Correlations

A Simple Two-Parameter Correlation Model for Aqueous Electrolyte Solutions across a Wide Range of Temperatures†

Xinlei Ge‡,§ and Xidong Wang*,||

Department of Physical Chemistry, University of Science and Technology Beijing, 100083, China, Department of Materials Science and Engineering, Royal Institute of Technology, SE 10044, Stockholm, Sweden, and College of Engineering, Peking University, Beijing 100871, China

In this paper, we focused on the correlation of the thermodynamic properties of aqueous solutions across a temperature range from (273.15 to 523.15) K by a simple two-parameter model. This model is based on the modified three-characteristic-parameter correlation (TCPC) model. The two parameters, *b*, distance of closest approach, and *S*, solvation parameter, represent the interactions between ions and ions-molecules, respectively. The results show that it can adequately correlate the activity coefficient and osmotic coefficient of the single electrolyte solutions. The set of two characteristic parameters for many electrolytes was obtained. We also obtained the temperature-dependent parameters for these electrolytes. In over 70 % of the cases, six to eight parameters are necessary for an electrolyte. Compared with the Pitzer model, our model also represented a good performance.

Introduction

In many industrial processes, such as chemical engineering, extraction, and distillation, etc., electrolyte solutions play an important role. The prediction of thermodynamic properties attracts much more attention, and many semiempirical models have been developed in the past century, such as the Bromley[1] model, Pitzer[2] equations, the hydration theory by Robinson and Stokes,[3,4] and the NRTL model,[5,6] etc. Meanwhile, many theories have been put forward based on the statistical mechanics with the rapid development of computer technology, focusing on three aspects, molecular simulation (Monte Carlo and molecular dynamics simulation), integral equation theory (Mean Spherical Approximation based theories,[7,8] etc.), and perturbation theory (SAFT,[9] etc.). Recently, a model without fitted parameters has been proposed,[10,11] but it is limited in the case of $\gamma \leq 1$, which is not sufficient to describe many strong electrolyte solutions. Although these theories are very useful for understanding the microscopic structure of electrolyte solutions, they have not been used widely for real solutions. The complex computation of a number of models also restricts their application and makes it very difficult to predict phase equilibrium. Moreover, these models usually still need adjustable parameters as the semiempirical models. Thus, it is still of central importance to develop the correlation models.

Lin and Lee[12] proposed a predictive three-characteristic-parameter correlation (TCPC) model for strong electrolytes in the low concentration range. Recently, we modified and extended this model to cover strong[13] and complex[14] aqueous electrolytes at 298.15 K across a wide concentration range, nonaqueous electrolytes at 298.15 K and other temperatures, and in mixed solvent systems.[15] We have showed that[13] the model with only two parameters (*b*, *S*) is enough to correlate the thermodynamic properties of aqueous solutions, especially for a concentration range that is not very high (generally below 6 mol·kg^{-1}). Since many real processes related with aqueous solutions are carried out at temperatures other than 298.15 K, the work here accounts for the temperature effects of this modified model with two parameters for correlation of mean activity coefficient and osmotic coefficient for aqueous electrolyte solutions. This work does not incorporate pressure effects because of the scarcity of relevant experimental data.

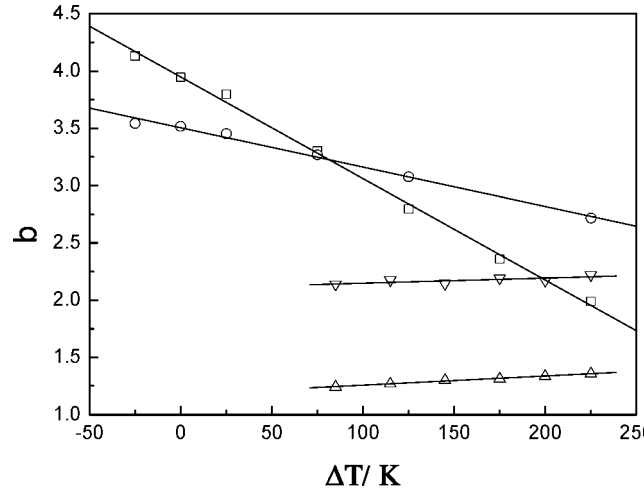

Figure 1. Linear change of the distance of closest approach parameter, *b*, against the temperature for some electrolytes. The solid lines are the results of linear fit. □, CsOH; ○, $MgCl_2$; △, KH_2PO_4; ▽, K_2HPO_4.

* Corresponding author. Tel.: +86 10 62334926. Fax: +86-10-62327283. E-mail address: xidong@coe.pku.edu.cn.
† Part of the special issue "Robin H. Stokes Festschrift".
‡ University of Science and Technology Beijing.
§ Royal Institute of Technology.
|| Peking University.

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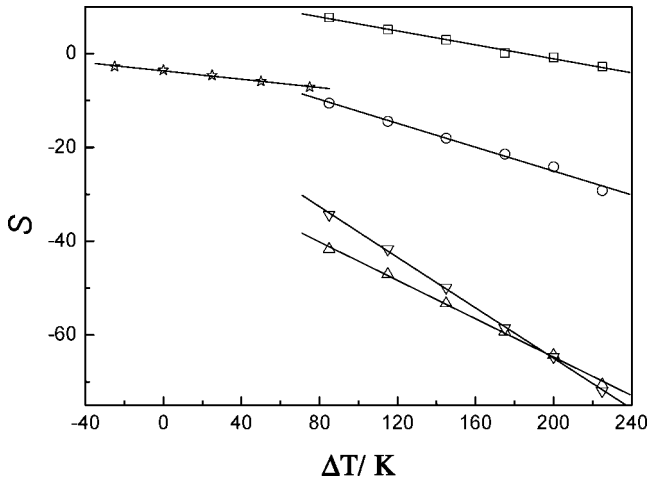

Figure 2. Linear change of the solvation parameter, *S*, against the temperature for some electrolytes. The solid lines are the results of linear fit. □, K_2HPO_4; ○, Na_2HPO_4; △, KH_2PO_4; ▽, NaH_2PO_4; ☆, $(NH_4)_2SO_4$.

Two-Parameter Model

An electrolyte molecule dissolved in the solvent would be dissociated into an anion and a cation. If the dissociation is complete, the potential energy of an ion can be simplified by considering the ion−ion interaction and ion−molecule interaction. Thus, the mean activity coefficient for a single salt is combined with the Pitzer long-range term and short-range solvation interaction

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^{\mathrm{PDH}} + \ln \gamma_{\pm}^{\mathrm{SV}} \tag{1}$$

The expression of the first term is

$$\ln \gamma_{\pm}^{\mathrm{PDH}} = -|z_+ z_-| A_\phi \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] \tag{2}$$

$$A_\phi = \frac{1}{3}(2\pi L d_{\mathrm{w}})^{1/2} \left(\frac{e^2}{DkT} \right)^{3/2} \tag{3}$$

The first term is the Pitzer−Debye−Hückel term, which can represent the ion−ion long-range interaction. Here, A_ϕ is the Debye−Hückel constant with a value of 0.392 at 298.15 K and *D* is the static dielectric constant at an absolute temperature *T* in Kelvin. *L* is Avogadro's number; d_{w} is the density of water; *k* is the Boltzmann 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 *b* is a distance parameter depending on the closest distance of approach of ions.

