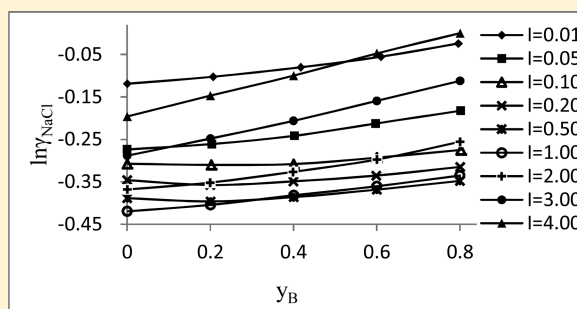# Mean Activity Coefficients of NaCl in NaCl + SrCl$_2$ + H$_2$O Ternary System at 298.15 K Determined by Potential Difference Measurements

Mei-Fang Zhou,[†,‡] Shi-Hua Sang,*[,†,‡] Qing-Zhu Liu,[†,‡] Dan Wang,[†,‡] and Chao Fu[†,‡]

[†]College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, P. R. China
[‡]Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu 610059, P. R. China

ABSTRACT: The mean activity coefficients for NaCl in the (NaCl + SrCl$_2$ + H$_2$O) ternary system were determined by electrode potential measurements of the cell without liquid junction: Na−ion selective electrode (ISE)|NaCl (m_A), SrCl$_2$ (m_B), H$_2$O|Cl−ion selective electrode (ISE) at the total ionic strengths ranging from (0.0100 up to 4.0000) mol·kg^{-1} at 298.15 K for different ionic strength fractions y_B of SrCl$_2$ with y_B = (0.0, 0.2, 0.4, 0.6, and 0.8). The activity coefficient results were interpreted based on the Pitzer model. The Pitzer ion interaction parameters $\theta_{Na^+·Sr^{2+}}$ and $\varphi_{Na^+·Cl^-·Sr^{2+}}$ were calculated. Furthermore, those parameters obtained with the Pitzer model were used to calculate the values of the mean activity coefficients of SrCl$_2$. In addition, the osmotic coefficients, solvent activity, and the excess Gibbs free energy for the mixed electrolyte system were also studied.

Plot of $ln\gamma_{\pm NaCl}$ vs y_B for different ionic strengths I.

1. INTRODUCTION

Electrolyte solutions exist widely in nature, and the study of the thermodynamics properties of mixed electrolyte solutions such as activity coefficients, osmotic coefficients, heat capacity, enthalpy, entropy, and excess free energy is becoming more and more popular. The investigation of those thermodynamics properties is of much interest not only to develop new thermodynamic models and test new electrolyte solution theories,[1,2] but also more importantly to contribute thermodynamic data to the scientific investigation[3−6] and development of applied research work on seawater and the brine industry.

In recent years, electrode potential measurements have become more and more popular in potential analysis because ion−selective electrodes have a wide range of linear response, high sensitivity, good selectivity, and good analysis speed, and automatic and continuous measurement and control is easily realized with this type of measurements. The Pitzer model also plays an important role in predicting the activity coefficient of each solute and osmotic coefficient of aqueous systems.[7] Research reports about activity coefficients calculated using the Pitzer equation[8−13] are increasing all over the word. In the early stages we studied the mean activity coefficients of NaBr in the NaBr + Na$_2$SO$_4$ + H$_2$O system, NaBr in the NaBr + Na$_2$B$_4$O$_7$ + H$_2$O system, NaBr in the NaBr + SrBr$_2$ + H$_2$O system, KBr in the KBr + K$_2$B$_4$O$_7$ + H$_2$O system, and KBr in the KBr + K$_2$SO$_4$ + H$_2$O system at 298.15 K by electrode potential techniques.[14−18]

Clegg[19] measured the Osmotic and Activity Coefficients of NaCl + SrCl$_2$ + H$_2$O at 298.15 K by isopiestic vapor-pressure measurements and obtained the ion-interaction parameters of $\theta_{Na^+·Sr^{2+}}$ and $\varphi_{Na^+·Cl^-·Sr^{2+}}$ for which the total ionic strength was constrained to the range of $I \leq 7$ mol·kg^{-1}. In this work, we determined the activity coefficients of NaCl in the NaCl + SrCl$_2$ + H$_2$O ternary system by electrode potential measurements at 298.15 K and in the (0.0100 to 4.0000) mol·kg^{-1} total ionic strength range, and the Pitzer's ion-interaction parameters of $\theta_{Na^+·Sr^{2+}}$ and $\varphi_{Na^+·Cl^-·Sr^{2+}}$ were evaluated by using the activity coefficients of NaCl in the NaCl + SrCl$_2$ + H$_2$O ternary system. Then the osmotic coefficients, solvent activity, and excess Gibbs free energy of this system were calculated.

