Correlation and Prediction of Activity and Osmotic Coefficients of Aqueous Electrolytes at 298.15 K by the Modified TCPC Model

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The modification and extension of a three-characteristic-parameter correlation model for calculating the thermodynamic properties including osmotic and mean activity coefficients of aqueous electrolytes at 298.15 K have been presented in this paper. The model can be reduced with two parameters: *b*, the approaching parameter, and *S*, the solvation parameter. Although the model adequately describes the thermodynamics with these two parameters, the third parameter, *n*, which is related to the distance between an ion and a solvent molecule, also can be regarded as an adjustable parameter. The two sets of parameters for 283 single salts in aqueous solutions up to saturation have been obtained from the regression of experimental values. Mean activity or osmotic coefficients of $RbNO_2$, $MgCl_2$, $Sm(ClO_4)_3$, and $ZnSO_4$, with these two sets of parameters, have been compared with the smoothed experimental data, which show good agreement. When the model with three parameters is employed, it gives a more accurate result, especially in case of high concentration. The comparison with Pitzer and the original TCPC model also illustrates the excellent performance of this modified model.

Introduction

Studies on the thermodynamic properties of electrolytes have received much attention over the past few decades and also much significant scientific progress have been made. The most widely used are Pitzer equations[1−5] with the introduction of short-range interaction between ions rather than the first Debye−Huckel model, which considers only the long-range ion interaction with the available prediction for very dilute solutions. The other widely developed models include the Bromley model,[6−8] NRTL model,[9,10] and MSA-based models.[11,12]

In 1993, Lin[13,14] published a predictive model with three parameters for the calculation of activity and osmotic coefficients of strong electrolytes in binary solutions. In this model, the Poisson−Boltzmann equation was employed to account for the long-range ion−ion interactions, and the concept of solvation was employed for the short-range ion−molecule interactions. All three parameters were expressed with physical significance. In 1998, Lin[15] modified their model with the Pitzer term instead of the complicated numerical solution of the differential equation. Lin and Lee[16,17] further assumed that the dielectric constant of water would not vary with the concentration of electrolytes, the model was reduced to be a two-ionic parameter approach, which can be applied to the calculations of both the mean ionic activity coefficient and the individual ion activity coefficient. Pazuki[18,19] utilized this model to predict the water activity and osmotic coefficients for many kinds of electrolyte solutions, and the DH term was used to replace the Pitzer term to establish a new predictive model for 144 electrolyes.[20] These TCPC-based models have also been widely applied to the calculation of vapor pressure[21,22] and vapor−liquid equilibrium[23−25] for both aqueous and nonaqueous solutions[26] of single or mixed electrolyte systems. And they have also been widely extended to other fields, such as medical chemistry,[27] biology, and biochemistry.[28,29]

However, the original model provides only the parameters suitable for a low concentration range (below 6 mol·kg^{-1}). Therefore, this work aims to obtain the parameters from the known experimental activity or osmotic coefficient data of single electrolytes over a wide range of concentration, up to nearly saturation. The form of the TCPC model proposed by Lin[15] was modified and extended for the calculation of activity and osmotic coefficients for 283 single salts and more than primitive 144 electrolyte solutions.

Theoretical Modeling

Lin and Lee[15] published their model for calculating the mean activity coefficient of aqueous electrolytes, which is a combination of the Pitzer long-range interaction and short-range solvation effect

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

The expression for the first term is

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

and

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

In the above equations, A_ϕ is the Debye−Huckel constant with a value of 0.392 at 298.15 K, and D is the static dielectric constant at temperature T. It should be noted that in the earlier model[15] D was considered to be an adjustable parameter, but

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in the present work, it is regarded as a constant.[16,17] N_0 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 the so-called approaching parameter depending on the closest distance of approach of the ions.

In this model, the occurrence of solvation is attributed to the phenomenon in which the ions are surrounded by solvent molecules. The interaction between a cation and a solvent molecule can be described as

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

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

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

where β and n can be determined by experimental data. Then eq 5 will be expressed in terms of ionic strength as

$$\Gamma_{cs} = \frac{h_{cs} z_+ e \mu I^{2n}}{\beta_+^2} \tag{6}$$

A dimensionless potential, $\Phi_{cs} = e\Gamma_{cs}/kT$ is defined for a cation and a surrounding molecule. By substituting eq 6 into Φ_{cs}, we obtain

$$\Phi_{cs} = h_{cs} z_+ \left(\frac{e^2 \mu}{\beta_+^2 kT}\right) I^{2n} \tag{7}$$

Similarly, a corresponding dimensionless potential for an anion due to solvation is obtained as

$$\Phi_{as} = h_{as} z_- \left(\frac{e^2 \mu}{\beta_-^2 kT}\right) I^{2n} \tag{8}$$

Then the charging process of this cation from 0 to z_+e is equal to the electrostatic potential of the surrounding ions, $kT \ln \gamma_+$. Accordingly, the cation activity coefficient can be calculated as follows:

$$\ln \gamma_+ = \frac{1}{kT}\int_0^{z+} (\psi_{cr} + \Gamma_{cs}) e \, dz = \int_0^{z+} (\Phi_{cr} + \Phi_{cs}) \, dz \tag{9}$$

The first term of the integrand considers that the contribution belongs to ions, whereas the second term is attributed to the solvation effect that is relevant in this context. Thus, neglecting Φ_{cr} and substituting Φ_{cs} into the equation, one obtains

$$\ln \gamma_+^{SV} = h_{cs}\left(\frac{e^2 \mu}{\beta_+^2 kT}\right) I^{2n} \left(\frac{z_+^2}{2}\right) \tag{10}$$

Similarly, the anion activity coefficient is

$$\ln \gamma_-^{SV} = h_{cs}\left(\frac{e^2 \mu}{\beta_-^2 kT}\right) I^{2n} \left(\frac{z_-^2}{2}\right) \tag{11}$$

According to the definition of the mean activity coefficient of an electrolyte

$$\ln \gamma_\pm^{SV} = \frac{\nu_+ \ln \gamma_+^{SV} + \nu_- \ln \gamma_-^{SV}}{\nu_+ + \nu_-} \tag{12}$$

the equation for estimating the mean activity coefficient, $\gamma_\pm^{SV}$, becomes

$$\ln \gamma_\pm^{SV} = \frac{S}{T} \frac{I^{2n}}{\nu_+ + \nu_-} \tag{13}$$

Equation 13 represents the interaction between the ion and the solvent molecule. A solvation parameter, S, that is a characteristic value indicating the tendency of solvation of an electrolyte in solution is defined as

$$S = \frac{e^2 \mu (h_{cs} \nu_+ z_+^2 \beta_-^2 + h_{as} \nu_- z_-^2 \beta_+^2)}{2k\beta_+^2 \beta_-^2} \tag{14}$$

The mean ionic activity coefficient can thus be written as

$$\ln \gamma_\pm = -|z_+ z_-| A_\phi \left[\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right] + \frac{S}{T}\frac{I^{2n}}{\nu_+ + \nu_-} \tag{15}$$

The osmotic coefficient of a solution, ϕ, is related to the mean activity of the electrolyte by

$$\phi = 1 + \frac{1}{m}\int_0^m m \, d \ln \gamma_\pm \tag{16}$$

With eq 15, it is reduced as

$$\phi = 1 - |z_+ z_-| A_\phi \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{S}{T(\nu_+ + \nu_-)} \frac{2n}{2n+1} I^{2n} \tag{17}$$

Evaluation of Parameters

On the basis of ion parameters b, S, and n, the mean activity and osmotic coefficients can be predicted. During the calculation, the values of the mean molal activity coefficients or osmotic coefficients are collected from the literature. Most of these investigations were carried out by the National Bureau of Standards. The different experimental values for the mean activity coefficients or osmotic coefficients obtained from different techniques were critically determined and adjusted to different equations. Then the smoothed values were obtained and recommended to be the standard values. In this paper, we also summarized some newly determined experimental activity or osmotic coefficient values from recent publications to improve some old experimental values.