The second term is used to represent the solvation effects between ions and solvent molecules. In this model, the specific interaction between ions and molecules is described by Coulomb's law, for a cation

$$\Gamma_{\mathrm{cs}} = \frac{h_{\mathrm{cs}} z_+ e \mu}{s^2} \tag{4}$$

where *s* is the distance between an ion and a solvent molecule. μ is the dipole moment of solvent, and h_{cs} is a proportional parameter. *s* is assumed to be inversely proportional to the ionic strength of solution

$$s = \beta_+ I^{-n} \tag{5}$$

where β_+ and *n* can be determined from experimental data.

The dimensionless potential is defined as

$$\Phi_{\mathrm{cs}} = e\Gamma_{\mathrm{cs}}/kT = h_{\mathrm{cs}} z_+ \left(\frac{e^2 \mu}{\beta_+^2 kT} \right) I^{2n} \tag{6}$$

A similar expression can be obtained for an anion. Then, the charging process can be carried out,[13] and the final expression of this term is the combination of anion−molecule interaction and cation−molecule interaction

$$\ln \gamma_{\pm}^{\mathrm{SV}} = \frac{S}{T} \frac{I^{2n}}{\upsilon_+ + \upsilon_-} \tag{7}$$

Here, *S* is defined as the solvation parameter. υ_+ and υ_- are the stoichiometric coefficients of the cation and anion, respectively.

And, the osmotic coefficient, Φ, can be calculated by

$$\phi = 1 - |z_+ z_-| A_\phi \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{S}{T(\upsilon_+ + \upsilon_-)} \frac{2n}{2n+1} I^{2n} \tag{8}$$

The activity of the solvent can be calculated as

$$\ln a_{\mathrm{s}} = -(\upsilon m M_{\mathrm{S}}/1000) \cdot \phi \tag{9}$$

In this model, (*b*, *S*, *n*) are the adjustable parameters. *b* is the distance of the closest approach parameter, which represents the closest distance between ions; *S* is the solvation parameter, which can describe the interactions between ions and solvent molecules including solvation effect or some kind of association effect of ions; and *n* is distance parameter related to the distance between the ion and solvent molecule. We have showed that *n* can be regarded as a constant, 0.645, in the case of a concentration range that is not very high (generally < 6 mol·kg^{-1}). Therefore, the model can be simplified to be a two-parameter model.

The parameters for the electrolyte solutions at different temperatures can be easily regressed from the literature data by the least-squares method with the application of MATLAB software. The objective functions are listed below

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

$$\delta = \left[\sum_i (\phi^{\mathrm{exptl}} - \phi^{\mathrm{calcd}})^2 / n_p \right]^{1/2} \tag{10}$$

After the characteristic parameters (*b*, *S*) are obtained, we can consider them to be simple polynomial functions. Then, the temperature-dependent parameters can be obtained.

$$b(T/\mathrm{K}) = b_0 + b_1 \cdot (\Delta T/\mathrm{K}) + b_2 \cdot (\Delta T/\mathrm{K})^2 + b_3 \cdot (\Delta T/\mathrm{K})^3 + b_4 \cdot (\Delta T/\mathrm{K})^4 \tag{11}$$

$$S(T/\mathrm{K}) = S_0 + S_1 \cdot (\Delta T/\mathrm{K}) + S_2 \cdot (\Delta T/\mathrm{K})^2 + S_3 \cdot (\Delta T/\mathrm{K})^3 + S_4 \cdot (\Delta T/\mathrm{K})^4 \tag{12}$$

In the above equations, $\Delta T = T - T_{\mathrm{r}}$; $T_{\mathrm{r}} = 298.15$ K; and b_i and S_i are the temperature-dependent parameters.

Results and Discussion

To obtain the parameters across a wide range of temperatures, A_Φ should be carefully determined. Pitzer et al.[16,17] recommended the values across a wide range of temperatures, and we can also calculate the values according to the functions proposed by Spencer et al.[18] and Moller[19] below or above 25 °C, respectively. During the optimization process, the experimental data, usually osmotic coefficient data, were employed to regress the parameters. In some cases, to cover a wider temperature range, the recommended mean activity coefficient data in the literature were used. The data sources are also shown in Tables 1 and 2.

Table 1. Calculated Parameters for 1−1 Type Electrolyte Solutions in a Temperature Range of (273.15 to 523.15) K

