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Thermodynamic Study on Mixed Electrolyte KCl and K_2SO_4 Aqueous Systems from EMF Measurements at 298.15 K

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Activity coefficients for potassium chloride in the $KCl + K_2SO_4 + H_2O$ ternary system were determined from electromotive force (emf) measurements of the cell: K ion selective electrode (ISE)|KCl (m_A), K_2SO_4 (m_B), H_2O|Ag|AgCl at 298.15 K and over total ionic strengths from 0.01 mol·kg^{-1} up to the saturated concentration 2.3 mol·kg^{-1}. The K^+ ion selective electrode (K-ISE) and Ag|AgCl electrode used in this work were prepared in our laboratory and had reasonably good Nernst responses, which demonstrate that the emf method can be applied to measure the above system with high precision in comparison with other methods. The experimental data were analyzed using the Harned rule and the Pitzer model. The Harned coefficients and the Pitzer binary and ternary ionic interaction parameters for the system have been evaluated. The experimental results obey the Harned rule, and the Pitzer model can be used to describe this aqueous system satisfactorily. The activity coefficients of K_2SO_4, the osmotic coefficients of the mixtures, and the excess free energy of mixing were also calculated. Finally, the mutual solubility of the mixed salts was predicted by way of the obtained Pitzer parameters.

Introduction

In western China, there are many salt lakes, most of which are aqueous solutions containing K^+, Na^+, Mg^{2+}, Li^+//Cl^-, SO_4^{2-}, and borate. To scientifically exploit these natural resources is of great strategic importance. The purpose of this present investigation is to obtain basic thermodynamic properties and seek more representative and accurate thermodynamic models for the title system related to the salt lakes by using a relatively convenient and fast method. In our next research plan, we will introduce some organic solvents to this mixture so as to achieve useful results for further research and application.

The determination of thermodynamic properties such as activity coefficients and osmotic coefficients for the mixed salt system $KCl + K_2SO_4 + H_2O$ is of much interest in the chemical industry, development of salt lakes and oceans, and biological or geological processes. Robinson has investigated this system at 298.15 K using an isopiestic method, and Pitzer et al. fitted these isopiestic experimental data to the Pitzer model, evaluating the values of the binary and ternary ion interaction parameters of the model.[1,2] Sarada[3] made emf measurements on the system at three ionic strengths (0.5, 1.0, and 2.0 mol·kg^{-1}). Christenson[4] also carried out a study on this system at one ionic strength (1.0 mol·kg^{-1}) from the emf measurements based on a glass electrode. However, the above measurements are not very systematic and complete, especially since the concentrations of KCl and K_2SO_4 in the mixture are not saturated and not appropriate to the natural brine.

Thus, an approximation to the natural salt lake brine has been made in the present work. The emf measurements were carried out and the activity coefficients were determined at the total ionic strengths (0.01, 0.05, 0.1, 0.5, 1.0, 2.0, and 2.3) mol·kg^{-1} and at a common temperature. The ionic strength fraction for K_2SO_4, y_B, in the system was selected as (0, 0.2, 0.4, 0.6, and 0.8) in order to assign experiments and treat results more rationally and easily.

Experimental Section

Potassium sulfate (K_2SO_4), analytical grade, was twice recrystallized from water before use. Potassium chloride (KCl), guarantee reagent grade and >99.99 mass % purity, was directly used without further purification. Both salts were heated to 473 K in a muffle furnace for about (5 to 8) h, and afterward the chemicals were stored over silica gel in a desiccator before use. The water was deionized and then redistilled in the presence of a small amount of $KMnO_4$. Its specific conductance was $<1.0 \times 10^{-4}$ S·m^{-1}.

The K ion selective electrode (K-ISE), which was a PVC membrane type electrode based on valinomycin and a proper amount of potassium tetraphenylboron as the active agent, was constructed in our laboratory. The related technique has been described elsewhere.[5] The Ag|AgCl electrode was a thermal−electrolytic type prepared in our lab according to Ives and Janz.[6] They both were calibrated before use and showed good Nernst response and selectivity. The ion analyzer used was Orion 868, whose resolution was ±0.1 mV.

The cell vessel was a double-walled glass bottle held at (298.15 ± 0.02) K by circulation of water from a thermostat. The solution in the vessel was stirred with a magnetic stirrer at a slow constant rate.

