kg^{1/2}\ mol^{1/2}$, respectively.

The activity of water can be determined from the following equation

$$\ln a_w = -(\upsilon m M_w/1000) \cdot \varphi \quad (9)$$

where $\upsilon = \upsilon_+ + \upsilon_-$ and M_w is the molecular weight of water ($g \cdot mol^{-1}$).

Bromley Model. The equation proposed by Bromley[2] for calculating the mean activity coefficient of an aqueous electrolyte solution is

$$\log \gamma_\pm = -\frac{A_m |Z_+ Z_-| I^{1/2}}{1 + I^{1/2}} + I \cdot \left[\frac{(0.06 + 0.6B)|Z_+ Z_-|}{(1 + 1.5I/|Z_+ Z_-|)^2} + B \right] \quad (10)$$

Here, A_m has a constant value of 0.5108 at 298.15 K. B is an adjustable parameter.

Modified TCPC Model. The three-characteristic-parameter correlation model proposed by Lin and Lee[10] was modified with the following equations for calculating the mean activity coefficient, osmotic efficient, and solvent activity for single electrolyte solutions

$$\ln \gamma_\pm = -|z_+ z_-| A_\varphi \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] + \frac{S}{T} \cdot \frac{I^{2n}}{\upsilon_+ + \upsilon_-} \quad (11)$$

$$\varphi = 1 - |z_+ z_-| A_\varphi \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{S}{T(\upsilon_+ + \upsilon_-)} \frac{2n}{2n+1} I^{2n} \quad (12)$$

$$\ln a_s = -(\upsilon m M_s/1000) \cdot \varphi \quad (13)$$

$$A_\varphi = \frac{1}{3}(2\pi L d_s)^{1/2} \left(\frac{e^2}{DkT} \right)^{3/2} \quad (14)$$

Here D is the static dielectric constant of the solvent at temperature T and L is Avogadro's number; d_S is the density of solvent; k is the Boltzmann constant; and e is the electronic charge. M_s is the molecular weight of solvent ($g \cdot mol^{-1}$). Other symbols are the same as the ones described above.

In eqs 11 to 13, the first term is the PDH long-range interaction term. b is an adjustable parameter in this model, which is dependent on the closest-distance of approach between ions. The second term is the expression of solvation effect. It was calculated on the basis of electrical potential law. S is defined as the "solvation parameter" that represents the solvation effect between ions and the solvent molecules. n was a parameter related to the distance between the ion and the solvent molecule.

The modifications are concentrated on the following aspects: (i) Treatment of the D value. In the original model, D was regarded as an adjustable parameter and can be regressed from the literature data. Actually, in most of the semiempirical models, such as Pitzer, Bromley, NRTL, etc., the solute is always treated as a medium with an invariable dielectric constant; here it was also employed as a solute-specific constant. (ii) Treatment of the S value. In the original model, S was treated as a value containing temperature; here it is independent of temperature, which hopefully will reduce the temperature dependence of the parameters. (iii) Treatment of the n value. In the original model, n was regarded as a constant, 0.645, in all cases to simplify the process of optimization. Since the concentration range is low ($< 6\ mol \cdot kg^{-1}$), it is acceptable for strong electrolytes, but we prove that it is necessary to take a change of n value into account for prediction in the high concentration range. Thus in our study, the two sets of parameters (b, S) and (b, S, n) were both obtained to compare with each other.

It also should be noted that the original TCPC model was developed on the consideration that electrolytes are completely dissociated into ions. This assumption was also employed in our model. For the complex electrolyte solutions, in a sort of way, one can also assume that the complex electrolyte molecule is dissociated completely in the low concentration range. But in the higher concentration range, n becomes a very important factor. With the consideration of n, it is also helpful to overcome the deviation from complete dissociation. In our opinion, the solvation effects included in our model are the most important for the calculation of complex electrolyte solutions. The results listed below show its feasibility.

Results and Discussion

The modified TCPC model was applied to correlate the experimental activity coefficient data or osmotic coefficient data for many complex electrolytes at 298.15 K, so that the adjustable parameters can be obtained by multiple regression analysis. The objective function is given below, and the optimization was performed by the least-squares method with MATLAB software

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

or

$$\delta = \left[\sum_i (\varphi^{exptl} - \varphi^{calcd})^2 / n_p \right]^{1/2} \quad (15)$$

Here δ is defined as the standard deviation; n_p is the number of experimental data points; and the subscripts of exptl and calcd refer to the experimental and calculated data, respectively. Two sets of parameters for our model, (b, S) and (b, S, n), are both listed in Table 1. Since parameters of the Pitzer or Bromley models for these electrolytes have not been reported in the literature, they were also regressed and tabulated in Table 1 to compare with our model. Most of the parameters in our model and the Pitzer and Bromley models were obtained from experimental mean activity coefficients, while some parameters were regressed from reported experimental osmotic coefficients. The standard deviations of different electrolytes by various models are listed in Table 2.

It should be noted that some negative S values were obtained, which may seem unreasonable. Actually, the S value can be regarded as representing the interactions between ions and solvent molecules. The negative S value represents the association effect of ions, equal to a negative solvation effect. In these cases, it indicates that the association of ions or incomplete dissociation is very significant for calculating the thermodynamic properties of these electrolytes.

As shown in Table 2, the results of standard deviations of our model show good consistency between the experimental

Table 1. Calculated Parameters for Aqueous Electrolyte Solutions at 298.15 K[a]