T/K	Mmax/mol·kg^{-1}	data	b	S	100·δ	refs
		HBr				
273.15	5.551	$\gamma_\pm$	3.8727	136.1593	4.65	20
283.15	5.551	$\gamma_\pm$	3.9613	138.0095	4.97	20
293.15	5.551	$\gamma_\pm$	4.0759	139.2532	5.20	20
298.15	5.551	$\gamma_\pm$	4.1204	139.8130	5.29	20
303.15	5.551	$\gamma_\pm$	4.1583	140.2200	5.33	20
313.15	5.551	$\gamma_\pm$	4.2046	140.9725	5.56	20
323.15	5.551	$\gamma_\pm$	4.2968	141.5627	5.75	20
333.15	5.551	$\gamma_\pm$	4.2759	142.6964	5.94	20
343.15	5.551	$\gamma_\pm$	4.2161	143.5410	6.48	20
		KCl				
273.15	4.0	Φ	2.6809	2.5679	1.51	21
283.15	4.0	$\gamma_\pm$	2.4142	7.8086	2.29	22
293.15	4.0	$\gamma_\pm$	2.5439	9.5570	2.07	22
298.15	4.0	$\gamma_\pm$	2.7588	7.1139	3.53	22
303.15	4.286	Φ	0.8534	28.0495	3.24	23
313.15	4.286	Φ	1.1532	31.7091	3.75	23
323.15	4.286	Φ	1.4285	29.0971	1.74	23
333.15	4.286	Φ	1.3714	33.1968	2.17	23
343.15	4.286	Φ	1.0195	42.1780	2.65	23
		LiCl				
273.15	6.0	Φ	4.8289	89.8136	0.21	24
298.15	6.0	Φ	4.9833	90.2852	0.27	24
323.15	6.0	Φ	4.9539	89.8484	0.35	24
348.15	6.0	Φ	4.8369	88.3053	0.39	24
373.15	6.0	Φ	4.6939	86.3223	0.45	24
		NaCl				
273.15	6.0	Φ	2.7351	31.9156	1.65	25
298.15	6.0	Φ	3.4933	37.2231	0.82	25
323.15	6.0	Φ	3.9455	40.3212	0.50	25
348.15	6.0	Φ	4.1673	41.5132	0.50	25
373.15	6.0	Φ	4.2989	41.0540	0.52	25
398.15	6.0	Φ	4.6409	43.8045	0.52	25
423.15	6.0	Φ	4.3478	35.9084	0.47	25
448.15	6.0	Φ	4.2622	31.4942	0.53	25
473.15	6.0	Φ	4.0767	26.0093	0.72	25
		NaI				
283.15	10	Φ	62.4060	55.1031	0.94	26
298.15	10	Φ	50.8194	55.5901	1.25	26
303.15	8.398	Φ	5.7585	64.4666	4.82	23
313.15	8.398	Φ	9.3261	64.9080	4.81	23
323.15	8.398	Φ	13.2722	66.1042	4.79	23
333.15	8.398	Φ	10.2185	68.7137	4.57	23
343.15	8.398	Φ	9.0945	71.1222	4.22	23
		NaBr				
283.15	9	Φ	4.5869	43.3425	1.11	26
298.15	9	Φ	5.5285	45.6321	1.40	26
303.15	7.981	Φ	3.9534	54.9917	4.72	23
313.15	7.981	Φ	5.5350	52.7238	3.28	23
323.15	7.981	Φ	8.6743	50.4853	1.76	23
333.15	7.981	Φ	8.3545	51.1411	1.62	23
343.15	7.981	Φ	21.7588	47.5182	2.48	23
		KF				
283.15	12	Φ	2.9112	39.4912	1.05	26
298.15	12	Φ	3.7159	39.2315	1.31	26
323.15	12	Φ	4.7513	36.6802	1.68	26
348.15	12	Φ	5.0830	32.9880	1.75	26
		CsI				
303.15	2.595	Φ	0.3569	101.1195	2.07	23
313.15	2.595	Φ	5.1994	−12.9826	1.68	23
323.15	2.595	Φ	4.1522	−6.1549	1.45	23
333.15	2.595	Φ	1.8971	20.6377	1.34	23
343.15	2.595	Φ	2.5754	12.6945	1.16	23
		CsCl				
303.15	8.590	Φ	58.4807	3.7779	9.69	23
313.15	8.590	Φ	23.5146	4.2934	7.20	23
323.15	8.590	Φ	10.8165	4.6792	4.11	23
333.15	8.590	Φ	8.8908	6.0260	3.30	23
343.15	8.590	Φ	5.9827	9.3979	1.81	23
		KI				
303.15	5.648	Φ	0.8024	36.6254	5.44	23
313.15	5.648	Φ	1.0375	36.6624	1.36	23
323.15	5.648	Φ	1.0906	47.1263	2.47	23
333.15	5.648	Φ	1.4450	44.1605	2.44	23
343.15	5.648	Φ	2.0721	40.0792	1.39	23
		RbCl				
303.15	6.949	Φ	2.0117	27.4371	2.56	23
313.15	6.949	Φ	2.2731	21.5584	2.11	23
323.15	6.949	Φ	2.3519	18.8883	1.57	23
333.15	6.949	Φ	2.4336	18.9875	1.46	23
343.15	6.949	Φ	2.5335	20.1707	0.99	23
		LiOH				
273.15	5.0	ln $\gamma_\pm$	1.7792	7.3501	3.29	27
298.15	5.0	ln $\gamma_\pm$	1.9026	6.5601	2.85	27
323.15	5.0	ln $\gamma_\pm$	1.8583	−0.8693	3.07	27
373.15	5.0	ln $\gamma_\pm$	1.6364	−22.8155	4.39	27
423.15	5.0	ln $\gamma_\pm$	1.4363	−48.1512	6.24	27
473.15	5.0	ln $\gamma_\pm$	1.2831	−72.6477	8.27	27
523.15	5.0	ln $\gamma_\pm$	1.1691	−93.2840	10.44	27
		NaOH				
273.15	17	$\log_{10}$	2.5678	58.4605	7.70	36
283.15	17	$\log_{10}$	3.0013	57.1262	8.02	36
293.15	17	$\log_{10}$	3.2269	55.8287	7.31	36
303.15	17	$\log_{10}$	3.5161	54.1050	7.20	36
