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Chemical Engineering Thermodynamics

A new model in correlating and calculating the solid–liquid equilibrium of salt–water systems☆



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ABSTRACT

In this work, a new activity coefficient model was deduced for the correlation of solid–liquid equilibrium (SLE) in electrolyte solutions. The new excess Gibbs energy equation for SLE contains two parts: the single electrolyte item and the mixed electrolyte item. Then a new hypothesis for the reference state of activity coefficients was proposed in the work. Literature data for single electrolyte solution and mixed electrolyte solution systems, with temperature spanning from 273.15 to 373.15 K, were successfully correlated using the developed model.

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1. Introduction

Electrolyte solutions are encountered in many natural and industrial processes. The activity coefficient model for electrolyte solutions is widely used in chemical engineering, geochemistry and other fields, such as seawater desalination, crystallization, corrosion studies, hydro-metallurgical studies, and environmental application. So, the study for electrolyte solutions is an important research topic.

A number of activity coefficient models for concentrated electrolyte solutions have been developed for calculating the thermodynamic properties of electrolyte solutions for engineering applications. Some examples are the ElecNRTL model of Chen *et al.* [1–3], Pitzer's model [4], the OLI MSE model of Wang *et al.* [5,6], the Lu–Maurer model of Lu *et al.* [7,8]. These models combine local composition activity coefficient models (the short-range interactions) with the Debye–Hückel's law [9] or modified Debye–Hückel's law (the long-range interactions). Thomsen *et al.* [10,11] and Xu *et al.* [12] studied vapor–liquid equilibrium (VLE), and the models can successfully correlate and predict VLE data in electrolyte solutions. These models mentioned above have been successfully used to calculate the thermodynamic properties of electrolyte solutions at high temperature and high concentrations.

However, describing the thermodynamic properties of electrolyte solutions using conventional thermodynamic models has been quite challenging. Modeling solid–liquid equilibrium for some multicomponent electrolyte solutions is still incomplete. For multicomponent electrolyte solutions, the complicated calculation and low accuracy are the major drawbacks of conventional model. Therefore, it is necessary to explore a new model to accurately and simply describe the thermodynamic properties of electrolyte solutions.

2. Model Description

A modified NRTL model [12] has been successfully proposed to correlate and predict VLE data for electrolyte solutions in our previous work. We obtained the final equation and tested this approach for water activity between 298.15 K and 415.85 K. In this work, a new model is proposed to calculate SLE data in electrolyte solutions.

2.1. Activity coefficient and the new reference

It is still assumed that the solute in the electrolyte solution exists as molecule like our previous work. The activity coefficient of solute in this work is the same meaning as the mean ionic activity coefficient in other model.

In this work, it is assumed that the new reference state of activity coefficients in this model is the activity of solute $a_i (= m_i \times \gamma_i) \rightarrow 1$ as $m_i \rightarrow$ the solubility. The reference is meaningful only to SLE, not to the other situations.

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Table 1
Results of correlation for mixed electrolyte solutions

System	T/K	Data points	This work		Reference and experiment
			$dY/\text{mol} \cdot \text{kg}^{-1}\text{①}$	$dP/\% \text{②}$	
$\text{K}_2\text{CO}_3\text{-KCl-H}_2\text{O}$	273.15–343.15	38	0.097	4.27	[13]
$\text{K}_2\text{SO}_4\text{-KCl-H}_2\text{O}$	273.15–373.15	45	0.019	3.06	[13]
$\text{KCl-CaCl}_2\text{-H}_2\text{O}$	273.15–373.15	62	0.17	5.8	[14,15,16]
$\text{KCl-MgCl}_2\text{-H}_2\text{O}$	273.15–373.15	66	0.09	3.3	[13,14,16]
$\text{KNO}_3\text{-KCl-H}_2\text{O}$	303.15–343.15	42	0.13	1.56	[17,18]
$\text{MgCl}_2\text{-CaCl}_2\text{-H}_2\text{O}$	298.15–348.15	55	0.29	4.6	[14,16,19]
$\text{MgSO}_4\text{-CaSO}_4\text{-H}_2\text{O}$	298.15–328.15	18	0.12	5.1	[20,21]
$\text{MgSO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$	273.15–339.15	64	0.009	0.77	[13]
$\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$	278.15–333.15	57	0.043	2.03	[22]
$\text{NaBr-KBr-H}_2\text{O}$	273.15–323.15	59	0.059	2.7	[13]
$\text{NaCl-CaCl}_2\text{-H}_2\text{O}$	273.15–373.15	27	0.206	5.2	[23]
$\text{NaCl-KCl-H}_2\text{O}$	273.15–373.15	67	0.034	0.64	[13,17,23]
$\text{NaCl-MgCl}_2\text{-H}_2\text{O}$	273.15–373.15	51	0.081	5.1	[13,23]
$\text{NaCl-Na}_2\text{SO}_4\text{-H}_2\text{O}$	288.15–373.15	70	0.042	3.03	[24,25]
$\text{NaCl-NaI-H}_2\text{O}$	273.15–348.15	45	0.2	4.2	[13]
$\text{NaI-KI-H}_2\text{O}$	273.15–323.15	52	0.11	2.2	[13]
$\text{NaCl-NaBr-H}_2\text{O}$	273.15–303.15	42	0.09	4.3	[26]
$\text{NaCl-KCl-MgCl}_2\text{-H}_2\text{O}$	293.15	24	0.055	3.7	[13]
Average difference			0.105	3.4	

① $dY = (1/N) \sum |P_{\text{exp}} - P_{\text{cal}}|$, where N is the number of data points.

② $dP = (1/N) \sum |P_{\text{exp}} - P_{\text{cal}}| / P_{\text{exp}} \times 100\%$, where N is the number of data points.

Because of the change of the activity coefficient's definition and the reference, it is not necessary to consider the situation of $m_i \rightarrow 0$. SLE literature data analysis is in the high concentration, the Debye–Hückel term is disregarded in this model.