	this work					Pitzer			Bromley
electrolytes	b	S (n = 0.645)	b	S	n	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	B
				1–1 Electrolytes					
$(CH_3)_4NCl$	2.0229	22.1336	1.4426	63.6810	0.4822	0.0579	0.0966	−0.0006	0.0311
$(CH_3)_4NBr$	1.1651	0.9487	2.6487	−130.2132	0.18015	−0.0460	0.1310	0.0110	−0.0338
$(CH_3)_4NF$	5.9756	156.9875	2.6261	264.6599	0.5258	0.2686	0.2364	−0.0008	0.2128
$(CH_3)_4NI$	1.5943	−488.6981	1.4413	−499.8599	0.6846	0.0691	−0.1131	−1.3466	3.9000
$(C_2H_5)_4NCl$	1.3611	65.4382	1.6403	40.0334	0.75025	0.0545	0.0885	0.0081	0.0594
$(C_2H_5)_4NBr$	0.6596	30.6456	0.7956	9.5254	0.87025	−0.0162	−0.1359	0.0065	−0.0026
$(C_2H_5)_4NF$	9.9881	270.2649	5.6571	330.1712	0.5925	0.3728	0.3491	0.0119	0.3423
$(C_2H_5)_4NI$	0.2453	−124.4186	22.5381	−653.2634	0.25045	−0.3942	0.0619	0.1255	−0.2549
$(C_3H_7)_4NBr$	0.6831	29.7238	0.6831	29.7238	0.6450	0.0034	−0.2308	0.0045	−0.0139
$(C_3H_7)_4NI$	0.2317	−612.3611	15.9119	−891.4826	0.3210	−0.7365	0.0958	0.3664	−0.4852
$(C_4H_9)_4NCl$	3.1404	6.2739	3.1404	6.2739	0.6450	0.0372	0.4111	−0.0012	0.0156
$(C_4H_9)_4NBr$	0.5597	−57.3470	21.6468	−511.9992	0.2144	−0.1786	−0.0080	0.0400	−0.1528
$(C_4H_9)_4NF$	17.6933	478.8478	6.2702	579.9987	0.5328	0.6172	0.3525	−0.0229	0.4822
$(HOCH_2CH_3)_4NBr$	0.7713	−4.6713	17.9510	−417.9364	0.16555	−0.0834	0.0634	0.0130	−0.0583
$(HOCH_2CH_3)_4NF$	2.7782	35.9180	2.4341	55.0240	0.5474	0.0850	0.2279	−0.0025	0.0494
$(n\text{-}C_3H_7)_4NF$	23.0240	358.6524	1.8609	652.4230	0.49025	0.5705	0.1580	−0.0080	0.4462
$(n\text{-}C_4H_9)_4NF$	17.6933	478.8534	5.9212	587.0003	0.52735	0.6174	0.3523	−0.0231	0.4822
$HTcO_4$	2.3931	88.4825	3.3044	41.9805	0.8484	0.0843	0.2807	0.0144	0.0969
$HReO_4$	2.4285	77.9596	2.7839	60.0700	0.7037	0.1001	0.2457	0.0062	0.0943
ChCl	1.8118	21.7247	2.1286	7.0243	0.9065	0.0029	1.5674	0.0049	−0.0102
Bu_4NBr	1.7643	−183.9533	16.1494	−493.571	0.24585	−0.3498	0.6186	0.1336	−0.1705
sec-Bu_4NBr	1.8018	−170.3016	17.6749	−488.028	0.2297	−0.3354	0.6111	0.1383	−0.1567
iso-Bu_5NBr	1.8426	−185.6487	17.0788	−488.688	0.2431	−0.3390	0.6136	0.1298	−0.1667
Bu_2Et_2NBr	2.0484	−144.2704	17.0106	−438.124	0.2129	−0.2734	0.5937	0.1157	−0.1228
$BuEt_3NBr$	1.8339	−155.3455	17.9419	−477.486	0.2149	−0.3116	0.5897	0.1354	−0.1464
NaGlu	2.3297	48.7016	2.7206	23.4367	0.8828	0.0602	0.2291	0.0080	0.0490
KGlu	2.5942	61.1903	2.9897	36.9890	0.84235	0.0808	0.2333	0.0094	0.0642
$MMANO_3$	1.7319	−10.5173	20.1984	−297.1911	0.18095	−0.0176	0.2732	0.0011	−0.0231
$DMANO_3$	1.8517	−10.2575	20.6697	−286.2350	0.1687	−0.0122	0.2372	0.0020	−0.0208
$TMANO_3$	1.3599	−3.4019	3.8503	−169.9468	0.1850	−0.0261	0.1813	0.0037	−0.0243
TmGuCl	1.9320	24.2383	2.2067	5.8856	1.00915	0.0238	0.2359	0.0049	0.0201
TmGuBr	1.1041	3.0200	1.1174	0.0025	2.4501	−0.0397	0.1411	0.0067	−0.0251
GuF	1.4553	−1.0423	5.1018	−191.3613	0.16325	−0.0210	0.2315	0.0033	−0.0177
$NaCF_3SO_3$	5.7364	35.5042	3.9284	86.0234	0.4316	0.1453	0.3222	−0.0147	0.0754
NH_4Br	2.8106	9.9311	2.6425	19.0497	0.5051	0.0517	0.2876	−0.0033	0.0194