2. EXPERIMENTAL SECTION

The apparatus used in this experiment were an AL104 electronic balance (U.S.Mettler-Toledo Group) with an accuracy of 0.1 mg; a UPT-II-20T (Shanghai XiRen Scientific instrument Co., Ltd.) UPT type ultrapure water machine; a Pxsj-216 ion meter (Leici Precision Scientific Instrument Co., Ltd.) with a precision of ±0.1 mV; a JB-1 blender (Leici Precision Scientific Instrument Co., Ltd.); a Bilon-HW-05 (Beijing Bi-Lang Co., Ltd.) constant temperature water-bath with an external circulation system for the circulation of water to keep the temperature constant and a precision of 0.01 K; a PNa-1-01 sodium ion selective electrode (Jiangfen Electroanalytical Instrument Co., Ltd.); a PCl-1-01 chloride ion selective electrode (Jiangfen Electroanalytical Instrument Co., Ltd.); and a 801 reference electrode (Jiangfen Electroanalytical Instrument Co., Ltd.). The Na-ISE was soaked

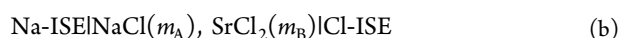for 30 min in a 10^{-2} mol·L^{-1} NaCl aqueous solution and washed with deionized water to a blank potential, static reading was performed on testing; the Cl-ISE was soaked for 2 h in a 10^{-3} mol·L^{-1} NaCl aqueous solution, then cleaned with deionized water; the reference electrode was a double junction saturated calomel electrode with the salt bridge filled with a G. R. grade saturated solution of potassium chloride.

Sodium chloride (NaCl) (Merck pro analysis, 99.99%) and strontium chloride (SrCl$_2$·6H$_2$O) (Jianglai biological, 99%) were heated at 375.15 K and 330.15 K in an oven for about 8 h to 12 h, respectively, and afterward stored over silica gel in desiccators and used without further purification. All aqueous solutions were prepared by using UPT type ultrapure water machine for which the specific conductance was less than 0.055 μs·cm^{-1}. Each concentration of the solutions was prepared at different ionic strength fractions y_B of SrCl$_2$ for each set of measurements by direct weighing of both the solute and the solvent.

The cell arrangements in this work were as follows:

$$\text{Na-ISE}|\text{NaCl}(m_0)|\text{Cl-ISE} \qquad (a)$$

$$\text{Na-ISE}|\text{NaCl}(m_A),\ \text{SrCl}_2(m_B)|\text{Cl-ISE} \qquad (b)$$

The above cells are without liquid junction. m_0 was the molalities of NaCl as single salts in water. m_A and m_B were the molalities of NaCl and SrCl$_2$ in the mixture, respectively. The temperature in the cell was maintained constant within $T = (298.15 \pm 0.01)$ K until the electrode potential was balanced, which changes less than 0.1 mV per 30 min.

Before determining the activity coefficients of a mixture, the electrode potential of cell (a) was measured so as to calibrate the electrode pair composing cell (a), and furthermore, obtain its standard potential and the Nernstian response slope. Then the electrode potential of cell (b) under different ionic strength was measured, and concentration was determined from low to high.

3. RESULTS AND DISCUSSION

3.1. The Performance of the Electrode. According to the galvanic cell (a), the (E_a) (electrode potential values of NaCl) of pure NaCl solution at 0.0010−5.0000 mol·kg^{-1} at $T = 298.15$ K was determined by The Nernstian equation of cell (a) and it can be expressed as follows:

$$
\begin{aligned}
E_a &= E^0 + \kappa \ln a_+ a_- \\
&= E^0 + \kappa \ln a_0 \\
&= E^0 + 2\kappa \ln m_0 \gamma_{0\pm\text{NaCl}}
\end{aligned} \qquad (1)
$$

where $k = RT/F$ is the electrode response slope. The R, F, and T respectively represent the gas constant, Faraday constant, and absolute temperature, E^0 stand for the standard electrode potential of cell (a) and $\gamma_{0\pm\text{NaCl}}$ is the mean activity coefficients of pure NaCl at 298.15 K at different m_0 values in water, and it is taken from the Handbook of Chemistry and physics.[20]