2.2. The excess Gibbs energy and modeling

The model for the excess Gibbs energy of SLE is expressed as a new formula in this paper. The model is proposed according to the excess Gibbs energy of Pitzer model. Two contributions of the new model are being considered to account for the excess Gibbs energy. The function of G_w^e is based on $\sum_i \sum_{j \neq i} (m_i m_j \lambda_{i,j})$ in the excess Gibbs energy function of Pitzer model, and G_w^e is adopted to account for the electrostatic interaction term between single electrolyte and water. The function of G_x^e is

based on $\sum_i \sum_{j \neq i} (m_i m_j m_k \Lambda_{i,j,k})$ in Pitzer's, and G_x^e is the electrostatic interaction term between salt and salt, which is usually used in multicomponent electrolyte solutions. It is assumed that solubility of every dissolved solid is affected by other solutes in multicomponent electrolyte solutions. For the calculation, water-salt parameters for electrolyte solutions are shared in single salt systems and mixed salt systems. The excess Gibbs energy is described as follows:

$$G^e = G_w^e + G_x^e \quad (1)$$

$$\frac{n_i G_w^e}{RT} = m_i E_i \quad (2)$$

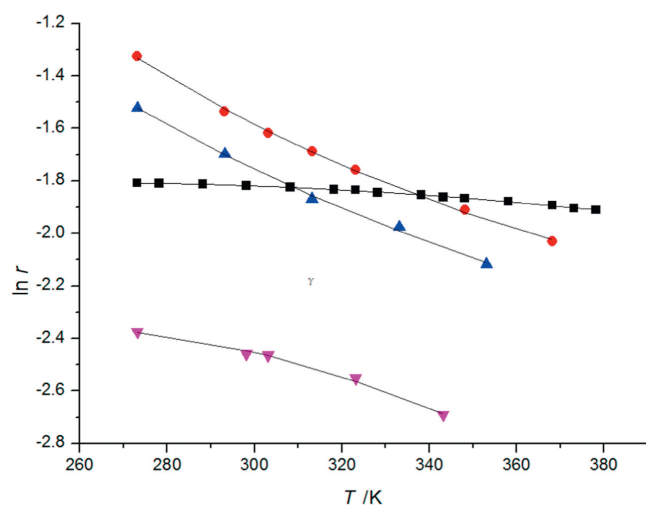


Fig. 1. The correlation of the activity coefficient for NaCl, KCl, KBr, K_2CO_3 solutions. Symbols (■, NaCl; ●, KCl; ▲, KBr; ▼, K_2CO_3): literature data [13]; lines: the correlation result of the new model.

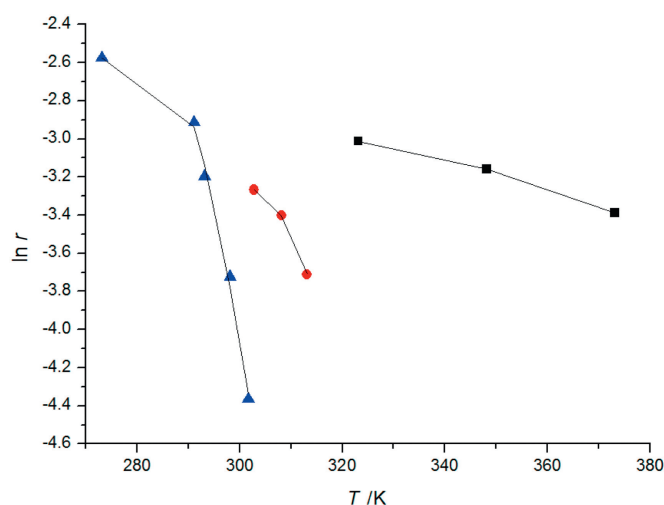


Fig. 2. The correlation of the activity coefficient for CaCl_2 solution. Symbols (■, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; ●, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$; ▲, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$): literature data [23]; lines: the correlation result of the new model.

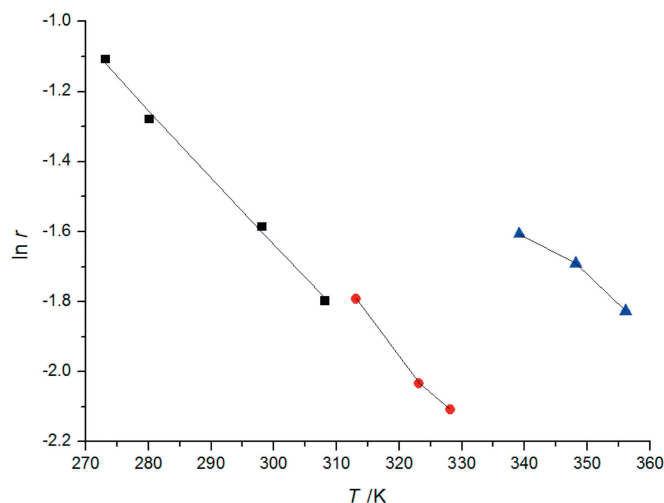


Fig. 3. The correlation of the activity coefficient for MgSO_4 solution. Symbols (■, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; ●, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$; ▲, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$): literature data [13,20]; lines: the correlation result of the new model.

$$\frac{n_i G_x^e}{RT} = \sum_i \sum_{j \neq i} (m_i m_j F_{i,j} + m_i m_j^{k_x} G_{i,j}) \quad (3)$$

where m_i and m_j are the molality of solute; E_i , $F_{i,j}$ and $G_{i,j}$ are the interaction parameters at a particular temperature; $k_x = 0.5$.

$$RT \ln \gamma_i = \left(\frac{\partial n_i G^e}{\partial n_i} \right) \quad (4)$$

In this work, we obtain the activity coefficient of solute from Eqs. (1)–(4), and the final equation can be written as follows:

$$\ln \gamma_i = E_i + \sum_{j \neq i} (F_{i,j} m_j + G_{i,j} m_j^{0.5}) \quad (5)$$

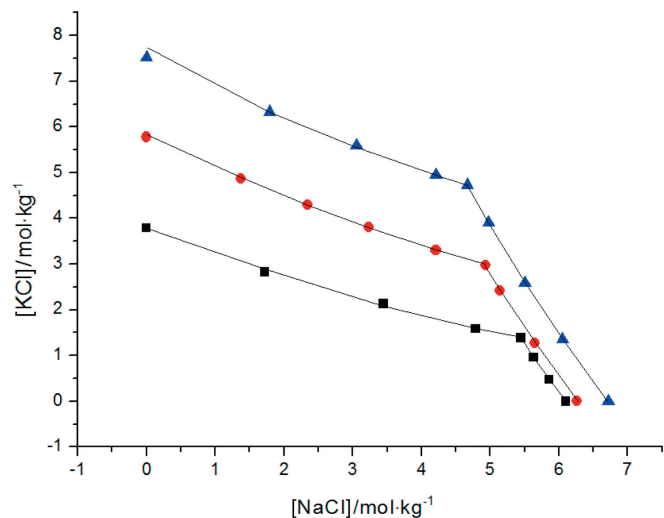


Fig. 4. The correlations of SLE data for NaCl – KCl – H_2O system. Symbols (■, $T = 273.15 \text{ K}$; ●, $T = 323.15 \text{ K}$; ▲, $T = 373.15 \text{ K}$): literature data [13,17,23]; lines: the correlation result of the new model.