LiMS	4.4565	55.2994	2.8658	119.0670	0.4617	0.1453	0.2855	−0.0088	0.0887
NaMS	3.1935	26.7125	3.0186	35.0645	0.5760	0.0357	1.7892	0.0001	0.0446
KMS	2.6558	6.5067	2.6844	4.9693	0.71105	0.0435	0.2752	−0.0031	0.0140
HTFMS	4.7368	114.5451	4.5230	120.9732	0.6290	0.1829	0.3230	0.0020	0.1512
LiTFMS	7.3404	111.6682	3.2756	219.0136	0.4660	0.2400	0.3127	−0.0139	0.1643
NaTFMS	4.6665	32.6061	2.5677	120.0700	0.3596	0.1295	0.2992	−0.0125	0.0663
KTFMS	2.2712	−14.5605	3.2365	−64.0134	0.3858	−0.0039	0.3587	−0.0012	−0.0198
NH_4MS	2.6519	16.1232	2.7891	7.3057	0.9073	0.0537	0.2398	−0.0023	0.0242
Me_4NMS	3.5060	70.9425	3.3657	77.6315	0.6176	0.1302	0.2648	−0.0018	0.0924
Et_4NMS	2.8750	95.052	3.1508	79.8424	0.6449	0.1285	0.2415	0.0017	0.0957
Bu_4NMS	6.2708	35.0049	0.5943	399.7581	0.2256	0.2081	0.2413	−0.0388	0.0827
HES	4.5209	74.5035	3.8359	100.0506	0.5562	0.1618	0.2926	−0.0087	0.1077
LiES	5.0788	77.9834	3.1439	152.0476	0.4572	0.1849	0.2873	−0.0141	0.1162
NaES	4.5414	52.4027	3.5582	90.1791	0.4889	0.1443	0.2989	−0.0123	0.0863
KES	3.0368	34.2348	3.2266	24.0252	0.7580	0.0807	0.2607	−0.0022	0.0491
NH_4ES	3.3883	30.7203	3.1128	44.6735	0.5357	0.1002	0.2567	−0.0093	0.0513
Me_4NES	3.8093	76.0092	3.1747	105.8209	0.5472	0.1524	0.2556	−0.0063	0.1014
Et_4NES	3.4547	96.1366	3.3733	100.1263	0.6322	0.1522	0.2498	0.0015	0.1164
Bu_4NES	6.8761	19.7097	0.1016	549.9993	0.2070	0.2052	0.2513	−0.0439	0.0711
H sul[A]	−0.1118	16.1479	4.4843	−509.7898	0.19325	−0.2957	−0.2673	0.1040	−0.2252
Na sul[A]	2.4633	−22.3152	21.3443	−329.541	0.16045	−0.077	1.2144	0.0114	***I***
K sul[A]	1.7742	−42.0600	23.2023	−335.8895	0.2342	−0.0706	0.2868	0.0082	−0.055
Li sul[A]	57.4892	16.6942	26.7226	47.1528	0.39495	0.1327	0.7937	−0.0140	0.0924
Me_4Gu sul[A]	2.9078	31.9709	2.7667	39.3684	0.59435	0.0790	0.2608	−0.0025	0.0462
Picolinic acid	10.2944	−13.1251	10.2944	−13.1251	0.6450	0.0061	0.9110	0.0010	0.0242
Na sulf[B]	2.5884	−4.4962	25.4188	−226.1378	0.13375	0.1118	0.1386	−0.0708	0.0185
K sulf[B]	2.5115	−13.9743	20.2414	−236.5900	0.16915	0.0079	0.2698	0.0017	−0.0021
H Ben[C]	3.3013	28.7469	3.6374	14.9846	0.83245	0.0711	0.3232	−0.0011	0.0486
Li Ben[C]	4.9455	39.2196	3.2301	99.9829	0.40975	0.1369	0.3174	−0.0138	0.0786
Na Ben[C]	3.5864	5.9151	3.2559	20.0916	0.31095	0.0993	0.2554	−0.0250	0.0429
Li 2,5-Dim[D]	2.4589	−19.2066	23.0632	−255.1499	0.1802	0.0049	0.2655	−0.0013	−0.0102
Na 2,5-Dim[D]	2.5980	−96.6617	22.9434	−307.3554	0.22805	−0.0696	0.3027	0.0393	−0.0344
H mes[E]	0.6196	−18.3527	20.1835	−465.4890	0.2018	−0.2013	0.2654	0.0372	−0.0889
Li mes[E]	1.3474	−17.2769	24.3557	−350.3533	0.18825	−0.0953	0.2778	0.0220	−0.0475
Na mes[E]	3.3676	−210.3428	3.8230	−225.0136	0.57815	−0.0266	0.2843	−0.0114	−0.0723
Li p-eth[F]	2.5381	−40.3322	23.7405	−276.2212	0.24245	−0.0682	0.4285	0.0134	−0.0305
Na p-eth[F]	2.9260	−135.6830	6.0301	−239.9839	0.44385	−0.0965	0.3770	−0.0102	−0.0855
H p-tol[G]	1.6716	1.0101	1.6266	0.0028	3.09355	−0.0367	0.2667	0.0127	−0.0152