Then this new model was employed to correlate the aforementioned experimental data, and parameters b, S, and n were evaluated by multiple regression analysis. The objective function is given below, and the optimization was performed by the least-squares method with the special application of MATLAB software:

$$\delta = \left[\sum_i \frac{(\ln \gamma_\pm^{exptl} - \ln \gamma_\pm^{calcd})^2}{n_p}\right]^{1/2} \text{ or } \delta = \left[\sum_i \frac{(\phi^{exptl} - \phi^{calcd})^2}{n_p}\right]^{1/2} \tag{18}$$

Here, δ is defined as the standard deviation (%), n_p is the number of experimental data points, and superscripts exptl and calcd refer to the experimental and calculated results, respectively. Most of the parameters were obtained from activity coefficients; a few sets of parameters were regressed from

Table 1. Calculated Parameters for 1-1 Electrolytes in H_2O at $T = 298.15$ K

electrolytes	M_{max}	np	b	S	$10^2\delta$	b_0	S_0	n	$10^2\delta$	refs
				($n = 0.645$)						
HCl	16.000	40	10.7090	74.0656	14.16	2.6630	202.0039	0.4758	6.30	30, 31
HBr	11.000	34	6.5822	122.2983	7.03	3.7544	179.6788	0.5691	4.55	31
HI	10.000	33	9.5918	134.0093	5.05	5.3413	186.5756	0.5764	2.30	31
$HClO_4$	16.000	39	5.3186	116.2511	6.63	3.5679	150.4983	0.6004	4.70	31
HNO_3	28.000	51	19.4478	13.2081	17.91	2.3109	198.0088	0.2894	9.40	31
LiCl	19.219	44	11.8581	64.6857	22.15	1.9304	232.1466	0.4458	12.41	30, 31
LiBr	20.000	43	10.6284	91.0308	22.19	2.0933	228.3532	0.5000	13.37	31
LiI	3.000	23	9.5919	134.0092	5.05	6.3035	121.0137	0.6816	1.62	31
LiOH	5.000	26	1.6256	8.4132	6.56	7.7432	−198.2412	0.1427	5.79	31
$LiClO_4$	4.500	26	5.9348	118.1541	2.13	5.4304	130.0342	0.6165	2.04	31
$LiNO_3$	20.000	43	12.4697	28.5148	15.44	2.3955	185.4101	0.3637	7.57	31
$LiNO_2$	19.900	47	13.1972	24.5179	14.26	3.3969	155.0694	0.3603	7.47	32
$LiClO_3$	4.200	20	3.9325	86.599	1.52	3.0342	125.8670	0.5409	0.80	33
$LiBrO_3$	5.000	21	2.9195	43.8336	0.80	3.0747	36.0094	0.6993	0.70	33
LiAc[a]	4.000	25	3.5139	42.2149	3.13	3.9185	24.4886	0.8294	2.88	31
NaF	1.000	17	3.4174	−95.6844	3.46	19.5050	−256.4171	0.2141	1.44	31
NaCl	6.000	30	3.0210	36.1573	3.63	3.5425	14.0326	0.8998	3.04	30, 31
NaBr	9.000	32	3.5307	47.49	3.38	3.4595	49.9861	0.6341	3.37	31
NaI	12.000	35	4.5605	58.9735	4.23	3.5752	84.7943	0.5759	3.39	31
NaOH	29.000	52	10.7325	36.4375	32.33	1.3407	229.9241	0.3942	20.59	31
$NaClO_3$	3.000	23	2.8370	−16.6908	4.09	17.6791	−215.6566	0.1776	2.20	31
$NaClO_4$	6.000	29	3.0096	14.8556	3.71	3.2748	2.9747	1.0930	3.35	31
$NaNO_3$	6.000	9	1.9873	−10.6356	3.10	14.5232	−254.7813	0.1755	1.50	34
$NaNO_2$	12.340	40	3.0209	4.2996	5.26	3.0859	1.6076	0.8414	5.21	32
$NaBrO_3$	2.617	23	2.3223	−46.7156	5.06	19.6252	−290.0764	0.2108	1.67	31
NaH_2PO_4	6.500	30	1.3415	−211927	9.24	18.7933	−355.5469	0.1972	4.06	31
NaH_2AsO_4	1.300	19	3.3011	−128.947	3.66	20.9093	−308.6072	0.2467	0.80	31
NaCNS	18.000	41	6.6633	28.7686	11.97	2.7719	117.2245	0.4228	7.89	31
NaAc[a]	3.500	24	4.2945	64.0634	2.48	4.6723	51.0027	0.7267	2.39	31
KF	17.500	41	3.4802	33.2784	6.86	2.5738	64.0029	0.5382	5.73	31
KCl	5.000	29	2.5989	11.4181	4.24	2.7650	1.2015	1.3535	3.88	31, 34
KBr	5.500	28	2.8135	13.6663	3.98	3.0352	2.2813	1.1739	3.64	31
KI	4.500	26	3.2137	17.8304	3.39	3.4704	5.4343	1.0340	3.16	31
KOH	20.000	43	7.8571	58.9937	15.83	2.2214	175.0002	0.4752	7.89	31, 35
$KClO_3$	0.700	13	3.4665	−292.508	3.48	17.5757	−369.8812	0.2691	0.95	31
$KBrO_3$	0.500	11	3.6909	−418.873	3.12	22.2756	−415.3636	0.2712	0.79	31
KNO_3	3.500	24	1.5311	−76.8747	7.24	25.2117	−412.6326	0.2446	0.94	31
KNO_2	34.120	62	1.9736	−3.8176	7.77	16.3589	−253.8073	0.1745	3.39	32
KH_2PO_4	1.800	20	1.7597	−143.318	6.29	23.3901	−438.2261	0.2530	1.12	31
KH_2AsO_4	1.300	18	2.5641	−166.56	4.73	19.8789	−376.4632	0.2589	1.00	31
KCNS	5.000	27	2.7131	0.5244	4.14	9.7537	−153.0942	0.1481	3.33	31
KPF_6	0.500	11	2.4274	−649.2133	4.31	22.8225	−615.1244	0.95	1.11	31
KAc[a]	3.500	24	4.5094	77.111	2.40	4.8812	65.2488	0.7033	2.38	31
RbF	3.500	24	3.7605	33.3734	2.88	4.0546	21.2275	0.8087	2.80	31
RbCl	7.800	32	2.3952	9.541	4.64	2.5461	1.6154	1.0766	4.36	31
RbBr	5.000	27	2.3770	2.664	4.75	8.7567	−159.5242	0.1455	4.02	31
RbI	5.000	27	2.3181	3.6877	4.89	7.3478	−143.8386	0.1464	4.25	31
$RbNO_3$	4.500	26	1.2917	−62.2403	8.59	21.0004	−418.8128	0.2437	1.37	31
$RbNO_2$	62.300	90	1.6063	−2.0439	8.88	17.3885	−269.6666	0.1715	2.98	32
RbAc[a]	3.500	24	4.5674	81.7406	2.39	4.7729	75.0088	0.6754	2.37	31
CsF	3.500	24	3.8859	57.0509	2.82	4.3347	39.1874	0.7839	2.60	31
CsCl	11.000	34	1.8858	8.2635	6.06	2.0087	1.1615	1.0601	5.66	30, 31
CsBr	5.000	27	1.9521	−1.5032	5.88	11.6601	−223.3121	0.1563	4.32	31
CsI	3.000	23	2.1239	−27.8979	5.25	19.4726	−280.1542	0.1881	2.36	31
CsOH	5.000	8	3.9753	87.8137	0.38	3.9753	87.8137	0.6450	0.38	35
$CsNO_3$	1.500	19	1.9550	−170.979	5.87	20.3969	−432.7524	0.2621	1.13	31
$CsNO_2$	36.000	63	2.5368	−2.9206	5.56	10.6039	−177.2364	0.1792	3.70	32
CsAc[a]	3.500	24	4.7820	82.7555	2.36	4.8062	81.9875	0.6485	2.36	31
$AgNO_3$	15.000	38	0.8535	−19.8039	15.53	21.7555	−436.6749	0.2214	4.54	31
TlCl	0.010	4	−3.2801	−169.6971	1.06	3.3624	−423.6378	0.3298	0.95	31
$TlClO_4$	0.500	11	3.2068	−461.564	3.49	16.3923	−440.7208	0.2839	1.06	31
$TlNO_3$	0.400	10	2.4949	−703.2850	3.80	17.0798	−573.8103	0.2949	1.16	31
TlAc[a]	6.000	29	1.8285	−15.1217	6.37	20.6486	−299.4823	0.1792	2.81	31
NH_4I	7.500	29	3.0461	606505	0.85	2.9810	13.5922	0.5904	0.82	36
NH_4Cl	7.405	32	2.7225	7.5004	4.00	2.8347	2.0781	0.9652	3.86	30, 31
NH_4ClO_4	2.100	22	1.8117	−67.0223	5.98	19.7631	−348.2867	0.2137	2.04	31
NH_4NO_3	25.954	49	1.3510	−6.3684	9.94	20.3806	−329.8858	0.1867	2.44	31
NH_4SCN	23.000	39	3.0472	−1.9443	1.95	1.2264	182.4071	0.0852	1.95	37
Et_4NNO_3	8.000	30	0.3645	7.3745	8.40	1.75481	−250.0415	0.1666	7.78	36
Me_4NNO_3	7.000	28	1.1216	6.0951	3.96	1.1742	0.1049	1.7271	3.43	36
$MeNH_3ClO_4$	4.000	19	1.3274	−30.563	3.41	19.9844	−360.0351	0.2051	1.18	38
$Me_2NH_2ClO_4$	7.500	26	1.0252	−22.4129	5.73	19.4992	−400.9702	0.2066	2.04	38
Me_3NHClO_4	1.800	14	0.9449	−115.916	3.14	23.1899	−498.5483	0.2502	0.56	38
GuCl	12.000	29	1.2787	−10.0571	6.79	21.7591	−348.8574	0.1858	3.31	39
Li(p-tol)[b]	4.500	26	2.9117	3.2463	4.03	10.7024	−145.3630	0.1432	3.61	31