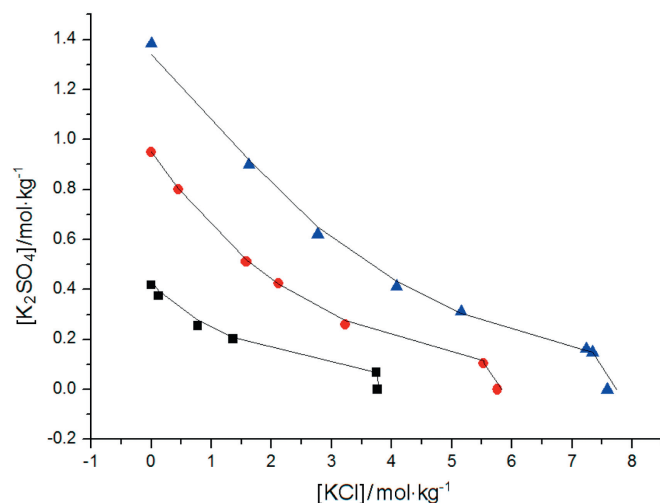


Fig. 5. The correlations of SLE data for K_2SO_4 – KCl – H_2O system. Symbols (■, $T = 273.15 \text{ K}$; ●, $T = 323.15 \text{ K}$; ▲, $T = 373.15 \text{ K}$): literature data [13]; lines: the correlation result of the new model.

We have tested this approach for SLE data between 273.15 K and 373.15 K. To correlate data at different temperatures, the following temperature dependence of the parameter E_i , $F_{i,j}$ and $G_{i,j}$ were used:

$$E_i = pa_{i-1}T + pa_{i-2}T^{0.5} + pa_{i-3}/T \quad (6)$$

$$F_{i,j} = pb_{i-j}T + pc_{i-j}T^{k_i} \quad (7)$$

$$G_{i,j} = pd_{i-j}T + pe_{i-j}T^{k_i} \quad (8)$$

where pa_{i-1} , pa_{i-2} and pa_{i-3} , are water–solute parameters, pb_{i-j} , pc_{i-j} , pd_{i-j} and pe_{i-j} , are solute–solute parameters, and k_i is the temperature parameter.

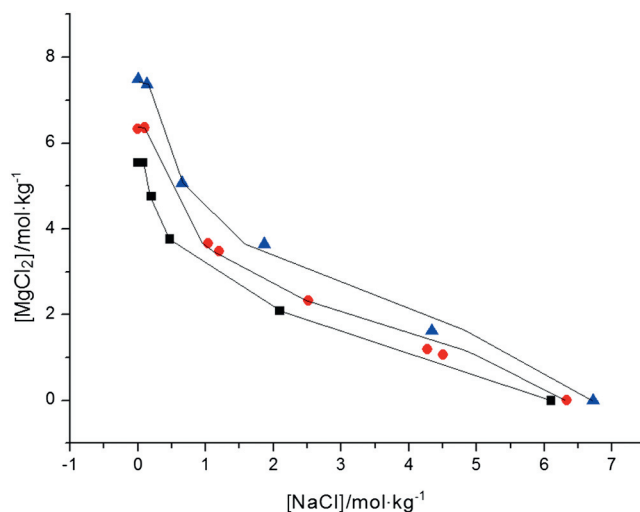


Fig. 6. The correlations of SLE data for NaCl – MgCl_2 – H_2O system. Symbols (■, $T = 273.15 \text{ K}$; ●, $T = 323.15 \text{ K}$; ▲, $T = 373.15 \text{ K}$): literature data [13,23]; lines: the correlation result of the new model.

Table 2

Comparison of the SLE data for single electrolyte solutions

System	T/K	Data points	This work		ElecNRTL		Pitzer	
			dY/mol·kg ⁻¹	dP/%	dY/mol·kg ⁻¹	dP/%	dY/mol·kg ⁻¹	dP/%
NaCl-H ₂ O	273.15–373.15	4	0.032	0.50	0.04	0.64	0.05	0.79
KCl-H ₂ O	273.15–373.15	4	0.077	1.01	0.058	0.96	0.42	3.57
CaCl ₂ -H ₂ O	273.15–373.15	4	0.13	1.65	0.46	6.09	0.35	3.41
K ₂ CO ₃ -H ₂ O	273.15–373.15	4	0.016	0.2	0.51	6.41	0.097	1.15
NaBr-H ₂ O	303.15–373.15	4	0.37	3.1	1.08	12	0.15	1.79
Na ₂ SO ₄ -H ₂ O	298.15–373.15	4	0.11	4.16	2.41	61.37	1.16	25.24
MgSO ₄ -H ₂ O	298.15–373.15	4	0.033	2.10	0.76	11.92	0.34	7.36
MgCl ₂ -H ₂ O	273.15–373.15	4	0.13	2.14	0.16	2.28	0.41	5.70
Average difference dY and dP			0.11	1.85	0.68	12.7	0.37	6.12

Table 3Literature and calculated values of the solubility of the NaCl–KCl–H₂O system