Table 1. Continued

	this work					Pitzer			Bromley
electrolytes	b	S (n = 0.645)	b	S	n	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	B
H p-bth[H]	1.0300	−17.1221	21.9102	−387.2545	0.19525	−0.1442	0.3080	0.0305	−0.0619
lysine	4.6859	88.4677	5.1679	76.2484	0.68475	0.1371	0.4129	0.0046	0.1256
arginine	32.2524	−103.3543	32.2524	−103.3543	0.6450	0.0312	0.8353	−0.0220	0.1018
lysHCl	1.0965	36.0540	1.2838	8.1549	1.20235	−0.0270	0.0782	0.0251	−0.0165
ArgHCl	0.6628	−9.0812	20.4787	−448.5980	0.1745	−0.1185	0.0480	0.0226	−0.0784
HisHCl	1.4624	−175.5622	20.1424	−429.4027	0.24495	−0.2622	0.2455	0.2124	−0.1371
CCl_3COOK[b]	5.4857	0.2672	4.1588	31.3469	0.2005	0.0855	0.4056	−0.0101	0.0294
CF_3COOK[b]	7.3057	−2.8114	7.4563	−3.2108	0.6291	0.0119	1.0704	−0.0003	***J***
CCl_3COONa[b]	9.3153	20.4672	0.3942	502.5763	0.2110	0.1323	0.4469	−0.0109	6.2900
CF_3COONa[b]	14.5962	16.0939	0.5378	502.9960	0.2021	0.1192	0.5600	−0.0073	0.0539
Et_4NI	0.2219	−179.3147	20.6578	−693.9790	0.2540	−0.4886	0.0617	0.2001	−0.2989
$BuEt_3NI$	25.8021	−819.6828	8.9096	−712.9900	0.7387	−0.1964	0.5198	−0.3875	−0.4595
$HepEt_3NI$	−0.2956	−108.6469	22.2578	−942.5830	0.2403	−0.6174	−0.1728	0.1523	−0.3655
$HexEt_3NI$	0.5382	−206.0547	20.9943	−680.2790	0.3009	−0.4648	0.2318	0.1163	−0.2775
$PenEt_3NI$	1.0201	−252.8996	20.8656	−615.6010	0.31095	−0.3804	0.2361	0.0955	−0.2521
$PrEt_3NI$	13.8935	−327.4788	28.6146	−379.378	0.5343	−0.0709	0.6091	−0.1205	−0.0909
				1–2, 2–1 Electrolytes					
$(NH_4)_2B_{10}H_{10}$	2.5905	8.2765	2.4378	31.9891	0.40915	0.1450	1.4543	−0.0178	0.0146
$Na_2B_{12}H_{12}$	4.1248	162.4389	3.4172	235.0167	0.5514	0.5481	1.4964	−0.0404	0.1555
$(TH)_2SO_4$	1.8578	10.8221	1.8954	5.9398	0.7432	0.0654	1.1748	−0.0016	***N***
Na_2WO_4	3.6058	20.6613	3.9657	1.6436	1.23675	0.1327	2.5969	−0.0011	0.0476
Na_2MoO_4	3.3747	21.5022	3.7032	2.0825	1.18675	0.1318	2.4412	−0.0012	0.0442
H m-ben[K]	5.1296	104.8623	5.2159	97.6633	0.6662	0.5121	1.5877	−0.0735	0.1284
Li m-ben[K]	5.0608	84.6993	4.6131	119.1647	0.56545	0.4579	1.6824	−0.0532	0.1114
Na m-ben[K]	4.5130	30.5777	4.6205	23.0191	0.7080	0.2964	1.8356	−0.0367	0.0622
H 4,4′-bib[L]	1.1894	66.1800	1.2403	44.5517	0.74685	0.0609	0.0100	0.0380	−0.0213
Li 4,4′-bib[L]	2.7859	4.3687	2.7619	0.0631	2.8275	0.1440	1.1016	0.0086	0.0169
Na 4,4′-bib[L]	26.6244	−69.5442	25.9094	−65.3245	0.7453	1.3033	2.5207	−1.7435	0.2974
H 1,14-dis[M]	0.1546	40.1834	0.1794	8.0168	1.07255	−0.0113	−14.3078	0.0416	−0.4720
$Ba(OH)_2$	1.7934	98.5231	1.9346	5.3390	1.8119	−0.0691	0.4522	0.2595	−0.0117
				3–1 Electrolytes					
$Al(ClO_4)_3$	4.2458	207.0617	4.9010	154.0625	0.6945	0.9059	5.6963	0.0207	0.1789
$Al(NO_3)_3$	2.0544	89.3121	1.6008	246.0127	0.4948	0.5048	2.0034	−0.0153	0.0599
$Co(en)_3(ClO_4)_3$	2.6646	−71.9500	7.6476	−900.283	0.1953	0.1364	3.3718	0.0546	−0.0076
$La(BrO_3)_3$[b]	3.0713	17.5084	3.3857	1.4002	0.55405	−0.0270	103.5659	0.0259	−
$Pr(BrO_3)_3$[b]	3.1362	20.1936	3.4120	3.2358	0.4948	−0.0177	84.1632	0.0287	−
$Nd(BrO_3)_3$[b]	3.0645	26.0858	3.4455	1.4604	0.60595	−0.0551	85.8109	0.0485	−
$Sm(BrO_3)_3$[b]	2.8952	32.6826	3.6185	2.1120	0.57545	−0.0341	92.3074	0.0447	−
$Eu(BrO_3)_3$[b]	3.1328	33.7878	3.7322	1.5228	0.62235	−0.0615	98.2250	0.0578	−
$Gd(BrO_3)_3$[b]	3.0901	44.4311	4.1144	2.1081	0.60725	−0.0601	114.8468	0.0654	−
$Tb(BrO_3)_3$[b]	3.2003	47.0840	4.1831	6.4849	0.50825	−0.0011	74.0123	0.0550	−
$Dy(BrO_3)_3$[b]	3.3317	54.0347	4.2251	10.7476	0.47395	0.0173	85.2176	0.0589	−
$Ho(BrO_3)_3$[b]	3.2557	70.5594	4.8957	9.3279	0.50805	−0.0084	109.4322	0.0808	−
$Er(BrO_3)_3$[b]	3.3354	85.6414	4.7434	23.9934	0.43625	0.0852	118.2586	0.0716	−
$Tm(BrO_3)_3$[b]	3.3800	96.0138	4.5139	40.7834	0.3970	0.1488	118.1959	0.0649	−
$Yb(BrO_3)_3$[b]	3.3282	100.0263	4.6168	38.9086	0.40325	0.1527	140.4127	0.0661	−
$Lu(BrO_3)_3$[b]	2.9308	95.6349	5.6227	12.0194	0.50135	0.0015	177.9995	0.0942	−
$Y(BrO_3)_3$[b]	3.4513	72.3989	5.6108	11.0299	0.4928	0.0220	104.0567	0.0736	−
$La(NO_3)_3$[b]	4.0343	19.5220	3.2529	76.9948	0.4836	0.2568	8.6198	−0.0081	0.0304
$Pr(NO_3)_3$[b]	3.7508	22.7310	2.9670	105.9629	0.4588	0.2762	8.2994	−0.0094	0.0329
$Eu(NO_3)_3$	3.8015	29.7474	2.6751	169.8080	0.4294	0.3273	7.6788	−0.0127	0.0403
$Y(NO_3)_3$	5.3316	31.2768	2.3819	389.9655	0.3509	0.3815	8.7981	−0.0149	0.0485
$Lu(NO_3)_3$	5.4046	32.2717	1.8379	648.6730	0.30435	0.4195	8.3830	−0.0178	0.0501
				4–1 Electrolytes					
$Pt(en)_3Cl_4$	2.4807	−52.1227	4.3009	−849.679	0.19455	0.5889	6.2013	−0.1051	−0.0089
$ThCl_4$	5.6880	82.8019	5.7635	75.9360	0.6595	1.1471	19.8116	−0.1240	0.1012
				3–2 Electrolytes					
$[Co(en)_3]_2(SO_4)_3$	2.2808	4.9497	2.3000	0.0244	1.45675	0.7091	24.4864	−0.0602	−0.0084
$Lu_2(SO_4)_3$	2.2586	29.3380	2.2505	34.0275	0.6199	1.1666	20.9549	−0.1610	−0.0073
				2–2 Electrolytes					
$CaCrO_4$[b]	2.9686	−11.0709	4.1770	−203.028	0.1982	***X***			0.0182

[a] **A**, sulfamate. **B**, sulfanilate. **C**, benzensulfonate. **D**, 2,5-dimethylbenzenesulfonate. **E**, mesitylenesulfonate. **F**, *p*-ethylbenzenesulfonate. **G**, *p*-toluenesulfonate. **H**, *p*-bthylbenzenesulfonate. **I**, $-7.3736 \cdot 10^{-4}$. **J**, $2.9997 \cdot 10^{-4}$. **K**, *m*-benzenedisulfonate. **L**, 4,4′-bibenzyldisulfonate. **M**, 1,14-disphenyltetradecanedisulfonate. **N**, $1.8806 \cdot 10^{-4}$. **X**. $\beta^{(0)} = 0.1251$, $\beta^{(1)} = 0.7691$, $\beta^{(2)} = -0.1309$, $C^{\varphi} = -0.0125$. [b] The parameters for these electrolytes by the modified TCPC model have been reported in our previous work.[11] But parameters of the Pitzer and Bromley models have not been reported before. For comparison, they are all presented here.

data and the calculated results. The discrepancy of the Bromley model for 1–1 electrolytes (0.0805) is acceptable but unacceptable for other kinds of electrolyte solutions (> 0.15). The modified model with two parameters (b, S) is acceptable (overall average 0.0394) for most electrolyte solutions; it is a little worse than the Pitzer model (overall average 0.0202). But our model