Figure 1 shows that the electrode constant E^0 is 16.343 and the electrode response slope k is 24.924 and the coefficient of determination (R^2) is 0.9999, so there really exists the good liner relation between E_a and $\ln a_{0\pm\text{NaCl}}$. The electrode potential values and molarities are listed in Table 1. As shown in Figure 1, E_a linearly increases with $\ln a_{0\pm\text{NaCl}}$ increasing, so we can say that the Na-ISE and Cl-ISE have a good linear Nernstian response, and it indicates that the electrode pairs used here have a satisfactory Nernstian response and are well suited for our measurements.
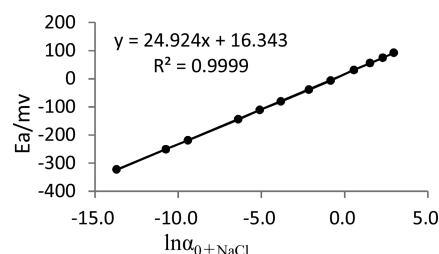

Figure 1. Plot of E_a vs $\ln a_{0\pm\text{NaCl}}$ for calibration of potassium and bromine selective electrode pair at 298.15 K.

Table 1. Calibration of Electrode Pair Na-ISE and Cl-ISE

$m_0{}^a$/mol·kg^{-1}	$\gamma_{0\pm\text{NaCl}}$	$\ln \alpha_{0\pm\text{NaCl}}$	$E_a{}^b$/mV
0.0011	0.965	−13.7045	−335.7
0.0050	0.928	−10.7504	−259.6
0.0100	0.903	−9.4165	−223.1
0.0498	0.822	−6.3902	−147.9
0.1001	0.779	−5.1021	−113.0
0.1998	0.734	−3.8399	−81.1
0.4998	0.681	−2.1555	−39.1
0.9994	0.657	−0.8414	−4.8
1.9702	0.668	0.5493	30.9
2.9980	0.714	1.5222	56.4
3.9938	0.783	2.2802	77.1
4.9942	0.874	2.9472	94.9

$^a m_0$ indicates the molalities of NaCl as single salts in water and standard uncertainties u with 0.68 level of confidence are follows: $u(m_0) = 0.0001$ mol·kg^{-1}, $u(T) = 0.01$ K, ^{b}The average uncertainties of emf were calculated according to data scatter: $u(E_a) = 0.4$ mV.

3.2. Experimental Mean Activity Coefficient of NaCl in the Mixture. According to the galvanic cell (b), we experiment to acquire the electrode potential values E_b of the NaCl in the ternary system (NaCl + SrCl$_2$ + H$_2$O) at $T = 298.15$ K and at different ionic strength $I = m_A + 3m_B$ ranging from (0.0100 to 4.0000) mol·kg^{-1}, and ionic strength fraction $y_B = 3m_B/(m_A + 3m_B) = 0.8, 0.6, 0.4, 0.2, 0.0$, concentration from low to high close to capacity. The Nernstian equation of cell (b) can be written as follows:

$$
\begin{aligned}
E_b &= E^0 + \kappa \ln \alpha_{\text{Na}^+} \cdot \alpha_{\text{Cl}^-} \\
&= E^0 + \kappa \ln m_A (m_A + 2m_B) \gamma_{\pm\text{NaCl}}^2
\end{aligned} \qquad (2)
$$

where $\gamma_{\pm\text{NaCl}}$ and $\gamma_{\pm\text{SrCl}_2}$ are the mean activity coefficient of NaCl and SrCl$_2$ in the cell (b), respectively. After arrangements, eq 2 can be expressed by the following formula:

$$
\ln \gamma_{\pm\text{NaCl}} = \frac{(E_b - E^0)}{2\cdot\kappa} - \frac{1}{2}\cdot\ln[m_A \cdot (m_A + 2m_B)] \qquad (3)
$$

Hence the mean activity coefficients of NaCl can be calculated through eq 3, and the related results of cell (b) are listed in Table 2.