313.15	17	$\log_{10}$	3.7333	52.1232	7.13	36
323.15	17	$\log_{10}$	3.8769	49.8406	7.11	36
333.15	17	$\log_{10}$	3.9069	47.3185	7.16	36
343.15	17	$\log_{10}$	3.8571	44.4792	7.29	36
373.15	5.0	ln $\gamma_\pm$	3.0885	44.4956	1.29	27
423.15	5.0	ln $\gamma_\pm$	2.7801	29.5707	2.08	27
473.15	5.0	ln $\gamma_\pm$	2.4196	11.1331	3.24	27
523.15	5.0	ln $\gamma_\pm$	2.0693	−7.8281	4.69	27
		KOH				
273.15	5.0	ln $\gamma_\pm$	3.3361	79.8015	0.72	27
298.15	5.0	ln $\gamma_\pm$	3.5361	83.6601	0.97	27
323.15	5.0	ln $\gamma_\pm$	3.4777	78.4521	1.09	27
373.15	5.0	ln $\gamma_\pm$	3.0680	61.1378	1.16	27
423.15	5.0	ln $\gamma_\pm$	2.6870	46.9960	1.88	27
473.15	5.0	ln $\gamma_\pm$	2.3456	37.6203	2.99	27
523.15	5.0	ln $\gamma_\pm$	2.0066	24.3514	4.50	27
		CsOH				
273.15	5.0	ln $\gamma_\pm$	4.1316	80.5086	0.96	27
298.15	5.0	ln $\gamma_\pm$	3.9444	87.8493	0.37	27
323.15	5.0	ln $\gamma_\pm$	3.7992	91.3475	0.65	27
373.15	5.0	ln $\gamma_\pm$	3.3019	89.9786	0.97	27
423.15	5.0	ln $\gamma_\pm$	2.7958	81.4170	1.63	27
473.15	5.0	ln $\gamma_\pm$	2.3604	69.3636	2.81	27
523.15	5.0	ln $\gamma_\pm$	1.9885	57.0392	4.37	27
		LiBr				
273.15	5.0	ln $\gamma_\pm$	4.6441	99.9234	1.20	28
298.15	5.0	ln $\gamma_\pm$	3.8479	115.0719	0.65	28
323.15	5.0	ln $\gamma_\pm$	3.8870	120.8577	0.55	28
373.15	5.0	ln $\gamma_\pm$	3.9116	120.7532	0.75	28
423.15	5.0	ln $\gamma_\pm$	3.5892	118.2699	0.91	28
473.15	5.0	ln $\gamma_\pm$	3.1875	113.2435	1.28	28
523.15	5.0	ln $\gamma_\pm$	2.8722	92.7278	1.81	28
		NaBr				
273.15	5.0	ln $\gamma_\pm$	2.9122	38.2271	1.64	28
298.15	5.0	ln $\gamma_\pm$	3.2193	50.8820	0.85	28
323.15	5.0	ln $\gamma_\pm$	3.5135	58.8024	0.82	28
373.15	5.0	ln $\gamma_\pm$	3.7005	67.6177	0.99	28
423.15	5.0	ln $\gamma_\pm$	3.6387	71.1886	1.11	28
473.15	5.0	ln $\gamma_\pm$	3.6807	69.4628	1.04	28
523.15	5.0	ln $\gamma_\pm$	3.9538	59.2719	0.61	28
		KBr				
273.15	5.0	ln $\gamma_\pm$	2.4056	9.5572	7.36	28
298.15	5.0	ln $\gamma_\pm$	2.7140	14.7324	1.51	28
323.15	5.0	ln $\gamma_\pm$	2.9724	21.1764	1.13	28
373.15	5.0	ln $\gamma_\pm$	3.2810	29.2771	0.99	28
423.15	5.0	ln $\gamma_\pm$	3.4593	30.9879	0.96	28
473.15	5.0	ln $\gamma_\pm$	3.4008	31.0389	1.12	28
523.15	5.0	ln $\gamma_\pm$	3.0759	29.6979	1.70	28
		CsBr				
273.15	5.0	ln $\gamma_\pm$	1.4277	6.9383	4.24	28
298.15	5.0	ln $\gamma_\pm$	1.7711	3.8953	3.28	28
323.15	5.0	ln $\gamma_\pm$	2.0749	4.6337	2.70	28
373.15	5.0	ln $\gamma_\pm$	2.5368	8.1066	2.12	28
423.15	5.0	ln $\gamma_\pm$	2.7698	11.5103	2.00	28
473.15	5.0	ln $\gamma_\pm$	2.7733	13.6862	2.24	28
523.15	5.0	ln $\gamma_\pm$	2.6129	13.9502	2.81	28
		KH_2PO_4				
383.15	6.0	ln $\gamma_\pm$	1.2417	−41.7442	7.70	29
413.15	6.0	ln $\gamma_\pm$	1.2697	−47.0456	8.05	29
443.15	6.0	ln $\gamma_\pm$	1.3009	−53.2842	8.58	29
473.15	6.0	ln $\gamma_\pm$	1.3123	−59.3281	9.14	29
498.15	6.0	ln $\gamma_\pm$	1.3348	−64.2857	8.62	29
523.15	6.0	ln $\gamma_\pm$	1.3589	−70.6214	10.47	29
		NaH_2PO_4				
383.15	6.0	ln $\gamma_\pm$	1.4176	−34.4091	6.66	29
413.15	6.0	ln $\gamma_\pm$	1.3978	−41.7036	7.30	29
443.15	6.0	ln $\gamma_\pm$	1.3727	−49.8951	8.07	29
473.15	6.0	ln $\gamma_\pm$	1.3460	−58.5478	8.98	29
498.15	6.0	ln $\gamma_\pm$	1.3045	−64.6999	9.84	29
523.15	6.0	ln $\gamma_\pm$	1.3211	−71.9751	10.72	29
		$NaBF_4$				
288.15	7.6831	$\gamma_\pm$	1.6435	−24.5205	6.78	30
298.15	8.3168	$\gamma_\pm$	1.7657	−20.6774	5.68	30
308.15	8.8454	$\gamma_\pm$	2.8150	−17.4355	4.54	30
		$NaCF_3SO_3$				
298.15	5.3755	Φ	11.1243	29.6289	1.98	31
323.15	4.3070	Φ	8.6415	35.6951	1.26	31