Table 1 (Continued)

electrolytes	M_{max}	np	b	S	$10^2\delta$	b_0	S_0	n	$10^2\delta$	refs
					($n = 0.645$)					
Na(*p*-tol)[b]	4.000	25	2.5715	−39.2746	4.61	18.1534	−265.8595	0.2264	1.03	31
Na(form)[c]	3.500	24	3.4286	19.4765	3.20	3.7098	5.4300	1.1584	2.92	31
Na(propion)[d]	3.000	23	4.7141	87.6127	2.40	4.9340	80.8444	0.6759	2.39	31
Na(butyr)[e]	3.500	24	6.1267	90.994	3.72	4.5050	134.9961	0.5154	3.22	31
Na(valer)[f]	2.000	21	5.0902	110.3097	2.53	5.0765	110.3870	0.6468	2.53	31
Na(capryl)[g]	3.000	14	2.4229	−181.285	13.98	20.6632	−419.2994	0.4013	10.76	31
Na(pelargon)[h]	2.500	14	−0.0040	−124.963	13.89	14.3583	−746.6784	0.2788	10.16	31
Na(capr)[i]	1.800	11	−0.3751	−148.937	9.18	13.2771	−993.4393	0.2784	5.70	31
NaH(malon)[j]	5.000	27	2.3467	−8.2267	4.91	16.7239	−232.2804	0.1649	2.87	31
NaH(succ)[k]	5.000	27	2.3572	4.9897	4.94	7.7862	−144.2902	0.1428	4.51	31
NaH(adip)[l]	0.700	13	4.1715	−103.075	2.85	19.7917	−219.5625	0.2093	1.45	31
K(*p*-tol)[b]	3.500	24	2.3829	−75.3951	5.27	22.4243	−333.2843	0.2651	0.75	31
KH(malon)[j]	5.000	27	2.0508	−22.4596	5.94	24.0010	−297.4403	0.1914	2.17	31
KH(succ)[h]	4.500	26	2.1968	−8.2907	5.45	16.2421	−239.4646	0.1677	3.39	31
KH(adip)[l]	1.000	16	3.6685	−74.8717	3.27	18.2807	−224.1702	0.2068	1.60	31
CCl_3COONa	9.000	26	9.3153	20.4672	6.84	0.3942	502.5763	0.2110	2.88	40
CCl_3COOK	8.000	25	5.4857	0.2672	3.41	4.1588	31.3469	0.2005	3.24	40
CF_3COONa	12.500	36	14.5962	16.0939	9.30	0.5378	502.9960	0.2021	4.48	41
CF_3COOK	58.000	89	7.3057	−2.8114	3.85	7.4563	−3.2108	0.6291	3.84	41
H_3PO_4[m]	23.524	24	24790	49	29.53	31.1025	179.2192	0.4277	8.87	42
citric acid[n]	8.000	22	75385	47	4.68	28.8874	129.8666	0.4047	2.79	43

[a] Acetate. [b] *p*-Toluenesulfonate. [c] Formate. [d] Propionate. [e] Butyrate. [f] Valerate. [g] Caprylate. [h] Pelargonate. [i] Caprate. [j] Malonate. [k] Succinate. [l] Adipate. [m] Calculated according to the equilibria: $H_3PO_4 = H^+ + H_2PO_4^-$ [n] $HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$

Table 2. Calculated Parameters for 1-2 Electrolytes in H_2O at $T = 298.15$ K

electrolytes	M_{max}	np	b	S	$10^2\delta$	b_0	S_0	n	$10^2\delta$	refs
					($n = 0.645$)					
Li_2SO_4	3.000	13	2.4408	19.5494	2.52	2.5841	2.7436	1.0765	1.55	45
$Li_2C_6H_4S_2O_6$	2.500	34	4.8069	83.4730	4.52	4.7297	90.0020	0.6270	4.50	46
$Li_2C_{14}H_{12}S_2O_6$	1.200	29	2.9782	−13.5231	7.55	9.5427	−434.9644	0.1682	5.82	46
Na_2SO_4	4.445	37	2.2951	−9.3723	13.88	8.1535	−514.8889	0.1700	9.50	45, 46
Na_2SO_3	2.058	33	2.7323	−28.0525	9.71	11.8161	−564.2486	0.1806	5.50	46
Na_2CO_3	3.115	38	2.5611	−14.7363	11.14	11.0390	−551.9787	0.1706	6.96	46
Na_2HPO_4	2.121	33	2.5789	−59.6896	11.07	19.6318	−758.3691	0.1974	3.59	46
Na_2CrO_4	4.363	42	2.5566	12.9157	12.21	2.7036	0.0130	2.0429	9.84	46
$Na_2S_2O_3$	4.052	41	2.4357	3.6527	12.18	5.3497	−298.9463	0.1526	9.44	46
$Na_2S_2O_6$	0.852	27	3.4191	−97.8151	7.08	18.5930	−646.2398	0.1957	3.46	46
$Na_2S_2O_8$	0.098	19	4.0144	−888.1040	3.11	20.1298	−830.7216	0.2371	1.48	46
$Na_2C_2H_4S_2O_6$	1.800	32	3.2537	19.6981	6.64	3.3698	2.6839	1.2468	6.39	46
$Na_2C_6H_4S_2O_6$	3.000	36	4.3246	30.0141	4.86	4.5515	13.3254	0.8269	4.67	46
$Na_2C_{14}H_{12}S_2O_6$	0.400	22	3.0462	−209.7000	5.55	20.6542	−760.6126	20.95	2.63	46
$Na_2C_{14}H_{12}S_2O_8$	0.400	22	3.0944	−638.6782	7.87	9.4383	−985.6674	0.3335	3.05	46
$Na_2B_{12}H_{12}$	1.729	31	4.6801	153.9368	4.25	4.8523	136.7699	0.6798	4.18	46
Na_2HAsO_4	1.029	29	3.5393	−96.0036	6.79	19.9085	−657.0949	0.1981	2.57	46
$Na_2C_4H_2O_4$(Fuma)[a]	2.077	33	2.8284	21.7473	8.72	2.9546	0.9133	1.5491	7.99	46
$Na_2C_2H_2O_4$(Male)[b]	2.879	36	2.2228	4.5174	11.95	4.8221	−310.5025	0.1598	9.71	46
K_2SO_4	0.800	8	2.0800	−51.9550	1.76	5.9898	−498.1185	0.2086	0.86	45
K_2HPO_4	0.873	27	3.0103	−111.8357	7.66	20.8050	−740.2638	0.1954	3.46	46
$K_2H_2P_2O_7$	3.070	37	2.4569	−33.1493	12.40	24.1831	−769.0996	0.1802	4.91	46
K_2HAsO_4	0.886	27	3.8274	−67.3553	5.88	21.1130	−581.5137	0.1792	3.23	46
K_2CrO_4	3.372	38	2.5411	−6.1863	11.02	6.8058	−395.3916	0.1704	8.19	46
$K_2Cr_2O_7$	0.507	24	17.1016	−290.2102	4.15	22.8902	−358.0192	0.4390	2.58	46
$K_2Pt(CN)_4$	0.948	28	4.9310	−71.4097	4.81	18.1263	−466.9720	0.1949	2.10	46
Rb_2SO_4	2.048	20	2.0084	−11.3969	6.93	5.1059	−417.9103	0.1820	4.89	47
$Rb_2S_2O_8$	0.075	17	3.3000	−1767.4	3.19	8.8339	−995.4220	0.3015	1.76	46
Cs_2SO_4	3.105	24	1.9190	11.7166	7.27	1.9850	0.6311	1.3103	6.47	47
Cs_2S_2O8	0.109	20	2.9000	−1463.8	3.68	6.6689	−968.2117	0.3126	2.24	46
$(NH_4)_2HPO_4$	3.107	37	1.4091	−41.8726	19.81	14.7662	−985.1794	0.1894	7.96	46
$(NH_4)_2B_{10}H_{10}$	3.807	40	3.0282	0.9021	7.92	5.3798	−219.5946	0.1507	6.85	46
$(CN_3H_6)_2CO_3$	2.613	35	1.7390	−56.9524	16.59	22.8585	−977.4960	0.1938	5.65	46
$C_2H_6S_2O_6$	5.500	46	6.3607	81.4803	10.80	4.1061	200.0055	0.4943	6.40	46
$C_6H_6S_2O_6$	1.800	32	4.6903	104.1349	4.17	4.8480	88.9510	0.6894	4.08	46