The cell arrangements in this work were as follows:

$$\text{K-ISE}|\text{KCl}\ (m_{A0})|\text{Ag}|\text{AgCl} \qquad (a)$$

$$\text{K-ISE}|\text{K}_2\text{SO}_4\ (m_{B0})|\text{Ag}|\text{AgCl} \qquad (b)$$

$$\text{K-ISE}|\text{KCl}\ (m_A),\ \text{K}_2\text{SO}_4\ (m_B)|\text{Ag}|\text{AgCl} \qquad (c)$$

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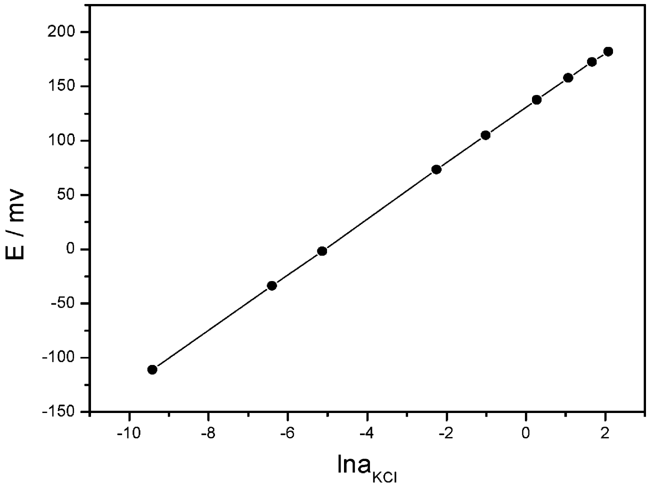

Figure 1. Response line of the K-ISE and the Ag|AgCl electrode pair.

These galvanic cells contained a single liquid without a liquid junction. Here m_{A0} and m_{B0} were the molalities of KCl and K_2SO_4 as single salts in water, respectively. m_A and m_B were the molalities of KCl and K_2SO_4 in the mixture, respectively.

Each concentration of the above solutions in all cells was prepared by directly weighing the materials, using a Sartorius electronic balance whose accuracy was 0.1 mg. In general, for each run the emf reached a stable equilibrium value with a fluctuation of ±0.2 mV after (0.5 to 1) h at all ionic strengths.

At first, the electromotive force (emf) of cell a was measured so as to calibrate the electrode pair composing cell a and, furthermore, obtain its standard potential and the Nernst response slope. And then the emf of cell c was measured in the sequence of the ionic strength fraction (y_B) of K_2SO_4 in the solutions. Finally, the emf of cell b was measured to obtain the selective coefficient (K^{pot}).

Results and Discussion

1. Calibration of the Electrode Pair of K-ISE and Ag|AgCl. For cell a, 21 measurements of m_{A0} from 0.0050 mol·kg^{-1} to 4.8114 mol·kg^{-1} (saturated) were selected to determine each corresponding potential (E_a). The Nernst equation for cell a can be expressed as

$$E_a = E° + k \ln a_{KCl}$$

or

$$E_a = E° + k \ln(m_{A0}^2 \gamma_{\pm A0}^2) \quad (1)$$

where $k = RT/F$ represents the theoretical Nernst slope. R, F, and T are the universal gas constant, the Faraday constant, and the absolute temperature, respectively. $\gamma_{\pm A0}$ designates the mean ionic activity coefficient of pure KCl at different m_{A0} values in water; its values were taken and calculated from Kim's data[7] when needed. $E°$ stands for the experimental standard potential of cell a. With a series of sets of E_a, m_{A0}, and $\gamma_{\pm A0}$, then E_a was plotted against ln a_{KCl} so as to check their linear relationship. As shown in Figure 1 and Table 1, it is clear that there really exists a good linear relation between E_a and ln $a_{KCl.}$ By way of this line, the $E°$ and k can be evaluated using a linear regression method. The value of E_a for each m_{A0} and the values of k and $E°$ along with the corresponding root-mean-square deviation (rmsd) and the linear correlation coefficient (R) are summarized in Table 1. The obtained values of k get quite close to the theoretical one (25.69) of the Nernst slope. Therefore, it is concluded that the electrode pairs used here have a satisfactory Nernst response and are well suitable for our measurements.