The parameters for different electrolytes at various temperatures along with the standard deviation (100·δ) are listed in Tables 1 and 2. From these tables, one can see that the obtained parameters can fit the literature data very well, especially for

Table 2. Calculated Parameters for 1−2, 2−1, and 2−2 Type Electrolytes in a Temperature Range of (273.15 to 523.15) K

T/K	Mmax/mol·kg^{-1}	data	b	S	100·δ	refs	T/K	Mmax/mol·kg^{-1}	data	b	S	100·δ	refs
			K_2HPO_4							$SrCl_2$			
383.15	6.0	ln $\gamma_\pm$	2.1378	7.7022	4.62	29	273.15	4.0	ln $\gamma_\pm$	3.0166	71.9818	1.81	34
413.15	6.0	ln $\gamma_\pm$	2.1748	5.1177	4.81	29	298.15	4.0	ln $\gamma_\pm$	3.1867	76.4230	1.22	34
443.15	6.0	ln $\gamma_\pm$	2.1447	2.9577	5.28	29	323.15	4.0	ln $\gamma_\pm$	3.2768	77.6442	1.65	34
473.15	6.0	ln $\gamma_\pm$	2.1931	0.1277	5.54	29	373.15	4.0	ln $\gamma_\pm$	3.2699	72.1904	2.41	34
498.15	6.0	ln $\gamma_\pm$	2.1706	−0.7987	6.06	29	423.15	4.0	ln $\gamma_\pm$	3.1142	59.7810	2.28	34
523.15	6.0	ln $\gamma_\pm$	2.2217	−2.7911	6.50	29	473.15	4.0	ln $\gamma_\pm$	2.9161	45.3527	1.85	34
			Na_2HPO_4				523.15	4.0	ln $\gamma_\pm$	2.7524	33.9882	1.54	34
383.15	6.0	ln $\gamma_\pm$	1.9560	−10.5512	7.38	29				$SrBr_2$			
413.15	6.0	ln $\gamma_\pm$	1.9803	−14.4053	7.74	29	303.15	3.340	Φ	55.1553	87.2	14.27	23
443.15	6.0	ln $\gamma_\pm$	1.9742	−18.0717	8.36	29	313.15	3.340	Φ	22.9308	88.7044	7.97	23
473.15	6.0	ln $\gamma_\pm$	1.9696	−21.4245	9.16	29	323.15	3.340	Φ	9.1821	95.6548	4.00	23
498.15	6.0	ln $\gamma_\pm$	2.0005	−24.1546	9.75	29	333.15	3.340	Φ	6.6655	99.5809	2.96	23
523.15	6.0	ln $\gamma_\pm$	2.0435	−29.1891	9.66	29	343.15	3.340	Φ	11.2082	96.5980	1.94	23
			$(NH_4)_2SO_4$							SrI_2			
273.15	6.0	Φ	2.3530	−2.7826	9.19	32	303.15	4.156	Φ	274.268	98.1	2.45	23
298.15	6.0	Φ	2.5663	−3.5112	8.54	32	313.15	4.156	Φ	138.971	98.0	1.99	23
323.15	6.0	Φ	2.7133	−4.6322	8.26	32	323.15	4.156	Φ	53.8657	99.4666	1.48	23
348.15	6.0	Φ	2.7519	−5.9349	8.40	32	333.15	4.156	Φ	17.6510	103.0764	1.82	23
373.15	6.0	Φ	2.6950	−7.1232	9.02	32	343.15	4.156	Φ	13.3159	107.0393	2.55	23
			Cs_2SO_4							$MgCl_2$			
298.15	3.1082	Φ	2.5461	7.5931	5.47	33	273.15	4.0	ln $\gamma_\pm$	3.5408	109.7150	0.64	34
323.15	3.5095	Φ	2.7554	12.3828	4.83	33	298.15	4.0	ln $\gamma_\pm$	3.5159	110.9725	0.79	34
			Rb_2SO_4				323.15	4.0	ln $\gamma_\pm$	3.4535	110.2694	1.01	34
298.15	2.048	Φ	2.7200	−17.2628	5.18	33	373.15	4.0	ln $\gamma_\pm$	3.2694	107.4684	1.08	34
323.15	3.0	Φ	2.6891	−2.6365	5.40	33	423.15	4.0	ln $\gamma_\pm$	3.0764	101.7271	1.39	34
			Na_2SO_4				523.15	4.0	ln $\gamma_\pm$	2.7150	75.8845	2.80	34
273.15	1.5	Φ	1.9984	−45.8561	3.07	21				$BaCl_2$			
			H_2SO_4				273.15	4.0	ln $\gamma_\pm$	3.2272	27.4805	4.69	34
273.15	10.0	Φ	2.0955	28.4037	6.18	21	298.15	4.0	ln $\gamma_\pm$	3.3757	33.6801	5.18	34
			$CaCl_2$				323.15	4.0	ln $\gamma_\pm$	3.4279	34.9857	5.32	34
303.15	6.019	Φ	11.1224	76.3032	7.51	23	373.15	4.0	ln $\gamma_\pm$	3.3644	31.1592	4.66	34
313.15	6.019	Φ	26.0450	73.2034	6.98	23	423.15	4.0	ln $\gamma_\pm$	3.1464	22.7540	3.31	34
323.15	6.019	Φ	36.4503	71.0876	6.85	23	473.15	4.0	ln $\gamma_\pm$	2.8728	12.3727	2.18	34
333.15	6.019	Φ	24.7423	69.8590	6.50	23	523.15	4.0	ln $\gamma_\pm$	2.6566	4.2732	2.02	34
343.15	6.019	Φ	25.5616	67.7451	6.05	23				$BaBr_2$			
			$CaBr_2$				303.15	3.398	Φ	34.96	51.8	4.34	23
303.15	4.596	Φ	189.352	95.8806	3.90	23	313.15	3.398	Φ	13.6920	55.3570	1.70	23
313.15	4.596	Φ	58.7089	95.8565	3.15	23	323.15	3.398	Φ	6.6658	61.2786	2.17	23
323.15	4.596	Φ	16.6999	96.5706	3.67	23	333.15	3.398	Φ	5.9960	63.5930	2.71	23
333.15	4.596	Φ	10.1975	97.3547	3.36	23	343.15	3.398	Φ	8.6009	59.5986	2.83	23
343.15	4.596	Φ	6.8508	99.3077	2.94	23				$Ca(NO_3)_2$			
			CaI_2				273.15	20	ln $\gamma_\pm$	7.3638	9.8998	15.14	35
303.15	2.915	Φ	11.4604	74.5559	5.51	23	298.15	20	ln $\gamma_\pm$	10.1583	9.7236	13.65	35
313.15	2.915	Φ	3.7236	89.1967	3.80	23	323.15	20	ln $\gamma_\pm$	11.8637	9.2353	12.76	35
323.15	2.915	Φ	3.1165	93.7986	3.70	23	348.15	20	ln $\gamma_\pm$	11.9277	8.5124	12.20	35
333.15	2.915	Φ	2.9588	97.0670	2.85	23	373.15	20	ln $\gamma_\pm$	10.9057	7.6940	11.75	35
343.15	2.915	Φ	2.9472	98.9513	2.75	23	393.15	20	ln $\gamma_\pm$	9.7472	7.0784	11.35	35
										$MgSO_4$			
							273.15	3.0	Φ	2.4807	15.5310	5.47	21

1−1 type electrolytes in Table 1. However, some relative large deviations also can be found, such as NaOH, KH_2PO_4, and NaH_2PO_4 in Table 1, and Na_2HPO_4 and $Ca(NO_3)_2$ in Table 2. In our opinion, these deviations can be attributed to the following aspects:

First, this work is based on the species being the stoichiometric composition. For some salts, a number of complex ions can exist in the solution simultaneously, such as $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $H_4P_2O_8^{2-}$, etc., in NaH_2PO_4, KH_2PO_4, Na_2HPO_4, and K_2HPO_4. The present model is limited to describe the very complicated systems.

Second, the calculated standard deviations for asymmetric electrolytes shown in Table 2 are worse than 1−1 type electrolytes. As well-known, in PDH term, the electric potential of a charged cation in a uniform electric field is described by the Boltzmann distribution. The solvation term is also established on the Coulomb force between spherical particles. But for some asymmetric electrolytes, the size difference of its anion and cation could be very large, and the shape is highly nonspherical that the charge density of ions in the solution can no longer be described by the Boltzmann distribution. Thus, some large deviations may be obtained.

Finally, the assumption of complete dissociation of this model is accurate for strong electrolyte solutions or the solutions with low concentration. Thus, good results are obtained for 1−1 electrolytes. However, for the weak electrolytes or the solution with high ionic strength, it is less accurate due to incomplete dissociation of electrolyte molecules or the association of ions. This is the situation for $Ca(NO_3)_2$ ($I = 60$ mol·kg^{-1}). For LiCl, we found the deviation is over 25 % for a concentration up to 18.5 mol·kg^{-1}, but for a concentration below 6 mol·kg^{-1}, the correlation is very good, as shown in Table 1.

According to eqs 11 and 12, the temperature-dependent parameters for these electrolyte solutions, along with the corresponding correlation coefficients, can be obtained, as listed in Table 3. The fitting temperature range is the same as shown in Tables 1 and 2. The absence of a parameter value indicates that it is not important.