[a] Sodium fumarate. [b] Sodium maleate.

osmotic coefficients. In the earlier model, n was a constant, 0.645, for all electrolyte systems, which brings about simplicity for optimization. For electrolytes at higher concentration, the fitting deviation will be high with this value. However, n should be an electrolyte-specific value despite the assumption for simple optimization because the concentration variation will influence the ion−molecule interaction. In this study, the set of parameters with $n = 0.645$ has been obtained, so the model can be reduced to be the model with two parameters, namely, the approaching parameter and the solvation parameter. Meanwhile, n could be regarded as an adjustable parameter; the three parameters for each electrolyte are also listed in Tables 1 to 6.

Table 3. Calculated Parameters for 2-1 Electrolytes in H_2O at $T = 298.15$ K

electrolytes	M_{max}	np	b	S	$10^2\delta$	b_0	S_0	n	$10^2\delta$	refs
				($n = 0.645$)						
$MgCl_2$	5.919	36	3.6024	110.1902	1.90	3.3156	127.0174	0.6224	1.06	48
$MgBr_2$	5.610	47	4.5840	129.4537	5.24	4.2266	148.6912	0.6216	4.96	49
MgI_2	5.010	45	4.8106	159.8795	4.59	4.5275	174.9512	0.6292	4.43	49
$Mg(NO_3)_2$	5.123	26	3.9965	77.7512	4.22	3.3844	120.5300	0.5720	2.67	50
$Mg(ClO_4)_2$	4.500	21	5.2122	163.6839	5.32	4.0301	226.5346	0.5872	3.28	51
$CaCl_2$	10.000	65	6.7158	61.3273	28.24	2.6803	260.0920	0.4476	18.79	49
$CaBr_2$	9.210	62	4.9110	105.3440	17.73	3.4120	170.0119	0.5763	15.00	49
CaI_2	1.915	38	4.4415	132.4132	4.34	4.7918	99.9750	0.7208	4.00	49
$Ca(NO_3)_2$	20.000	23	4.2857	11.9865	18.67	2.5459	125.8526	0.3788	11.10	52
$SrCl_2$	4.083	42	3.5348	69.6187	6.89	3.7759	49.9957	0.7078	6.60	49
$SrBr_2$	2.123	40	4.0066	88.2535	5.27	4.5517	40.0479	0.8496	4.34	49
SrI_2	1.970	38	4.5106	119.0206	4.34	4.9576	79.9973	0.7521	3.82	49
$BaCl_2$	2.000	12	3.0821	48.6672	0.36	3.0577	51.5110	0.6319	0.35	30
$BaBr_2$	2.321	42	3.7309	64.1377	5.51	4.0805	31.0113	0.8239	5.01	49
BaI_2	1.998	38	4.5297	108.7583	4.22	4.8562	80.0076	0.7269	3.99	49
$MnCl_2$	7.699	55	5.6479	35.2692	13.37	3.4896	159.9827	0.4237	8.96	53
$MnBr_2$	5.640	47	6.0902	80.0128	12.82	3.7969	209.9965	3.4858	8.32	53
$Mn(ClO_4)_2$	3.456	38	5.7606	174.9947	3.12	5.6699	179.6224	0.6397	3.12	53
$NiCl_2$	5.714	48	4.1252	74.7718	10.17	3.7134	140.0036	0.5409	8.33	54
$NiBr_2$	4.693	43	4.7275	118.4371	6.13	4.2216	150.0000	0.6024	5.67	54
$Ni(ClO_4)_2$	3.501	39	4.9726	176.9271	3.75	5.2614	160.0016	0.6654	3.55	54
$Ni(NO_3)_2$	4.623	43	4.1029	75.8773	5.00	4.2537	66.1773	0.6700	4.95	54
$CoCl_2$	4.118	41	4.2677	75.7842	6.46	4.1143	87.2168	0.6183	6.35	54
$CoBr_2$	5.672	48	5.8767	99.3364	9.79	3.9643	199.9636	0.5292	7.94	54
$Co(NO_3)_2$	5.790	49	4.1145	66.6389	6.12	3.8215	84.7492	0.6053	5.90	54
$Co(ClO_4)_2$	3.514	39	5.1612	176.0365	3.59	5.2624	169.9434	0.6522	3.55	54
$CuCl_2$	5.750	47	4.0997	21.3252	7.06	3.7431	47.5279	0.5129	6.56	53
$CuBr_2$	3.606	39	5.3216	55.7680	7.57	4.2854	132.1189	0.4792	6.33	53
$Cu(ClO_4)_2$	3.557	39	4.9379	163.1114	3.94	4.9882	159.9888	0.6489	3.93	53
$Cu(C_7H_7O_3S)_2$	0.800	26	3.6946	−84.7321	4.31	19.2434	−596.0920	2.83	0.52	53
$FeCl_2$	2.050	33	3.6024	80.2881	6.19	3.9556	38.4726	0.8414	5.50	54
ZnF_2	0.142	20	2.7000	−1122.5000	4.90	8.7898	−992.8423	0.2925	2.06	55
$ZnCl_2$	23.193	117	3.8571	8.4343	20.01	2.5249	69.0252	0.4593	15.94	55, 56
$ZnBr_2$	20.100	105	9.2891	15.1727	18.45	4.1120	109.0121	0.4215	11.80	55
ZnI_2	11.892	72	16.9741	22.2609	12.84	7.4638	119.9647	0.4231	9.15	55
$Zn(ClO_4)_2$	4.311	43	4.7811	172.0634	4.75	4.5732	184.2722	0.6324	4.68	55
$Zn(NO_3)_2$	7.103	53	5.0861	64.2578	8.55	3.9427	119.9882	0.5484	6.21	55
$Zn(C_7H_7O_3S)_2$	0.300	21	3.5877	−200.8860	4.54	22.2354	−676.3877	0.2039	1.98	55
$Cd(ClO_4)_2$	1.928	32	4.4231	132.9021	4.79	4.9821	81.0019	0.7829	3.93	55
$Cd(NO_3)_2$	2.638	35	3.8830	39.9494	5.58	4.0740	21.2660	0.7943	5.30	55
$Cd(C_7H_7O_3S)_2$	0.600	24	3.6847	−121.0707	4.71	23.1138	−653.0288	0.1912	2.20	55
$PbCl_2$	0.039	13	−0.7000	−2218.4000	2.95	0.0810	−998.9993	0.3757	2.06	53
$Pb(NO_3)_2$	1.988	33	1.7184	−67.3731	15.01	19.5633	−970.3734	0.1920	5.88	53
UO_2Cl_2	3.174	37	4.5424	80.2918	3.91	4.5424	80.2918	0.6450	3.91	53
$UO_2(ClO_4)_2$	5.458	46	7.7533	206.7425	14.92	4.1793	354.9643	0.5528	8.67	53
$UO_2(NO_3)_2$	5.511	47	7.9946	56.0113	19.48	3.3233	330.0621	0.3649	12.05	53
$[Co(NH_3)_5NO_2]Cl_2$	0.100	19	8.6000	−2246.0000	1.52	18.5000	−1333.7000	0.4000	1.21	54
$[Co(NH_3)_5Cl]Cl_2$	0.008	8	2.9946	−97.5683	1.39	25.3312	−909.6156	0.2536	0.63	54
$[Co(NH_3)_5F]Cl_2$	1.000	28	2.6106	−119.2495	9.16	24.7429	−852.2632	0.1958	3.22	54
$[Co(NH_3)_5Cl](ClO_4)_2$	0.100	19	4.1000	−1284.8000	3.36	16.1229	−991.3599	0.2757	1.15	54
$A(NO_3)_2$[a]	0.400	22	2.3455	−312.6992	7.15	17.7134	−924.8939	0.2268	2.18	54
$A(I_2)$[a]	0.500	23	2.3798	−227.9561	7.62	26.6173	−945.8165	0.2090	2.96	54
$A(Br_2)$[a]	1.200	29	2.4327	−93.9419	10.11	21.0530	−828.5345	0.1927	4.22	54
$A(Cl_2)$[a]	2.400	34	2.1690	−18.1774	12.16	9.9416	−610.1608	0.1729	7.53	54
$B(NO_3)_2$[b]	0.050	14	3.2000	−2290.2000	2.39	8.60701	−987.7751	0.3039	1.26	54
$B(I_2)$[b]	0.100	19	3.4000	−1200.2000	3.76	13.9140	−973.0655	0.2684	1.77	54
B(Br2)[b]	0.600	24	2.4904	−186.4830	8.02	23.2260	−885.9179	0.2061	3.18	54
$B(Cl_2)$[b]	0.600	24	2.2125	−165.0083	8.43	24.6461	−919.9890	0.1988	3.98	54
$C(NO_3)_2$[c]	2.500	34	1.9090	−52.4023	14.57	23.4283	−924.1464	0.1876	5.18	54
$C(I_2)$[c]	0.800	26	2.4629	−163.4988	8.92	22.3995	−898.6875	0.2060	3.18	54
$C(Br_2)$[c]	0.800	26	2.2786	−138.0495	9.76	26.4255	−921.5766	0.1942	4.06	54
$C(Cl_2)$[c]	2.500	34	2.1577	−17.8285	12.24	10.1712	−617.9236	0.1724	7.37	54
$D(NO_3)_2$[d]	0.600	24	2.3061	−266.2785	8.60	18.3043	−966.1372	0.2299	2.73	54
$D(I_2)$[d]	0.600	24	2.3688	−292.6496	8.27	18.7113	−988.8720	0.2353	2.49	54
$D(Br_2)$[d]	1.000	28	2.1718	−178.8398	11.08	20.6938	−989.5971	0.2182	3.21	54
$D(Cl_2)$[d]	2.800	36	2.0198	−35.9580	14.54	24.1604	−870.9774	0.1782	6.14	54
$E(NO_3)_2$[e]	0.800	26	2.3089	−211.4851	9.71	21.3668	−978.2859	0.2205	2.93	54
$E(I)_2$[e]	0.300	21	2.4853	−456.8225	5.91	19.3461	−990.6448	0.2427	1.81	54
$E(Br_2)$[e]	2.400	34	1.8887	−58.6502	15.25	26.6673	−959.7391	0.1907	5.26	54
$E(Cl_2)$[e]	2.400	34	2.1377	−38.5128	13.23	20.8744	−819.4416	0.1792	6.08	54