The relationship between the mean activity coefficients $\gamma_{\pm\text{NaCl}}$ for ternary system (NaCl + SrCl$_2$ + H$_2$O) and the ionic strength fraction y_B of SrCl$_2$ is shown in Figure 2. Seen from Figure 2, $\ln \gamma_{\pm\text{NaCl}}$ decreases with the increase of I within a range of I less than 1.0000 mol·kg^{-1}, $\ln \gamma_{\pm\text{NaCl}}$ increased with the increase of I within a range of I more than 1.0000 mol·kg^{-1}.

3.3. Pitzer Equation. In this article, we took the modified form of the Pitzer equation suggested by Harvie and Weare[21,22] to fit the experimental data. For the mixed solution studied,

Table 2. Experimental Mean Activity Coefficients of NaCl in the Mixture at T = 298.15 K

I^a/mol·kg^{-1}	y_B	$m_A{}^a$/mol·kg^{-1}	$m_b{}^a$/mol·kg^{-1}	$E_b{}^b$/mV	$\gamma_{\pm NaCl}{}^b$
0.0100	0	0.0100	0	−219.2	0.8878
0.0100	0.2068	0.0079	0.0007	−225.9	1.0305
0.0107	0.4170	0.0062	0.0015	−231.1	1.0572
0.0098	0.6096	0.0038	0.0020	−246.2	1.0944
0.0100	0.7960	0.0020	0.0027	−261.6	1.1407
0.0498	0	0.0498	0.0000	−146.8	0.8245
0.0506	0.2036	0.0403	0.0034	−152.8	0.8386
0.0504	0.4026	0.0301	0.0068	−161.1	0.8597
0.0501	0.5971	0.0202	0.0100	−171.7	0.8909
0.0499	0.8013	0.0099	0.0133	−190.2	0.9292
0.1001	0	0.1001	0.0000	−113.7	0.7803
0.1003	0.2021	0.0800	0.0068	−121.1	0.7821
0.0996	0.3997	0.0598	0.0133	−130.3	0.7883
0.0993	0.5998	0.0397	0.0198	−141.8	0.8062
0.0991	0.8019	0.0196	0.0265	−160.7	0.8313
0.1998	0	0.1998	0.0000	−81.2	0.7351
0.1999	0.1996	0.1600	0.0133	−89.0	0.7305
0.2001	0.3991	0.1203	0.0266	−97.5	0.7408
0.2004	0.5988	0.0804	0.0400	−108.8	0.7566
0.2001	0.7999	0.0400	0.0534	−127.4	0.7814
0.4998	0	0.4998	0.0000	−37.6	0.6849
0.4994	0.2002	0.3994	0.0333	−45.3	0.6832
0.5005	0.3999	0.3003	0.0667	−53.7	0.6938
0.4978	0.6001	0.1991	0.0996	−65.2	0.7115
0.5002	0.7995	0.1003	0.1333	−83.3	0.7349
0.9994	0	0.9994	0.0000	−4.6	0.6499
0.9999	0.2001	0.7998	0.0667	−11.1	0.6627
0.9982	0.4003	0.5986	0.1332	−19.1	0.6812
0.9988	0.6003	0.3992	0.1998	−30.1	0.7011
0.9997	0.7998	0.2001	0.2665	−48.2	0.7274
1.9702	0	1.9702	0.0000	31.8	0.6683
1.9959	0.1994	1.5979	0.1327	26.0	0.6818
2.0009	0.3989	1.2027	0.2661	18.4	0.7027
1.9972	0.6000	0.7990	0.3994	7.6	0.7285
1.9951	0.8000	0.3991	0.5320	−9.8	0.7684
2.9980	0	2.9980	0.0000	56.7	0.7121
3.0035	0.2003	2.4018	0.2006	51.5	0.7438
2.9927	0.4001	1.7952	0.3992	44.4	0.7792
3.0019	0.6000	1.2008	0.6004	34.8	0.8218
2.9952	0.8000	0.5992	0.7987	17.6	0.8712
3.9934	0	3.9934	0.0000	75.6	0.7715
4.0124	0.1999	3.2104	0.2673	71.0	0.8127
3.9944	0.4001	2.3963	0.5327	64.1	0.8557
3.9941	0.6002	1.5969	0.7991	54.6	0.9074
4.0145	0.7999	0.8031	1.0705	37.8	0.9620