From Table 3, in 70 % of the cases, the change of (b, S) can be represented by a 2- or 3-order polynomial, which means six or eight parameters are sufficient to predict the thermodynamic properties of an electrolyte solution across a temperature range of (273.15 to 523.15) K in a concentration range of (0 to 20) mol·kg^{-1}. Furthermore, the distance of the closest approach

Table 3. Temperature-Dependent Parameters of the Simple Two-Parameter Model

system	b_0	b_1	b_2	b_3	b_4	R	S_0	S_1	S_2	S_3	S_4	R
HBr	4.11397	$9.36\cdot10^{-2}$	$-6.3022\cdot10^{-5}$	$-2.06821\cdot10^{-6}$		0.99117	139.78067	$9.454\cdot10^{-2}$	$-1.35\cdot10^{-3}$	$2.52303\cdot10^{-5}$		0.99867
LiCl	4.98132	$2.02\cdot10^{-3}$	$-1.41109\cdot10^{-4}$	$8.416\cdot10^{-7}$		0.99968	90.24089	$-1.48\cdot10^{-3}$	$-6.87486\cdot10^{-4}$			0.99694
KCl[a]	2.75857	$5.279\cdot10^{-2}$	$1.99\cdot10^{-3}$			1.00000	7.1139	$-7.9008\cdot10^{-1}$	$-6.565\cdot10^{-2}$	$-1.07\cdot10^{-3}$		1.00000
KCl[b]	$6.9151\cdot10^{-1}$	$2.935\cdot10^{-2}$	$5.20946\cdot10^{-4}$			0.99260	15.76	3.59526	$-2.6144\cdot10^{-1}$	$0.71\cdot10^{-2}$	$-6.17229\cdot10^{-5}$	1.00000
NaCl	3.40479	$2.078\cdot10^{-2}$	$-9.8779\cdot10^{-5}$			0.97139	36.98427	$1.7062\cdot10^{-1}$	$-1.35\cdot10^{-3}$			0.94524
NaI	10.88152	−1.88306	$2.0332\cdot10^{-1}$	$-6.67\cdot10^{-3}$	$6.79492\cdot10^{-5}$	1.00000	64.40706	$-1.981\cdot10^{-2}$	$3.82\cdot10^{-3}$			0.99476
NaBr	11.3848	−2.51339	2.4429·10−1	−8.24·10−3	$9.25\cdot10^{-5}$	1.00000	52.49666	$9.6496\cdot10^{-1}$	$-1.1126\cdot10^{-1}$	$3.82\cdot10^{-3}$	$-4.18246\cdot10^{-5}$	1.00000
KF	5.535	$1.3186\cdot10^{-1}$	$1.01\cdot10^{-3}$	$-5.03166\cdot10^{-5}$		0.99899	52.7238	$-1.3254\cdot10^{-1}$	$1.42\cdot10^{-3}$	$1.19093\cdot10^{-5}$		0.99760
CsI	−5.58114	1.48055	$-6.196\cdot10^{-2}$	$7.35258\cdot10^{-4}$		0.99971	221.81111	−29.64033	1.13883	$-1.297\cdot10^{-2}$		0.99634
CsCl	87.98091	−6.8449	$1.9881\cdot10^{-1}$	$-1.94\cdot10^{-3}$		1.00000	3.13829	$1.6701\cdot10^{-1}$	$-8.7\cdot10^{-3}$	$1.79567\cdot10^{-4}$		1.00000
KI	$6.1228\cdot10^{-1}$	$4.887\cdot10^{-2}$	$-2.07\cdot10^{-3}$	$3.78917\cdot10^{-5}$		0.99617	57.86263	−6.6409	0.55509	$-1.603\cdot10^{-2}$	$1.50712\cdot10^{-4}$	1.00000
RbCl	1.80334	$4.916\cdot10^{-2}$	$-1.48\cdot10^{-3}$	$1.67333\cdot10^{-5}$		0.99736	32.07407	−1.04613	$2.535\cdot10^{-2}$	$-1.7705\cdot10^{-4}$		0.99956
LiOH	1.88813	$1.2\cdot10^{-3}$	$-1.0014\cdot10^{-4}$	$6.44442\cdot10^{-7}$	$-1.27278\cdot10^{-9}$	0.99863	3.85717	$-3.3424\cdot10^{-1}$	$-4.84953\cdot10^{-4}$			0.99296
NaOH	3.50344	$2.405\cdot10^{-2}$	$-5.74077\cdot10^{-4}$	$3.50262\cdot10^{-6}$	$-6.89876\cdot10^{-9}$	0.96952	54.63047	$-1.3264\cdot10^{-1}$	$-6.39214\cdot10^{-4}$			0.99368
KOH	3.46454	$6.83455\cdot10^{-4}$	$-8.2197\cdot10^{-5}$	$2.26049\cdot10^{-7}$		0.99038	80.6128	$-1.1321\cdot10^{-1}$	$-1.85\cdot10^{-3}$	$5.61517\cdot10^{-6}$		0.99008
CsOH	3.94898	$-8.87\cdot10^{-3}$				0.99719	87.64795	2.0796	$-2.72\cdot10^{-3}$	$5.29566\cdot10^{-6}$		0.99981
LiBr	3.98803	$-1.422\cdot10^{-2}$	$3.29266\cdot10^{-4}$	$-2.62294\cdot10^{-6}$	$5.97146\cdot10^{-9}$	0.99001	114.83386	$3.8989\cdot10^{-1}$	$-0.69\cdot10^{-2}$	$4.53479\cdot10^{-5}$	$-1.08168\cdot10^{-7}$	0.99965
NaBr	3.26271	$1.192\cdot10^{-2}$	$-1.0821\cdot10^{-4}$	$3.06138\cdot10^{-7}$		0.99508	49.51086	$3.5412\cdot10^{-1}$	-1.38810^{-3}			0.99088
KBr	2.71075	$1.12\cdot10^{-2}$	$-4.22973\cdot10^{-5}$			0.99771	15.81624	$2.4606\cdot10^{-1}$	$-1.17\cdot10^{-3}$	$1.55773\cdot10^{-6}$		0.99417
CsBr	1.77779	$1.314\cdot10^{-2}$	$-4.20176\cdot10^{-5}$			0.99967	4.32642	$-4.089\cdot10^{-2}$	$1.97\cdot10^{-3}$	$-1.21395\cdot10^{-5}$	$2.23058\cdot10^{-8}$	0.99580
KH_2PO_4	1.17633	$-8.04554\cdot10^{-4}$				0.99006	−23.78166	$-2.0489\cdot10^{-1}$				0.99778
NaH_2PO_4	2.40057	$-2.941\cdot10^{-2}$	$3.21762\cdot10^{-4}$	$-1.53901\cdot10^{-6}$	$2.64501\cdot10^{-9}$	0.99086	−11.10104	$-2.6944\cdot10^{-1}$				0.00939
$NaBF_4$	1.7657	$5.858\cdot10^{-2}$	$4.64\cdot10^{-3}$			1.00000	−20.8778	$3.5425\cdot10^{-1}$				0.99880
$NaCF_3SO_3$	11.1243	$-9.931\cdot10^{-2}$				1.00000	29.6289	$2.4265\cdot10^{-1}$				1.00000
K_2HPO_4	2.10158	$4.58416\cdot10^{-4}$				0.77805	13.76789	$-7.438\cdot10^{-2}$				0.99617
Na_2HPO_4	1.5645	$9.01\cdot10^{-3}$	$-6.44643\cdot10^{-5}$	$1.50799\cdot10^{-7}$		0.99002	$4.261\cdot10^{-1}$	$-1.2736\cdot10^{-1}$				0.99567
$(NH_4)_2SO_4$	2.57528	$7.19\cdot10^{-3}$	$-7.41486\cdot10^{-5}$			0.99879	−3.68633	$-4.442\cdot10^{-2}$				0.99079
Cs_2SO_4	2.5461	$8.37\cdot10^{-3}$				1.00000	7.5931	$1.9159\cdot10^{-1}$				1.00000
Rb_2SO_4	2.72	$-1.24\cdot10^{-3}$				1.00000	−17.2628	$5.8505\cdot10^{-1}$				1.00000
$CaCl_2$	21.74931	−4.53065	$5.7734\cdot10^{-1}$	$-2.034\cdot10^{-2}$	$2.17652\cdot10^{-4}$	1.00000	77.62272	$-3.0671\cdot10^{-1}$	$2.04\cdot10^{-3}$			0.99091
$CaBr_2$	298.55896	−25.42994	$7.4145\cdot10^{-1}$	$-7.12\cdot10^{-3}$		0.99974	96.12755	$-6.02\cdot10^{-2}$	$2.87\cdot10^{-3}$			0.99229
$BaBr_2$	52.02209	−3.93924	$1.0719\cdot10^{-1}$	$-9.13925\cdot10^{-4}$		0.99944	51.83715	$-2.0293\cdot10^{-1}$	$4.084\cdot10^{-2}$	$-7.22783\cdot10^{-4}$		0.99829
$SrBr_2$	72.80094	−4.06897	$6.055\cdot10^{-2}$			0.99183	89.82275	$-8.5515\cdot10^{-1}$	$6.865\cdot10^{-2}$	$-1.03\cdot10^{-3}$		0.99736
SrI_2	354.77474	−17.53276	$2.2201\cdot10^{-1}$			0.99923	98.51508	$-1.372\cdot10^{-1}$	$7.33\cdot10^{-3}$			0.99624
CaI_2	21.83374	−2.7114	$1.4288\cdot10^{-1}$	$-3.24\cdot10^{-3}$	$2.65708\cdot10^{-5}$	1.00000	63.26001	2.63251	$-7.327\cdot10^{-2}$	$7.21233\cdot10^{-4}$		0.99713
$SrCl_2$	3.18463	$5.01\cdot10^{-3}$	$-6.13325\cdot10^{-5}$	$1.35848\cdot10^{-7}$		0.99969	76.52916	$1.1223\cdot10^{-1}$	$-2.76\cdot10^{-3}$	$6.32137\cdot10^{-6}$		0.99997
$MgCl_2$	3.50524	$-3.44\cdot10^{-3}$				0.99105	110.65789	$2.132\cdot10^{-2}$	$7.79084\cdot10^{-4}$			0.99912
$BaCl_2$	3.36987	$3.92\cdot10^{-3}$	$-6.36047\cdot10^{-5}$	$1.42601\cdot10^{-7}$		0.99989	32.96984	$1.3662\cdot10^{-1}$	$-2.48\cdot10^{-3}$	$5.80477\cdot10^{-6}$		0.99862
$Ca(NO_3)_2$	10.14301	$8.493\cdot10^{-2}$	$-9.55258\cdot10^{-4}$			0.99124	9.65305	−1.518·10−2	$-1.32317\cdot10^{-4}$			0.99664