Table 2. Standard Deviation (δ) for Different Electrolytes by Various Models

electrolytes	mmax mol·kg^{-1}	data	this work two	this work three	Pitzer	Bromley	refs.
			1–1 Electrolytes				
$(CH_3)_4NCl$	19	ln $\gamma_\pm$	0.0623	0.0422	0.0352	0.0758	13
$(CH_3)_4NBr$	5.5	ln $\gamma_\pm$	0.0457	0.0425	0.0264	0.0576	13
$(CH_3)_4NF$	7	ln $\gamma_\pm$	0.0536	0.0134	0.0083	0.0706	14
$(CH_3)_4NI$	0.25	ln $\gamma_\pm$	0.0036	0.0034	0.0004	0.0456	13
$(C_2H_5)_4NCl$	9	ln $\gamma_\pm$	0.0470	0.0395	0.0439	0.0726	13
$(C_2H_5)_4NBr$	12	ln $\gamma_\pm$	0.0777	0.0656	0.0736	0.0993	13
$(C_2H_5)_4NF$	5.5	ln $\gamma_\pm$	0.0301	0.0114	0.0137	0.0690	15
$(C_2H_5)_4NI$	1.9	ln $\gamma_\pm$	0.0573	0.0222	0.0174	0.0406	13
$(C_3H_7)_4NBr$	9	ln $\gamma_\pm$	0.0676	0.0676	0.0785	0.0721	13
$(C_3H_7)_4NI$	0.5	ln $\gamma_\pm$	0.0116	0.0021	0.0009	0.0299	13
$(C_4H_9)_4NCl$	15	ln $\gamma_\pm$	0.0378	0.0378	0.0529	0.1110	13
$(C_4H_9)_4NBr$	2.5	ln $\gamma_\pm$	0.0361	0.0146	0.0217	0.0359	14
$(C_4H_9)_4NF$	1.6	ln $\gamma_\pm$	0.0223	0.0054	0.0052	0.0399	14
$(HOCH_2CH_3)_4NBr$	6.5	ln $\gamma_\pm$	0.0624	0.0493	0.0302	0.0606	16
$(HOCH_2CH_3)_4NF$	6.5	ln $\gamma_\pm$	0.0119	0.0076	0.0032	0.0706	16
$(n\text{-}C_3H_7)_4NF$	5	ln $\gamma_\pm$	0.1131	0.0472	0.0410	0.0583	15
$(n\text{-}C_4H_9)_4NF$	1.6	ln $\gamma_\pm$	0.0223	0.0055	0.0052	0.0399	15
$HTcO_4$	5.5	ln $\gamma_\pm$	0.0392	0.0249	0.0254	0.0663	17
$HReO_4$	8	ln $\gamma_\pm$	0.0217	0.0178	0.0166	0.0720	17
ChCl	7.124	φ	0.0165	0.0122	0.0127		18
Bu_4NBr	1.0666	φ	0.0170	0.0025	0.0034		19
sec-Bu_4NBr	1.0325	φ	0.0160	0.0031	0.0034		19
iso-Bu_5NBr	1.0505	φ	0.0158	0.0034	0.0044		19
Bu_2Et_2NBr	0.9752	φ	0.0119	0.0015	0.0025		19
$BuEt_3NBr$	1.0052	φ	0.0146	0.0026	0.0034		19
NaGlu	4	ln $\gamma_\pm$	0.0174	0.0115	0.0064	0.0588	20
KGlu	3	ln $\gamma_\pm$	0.0121	0.0067	0.0026	0.0532	20
$MMANO_3$	9.5	ln $\gamma_\pm$	0.0368	0.0132	0.0081	0.0819	21
$DMANO_3$	6	ln $\gamma_\pm$	0.0272	0.015	0.0072	0.0717	21
$TMANO_3$	8.5	ln $\gamma_\pm$	0.0436	0.0345	0.0191	0.0693	21
TmGuCl	6.5	ln $\gamma_\pm$	0.0277	0.0187	0.0101	0.0695	22
TmGuBr	8.5	ln $\gamma_\pm$	0.0575	0.0505	0.0254	0.0679	22
GuF	9.3	ln $\gamma_\pm$	0.0454	0.0411	0.0144	0.0713	23
$NaCF_3SO_3$	5.3735	ln $\gamma_\pm$	0.0273	0.0182	0.0079	0.1159	24
NH_4Br	7.5	ln $\gamma_\pm$	0.0127	0.0122	0.0029	0.0923	25
LiMS	5.5	ln $\gamma_\pm$	0.0247	0.0098	0.0029	0.0853	26
NaMS	5.5	ln $\gamma_\pm$	0.0111	0.0098	0.0073	0.0802	26
KMS	6.5	ln $\gamma_\pm$	0.0117	0.0116	0.0028	0.0831	26
HTFMS	4.5	ln $\gamma_\pm$	0.0051	0.0033	0.0067	0.0723	26
LiTFMS	4.5	ln $\gamma_\pm$	0.0337	0.0041	0.0028	0.0826	26
NaTFMS	5.5	ln $\gamma_\pm$	0.0272	0.0124	0.0048	0.0931	26
KTFMS	11	ln $\gamma_\pm$	0.0221	0.0065	0.0096	0.0981	26
NH_4MS	4	ln $\gamma_\pm$	0.0112	0.0097	0.0033	0.0774	27
Me_4NMS	4	ln $\gamma_\pm$	0.0102	0.0100	0.0052	0.0783	27
Et_4NMS	4	ln $\gamma_\pm$	0.0134	0.0121	0.0085	0.0735	27
Bu_4NMS	4	ln $\gamma_\pm$	0.0582	0.0392	0.0152	0.1017	27
HES	4	ln $\gamma_\pm$	0.0137	0.007	0.0040	0.0854	27
LiES	4	ln $\gamma_\pm$	0.0235	0.0098	0.0052	0.0878	27
NaES	4	ln $\gamma_\pm$	0.0141	0.0065	0.0045	0.0893	27
KES	4	ln $\gamma_\pm$	0.0105	0.0096	0.0103	0.0791	27
NH_4ES	4	ln $\gamma_\pm$	0.0122	0.0109	0.0039	0.0828	27
Me_4NES	4	ln $\gamma_\pm$	0.0170	0.0134	0.0073	0.0794	27
Et_4NES	4	ln $\gamma_\pm$	0.0155	0.0152	0.0121	0.0741	27
Bu_4NES	4	ln $\gamma_\pm$	0.0610	0.040	0.0157	0.1076	27
H sul[A]	2.2	ln $\gamma_\pm$	0.0506	0.0278	0.0269	0.0505	28
Na sul[A]	4	φ	0.0187	0.0040	0.0068		28
K sul[A]	4.3	ln $\gamma_\pm$	0.0394	0.0091	0.0017	0.0702	28
Li sul[A]	6	ln $\gamma_\pm$	0.0098	0.0037	0.0274	0.1722	29
Me_4Gu sul[A]	6	ln $\gamma_\pm$	0.0116	0.0113	0.0040	0.0777	29
Picolinic acid	8	ln $\gamma_\pm$	0.0682	0.0682	0.0171	0.1692	30
Na sulf[B]	1.1	ln $\gamma_\pm$	0.0095	0.0092	0.0094	0.0377	28
K sulf[B]	3	ln $\gamma_\pm$	0.0168	0.0045	0.0053	0.0622	28
H Ben[C]	5	ln $\gamma_\pm$	0.0094	0.0032	0.0084	0.0802	31
Li Ben[C]	4.5	ln $\gamma_\pm$	0.0163	0.0042	0.0084	0.0873	31
Na Ben[C]	2.5	ln $\gamma_\pm$	0.0052	0.0046	0.0021	0.0627	31
Li 2,5-Dim[D]	3.5	ln $\gamma_\pm$	0.0160	0.0054	0.0041	0.0665	31
Na 2,5-Dim[D]	1	ln $\gamma_\pm$	0.0128	0.0046	0.0016	0.0442	31
H mes[E]	5.5	ln $\gamma_\pm$	0.1256	0.0970	0.0289	0.0828	31
Li mes[E]	4.5	ln $\gamma_\pm$	0.1546	0.1485	0.1424	0.0900	31
Na mes[E]	1	ln $\gamma_\pm$	0.0028	0.0016	0.0014	0.0534	31
Li p-eth[F]	4	ln $\gamma_\pm$	0.0552	0.0365	0.0288	0.083	31
Na p-eth[F]	2.5	ln $\gamma_\pm$	0.0279	0.0163	0.0210	0.0777	31
H p-tol[G]	5	ln $\gamma_\pm$	0.0439	0.0382	0.0039	0.0660	32