[a] A−$[Co(NH_3)_5CH_3CH_2COO]$. [b] B−$[Co(NH_3)_5CH_3COO]$. [c] C−$[Co(NH_3)_5(CH_3)_2CHCOO]$. [d] D−*cis*-$[CO(C_2H_8N_2)NH_3NO_2]$. [e] E−*trans*-$[CO(C_2H_8N_2)NH_3NO_2]$

Table 4. Calculated Parameters for 3-1 and 1-3 Electrolytes in H_2O at $T = 298.15$ K

electrolytes	M_{max}	np	b	S	$10^2\delta$	b_0	S_0	n	$10^2\delta$	refs
				($n = 0.645$)						
$LaCl_3$	3.8944	25	4.0925	76.9867	8.25	3.1226	184.5054	0.5195	4.16	57
$La(ClO_4)_3$	4.5000	20	4.9346	139.4031	12.08	3.4482	260.2924	0.5565	6.16	58
$La(NO_3)_3$	6.4738	38	3.8129	22.2132	4.76	3.2498	71.9976	0.4974	1.08	59
$La(C_2H_5SO_4)_3$	1.1000	11	4.1123	109.3914	1.61	3.6020	197.9807	0.5189	0.43	60
$PrCl_3$	3.8969	25	4.0124	80.5510	7.29	3.1664	171.9993	0.5356	3.84	57
$Pr(ClO_4)_3$	4.5000	20	4.7744	141.5753	10.63	3.5592	238.0500	0.5711	5.69	58
$Pr(NO_3)_3$	6.2861	37	3.6875	24.7770	6.12	2.9709	100.9091	0.4689	1.31	59
$Pr(C_2H_5SO_4)_3$	0.8000	8	4.0298	121.5895	0.69	3.7912	165.9902	0.5680	0.12	60
$NdCl_3$	3.9307	25	3.8894	82.6914	7.06	3.0827	172.9812	0.5387	3.70	57
$Nd(ClO_4)_3$	4.5000	20	4.6741	143.1895	9.72	3.5070	238.0503	0.5728	5.01	58
$Nd(NO_3)_3$	6.2598	37	3.6968	25.3606	7.10	2.8786	118.0141	0.4531	1.75	59
$Nd(C_2H_5SO_4)_3$	1.1000	11	4.1189	110.7794	1.23	3.7322	175.0045	0.5465	0.37	60
$DyCl_3$	3.6302	24	4.0820	92.6838	6.39	3.3002	173.8896	0.5524	3.65	57
$Dy(ClO_4)_3$	4.5000	20	4.9792	152.8828	11.90	3.5293	265.9833	0.5663	6.11	58
$Dy(C_2H_5SO_4)_3$	1.1000	11	4.5919	126.4241	1.61	4.0053	213.0033	0.5330	0.31	60
$HoCl_3$	3.6987	24	4.1311	94.0838	6.09	3.3870	167.9876	0.5597	3.51	57
$Ho(ClO_4)_3$	4.5000	20	5.1685	154.1702	10.93	3.8074	250.0073	0.5761	6.33	58
$Ho(C_2H_5SO_4)_3$	1.1000	11	4.3458	125.0512	1.57	3.8112	209.9980	0.5338	0.36	60
$ErCl_3$	3.7840	24	4.0210	95.4987	6.08	3.3575	161.9523	0.5673	3.59	57
$Er(ClO_4)_3$	4.5000	20	5.1368	155.3233	10.91	3.7491	254.9532	0.5745	6.37	58
$Er(NO_3)_3$	7.2709	42	5.2666	29.9765	16.69	2.3164	410.0192	0.3417	3.05	61
$Er(C_2H_5SO_4)_3$	1.1000	11	4.3617	127.6941	1.61	3.8289	211.7333	0.5364	0.37	60
$TmCl_3$	3.8814	25	3.9941	95.7643	6.56	3.2458	172.0431	0.5600	3.62	57
$Tm(ClO_4)_3$	4.5000	20	5.0050	157.0782	12.41	3.6823	254.8830	0.5761	8.57	58
$Tm(NO_3)_3$	5.9526	35	4.9337	35.3098	14.43	2.3809	394.9841	0.3505	2.92	61
$Tm(C_2H_5SO_4)_3$	1.1000	11	4.2949	125.6529	1.48	3.8001	204.7957	0.5400	0.36	60
$SmCl_3$	3.6414	24	3.8954	85.3876	5.92	3.2002	162.0001	0.5509	3.18	57
$Sm(ClO_4)_3$	4.5000	20	4.8205	148.1548	9.25	3.6749	234.9568	0.5793	4.93	58
$Sm(NO_3)_3$	4.2744	27	3.4057	34.0758	4.32	2.9387	94.9978	0.5025	1.67	61
$Sm(C_2H_5SO_4)_3$	0.8000	8	4.3311	129.9814	0.89	3.9771	190.9750	0.5504	0.07	60
$EuCl_3$	3.5839	23	3.8814	87.9613	5.63	3.2125	163.0029	0.5534	2.99	57
$Eu(C_2H_5SO_4)_3$	1.1000	11	4.3410	116.1269	1.25	3.9325	179.9654	0.5503	0.27	60
$GdCl_3$	3.5898	23	3.9035	90.1557	5.83	3.2081	167.9957	0.5525	3.09	57
$Gd(ClO_4)_3$	4.5000	20	4.9276	148.5906	10.70	3.5607	255.9908	0.5683	5.04	58
$Gd(NO_3)_3$	4.3701	27	3.5956	37.1043	4.58	3.0288	106.0274	0.4993	1.45	61
$Gd(C_2H_5SO_4)_3$	0.8000	8	4.2290	132.8269	0.82	3.9216	187.0208	0.5605	0.12	60