[a] Temperature range of 273.15 K to 298.15 K. [b] Temperature range of 303.15 K to 343.15 K.

Table 4. Standard Deviations from the Simple Two-Parameter Model[a]

system	Mmax / mol·kg^{-1}	temperature range / K	present 100·δ	Mmax / mol·kg^{-1}	temperature range / K	Pitzer 100·δ	M-Pitzer 100·δ
HBr	5.551	273.15 to 343.15	5.49	1.000	273.15 to 333.15	1.5	3.2
KCl	5.1776	273.15 to 343.15	2.33	4.000	273.15 to 313.15	1.7	0.78
NaCl	6.000	273.15 to 473.15	0.78	4.000	273.15 to 473.15	2.0	0.25
NaI	10.000	283.15 to 343.15	3.91	8.398	298.15 to 343.15	1.1	3.2
NaBr	9.000	283.15 to 343.15	2.49	7.981	298.15 to 498.15	2.9	2.6
KF	12.000	283.15 to 348.15	1.48				
CsI	2.595	303.15 to 343.15	1.57	2.595	298.15 to 343.15	3.0	3.0
CsCl	8.590	303.15 to 343.15	5.95	8.590	298.15 to 343.15	5.2	8.7
KI	5.648	303.15 to 343.15	1.62	5.648	298.15 to 343.15	3.8	5.3
RbCl	6.949	303.15 to 343.15	1.82	6.949	298.15 to 343.15	3.0	3.0
LiOH	5.0	273.15 to 523.15	5.92	7.219	298.15 to 473.15	0.28	3.5
NaOH	17.0	273.15 to 523.15	6.91	7.298	273.15 to 623.15	7.8	7.2
KOH	5.0	273.15 to 523.15	2.24	17.000	273.15 to 623.15	27.0	25.0
CsOH	5.0	273.15 to 523.15	2.10	5.921	298.15 to 473.15	4.1	4.2
LiBr	5.0	273.15 to 523.15	0.97	5.387	298.15 to 473.15	2.4	5.4
LiCl	6.0	273.15 to 373.15	0.34				
NaBr	5.0	273.15 to 523.15	0.79	7.981	298.15 to 498.15	2.9	2.6
KBr	5.0	273.15 to 523.15	3.02	7.434	273.15 to 498.15	7.3	7.1
CsBr	5.0	273.15 to 523.15	2.02	8.277	273.15 to 523.15	2.3	1.7
KH_2PO_4	6.0	383.15 to 523.15	8.81				
NaH_2PO_4	6.0	383.15 to 523.15	7.72				
$NaBF_4$	8.8454	288.15 to 308.15	5.72				
$NaCF_3SO_3$	5.3755	298.15 to 323.15	1.66				
K_2HPO_4	6.0	383.15 to 523.15	5.51				
Na_2HPO_4	6.0	383.15 to 523.15	8.72				
$(NH_4)_2SO_4$	6.0	273.15 to 373.15	7.93				
Cs_2SO_4	3.5095	298.15 to 323.15	5.15				
Rb_2SO_4	3.0	298.15 to 323.15	5.30				
CaI_2	2.915	303.15 to 343.15	3.85	2.915	298.15 to 343.15	7.2	6.2
$SrCl_2$	4.000	273.15 to 523.15	1.86	3.203	298.15 to 343.15	7.0	6.9
$MgCl_2$	4.000	273.15 to 523.15	1.47	4.801	298.15 to 573.15	17.0	5.0
$BaCl_2$	4.000	273.15 to 523.15	4.12	1.500	298.15 to 333.15	7.2	2.2
$Ca(NO_3)_2$	20.000	273.15 to 393.15	12.87	20.000	273.15 to 393.15	14.0	4.7
$CaCl_2$	6.019	303.15 to 343.15	6.80	7.031	298.15 to 343.15	7.3	7.3
$CaBr_2$	4.596	303.15 to 343.15	3.42	4.596	298.15 to 343.15	6.3	3.9
$BaBr_2$	3.398	303.15 to 343.15	2.89	3.398	298.15 to 343.15	3.1	3.7
$SrBr_2$	3.340	303.15 to 343.15	7.69	3.340	298.15 to 343.15	9.1	6.5
SrI_2	4.156	303.15 to 343.15	2.10	4.156	298.15 to 343.15	3.1	4.5