Literature solubility /mol·(kg H ₂ O) ⁻¹				This work (correlated)		This work (predicted)		ElecNRTL		Pitzer	
T /K	NaCl	KCl	Solid Phases	NaCl	KCl	NaCl	KCl	NaCl	KCl	NaCl	KCl
273.15	6.10	0.00	NaCl	6.10		6.10		6.14		6.13	
273.15	5.63	0.96	NaCl	5.63		5.50		5.85		5.55	
273.15	5.44	1.39	NaCl + KCl	5.43	1.40	5.6	1.20	5.85	1.11	5.48	1.08
273.15	3.45	2.13	KCl		2.08		2.30		1.68		1.86
273.15	0.00	3.79	KCl		3.78		3.91		3.77		3.82
298.15	6.16	0.00	NaCl	6.15		6.15		6.13		6.10	
298.15	5.42	1.57	NaCl	5.40		5.6		5.56		5.18	
298.15	5.10	2.18	NaCl + KCl	5.12	2.17	5.41	2.50	5.54	1.62	5.06	1.78
298.15	2.95	3.13	KCl		3.09		3.30		2.77		2.84
298.15	0.00	4.84	KCl		4.80		5.01		4.79		4.80
348.15	6.47	0.00	NaCl	6.46		6.46		6.48		6.44	
348.15	5.29	2.49	NaCl	5.30		5.45		5.45		5.05	
348.15	4.74	3.85	NaCl + KCl	4.75	3.87	4.80	3.79	5.08	3.51	4.51	3.55
348.15	2.68	4.91	KCl		4.94		5.21		4.82		4.70
348.15	0.00	6.67	KCl		6.80		6.89		6.70		6.71
373.15	6.71	0.00	NaCl	6.70		6.70		6.73		6.70	
373.15	4.97	3.91	NaCl	4.97		5.31		5.12		4.64	
373.15	4.67	4.74	NaCl + KCl	4.67	4.73	4.91	4.51	4.93	4.45	4.37	4.50
373.15	1.79	6.33	KCl		6.32		6.55		6.27		5.11
373.15	0.00	7.52	KCl		7.70		7.95		7.53		7.61
Average difference dY and dP				0.026	0.56	0.17	3.5	0.20	5.8	0.20	5.59

The model is useful only to the calculation of SLE in aqueous salt solutions, it is useful for simple calculations when a comprehensive, multi-property models is not needed

and only solubility need to be calculated. Therefore, multiple properties are not considered in this model, such as vapor–liquid equilibria.

Table 4Literature and calculated values of the solubility of the KCl–K₂CO₃–H₂O system

Literature solubility/mol·(kg H ₂ O) ⁻¹				This work (correlated)		This work (predicted)		ElecNRTL		Pitzer	
T /K	KCl	K ₂ CO ₃	Solid phases	KCl	K ₂ CO ₃	KCl	K ₂ CO ₃	KCl	K ₂ CO ₃	KCl	K ₂ CO ₃
273.15	3.76	0.00	KCl	3.78		3.78		3.77		3.77	
273.15	1.25	3.85	KCl	1.10		0.98		0.76		1.44	
273.15	0.70	5.11	KCl	0.63		0.59		0.03		0.90	
273.15	0.21	7.66	KCl + K ₂ CO ₃ ·1.5H ₂ O	0.20	7.66	0.18	7.90	0.02	6.85	0.33	7.55
273.15	0.00	7.75	K ₂ CO ₃ ·1.5H ₂ O		7.76		7.76		6.85		7.78
323.15	5.75	0.00	KCl	5.80		5.80		5.77		5.59	
323.15	2.52	3.76	KCl	2.25		1.95		2.50		1.75	
323.15	0.84	6.86	KCl	0.81		0.77		0.60		0.57	
323.15	0.43	8.64	KCl + K ₂ CO ₃ ·1.5H ₂ O	0.44	8.64	0.40	9.1	0.60	6.86	0.30	8.39
323.15	0.00	8.78	K ₂ CO ₃ ·1.5H ₂ O		8.80		8.8	0.00	8.62	0.00	8.20
343.15	6.49	0.00	KCl	6.60		6.60		6.52		6.02	
343.15	2.56	4.34	KCl	2.47		2.10		4.65		1.58	
343.15	0.77	8.67	KCl	0.76		0.65		1.15		0.31	
343.15	0.60	9.43	KCl + K ₂ CO ₃ ·1.5H ₂ O	0.61	9.43	0.55	9.1	1.02	9.43	0.28	8.91
343.15	0.00	9.64	K ₂ CO ₃ ·1.5H ₂ O		9.60		9.60	0.00	9.42		9.13
Average difference dY and dP				0.05	2.64	0.15	4.5	0.47	20.16	0.34	12.8

Table 5
Literature and calculated values of the solubility of the NaCl–MgCl₂–H₂O system

Literature solubility/mol · (kg H ₂ O) ^{−1}				This work		ElecNRTL		Pitzer	
T /K	NaCl	MgCl ₂	Solid Phases	NaCl	MgCl ₂	NaCl	MgCl ₂	NaCl	MgCl ₂
273.15	6.10	0	NaCl	6.10		6.15		5.96	
273.15	2.09	2.08	NaCl	2.12		2.19		2.24	
273.15	0.47	3.75	NaCl	0.47		0.49		0.63	
273.15	0.079	5.54	NaCl + MgCl ₂ · 6H ₂ O	0.082	5.55	0.11	5.58	0.11	5.49
273.15	0	5.60	MgCl ₂ · 6H ₂ O		5.64		5.56		5.53
298.15	6.16	0.00	NaCl	6.16		6.14		6.10	
298.15	1.86	2.53	NaCl	1.73		1.92		1.76	
298.15	0.53	3.97	NaCl	0.52		0.63		0.55	
298.15	0.091	5.81	NaCl + MgCl ₂ · 6H ₂ O	0.10	5.80	0.16	5.81	0.095	5.68
298.15	0.00	5.84	MgCl ₂ · 6H ₂ O		5.84		5.79		5.72
343.15	6.44	0.00	NaCl	6.42		6.44		6.48	
343.15	1.94	3.10	NaCl	1.66		1.80		1.37	
343.15	0.61	4.41	NaCl	0.67		0.80		0.46	
343.15	0.12	6.67	NaCl + MgCl ₂ · 6H ₂ O	0.13	6.68	0.23	6.81	0.067	6.28
343.15	0.00	6.68	MgCl ₂ · 6H ₂ O		6.70		6.71		6.30
373.15	6.71	0.00	NaCl	6.70		6.74		6.83	
373.15	4.34	1.63	NaCl	4.81		4.03		3.57	
373.15	0.14	7.37	NaCl + MgCl ₂ · 6H ₂ O	0.15	7.37	0.217	7.94	0.044	6.93
373.15	0.00	7.50	MgCl ₂ · 6H ₂ O		7.43		7.66		6.94
Average difference dY and dP				0.052	1.04	0.1	1.61	0.2	2.4

Table 6
Literature and calculated values of the solubility of the NaCl–Na₂SO₄–H₂O system