$TbCl_3$	3.5733	23	3.9787	92.4627	5.72	3.2796	168.9791	0.5553	3.26	57
$Tb(ClO_4)_3$	4.6196	29	5.5103	147.6444	14.11	3.4520	290.0355	0.5515	6.49	62
$Tb(NO_3)_3$	4.5320	28	3.8263	36.9916	5.58	3.0778	125.6942	0.4779	1.18	61
$YbCl_3$	4.0018	26	4.0181	95.4192	7.16	3.2370	172.9304	0.5597	3.85	57
$Yb(ClO_4)_3$	4.5000	20	4.9607	156.9708	11.09	3.6361	256.8650	0.5749	6.05	58
$Yb(NO_3)_3$	7.9115	45	6.0804	29.3844	22.76	1.6257	789.6905	0.2835	5.31	61
$Yb(C_2H_5SO_4)_3$	1.2000	12	4.4924	127.7401	1.93	3.8983	215.1765	0.5365	0.47	60
$LuCl_3$	4.1239	26	4.0494	95.4644	7.10	3.2447	174.3457	0.5588	3.84	57
$Lu(ClO_4)_3$	4.0000	19	4.6643	164.0388	7.49	3.7967	232.1834	0.5938	4.87	58
$Lu(C_2H_5SO_4)_3$	1.2000	12	4.5216	127.7959	1.99	3.8661	224.9653	0.5278	0.49	60
YCl_3	3.9478	25	4.0951	94.7003	6.90	3.2658	178.0028	0.5537	3.69	57
$Y(C_2H_5SO_4)_3$	1.2000	12	4.4355	123.9935	1.96	3.7937	221.9924	0.5245	0.46	60
$Al(ClO_4)_3$	3.0000	25	4.2458	207.0617	6.76	4.9010	154.0625	0.6945	4.83	63
$K_3Co(cn)_6$	1.3110	15	2.7140	90.0195	4.67	2.7140	9.0195	0.645	4.67	64
$Co(en)_3(NO_3)_3$	0.2749	9	2.3372	−193.6667	4.67	6.2857	-996.5800	0.2269	2.37	64
$Co(pn)_3(ClO_4)_3$	0.2612	9	2.4912	−213.7980	4.63	6.6096	-993.1090	0.2321	2.28	64
$La(BrO_3)_3$[a]	1.837	14	3.0713	17.5084	1.25	3.3857	1.4002	1.1081	0.52	65
$Pr(BrO_3)_3$[a]	1.805	17	3.1362	20.1936	1.35	3.4120	3.2358	0.9896	0.57	65
$Nd(BrO_3)_3$[a]	1.762	11	3.0645	26.0858	2.33	3.4455	1.4604	1.2119	0.97	65
$Sm(BrO_3)_3$[a]	1.883	26	2.8952	32.6826	2.01	3.6185	2.1120	1.1509	0.73	65
$Eu(BrO_3)_3$[a]	1.880	14	3.1328	33.7878	3.01	3.7322	1.5228	1.2447	0.32	65
$Gd(BrO_3)_3$[a]	1.882	11	3.0901	44.4311	3.56	4.1144	2.1081	1.2145	0.88	65
$Tb(BrO_3)_3$[a]	1.624	20	3.2003	47.0840	1.66	4.1831	6.4849	1.0165	0.94	65
$Dy(BrO_3)_3$[a]	1.791	19	3.3317	54.0347	2.96	4.2251	10.7476	0.9479	1.89	65
$Ho(BrO_3)_3$[a]	1.858	23	3.2557	70.5594	3.65	4.8957	9.3279	1.0161	1.68	65
$Er(BrO_3)_3$[a]	2.184	31	3.3354	85.6414	3.29	4.7434	23.9934	0.8725	0.97	65
$Tm(BrO_3)_3$[a]	2.050	20	3.3800	96.0138	2.46	4.5139	40.7834	0.7940	1.01	65
$Yb(BrO_3)_3$[a]	2.119	22	3.3282	100.0263	2.95	4.6168	38.9086	0.8065	1.46	65
$Lu(BrO_3)_3$[a]	2.160	17	2.9308	95.6349	5.23	5.6227	12.0194	1.0027	0.93	65
$Y(BrO_3)_3$[a]	1.836	16	3.4513	72.3989	2.69	5.6108	11.0299	0.9856	1.17	65

[a] Calculated by φ data; $\delta = \left[\sum_i \frac{(\phi^{\text{exptl}} - \phi^{\text{calcd}})^2}{n_p}\right]^{1/2}$.

Table 5. Calculated Parameters for 1-4 Electrolytes in H_2O at $T = 298.15$ K

electrolytes	M_{max}	np	b	S	$10^2\delta$	b_0	S_0	n	$10^2\delta$	refs
					($n = 0.645$)					
$K_4P_2O_7$	2.300	23	3.9129	11.5323	6.12	4.1382	0.0295	1.5919	3.66	66
$K_4W(CN)_8$	1.500	12	3.3819	−10.2106	8.11	4.82244	−479.9760	0.1803	6.38	67
K_4ATP	2.400	24	1.0651	9.9498	8.30	4.2838	0.0036	1.8931	5.84	68
$Na_4P_2O_7$	0.230	3	4.7693	−172.8850	1.05	10.2859	−999.6891	0.2451	0.64	68
Na_4ATP	2.800	28	3.5087	4.3618	12.29	3.5699	0.0001	2.3750	10.03	68
$[N(Me)_4]_4Mo(CN)_8$	1.440	12	2.7861	2.2406	7.24	2.7682	0.0382	1.5616	6.68	67