$^a I$, m_A, and m_B indicate the total ionic strength for NaCl + SrCl$_2$ + H$_2$O ternary system and the molalities of NaCl and SrCl$_2$ in the mixture, respectively. Standard uncertainties u with 0.68 level of confidence are as follows: $u(I)$ = 0.0001 mol·kg^{-1}, $u(m_A)$ = 0.0001 mol·kg^{-1}, $u(m_B)$ = 0.0001 mol·kg^{-1}, $u(T)$ = 0.01 K. ^{b}The average uncertainties of emf were calculated according to data scatter: $u(E_b)$ = 0.9 mV, $u(\gamma_{\pm NaCl})$ = 0.0136.
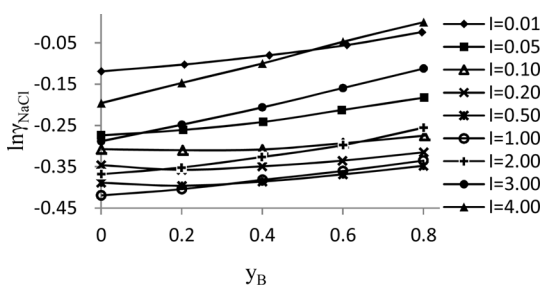
Figure 2. Plot of ln $\gamma_{\pm NaCl}$ vs y_B for different ionic strengths I.

the mean activity coefficients $\gamma_{\pm NaCl}$ and $\gamma_{\pm SrCl_2}$ and the osmotic coefficients Φ can be derived as follows after a series of substitutions and rearrangements. For ionic activity coefficients the corresponding relations are (4 to 6):

$$\ln \gamma_{\pm NaCl} = 2(m_A + m_B)\beta_{NaCl}^{(0)} + m_B\beta_{SrCl_2}^{(0)} + 2(m_A + m_B)g(2\sqrt{I})\beta_{NaCl}^{(1)}$$
$$+ m_B g(2\sqrt{I})\beta_{SrCl_2}^{(1)} + (1.5m_A^2 + 4m_A m_B + 2m_B^2)C_{NaCl}^{\phi}$$
$$+ \frac{\sqrt{2}}{2(m_A m_B + 2m_B^2)}C_{SrCl_2}^{\phi} + m_B\theta + m_B^E\theta$$
$$+ (1.5m_A m_B + m_B^2)\phi + F \qquad (4)$$

$$3\ln \gamma_{\pm SrCl_2} = 4(m_A + 2m_B)\left(m_A C^{\varphi}_{NaCl} + \frac{\sqrt{2}}{2m_B C^{\varphi}_{SrCl_2}}\right)$$
$$+ 4m_A \beta^{(0)}_{NaCl} + (2m_A + 8m_B)\beta^{(0)}_{SrCl_2}$$
$$+ \frac{\sqrt{2}}{2(m_A + 2m_B)^2 C^{\varphi}_{SrCl_2}} + 4m_A g(2\sqrt{I})\beta^{(1)}_{NaCl}$$
$$+ (2m_A + 8m_B)g(2\sqrt{I})\beta^{(1)}_{SrCl_2} + 2m_A\theta$$
$$+ 2m_A^E\theta + (6m_A m_B + m_A^2)\varphi + 6F \qquad (5)$$

$$F = -A_\phi\left\{\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2\ln(1 + 1.2\sqrt{I})}{1.2}\right\}$$
$$+ (m_A + 2m_B)g'(2\sqrt{I})(m_A\beta^{(1)}_{NaCl} + m_B\beta^{(1)}_{SrCl_2})/I$$
$$+ 2m_A m_B^E\theta' \qquad (6)$$

In these eqs 4 to 6, $I = m_A + 3m_B$ is the total ionic strength on a molality scale, A_φ denotes the Debye–Huckel parameter for the osmotic function with value of 0.3915 kg$^{1/2}$·mol$^{-1/2}$ for an aqueous solution at $T = 298.15$ K.[23] The β^0, β^1, and C^φ are the parameters of the Pitzer equation for single salt electrolyte solutions. These parameters were taken from the literature[24] and are presented in Table 3. The Pitzer's ion-

Table 3. Values of the Pitzer's Pure-Electrolyte Parameters β^0, β^1, and C^φ for NaCl and SrCl$_2$ at 298.15 K