Literature solubility /mol · (kgH ₂ O) ^{−1}				This work		ElecNRTL		Pitzer	
T/K	NaCl	Na ₂ SO ₄	Solid phases	NaCl	Na ₂ SO ₄	NaCl	Na ₂ SO ₄	NaCl	Na ₂ SO ₄
298.15	3.268	1.459	Na ₂ SO ₄ · 10H ₂ O + Na ₂ SO ₄		1.45		1.19		1.24
298.15	3.968	1.146	Na ₂ SO ₄		1.15		0.83		1.07
298.15	4.534	0.890	Na ₂ SO ₄		0.94		0.61		0.88
298.15	5.309	0.703	Na ₂ SO ₄		0.70		0.41		0.66
298.15	5.537	0.700	Na ₂ SO ₄		0.65		0.37		0.62
298.15	5.640	0.693	Na ₂ SO ₄ + NaCl	5.61	0.62	5.74	0.16	5.48	0.62
298.15	5.776	0.469	NaCl	5.76		5.81		5.63	
298.15	5.913	0.238	NaCl	5.93		5.95		5.86	
298.15	6.087	0.000	NaCl	6.15		6.14		6.1	
323.15	1.881	2.053	Na ₂ SO ₄		2.17		1.56		1.87
323.15	3.791	1.096	Na ₂ SO ₄		1.15		0.59		1.37
323.15	5.855	0.554	Na ₂ SO ₄ + NaCl	5.86	0.62	6.25	0.17	5.51	0.77
323.15	6.027	0.250	NaCl	6.06		6.27		6.03	
373.15	0.000	2.975	Na ₂ SO ₄				2.18		2.53
373.15	1.603	1.981	Na ₂ SO ₄				1.23		1.42
373.15	3.019	1.244	Na ₂ SO ₄				0.57		0.83
373.15	4.075	0.839	Na ₂ SO ₄				0.31		0.56
373.15	6.352	0.445	Na ₂ SO ₄ + NaCl	6.40		6.75	0.093	6.48	0.26
373.15	6.496	0.268	NaCl	6.49		6.60			
373.15	6.714	0.000	NaCl	6.70		6.75		6.71	
Average difference dY and dP				0.036	2.78	0.26	22.5	0.12	7.80

2.3. The calculations for SLE

We obtain the activity coefficient expression of solute from Eqs. (1)–(4), the expression for the solute is as follow:

$$\ln \gamma_i = pa_{i-1}T + pa_{i-2}T^{0.5} + pa_{i-3}/T + \sum_{j,j \neq i} (pb_{i-j}T + pc_{i-j}T^{k_i}m_j + pd_{i-j}T + pe_{i-j}T^{k_i}m_j^{0.5}) \quad (9)$$

$$a_i = m_i \gamma_i \quad (10)$$

We obtain the activity expression from Eq. (10), and the activity of solute is as follow:

$$a_i = m_i \exp \left(pa_{i-1}T + pa_{i-2}T^{0.5} + pa_{i-3}/T + \sum_{j,j \neq i} (pb_{i-j}T + pc_{i-j}T^{k_i}m_j + pd_{i-j}T + pe_{i-j}T^{k_i}m_j^{0.5}) \right) \quad (11)$$

Then, based on the reference state of activity coefficients ($a_i \rightarrow 1$ as $m_i \rightarrow$ the solubility) in this model, the solubility of corresponding solute is obtained. The expression of calculation is as follow:

$$m_x \exp \left(pa_{i-1}T + pa_{i-2}T^{0.5} + pa_{i-3}/T + \sum_{j,j \neq i} (pb_{i-j}T + pc_{i-j}T^{k_i}m_j + pd_{i-j}T + pe_{i-j}T^{k_i}m_j^{0.5}) \right) = 1 \quad (12)$$

where m_x is the solubility of solute.

From Eqs. (9) to (12), we can calculate the solubility m_x of corresponding solute. The software of this calculation is 1stopt 6.0, and the computational algorithm is Universal Global Algorithm.

Table 7

Literature and calculated values of the solubility of the NaCl–KCl–MgCl₂–H₂O System

T / K	Literature solubility/mol·(kg H ₂ O) ⁻¹				This work			ElecNRTL			Pitzer		
	NaCl	KCl	MgCl ₂	Solid Phases	NaCl	KCl	MgCl ₂	NaCl	KCl	MgCl ₂	NaCl	KCl	MgCl ₂
293.15	2.66	1.27	1.65	NaCl + KCl	2.51	1.25		2.93	0.95		2.52	1.38	1.64
293.15	2.14	1.46	1.59	KCl		1.48			1.234			1.55	1.59
293.15	0	2.47	1.59	KCl		2.45			2.29			2.35	1.60
293.15	3.37	1.59	1.14	NaCl + KCl	3.42	1.55		3.67	1.156		3.22	1.60	1.14
293.15	0.44	0.54	3.93	NaCl + KCl + KCl·MgCl ₂ ·6H ₂ O	0.45	0.58	3.92	1.09	0.35	3.17	0.50	0.55	3.93
293.15	0.35	0.25	4.31	NaCl + KCl·MgCl ₂ ·6H ₂ O	0.35		4.28	0.47		4.31	0.38		4.32
293.15	0.09	0.02	5.76	NaCl + KCl·MgCl ₂ ·6H ₂ O	0.11		5.85	0.17		5.824	0.09		5.65
293.15	3.89	0.06	1.07	NaCl		4.28		4.19			3.96		
293.15	3.64	0.96	1.06	NaCl	3.65			3.88			3.59		
293.15	3.33	1.58	1.06	NaCl + KCl	3.57	1.59		3.8	1.189		3.33	1.64	
293.15	2.05	2.12	1.06	KCl		1.99			1.88		2.05	2.14	
293.15	0.12	2.98	1.05	KCl		3.05			3.09		0.12	3.09	
293.15	2.15	0.1	2.1	NaCl	2.11			2.49			2.30		
293.15	1.96	0.79	2.1	NaCl	1.84			2.32			2.08		
293.15	1.88	1.14	2.11	NaCl + KCl	1.8	1.19		2.29	0.765		1.96	1.19	
293.15	1.16	1.35	2.12	KCl		1.37			1.06			1.42	
293.15	0.14	1.8	2.11	KCl		1.79			1.49			1.80	
293.15	0.86	0.07	3.19	NaCl	0.95			1.17			1.00		
293.15	0.84	0.46	3.17	NaCl	0.84			1.15			0.90		
293.15	0.81	0.88	3.18	NaCl + KCl	0.81	0.85		1.14	0.41		0.81	0.79	
293.15	0.39	1.04	3.15	KCl		0.96			0.514			0.92	
293.15	0.04	1.14	3.2	KCl		1.07			0.545			0.90	
293.15	0.44	0.54	3.94	NaCl + KCl + KCl·MgCl ₂ ·6H ₂ O	0.45	0.54	3.93	0.6	0.23	4	0.49	0.53	4.00
293.15	0.19	0.08	5.63	NaCl + KCl·MgCl ₂ ·6H ₂ O	0.17		5.62	0.17		5.45	0.09		5.16
Average difference dY and dP					0.055	3.7		0.28	24.20		0.082	6.57	

3. Results and Discussion

3.1. Correlation of the SLE in electrolyte solutions

The model described above was used to correlate SLE data for thirty-six electrolyte solutions at temperature between 273.15 K and 373.15 K.