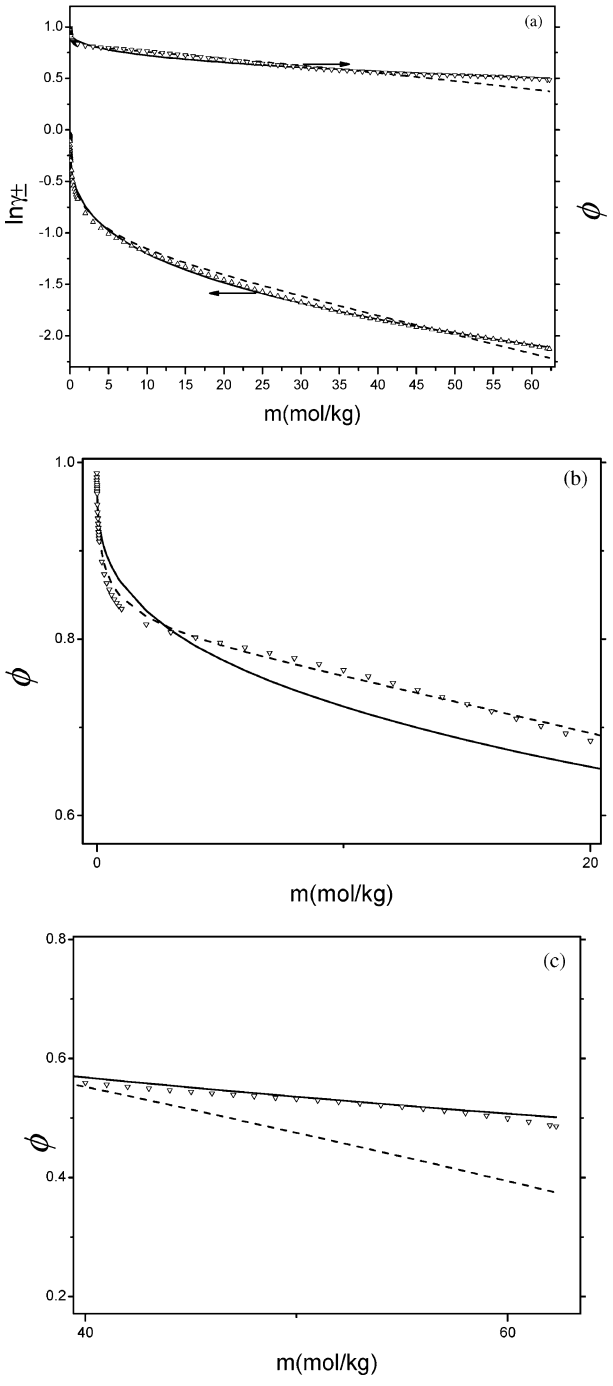

Figure 1. Experimental and calculated mean activity coefficients and osmotic coefficient of $RbNO_2$ aqueous solutions at 298.15 K. △, Experimental data for the mean activity coefficient;[32] ▽, osmotic coefficient.[32] The solid and dashed lines are calculated from the present model with three parameters and two parameters, respectively.

Calculated Results

As mentioned above, the parameters of different electrolytes are summarized in Tables 1 to 6 with the standard deviation (δ). The same set of parameters also can be used to predict the osmotic coefficients of the electrolytes. Figures 1 to 4 give some typical calculated results of mean activity and osmotic coefficients for $RbNO_2$, $MgCl_2$, $Sm(ClO_4)_3$, and $ZnSO_4$, respectively. From these Figures, it can be seen that the present models fit the experimental data very well across the whole range of concentration. Generally speaking, the model with three parameters performs better than does the two-parameter model. Detailed observations in Figure 1b,c show that the two-parameter model ($n = 0.645$) fits the experimental data better than does the model with three parameters at low concentration, but the results are opposite at high concentration. Similar phenomena can be found in predictions of activity and osmotic coefficients of other electrolytes. One can use the different sets of parameters according to different demands. As shown in Tables 1 to 6, there are also some systems with a large discrepancy just like the results in Lin.[15] First, for some electrolytes such as LiBr and rare earth perchlorates, the experimental data at high concentration are very high. For instance, the activity coefficient is 486 for LiBr ($m = 20$ mol·kg^{-1}) and 794.6 ($m = 4.5$ mol·kg^{-1}) for $Sm(ClO_4)_3$. In this case, the small deviation at high ionic strength easily leads to a large error, but the discrepancy is not very significant over the whole range of concentration, as shown in Figure 4. Second, for some special electrolytes with an organic anion or cation, for example, sodium carylate or sodium pelargonate, the size of the anion or cation is much larger than the ion of opposite sign, so the Boltzmann distribution may not be suitable for the charging process. Finally, for some electrolytes such as $ZnCl_2$ and $SrCl_2$, they will form several different complex ions in water, not just the simple anion

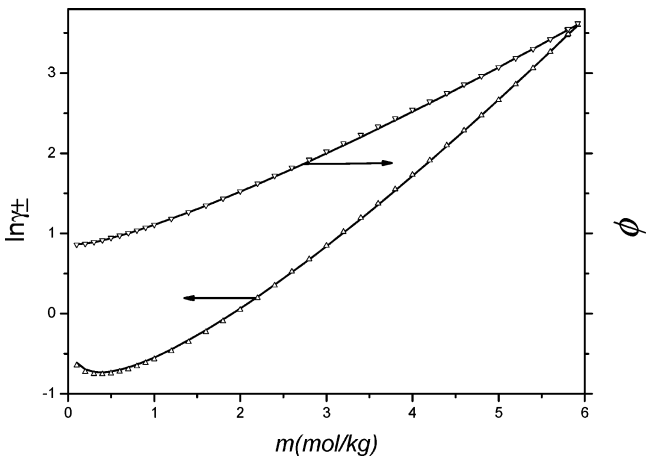

Figure 2. Experimental and calculated mean activity coefficients and osmotic coefficient of $MgCl_2$ aqueous solutions at 298.15 K. △, Experimental data for the mean activity coefficient;[48] ▽, osmotic coefficient.[48] The solid lines are calculated from the present model with three parameters.

Table 6. Calculated Parameters for 2-2 Electrolytes in H_2O at $T = 298.15$ K

electrolytes	M_{max}	np	b	S	$10^2\delta$	b_0	S_0	n	$10^2\delta$	refs
					($n = 0.645$)					
$CdSO_4$	3.500	16	1.8148	16.5049	3.66	1.9075	2.3792	0.9978	1.28	69
$BeSO_4$	4.000	17	1.7800	30.4714	0.91	1.7730	31.9923	0.6370	0.87	69
$CaSO_4$	0.020	5	0.4000	−3765.6000	9.41	3.7734	993.7385	0.2512	7.02	69
$CoSO_4$	0.100	7	2.1226	−684.4149	12.75	9.5692	−979.8825	0.2214	6.32	69
$MgSO_4$	3.000	15	2.0489	20.4444	2.75	2.1389	6.4328	0.8629	1.94	45
$MnSO_4$	4.000	17	1.8731	19.2167	3.97	1.9897	3.3404	0.9473	0.68	45
$NiSO_4$	2.500	14	1.8493	16.0246	3.15	1.9404	1.1474	1.1972	0.65	45
$CuSO_4$	1.400	11	1.7848	14.4541	0.72	1.8234	4.3885	0.9469	0.23	45
$ZnSO_4$	3.500	17	1.8744	21.8461	4.70	2.0189	2.3298	1.0529	0.92	45
$CaCrO_4$	1.112	9	2.9686	−11.0709	2.86	4.1770	−203.0283	0.1982	2.26	70

and cation. For example, $ZnCl_2$ will dissolve into Zn^{2+}, Cl^-, $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$, and $ZnCl_4^{2-}$.[15] The present model is limited in its ability to describe these very complicated systems, and corresponding modifications may be necessary.

Comparison with Other Models

As is well known, the Pitzer model is the most common model. The calculated mean activity coefficients and osmotic coefficients of $AgNO_3$, $MgCl_2$, and $La(ClO_4)_3$ from our results and the original TCPC model or the Pitzer ion interaction parameters are shown in Figures 5 to 7. These figures show the good performance of the present model with two or three parameters, which is at least as good as for the Pitzer model. Pitzer parameters were obtained from the same experimental data and concentration range. It should be noted that Pitzer ion interaction parameters were obtained from osmotic coefficient experimental data. For some electrolytes, the Pitzer model gives better results than the present model for predicting the osmotic coefficients. Because the original TCPC model is limited in its range of concentration (<6 mol·kg^{-1}), it shows a large deviation for the calculation at higher concentration, which can be seen in Figure 5.