	$\beta^{(0)}$	$\beta^{(1)}$	C^φ		
electrolyte	kg·mol^{-1}	kg·mol^{-1}	kg^2·mol^{-2}	σ	ref
NaCl	0.07722	0.25183	0.00106	0.00064	24
SrCl$_2$	0.28170	1.61666	−0.00071	0.00392	24

interaction parameters of $\theta_{Na^+\cdot Sr^{2+}}$ and $\theta_{Na^+\cdot Cl^-\cdot Sr^{2+}}$ indicate the unknown mixing ion-interaction parameters which should be determined.

$$\Phi = [m_A(m_A + 2m_B)\beta^{(0)}_{NaCl} + m_B(m_A + 2m_B)\beta^{(0)}_{SrCl_2}$$
$$+ m_A(m_A + 2m_B)\exp(-2\sqrt{I})\beta^{(1)}_{NaCl}$$
$$+ m_A(m_A + 2m_B)\exp(-2\sqrt{I})\beta^{(1)}_{SrCl_2}$$
$$+ m_A(m_A + 2m_B)^2 C^\varphi_{NaCl} + \frac{\sqrt{2}}{2m_B(m_A + 2m_B)^2 C^\varphi_{SrCl_2}}$$
$$+ 2m_A m_B(^E\theta + \theta + ^E\theta'I) + 2m_A m_B(m_A + 2m_B)\varphi$$
$$- A_\varphi I^{1.5}/(1 + 1.2\sqrt{I})]/(m_A + 1.5m_B) + 1 \qquad (7)$$

where the $^E\theta_{Na,Sr_2}$ and its ionic strength derivative $^E\theta'_{Na,Sr_2}$ stand for the unsymmetrical higher-order electrostatic terms of the Pitzer equation, which can be calculated according to the empirical formula,[6] and their values depend only on the total ionic strength I and the valences of the ions. And all the other parameters are constants and they have their usual significance.[1,5,7] Through eq 4, the Pitzer's ion-interaction parameters of $\theta_{Na^+\cdot Sr^{2+}}$ and $\varphi_{Na^+\cdot Cl^-\cdot Sr^{2+}}$ evaluated by using multiple linear regression technique and the values given in Table 4. Then, the activity coefficients of SrCl$_2$ fractions were calculated by substituting the regressed mixing ionic parameters from eqs 5. These outcomes are also together listed in Table 5.

Table 4. Values of the Pitzer Mixing Interaction Parameters $\theta_{Na^+\cdot Sr^{2+}}$, $\varphi_{Na^+\cdot Cl^-\cdot Sr^{2+}}$ for the NaCl + SrCl$_2$ + H$_2$O Ternary System at 298.15 K

I/mol·kg^{-1}	$\theta_{Na^+\cdot Sr^{2+}}$	$\varphi_{Na^+\cdot Cl^-\cdot Sr^{2+}}$	R^2	ref
0.0100−4.0000	0.0781	0.0925	0.9774	This work

Table 5. Mean Activity Coefficients $\gamma_{\pm SrCl_2}$, the Osmotic Coefficients Φ, Solvent Activity a_W, and Excess Gibbs Free Energies G^E at $T = 298.15$ K