Results of seventeen mixed electrolyte solutions are presented in Table 1. The results show that for all seventeen systems: $dY \leq 0.29 \text{ mol} \cdot \text{kg}^{-1}$ and the average of $dY = 0.105 \text{ mol} \cdot \text{kg}^{-1}$, $dP \leq 5.8\%$, and the average of $dP = 3.4\%$.

dY and dP were used:

$$dY = (1/N) \sum |P_{\text{exp}} - P_{\text{cal}}| \quad (11)$$

$$dP = (1/N) \sum |P_{\text{exp}} - P_{\text{cal}}| / P_{\text{exp}} \times 100\% \quad (12)$$

The correlation of the activity coefficient of NaCl, KCl, KBr, K₂CO₃ is shown in Fig. 1, and the results of CaCl₂ and MgSO₄ are shown in Figs. 2 and 3, respectively. The correlations of SLE data over the solutions of NaCl–KCl–H₂O, K₂SO₄–KCl–H₂O and NaCl–MgCl₂–H₂O at different temperature are shown in Figs. 4, 5 and 6, respectively. For these electrolyte solution systems, the model provides satisfactory results. In this work, Tables 8 and 9 present the values of the parameters introduced in Eq. (9), the water–solute parameters are listed in Table 8, the solute–solute parameters are listed in Table 9.

3.2. Prediction of the SLE in mixed electrolyte solutions

The predictive capability of the model was examined by calculating SLE in mixed electrolyte solution systems using values of the parameters obtained from the correlation of binary electrolyte solution systems. The prediction of SLE data over the solutions of NaCl + KCl + H₂O and KCl–K₂CO₃–H₂O are shown in Tables 4 and 5, respectively.

Table 8

Water–salt parameters for electrolyte solutions

System	pa_{i-1}	pa_{i-2}	pa_{i-3}
CaCl ₂ ·2H ₂ O	0.0242	−0.7770	1004.2229
CaCl ₂ ·4H ₂ O	−2.1808	50.3959	−66,574.4435
CaCl ₂ ·6H ₂ O	−2.3994	53.4066	−62,780.7400
CaSO ₄ ·2H ₂ O	0.4174	−9.6198	13,670.9649
CaSO ₄	0.6962	−17.2572	29,185.1172
K ₂ CO ₃	−0.0244	0.4244	−742.3316
K ₂ SO ₄ ·H ₂ O	−0.4639	10.1370	−10,929.8000
K ₂ SO ₄	0.0393	−1.0667	2111.6339
KBr	0.0068	−0.3160	502.7296
KCl	0.0110	−0.4134	678.7843
KI	0.0330	−0.9094	1089.1905
KNO ₃	0.0802	−2.3372	4517.2576
MgCl ₂ ·6H ₂ O	−0.0575	1.1471	−1618.5699
MgCl ₂ ·8H ₂ O	−1.4916	31.7260	−32,911.0151
MgCl ₂ ·12H ₂ O	−2.2508	46.0785	−42,138.7408
MgSO ₄ ·6H ₂ O	0.3653	−9.0441	13,738.8296
MgSO ₄ ·7H ₂ O	−0.1146	2.3491	−2378.5617
MgSO ₄	−0.3301	7.9849	−12,445.6728
NaBr·2H ₂ O	−0.0584	1.1114	−1309.5340
NaBr	0.0078	−0.2929	100.1064
NaCl	−0.0032	−0.0025	−241.1376
NaI·2H ₂ O	−0.0998	2.0254	−2475.9840
NaI	0.1013	−2.6925	4184.2399
Na ₂ SO ₄ ·10H ₂ O	−0.5395	11.2317	−10,193.0890
Na ₂ SO ₄	0.2587	−6.6061	10,804.9482
KCl–CaCl ₂	−0.0028	−1.7031	0.7681
α–KCl–CaCl ₂	0.0005	−0.1888	−1.6382
2KCl–CaCl ₂ ·2H ₂ O	0.2488	−4.3310	2.1560
KCl–MgCl ₂ ·6H ₂ O	−0.1583	0.6613	13,141.9493
CaCl ₂ ·MgCl ₂ ·6H ₂ O	−1.8914	40.3676	−37,769.6400
K ₂ SO ₄ ·MgSO ₄ ·2H ₂ O	0.0094	−0.7402	4455.2703
K ₂ SO ₄ ·MgSO ₄ ·6H ₂ O	−0.1617	3.4573	−2563.9369
Na ₂ SO ₄ ·MgSO ₄ ·2.5H ₂ O	18.8391	−353.9377	42.2690
Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O	−1.0550	18.7487	3688.1585
NaCl·NaBr	−0.0238	0.4119	1028.3250
NaCl·NaBr·2H ₂ O	−1.6159	34.1488	−30,522.2100