Table 2. Continued

electrolytes	mmax / mol·kg^{-1}	data	this work: two	this work: three	Pitzer	Bromley	refs.
H p-bth^{H}	5	ln $\gamma_{\pm}$	0.0918	0.0714	0.0142	0.0717	32
lysine	5.5	ln $\gamma_{\pm}$	0.0314	0.0303	0.0211	0.0912	33
arginine	1.6	ln $\gamma_{\pm}$	0.0268	0.0268	0.0100	0.1033	33
lysHCl	3.5	ln $\gamma_{\pm}$	0.0308	0.0228	0.0177	0.0434	33
ArgHCl	5	ln $\gamma_{\pm}$	0.0610	0.0445	0.0260	0.0561	33
HisHCl	0.7	ln $\gamma_{\pm}$	0.0160	0.0067	0.0011	0.0343	33
CCl_3COOK	8	ln $\gamma_{\pm}$	0.0341	0.0324	0.0230	0.1217	34
CF_3COOK	58	ln $\gamma_{\pm}$	0.0385	0.0384	0.1072	0.1915	35
CCl_3COONa	9	ln $\gamma_{\pm}$	0.0684	0.0288	0.0377	0.1385	34
CF_3COONa	12.5	ln $\gamma_{\pm}$	0.0930	0.0448	0.0333	0.1645	35
Et_4NI	1.4419	ln $\gamma_{\pm}$	0.0597	0.0196	0.0158	0.0476	36
$BuEt_3NI$	1.8108	ln $\gamma_{\pm}$	0.0382	0.0037	0.0272	0.1975	36
$HepEt_3NI$	3	ln $\gamma_{\pm}$	0.1953	0.0642	0.0552	0.1017	36
$HexEt_3NI$	2.344	ln $\gamma_{\pm}$	0.0907	0.0338	0.0013	0.0704	36
$PenEt_3NI$	1.6875	ln $\gamma_{\pm}$	0.0499	0.0097	0.0011	0.0630	36
$PrEt_3NI$	1.4619	ln $\gamma_{\pm}$	0.0253	0.0180	0.0301	0.1213	36
Average			***0.0367***	***0.0225***	***0.0173***	***0.0805***	
			1–2, 2–1 Electrolytes				
$(NH_4)_2B_{10}H_{10}$	3.5	ln $\gamma_{\pm}$	0.0101	0.0079	0.0122	0.1369	14
$Na_2B_{12}H_{12}$	1.6	ln $\gamma_{\pm}$	0.0167	0.0042	0.0087	0.0970	14
$(TH)_2SO_4$	6	ln $\gamma_{\pm}$	0.0215	0.0208	0.0086	0.1041	37
Na_2WO_4	2.5	ln $\gamma_{\pm}$	0.0330	0.0271	0.0237	0.1171	38
Na_2MoO_4	2.5	ln $\gamma_{\pm}$	0.0322	0.0270	0.0245	0.1110	38
H m-ben^{K}	1.6	ln $\gamma_{\pm}$	0.0225	0.0223	0.0156	0.1973	39
Li m-ben^{K}	2.5	ln $\gamma_{\pm}$	0.0298	0.0243	0.0224	0.2301	39
Na m-ben^{K}	3	ln $\gamma_{\pm}$	0.0265	0.0257	0.0269	0.2547	39
H 4,4′-bib^{L}	2	ln $\gamma_{\pm}$	0.0198	0.0168	0.0186	0.1280	39
Li 4,4′-bib^{L}	1.2	ln $\gamma_{\pm}$	0.0426	0.0380	0.0101	0.1643	39
Na 4,4′-bib^{L}	0.4	ln $\gamma_{\pm}$	0.0040	0.0039	0.0232	0.1349	39
H 1,14-dis^{M}	2	φ	0.0233	0.0153	0.0153	0.6727	39
Ba(OH)	0.2296	ln $\gamma_{\pm}$	0.0579	0.05	0.0279	0.1096	40
Average			***0.0261***	***0.0218***	***0.0183***	***0.1891***	
			3–1 Electrolytes				
$Al(ClO_4)_3$	3	ln $\gamma_{\pm}$	0.0676	0.0483	0.0795	0.4199	41
$Al(NO_3)_3$	3.1607	ln $\gamma_{\pm}$	0.0989	0.0598	0.0454	0.134	42
$Co(en)_3(ClO_4)_3$	0.5404	ln $\gamma_{\pm}$	0.0665	0.0424	0.0076	0.2193	43
$La(BrO_3)_3$	1.837	φ	0.0125	0.0052	0.0045		44
$Pr(BrO_3)_3$	1.805	φ	0.0135	0.0057	0.0047		44
$Nd(BrO_3)_3$	1.762	φ	0.0233	0.0097	0.0079		44
$Sm(BrO_3)_3$	1.883	φ	0.0201	0.0073	0.0066		44
$Eu(BrO_3)_3$	1.88	φ	0.0301	0.0032	0.0028		44
$Gd(BrO_3)_3$	1.882	φ	0.0356	0.0088	0.0082		44
$Tb(BrO_3)_3$	1.624	φ	0.0166	0.0094	0.0094		44
$Dy(BrO_3)_3$	1.791	φ	0.0296	0.0189	0.0190		44
$Ho(BrO_3)_3$	1.858	φ	0.0365	0.0168	0.0169		44
$Er(BrO_3)_3$	2.184	φ	0.0329	0.0097	0.0084		44
$Tm(BrO_3)_3$	2.05	φ	0.0246	0.0101	0.0100		44
$Yb(BrO_3)_3$	2.119	φ	0.0295	0.0146	0.0139		44
$Lu(BrO_3)_3$	2.16	φ	0.0523	0.0093	0.0093		44
$Y(BrO_3)_3$	1.836	φ	0.0269	0.0117	0.0115		44
$Eu(NO_3)_3$	6.3858	ln $\gamma_{\pm}$	0.0948	0.0283	0.0439	0.2606	45
$Y(NO_3)_3$	7.2103	ln $\gamma_{\pm}$	0.1685	0.0309	0.0719	0.3147	45
$La(NO_3)_3$	8.4591	ln $\gamma_{\pm}$	0.0712	0.0287	0.0916	0.3147	46
$Pr(NO_3)_3$	7.661	ln $\gamma_{\pm}$	0.0803	0.018	0.0728	0.2208	47
$Lu(NO_3)_3$	7.5961	ln $\gamma_{\pm}$	0.2268	0.0617	0.0782	0.2623	47
Average			***0.0572***	***0.0208***	***0.0284***	***0.2683***	
			4–1 Electrolytes				
$Pt(en)_3Cl_4$	0.33	ln $\gamma_{\pm}$	0.0603	0.0463	0.0103	0.255	48
$ThCl_4$	1.6	ln $\gamma_{\pm}$	0.0293	0.0287	0.0527	0.3709	49
Average			***0.0448***	***0.0375***	***0.0315***	***0.313***	
			3–2 Electrolytes				
$[Co(en)_3]_2(SO_4)_3$	1.844	ln $\gamma_{\pm}$	0.0942	0.0882	0.0798	0.5562	50
$Lu_2(SO_4)_3$	0.8942	ln $\gamma_{\pm}$	0.008	0.0078	0.0423	0.1999	51
Average			***0.0511***	***0.048***	***0.0611***	***0.3781***	
			2–2 Electrolytes				
$CaCrO_4$	1.112	ln $\gamma_{\pm}$	0.0286	0.0226	0.0071	0.1669	52
Overall Average			***0.0394***	***0.0226***	***0.0202***	***0.1551***	