I^a					$G^E \cdot 10^{4b}$
kg·mol^{-1}	y_B	$\gamma_{\pm SrCl_2}$ ^{b}	Φ^b	a_w ^{b}	Kj/mol
0.0100	0	0.7458	0.9678	0.9997	−0.0004
0.0100	0.2068	0.7416	0.9640	0.9997	−0.0004
0.0107	0.4170	0.7317	0.9582	0.9997	−0.0005
0.0098	0.6096	0.7380	0.9543	0.9998	−0.0005
0.0100	0.7960	0.7335	0.9468	0.9998	−0.0006
0.0498	0	0.5846	0.9429	0.9983	−0.0035
0.0506	0.2036	0.5720	0.9367	0.9985	−0.0040
0.0504	0.4026	0.5630	0.9293	0.9987	−0.0044
0.0501	0.5971	0.5567	0.9204	0.9988	−0.0049
0.0499	0.8013	0.5520	0.9081	0.9990	−0.0054
0.1001	0	0.5163	0.9312	0.9966	−0.0092
0.1003	0.2021	0.4995	0.9245	0.9970	−0.0102
0.0996	0.3997	0.4869	0.9164	0.9974	−0.0112
0.0993	0.5998	0.4767	0.9059	0.9977	−0.0125
0.0991	0.8019	0.4682	0.8913	0.9981	−0.0141
0.1998	0	0.4616	0.9220	0.9934	−0.0235
0.1999	0.1996	0.4373	0.9154	0.9941	−0.0254
0.2001	0.3991	0.4172	0.9067	0.9948	−0.0281
0.2004	0.5988	0.4008	0.8950	0.9955	−0.0318
0.2001	0.7999	0.3880	0.8787	0.9962	−0.0361
0.4998	0	0.4290	0.9195	0.9836	−0.0770
0.4994	0.2002	0.3851	0.9148	0.9853	−0.0808
0.5005	0.3999	0.3503	0.9071	0.9870	−0.0893
0.4978	0.6001	0.3231	0.8951	0.9888	−0.1011
0.5002	0.7995	0.3015	0.8774	0.9906	−0.1176
0.9994	0	0.4710	0.9342	0.9669	−0.1796
0.9999	0.2001	0.3923	0.9351	0.9701	−0.1825
0.9982	0.4003	0.3336	0.9308	0.9736	−0.1998
0.9988	0.6003	0.2898	0.9199	0.9771	−0.2309
0.9997	0.7998	0.2571	0.9098	0.9807	−0.2842
1.9702	0	0.7224	0.9812	0.9327	−0.3848
1.9959	0.1994	0.5309	1.0029	0.9371	−0.3680
2.0009	0.3989	0.3986	1.0113	0.9433	−0.3393
1.9972	0.6000	0.3085	1.0037	0.9507	−0.4761
1.9951	0.8000	0.2478	1.0396	0.9587	−0.5927
2.9980	0	1.2050	1.0442	0.8933	−0.5796
3.0035	0.2003	0.8764	1.0956	0.8988	−0.4916
2.9927	0.4001	0.5698	1.1210	0.9078	−0.4409
3.0019	0.6000	0.3924	1.1207	0.9186	−0.6727
2.9952	0.8000	0.2822	1.1836	0.9322	−0.8462
3.9934	0	1.9698	1.1132	0.8520	−0.7286
4.0124	0.1999	1.4889	1.2071	0.8546	−0.5798
3.9944	0.4001	0.9333	1.2569	0.8653	−0.5295
3.9941	0.6002	0.5572	1.2628	0.8806	−0.8200
4.0145	0.7999	0.3571	1.3459	0.8998	−1.0770

^{a}I indicates the total ionic strength for NaCl + SrCl$_2$ + H$_2$O ternary system and standard uncertainties u with 0.68 level of confidence are follows: $u(I) = 0.0001$ mol·kg^{-1}, $u(T) = 0.01$ K. ^{b}The average uncertainties of the mean activity coefficients of SrCl$_2$, osmotic coefficient, solvent activity, and excess Gibbs free energy were calculated in according to data scatter: $u(\gamma_{\pm SrCl_2}) = 0.0157$, $u(\Phi) = 0.0065$, $u(a_W) = 0.0003$ and $u(G^E) = 0.0033$.

3.4. Excess Gibbs Free Energy and Activity of Water.

The excess Gibbs free energy (G^E) and solvent activity (a_w) are calculated from the following relations:

$$G^E = RT[\nu_A m_A (1 - \Phi + \ln \gamma_A) + \nu_B m_B (1 - \Phi + \ln \gamma_B)] \tag{8}$$

$$a_W = \exp\left[-\Phi \cdot M_W \cdot \sum_i \frac{m_i}{1000}\right] \tag{9}$$

where m_A and m_B are the total number of anions and cations of the electrolyte produced by dissociation of one molecule of NaCl and SrCl$_2$, respectively. M_W and m_i are the molecular mass of water (18.0153 g·mol^{-1}) and molality of the solute species, respectively. The results of G^E and a_W were listed in Table 5.