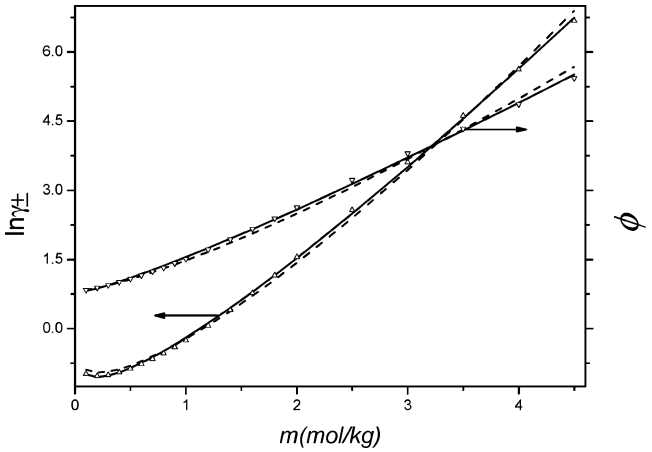

Figure 3. Experimental and calculated mean activity coefficients and osmotic coefficient of $Sm(ClO_4)_3$ aqueous solutions at 298.15 K. △, Experimental data for the mean activity coefficient;[58] ▽, osmotic coefficient.[58] The solid and dashed lines are calculated from the present model with three parameters and two parameters, respectively.

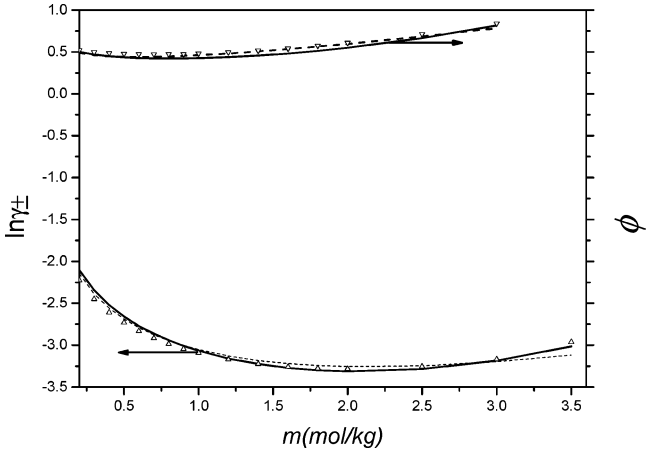

Figure 4. Experimental and calculated mean activity coefficients and osmotic coefficient of $ZnSO_4$ aqueous solutions at 298.15 K. △, Experimental data for the mean activity coefficient;[45] ▽, osmotic coefficient.[45] The solid and dashed lines are calculated from the present model with three parameters and two parameters, respectively.

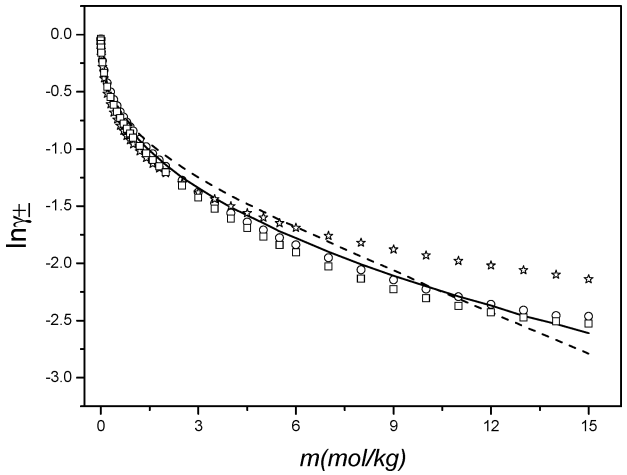

Figure 5. Comparison between experimental and calculated mean activity coefficients of $AgNO_3$ aqueous solutions at 298.15 K. ○, Experimental data;[31] □, Pitzer model;[4] ☆, TCPC model. The solid and dashed lines are calculated from the present model with three parameters and two parameters, respectively.

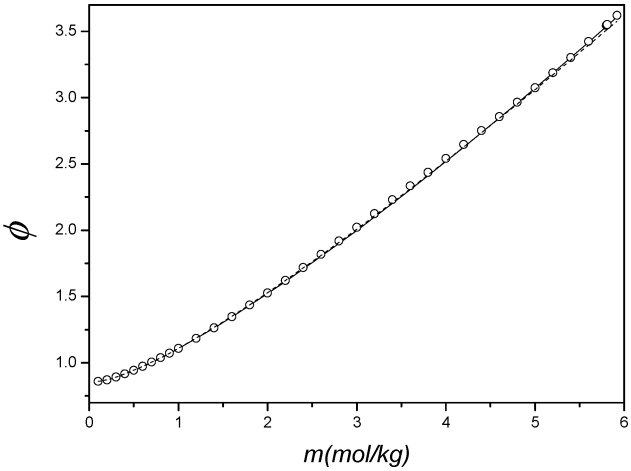

Figure 6. Comparison of experimental and calculated osmotic coefficients of $MgCl_2$ aqueous solutions at 298.15 K. ○, Experimental data.[48] The solid and dashed lines are calculated from the present model with three parameters and two parameters, respectively.

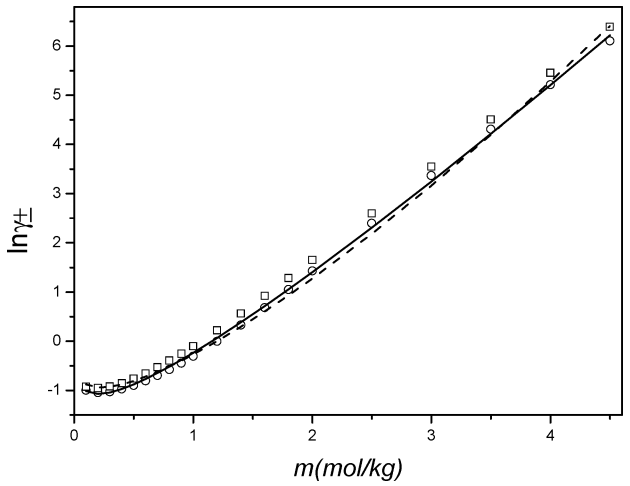

Figure 7. Comparison of experimental and calculated mean activity coefficients of $La(ClO_4)_3$ aqueous solutions at 298.15 K. ○, Experimental data;[31] □, Pitzer model.[4] The solid and dashed lines are calculated from the present model with three parameters and two parameters, respectively.

Conclusions

The original TCPC model for predicting the mean activity coefficients or osmotic coefficient of aqueous electrolyte solutions was modified and extended to be used over a larger range of concentration, generally up to saturation. The model can be formulated with two parameters: *b*, the approaching parameter, and *S*, the solvation parameter. Another parameter *n*, which is related to the distance between an ion and a solvent molecule, also can be regarded as an adjustable parameter. The two sets of parameters were both obtained from the reported experimental data of mean activity coefficients or osmotic coefficients at $T = 298.15$ K. The calculated results for some typical salts such as $RbNO_2$, $MgCl_2$, $Sm(ClO_4)_3$, and $ZnSO_4$ are in good agreement with available smoothed experimental data. The model with adjustable *n* values shows more accurate results than the model only with *b* and *S*, where *n* is a constant, 0.645, especially at high concentration.

The most common semiempirical Pitzer model was also employed to calculate the mean activity and osmotic coefficients for $AgNO_3$, $MgCl_2$, and $La(ClO_4)_3$ aqueous solutions. Also, the original TCPC model was used for comparison with the present model. The results show that the model proposed in this study is on par with the Pitzer model for many single salts whereas the earlier model parameters are not suitable for predicting the thermodynamic properties at high concentration.

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