with three parameters (b, S, n) (overall average 0.0226) is almost as good as the Pitzer model. Especially, it shows a smaller value of standard deviation (0.0208 and 0.0480) than the Pitzer model (0.0284 and 0.0611) in calculations of 3–1 and 3–2 electrolytes. Because the number of parameters in our model is the same as the Pitzer model, however, they have clear physical significance,

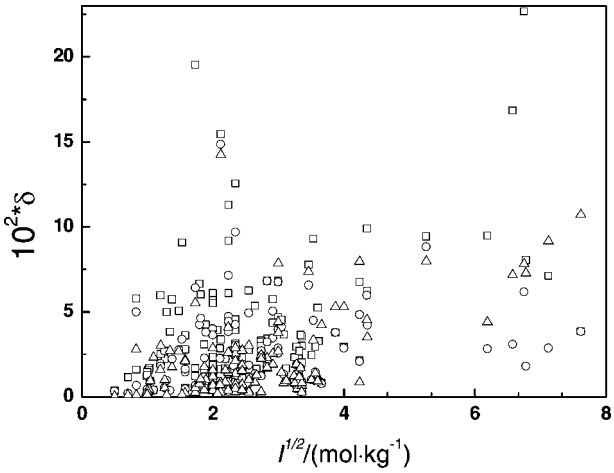

Figure 1. Standard deviations of different electrolytes calculated by various models at 298.15 K. □ and ○, the results of this work with two and three parameters, respectively; Δ, the calculated results with Pitzer the model.

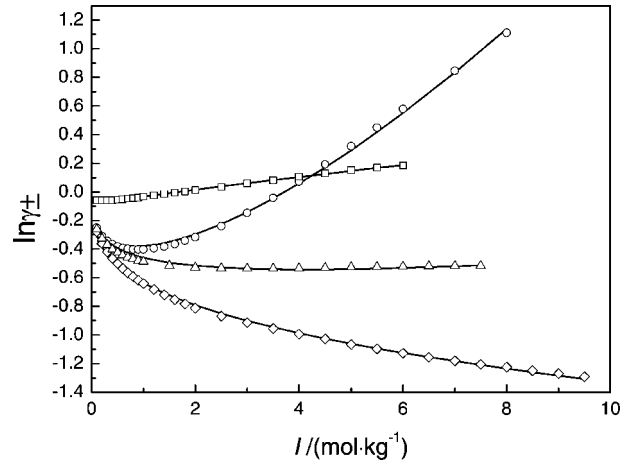

Figure 3. Comparison of calculated and experimental mean activity coefficient data for different 1–1 electrolytes at 298.15 K. The solid lines are calculated from the present work with three parameters. □, experimental data for Li sulfamate;[29] ○, $HReO_4$;[17] Δ, NH_4Br;[25] ◇, $MMANO_3$.[21]

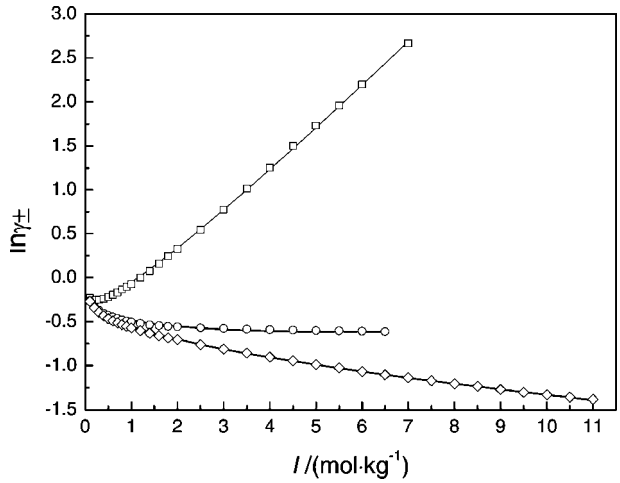

Figure 2. Comparison of calculated and experimental mean activity coefficient data for different 1–1 electrolytes at 298.15 K. The solid lines are calculated from the present work with three parameters. □, experimental data for $(CH_3)_4NF$;[14] ○, KMS;[26] ◇, KTFMS.[26]

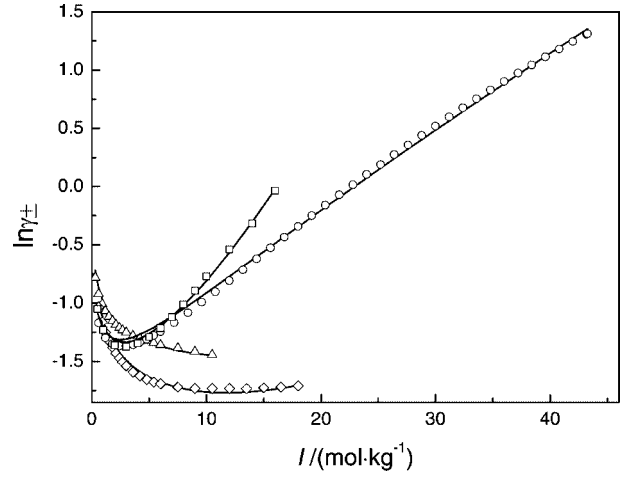

Figure 4. Comparison of calculated and experimental mean activity coefficient data for other types of electrolytes at 298.15 K. The solid lines are calculated from the present work with three parameters. □, experimental data for $ThCl_4$;[49] ○, $Y(NO_3)_3$;[45] Δ, $(NH_4)_2B_{10}H_{10}$;[14] ◇, $(TH)_2SO_4$.[37]

so one can find out that this model is on par with the Pitzer model for those electrolytes.