Figure 3 shows the plot of the osmotic coefficient against total ionic strength. It can be seen that the osmotic coefficient of water
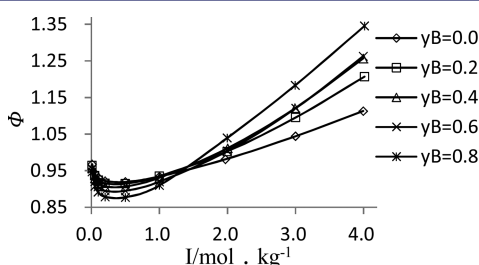
Figure 3. Plot of the osmotic coefficients Φ of water against total ionic strength I of the NaCl + SrCl$_2$+ H$_2$O ternary system at different ionic strength fraction y_B of SrCl$_2$ in the mixture at T = 298.15 K.

is first decreased and then increased by increasing the total ionic strength I in the mixture. Figures 4 to 6 show the changes of the mean activity coefficients of SrCl$_2$, solvent activity, and the excess Gibbs free energy plots as a function of total ionic strength for
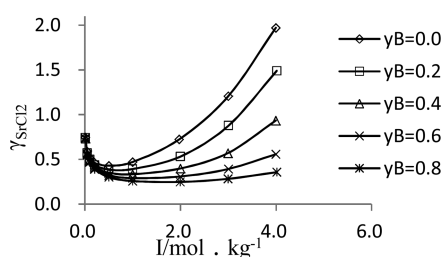

Figure 4. Plot of the values of the mean activity coefficients $\gamma_{\pm SrCl_2}$ for SrCl$_2$ against total ionic strength I of the NaCl + SrCl$_2$+ H$_2$O ternary system at different ionic strength fractions y_B of SrCl$_2$ in the mixture at T = 298.15 K.
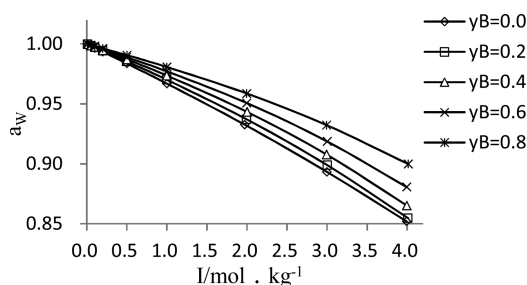

Figure 5. Plot of the solvent activity a_W against total ionic strength I of the NaCl + SrCl$_2$+ H$_2$O ternary system at different ionic strength fractions y_B of SrCl$_2$ in the mixture at T = 298.15 K.
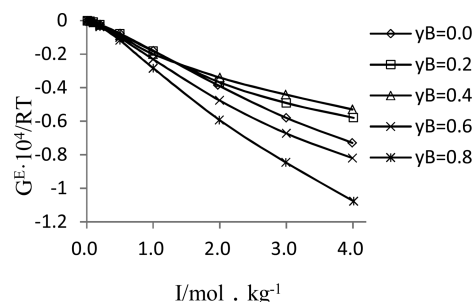

Figure 6. Plot of the excess Gibbs free energy G^E for mixed electrolyte solution against total ionic strength I of the NaCl + SrCl$_2$+ H$_2$O ternary system at different ionic strength fractions y_B of SrCl$_2$ in the mixture at T = 298.15 K.

all of the mixed electrolyte systems investigated, respectively. Figure 6 shows that the excess Gibbs free energy of solution is reduced by increasing total ionic strength.

4. CONCLUSION

The thermodynamic investigation of the NaCl + SrCl$_2$ + H$_2$O ternary system was studied by electrode potential method using Na-ISE and Cl-ISE at 298.15 K. The mean activity coefficients of NaCl in pure and mixed solution were determined by the cells without liquid junction. According to the obtained electrode constant and the response slope, the mean activity coefficients of NaCl in NaCl + SrCl$_2$ + H$_2$O system were calculated using the Nernstian equation. Pitzer ion interaction parameters $\theta_{Na^+ \cdot Sr^{2+}}$ and $\varphi_{Na^+ \cdot Cl^- \cdot Sr^{2+}}$ were calculated by Matlab linear regression method. And then the osmotic coefficients Φ, solvent activity a_W and the excess Gibbs free energy G^E of the system were calculated using these mixing parameters and the Pitzer model. The results showed that the Pitzer model can be used to describe this aqueous system satisfactorily. The results of present investigations indicate that Pitzer model could correlate the experimental results, and the result in this work can provide basic thermodynamic reference data for further research applications.

■ AUTHOR INFORMATION

Corresponding Author
*Tel.: +86 28 84079634. Fax: +86 28 84079074. E-mail: sangsh@cdut.edu.cn, sangshihua@sina.com.cn.

Notes

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