[a] Deviations from Pitzer and modified Pitzer models are from ref 37.

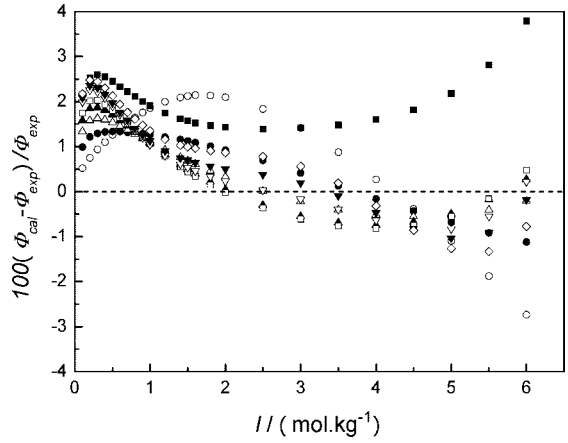

Figure 3. Relative deviations of calculated osmotic coefficient for NaCl at different temperatures by using the temperature-dependent parameters. ○, 273.15 K; ●, 298.15 K; △, 323.15 K; ▲, 348.15 K; □, 373.15 K; ■, 398.15 K; ▽, 423.15 K; ▼, 448.15 K; ♦, 473.15 K.

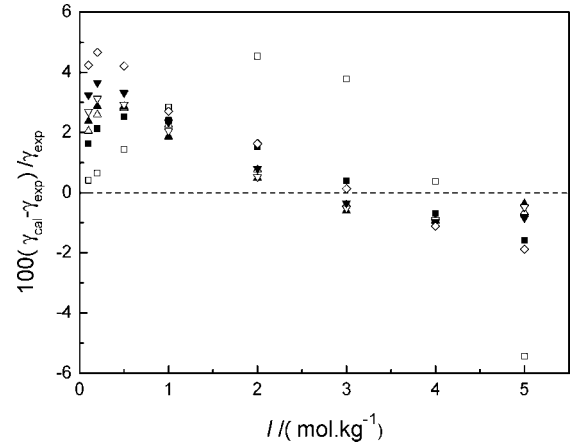

Figure 4. Relative deviations of calculated mean activity coefficient for KBr at different temperatures by using the temperature-dependent parameters. □, 273.15 K; ■, 298.15 K; △, 323.15 K; ▲, 373.15 K; ▽, 423.15 K; ▼, 473.15 K; ◇, 523.15 K.

parameter, b, or solvation parameter, S, for some electrolytes represents a simple linear change against temperature, such as CsOH, KH_2PO_4, $MgCl_2$, etc., as shown in Figures 1 and 2.

We also compared our model to the Pitzer equations. Pērez-Villaseñor et al.[37] have established the temperature dependence of a modified Pitzer model and the original one. By using the temperature-dependent parameters in Table 3, we obtained the standard deviations for each electrolyte system and listed them in Table 4, along with the results obtained by Pērez-Villaseñor et al.[37] For all the same systems in Table 4, the average standard deviation is 3.6 % from our model, 5.9 % from the original Pitzer model, and 5.1 % from the modified one. In about 80 % of the cases, the performance of our model is better than the Pitzer model. For some 2−1 type electrolytes with the same data source, such as $CaCl_2$, $CaBr_2$, $SrCl_2$, and $BaBr_2$, etc., the performance of our model is better. It should be noted that the

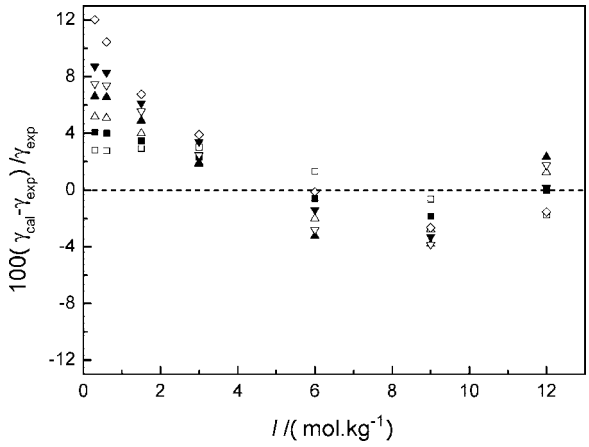

Figure 5. Relative deviations of calculated mean activity coefficient for $SrCl_2$ at different temperatures by using the temperature-dependent parameters. □, 273.15 K; ■, 298.15 K; △, 323.15 K; ▲, 373.15 K; ▽, 423.15 K; ▼, 473.15 K; ◇, 523.15 K.

number of parameters of the original Pitzer model used for these systems in their work is eight to ten parameters. Thus, we may have the conclusion that the performance of our model is fairly good for these systems.

Figures 3 to 5 show the distributions of the relative deviations against the concentration for NaCl, KBr, and $SrCl_2$ at a temperature range of (273.15 to 523.15) K by using the temperature-dependent parameters. From these figures, one can see that most of the realtive errors are within 10 %. The range of deviations for NaCl and KBr is smaller than that of $SrCl_2$. Another finding is that the relative large deviations always can be found at a higher temperature.

Conclusions

A simple model with two characteristic parameters, distance of closest approach parameter, *b*, and solvation parameter, *S*, was proposed to correlate the mean activity coefficient and osmotic coefficient for many aqueous electrolyte solutions across a temperature range of (273.15 to 523.15) K in a concentration range of (0 to 20) mol·kg^{-1}. We obtained the characteristic parameters for these electrolytes at different temperatures. The temperature-dependent parameters for some electrolytes are also obtained in this work. Generally, six to eight parameters are enough to describe the properties of the electrolytes across a wide temperature range. This model also showed a good performance when compared with the Pitzer equations, which means it is a good alternative for calculating the thermodynamic properties of electrolyte solutions.

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