Figure 1 shows the distribution of standard deviations of all studied electrolytes calculated by the new model and Pitzer model, respectively. Most of the values were within 5 %. Some large deviations were calculated from the new model with two parameters (*b*, *S*), while the model with three parameters (*b*, *S*, *n*) showed a much smaller value. It implies that it is rational and beneficial to describe the electrolyte properties by regarding *n* as an adjustable parameter. For some electrolytes with very high ionic strength, such as $La(NO_3)_3$, $Pr(NO_3)_3$, and $Y(NO_3)_3$, etc., in Figure 1, the new model with three parameters is better than that of the Pitzer model. To some extent, this phenomenon indicates that the solvation effect plays an important role in the case of high ionic strength.

Figures 2 to 4 show the examples of calculated and experimental mean activity coefficients of different electrolyte solutions. These figures show that our model with three parameters is very suitable for calculating the mean activity coefficient. The same set of parameters regressed from the mean activity coefficients also can be used to predict the osmotic coefficient and water activity, as shown in Figures 5 to 7. The good agreement between the experimental and calculated data also clearly indicates that our model is a very useful tool to estimate the osmotic coefficient and water activity of these aqueous electrolyte solutions.

Conclusions

The TCPC model first proposed by Lin and Lee[10] for estimating the thermodynamic properties of strong electrolyte solutions was extended to correlate many complex aqueous electrolyte solutions over a large range of concentrations at 298.15 K. It can be reduced with two parameters (*b*, *S*) or three parameters (*b*, *S*, *n*), where *n* also can be regarded as an adjustable parameter to describe the distance between the ion and solvent molecules. We obtained the parameters of our model, and Pitzer and Bromley models and tabulated the standard deviations for each electrolyte, respectively. Results of standard deviations show that the modified model with two parameters is good but a little worse than the Pitzer model. Our model with three parameters is almost as good as the Pitzer model and even better than it in estimating the properties of 3–1 type electrolyte solutions. The Bromley model is acceptable for 1–1 type electrolyte solutions to some extent but unacceptable for correlating the properties of other types of electrolyte solutions. Some typical examples of comparisons between

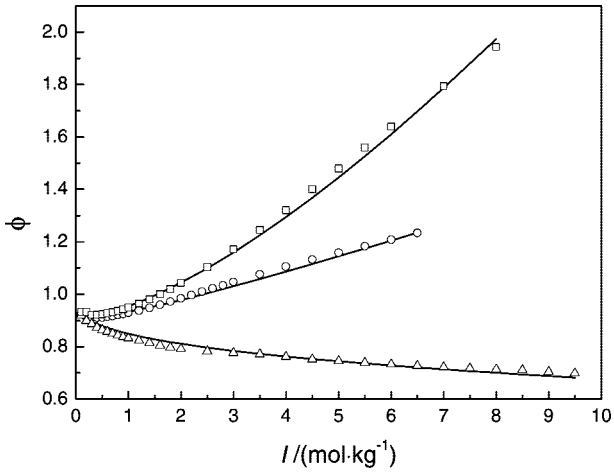

Figure 5. Comparison of calculated and experimental osmotic coefficient data for 1–1 electrolytes at 298.15 K. The solid lines are calculated from the present work with three parameters. □, experimental data for $HReO_4$;[17] ○, $(HOCH_2CH_3)_4NF$;[16] Δ, $MMANO_3$.[21]

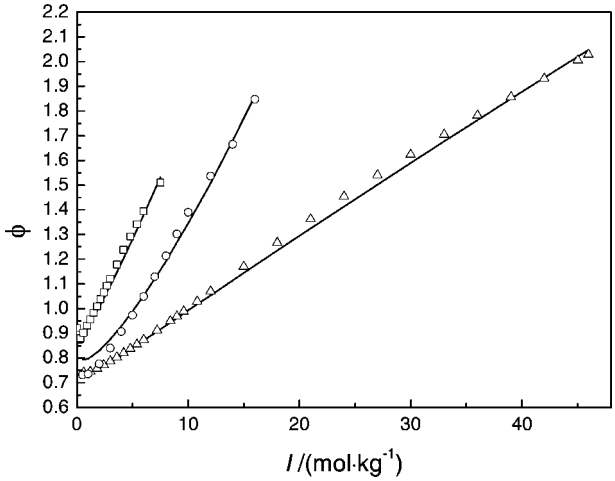

Figure 6. Comparison of calculated and experimental osmotic coefficient data for other types of electrolytes at 298.15 K. The solid lines are calculated from the present work with three parameters. □, experimental data for Li *m*-benzenedisulfonate;[39] ○, $ThCl_4$;[49] Δ, $MMANO_3$.[45]

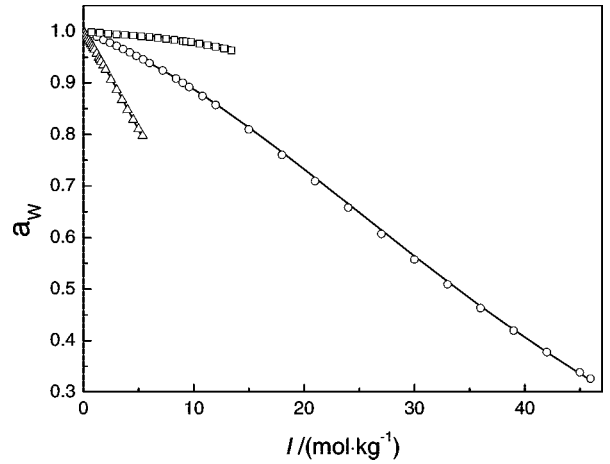

Figure 7. Comparison of calculated and experimental water activity for different electrolytes at 298.15 K. The solid lines are calculated from the present work with three parameters. □, experimental data for $Lu_2(SO_4)_3$;[51] ○, $Pr(NO_3)_3$; [47] Δ, $NaCF_3SO_3$.[24]

experimental data and calculated results with our model make it clear that our model is very good in estimating the mean activity coefficients, osmotic coefficients, and water activity of those complex aqueous electrolyte solutions.

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