Table 9

Salt-salt parameters for electrolyte solutions

Crystal	Salts	$pb_{\text{crystal-salt}}$	$pc_{\text{crystal-salt}}$	$pd_{\text{crystal-salt}}$	$pe_{\text{crystal-salt}}$	k_i
K ₂ CO ₃ -KCl						
KCl	K ₂ CO ₃	0.01994	−0.004150	−0.01967	0.004186	1.2600
K ₂ CO ₃ ·2H ₂ O	KCl	−0.003129	1.4771	0.001971	−0.8427	−0.08058
K ₂ SO ₄ -KCl						
KCl	K ₂ SO ₄	0.02366	−5.993 × 10 ^{−5}	−0.007838	2.1117 × 10 ^{−5}	2.0337
K ₂ SO ₄	KCl	−0.0003347	1.2925	−0.002696	2.2594	−0.1661
KCl-CaCl ₂						
KCl	CaCl ₂	−0.0007506	5.949 × 10 ¹⁸	0.002714	−6.2744	−7.8261
CaCl ₂ ·2H ₂ O	KCl	−0.001335	0.09440	0.0007133	0.04731	0.03474
CaCl ₂ ·4H ₂ O	KCl	−0.002088	118.6813	0.2143	−14455.5423	−0.9350
CaCl ₂ ·6H ₂ O	KCl	0.0103133	−8.3628	0.01472	11.8875	−0.1932
KCl·CaCl ₂	KCl	0.002594	−0.4546	−0.01216	−52988.98	−2.6959
KCl·CaCl ₂	CaCl ₂	−0.009464	1.2169	0.06379	−0.5645	−2.6959
α-KCl·CaCl ₂	KCl	−0.0008419	−5.115 × 10 ^{−6}	0.000876	5.8185 × 10 ^{−7}	9.7598 × 10 ^{−6}
α-KCl·CaCl ₂	CaCl ₂	0.001	−1.2756 × 10 ^{−5}	0.00116	−0.9625	9.7598 × 10 ^{−6}
2KCl·CaCl ₂ ·2H ₂ O	KCl	0.001125	−0.4266	−0.00739	0.1185	−50.3992
2KCl·CaCl ₂ ·2H ₂ O	CaCl ₂	0.0009074	9.7403	−0.00621	2.5543	−50.3992
KCl-MgCl ₂						
KCl	MgCl ₂	0.001158	5.355 × 10 ¹⁰	−0.001144	4.1406 × 10 ¹⁰	−4.6236
MgCl ₂ ·6 H ₂ O	KCl	0.01015	−1.2263 × 10 ³¹	−0.00235	2.7559 × 10 ³⁰	−12.3414
KCl·MgCl ₂ ·6 H ₂ O	MgCl ₂	−0.01838	2697.098	0.0959	−13837.6719	−1.0682
KCl·MgCl ₂ ·6 H ₂ O	KCl	−0.01807	5180.623	0.01776	−7283.0728	−1.0682
KNO ₃ -KCl						
KCl	KNO ₃	0.002573	−0.000901	−0.006199	0.002236	1.1768
KNO ₃	KCl	0.002129	−0.0001732	0.003088	−0.0002592	1.4182
MgCl ₂ -CaCl ₂						
CaCl ₂ ·2H ₂ O	MgCl ₂	0.0005794	−0.1796	0.003230	−0.9824	0.005009
CaCl ₂ ·4H ₂ O	MgCl ₂	−28.0484	31362.12	−0.06493	45.4066	−0.2248
CaCl ₂ ·6H ₂ O	MgCl ₂	0.05821	−19.8619	0.01225	−3.4229	−0.02226
MgCl ₂ ·6 H ₂ O	CaCl ₂	0.01297	−0.0006110	−0.01238	0.0006276	1.5244
CaCl ₂ ·MgCl ₂ ·6 H ₂ O	MgCl ₂	0.5615	−0.2461	−3.2033	1.4015	1.1437
CaCl ₂ ·MgCl ₂ ·6 H ₂ O	CaCl ₂	−0.4822	0.2115	1.6585	−0.7279	1.1437
MgSO ₄ -CaSO ₄						
MgSO ₄ ·7H ₂ O	CaSO ₄	0.5991	−815596.8203	−0.01726	17456.799	−1.499
CaSO ₄ ·2H ₂ O	MgSO ₄	−0.01369	0.0001338	0.03503	−0.000314	1.8277
MgSO ₄ -K ₂ SO ₄						
K ₂ SO ₄	MgSO ₄	0.0002575	−7897507.032	0.0002126	−4485546.319	−3.0856
MgSO ₄ ·H ₂ O	K ₂ SO ₄	0.02287	−5.9055	0.0001384	0.004312	0.05323
MgSO ₄ ·6H ₂ O	K ₂ SO ₄	−0.0001632	−1.7481	−0.0002618	3.6954	−0.6313
MgSO ₄ ·7H ₂ O	K ₂ SO ₄	0.001055	1.7175 × 10 ^{−86}	−0.0007205	−1.2334 × 10 ^{−86}	34.3528
K ₂ SO ₄ ·MgSO ₄ ·2H ₂ O	MgSO ₄	0.2352	−0.06617	−0.7994	0.2249	1.2184
K ₂ SO ₄ ·MgSO ₄ ·2H ₂ O	K ₂ SO ₄	−0.5321	0.1509	0.9212	−0.2631	1.2184
K ₂ SO ₄ ·MgSO ₄ ·6H ₂ O	MgSO ₄	0.01159	−3662.927	−0.03204	10234.57	−1.2887
K ₂ SO ₄ ·MgSO ₄ ·6H ₂ O	K ₂ SO ₄	−0.01868	5219.150	0.05371	−23115.4334	−1.2887
Na ₂ SO ₄ -KI						
KI	Na ₂ SO ₄	−2.9292	0.5548	1.0091	1.8537	0.4996
Na ₂ SO ₄ ·10H ₂ O	KI	−0.2833	−1.4409	0.6491	1.3686	−1.7958
Na ₂ SO ₄ -MgSO ₄						
Na ₂ SO ₄	MgSO ₄	−0.009773	8.4786 × 10 ¹¹	0.01738	−1.4395 × 10 ¹²	−4.5925
Na ₂ SO ₄ ·10H ₂ O	MgSO ₄	0.000889	−0.3047	0.01758	−6.4955	
MgSO ₄ ·6H ₂ O	Na ₂ SO ₄	−0.01078	2.4661	−0.004849	1.1129	0.06236
MgSO ₄ ·7H ₂ O	Na ₂ SO ₄	0.0008796	9473678.8170	−0.0006516	1.0413 × 10 ¹⁹	−8.2048
Na ₂ SO ₄ ·MgSO ₄ ·2.5H ₂ O	Na ₂ SO ₄	−0.1036	7300.1025	114.9325	−7163254.87	−0.8817
Na ₂ SO ₄ ·MgSO ₄ ·2.5H ₂ O	MgSO ₄	−15.6137	972383.0321	0.007907	970.8212	−0.8817
Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O	Na ₂ SO ₄	−0.1009	33.3523	0.3857	−127.6306	−0.0001968
Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O	MgSO ₄	−0.01741	7.9362	0.1848	−67.0097	−0.0001968
NaBr-KBr						
NaBr	KBr	−0.1708	3.5546	−0.04066	0.8365	0.4751
NaBr·6H ₂ O	KBr	0.0002078	1.5738 × 10 ⁶⁸	−8.5386 × 10 ^{−5}	2.7346 × 10 ⁴¹	−28.5519
KBr	NaBr	−0.001995	2.4864	0.001748	−1.8188	−0.1982
NaCl-CaCl ₂						
NaCl	CaCl ₂	−0.0002093	2.0235 × 10 ¹⁹	0.002175	−2.5652 × 10 ¹⁹	−7.9013
CaCl ₂ ·6H ₂ O	NaCl	0.006851	0.4493	−0.008211	0.6363	0.1410
CaCl ₂ ·2H ₂ O	NaCl	0.02322	−9.5101	−0.01877	8.2385	−0.07412
NaCl-KCl						
NaCl	KCl	0.002293	−0.000742	−6.914 × 10 ^{−5}	2.1031 × 10 ^{−5}	1.1742

Table 9 (continued)

Crystal	Salts	$pb_{\text{crystal-salt}}$	$pc_{\text{crystal-salt}}$	$pd_{\text{crystal-salt}}$	$pe_{\text{crystal-salt}}$	k_i
KCl	NaCl	−0.0001425	5719.334	0.000337	−3827.293	−1.7857
NaCl-MgCl ₂	MgCl ₂	−0.00167	29.3024	0.000747	−21.3666	0.5118
MgCl ₂ ·6H ₂ O	NaCl	0.01221	−11096770.79	−0.004196	4044177.004	−2.634
NaCl-Na ₂ SO ₄	Na ₂ SO ₄	−0.0004639	1.5326	0.000111	−0.04864	−0.3244
NaCl	NaCl	−0.000545	7.8458×10^{18}	0.005207	-2.5959×10^{19}	−7.694
Na ₂ SO ₄ ·10H ₂ O	NaCl	0.00621	-2.0494×10^{10}	−0.0134	4.7857×10^{10}	−4.0669
NaCl-NaI	NaI	−0.0005897	105176.65	0.001352	−115,915.649	−2.2115
NaCl	NaCl	0.003707	-2.2042×10^{-77}	−0.00266	2.0491×10^{-77}	30.2611
NaI·2H ₂ O	NaCl	0.003707	-2.2042×10^{-77}	−0.00266	2.0491×10^{-77}	30.2611
NaI-KI	NaI	0.002698	-2.9629×10^{-6}	−0.00176	1.8844×10^{-6}	2.1462
KI	KI	0.0001874	-4.4117×10^{27}	-7.379×10^{-5}	4.3829×10^{177}	−73.2743
NaI·2H ₂ O	KI	0.0001874	-4.4117×10^{27}	-7.379×10^{-5}	4.3829×10^{177}	−73.2743
NaCl-NaBr	NaCl	−0.8606	−0.7711	0.4303	−0.00926	0.9761
NaBr·2H ₂ O	NaCl	−0.0024	−3.3118	−0.07141	2.6212	−1.0939
NaCl-NaBr	NaBr	8.2679×10^{-6}	970.1999	0.07808	−3382.060	−1.0939
NaCl-NaBr·2H ₂ O	NaCl	−263.101	−5564.21	45.4328	−9194.699	−1.4926
NaCl-NaBr·2H ₂ O	NaBr	263.1208	−2884.066	−45.4733	−9.0608	−1.4926

3.3. Comparison with other methods

Eight single electrolyte solution systems and five mixed electrolyte solution systems were selected for comparison with ElecNRTL, Pitzer and the proposed model in this work, as these system had been previously studied using other methods. However, the ElecNRTL and Pitzer models are comprehensive thermodynamic models that reproduce multiple properties, including vapor–liquid equilibria, activity coefficients, and caloric properties in addition to solubility, the new model is useful for simple calculations when a comprehensive, multi-property model is not need and only solubility data need to be correlated.

Results of comparisons for single electrolyte solution systems are shown in Table 2, where dY and dP are listed. Note that the maximum dY(=0.37 mol·kg^{−1}) and the maximum dP(=4.16%) of the model in this work are less than ElecNRTL's (dY = 2.41 mol·kg^{−1}, dP = 61.37%) and Pitzer's (dY = 1.16 mol·kg^{−1}, dP = 25.24%). Similarly, the average dY(=0.11 mol·kg^{−1}) and the average dP(=1.85%) of the model are less than ElecNRTL's (dY = 0.68 mol·kg^{−1}, dP = 12.7%) and Pitzer's (dY = 0.37 mol·kg^{−1}, dP = 6.12%).

Results of comparisons for mixed electrolyte solution systems are shown in Tables 3–7. These systems are NaCl–KCl–H₂O, KCl–K₂CO₃–H₂O, NaCl–MgCl₂–H₂O, NaCl–Na₂SO₄–H₂O and NaCl–KCl–MgCl₂–H₂O, respectively. The average dY(=0.026, 0.05, 0.052, 0.036, 0.055 mol·kg^{−1}) and the average dP(=0.56, 2.64, 1.04, 2.78, 3.7%) of this work are less than ElecNRTL's (dY = 0.20, 0.47, 0.1, 0.26, 0.28 mol·kg^{−1}, dP = 5.8, 20.16, 1.61, 22.5, 24.2%) and Pitzer's (dY = 0.20, 0.34, 0.2, 0.12, 0.082 mol·kg^{−1}, dP = 5.59, 12.8, 2.4, 7.8, 6.57%).

These comparisons show that the model in this work can be used to correlate SLE data over wide ranges of temperatures and concentrations, and the results are better than ElecNRTL's and Pitzer's.

4. Conclusions

In this work, a new model is developed for the calculation of SLE in electrolyte solutions. A new excess Gibbs energy equation for SLE and a new assumption for the reference state of activity coefficients are proposed in the model. The new model was applied to single electrolyte solution and mixed electrolyte solution systems containing a variety of salts at wide ranges of temperature, and the results yielded compared well with literature data and with published models. The model can

successfully correlate SLE data in electrolyte solutions, and the results are better than ElecNRTL's and Pitzer's.

Nomenclature

a	activity
cal	calculation
dY	average absolute error, mol·kg ^{−1}
dP	average relative error, %
exp	experiment
G^e	excess Gibbs energy, J·mol ^{−1}
G_w^e	electrostatic interaction between single electrolyte and water, J·mol ^{−1}
G_x^e	electrostatic interaction term between salt and salt, J·mol ^{−1}
i	component i
j	component j
k_i	temperature parameter
k_x	exponential parameter
m	molality, mol·kg ^{−1}
m_x	solubility, mol·kg ^{−1}
n_t	integral molar quantity, mol
pa	water–solute parameter
pb, pc, pd, pe	solute–solute parameters
R	gas constant, J·mol ^{−1} ·kg ^{−1}
T	temperature, K
γ	activity coefficients

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