2. Selective Coefficient of the Ag|AgCl Electrode for SO_4^{2-} Ion. The Ag|AgCl electrode is, indeed, also a ion selective electrode. Its selectivity for Cl$^-$ is not unique in the aqueous mixture of KCl and K_2SO_4, whereas it could be interfered with by SO_4^{2-}. So, in this case, the disturbance extent, that is, the selective coefficient K^{pot} of electrode Ag|AgCl for SO_4^{2-} should be determined first. Through combining the Nernst principle and reordering the relevant terms, the K^{pot} for the given system can be calculated from the following formula:

$$K^{pot} = [\exp\{(E_b - E°)/k\}]/\{2(m_{B0}\gamma_{\pm B0})^{3/2}\} \quad (2)$$

in which $\gamma_{\pm B0}$ refers to the mean ionic activity coefficient of pure K_2SO_4 in water at 298.15 K, and its value was taken and calculated according to the cited literature.[7] E_b is the emf value of cell b at each measurement. Here we chose four measurements of m_{B0} (0.05, 0.1, 0.25, and 0.5) mol·kg^{-1} to measure E_b. Through calculation the average value of K^{pot} is found to be less than 1.0×10^{-4}.

3. Experimental Mean Activity Coefficients of KCl in the Mixture. Cell c was employed to determine the emf values E_m of KCl and K_2SO_4 as mixed salts in the mixture at 298.15 K and at different ionic strengths I and mole fractions y_B. Here $y_B = I_B/I = 3m_B/(m_A + 3m_B)$. The experimental mean activity coefficients of KCl (see Table 2) in the mixture are derived from the following Nernst equation:

$$E_m = E° + k \ln\{\gamma_{\pm A}^2 m_A(m_A + 2m_B) + K^{pot}\gamma_{\pm B}^{3/2} m_{\pm B}^{1/2}(m_A + 2m_B)\} \quad (3)$$

where $\gamma_{\pm A}$ and $\gamma_{\pm B}$ refer to the mean activity coefficients of KCl and K_2SO_4, respectively, in cell c. Since K^{pot} is so small that the second term within brackets on the right of eq 3 can be neglected without leading to an appreciable error, so we get the simplified form of eq 3

$$E_m = E° + k \ln\{m_A(m_A + 2m_B)\gamma_{\pm A}^2\} \quad (4)$$

After rearrangements, it becomes

$$\ln \gamma_{\pm A} = (E_m - E°)/(2k) - {}^1/_2 \ln\{m_A(m_A + 2m_B)\} \quad (5)$$

Accordingly, the mean activity coefficients of KCl in the aqueous mixture can be calculated through eq 5, and the related results of cell c are collected in Table 2.

4. Application and Testing of Some Electrolyte Solution Theories. (I) The Harned Rule. The Harned rule[8] is one of the earliest proposed and the simplest-formed treatments for strong electrolyte aqueous mixtures. When the total ionic strength remains constant, the activity coefficient of an electrolyte in the mixture is a simple function of the total ionic strength I of the solution. In relation to the studied electrolytic system, the Harned rule can be written as the following equation:

$$\ln \gamma_{\pm A} = \ln \gamma_{\pm A0} - \alpha_{AB} y_B - \beta_{AB} y_B^2 \quad (6)$$

where α_{AB} and β_{AB} represent the Harned interaction coefficients, which are dependent on both ionic strength and temperature, and $\gamma_{\pm A0}$ are the mean activity coef-

Table 1. Calibration of the Electrode Pair K-ISE|Ag|AgCl

m/mol·kg^{-1}	0.0100	0.0500	0.1000	0.5000	1.0000	2.0000	3.0000	4.0000	4.8114
E_a/mV	−109.1	−32.9	−1.8	73.4	105.7	137.7	157.1	171.6	181.8
K					25.51				
$E°$/mV					130.3				
R					0.9999				
rmsd					0.5070				

Table 2. Experimental Mean Activity Coefficients of KCl in the Mixture at 298.15 K

I/mol·kg^{-1}	y_B	m_A/mol·kg^{-1}	m_B/mol·kg^{-1}	E_m/mV	$\gamma_{\pm KCl}$
0.01	0.0	0.0100	0.0000	−110.9	0.9009
	0.2	0.0080	0.0007	−118.3	0.8999
	0.4	0.0060	0.0013	−127.9	0.9001
	0.6	0.0040	0.0020	−140.2	0.8988
	0.8	0.0020	0.0027	−160.1	0.8973
0.05	0.0	0.0500	0.0000	−33.6	0.8152
	0.2	0.0400	0.0033	−41.2	0.8139
	0.4	0.0300	0.0067	−50.5	0.8116
	0.6	0.0200	0.0100	−63.2	0.8092
	0.8	0.0100	0.0133	−83.3	0.8064
0.10	0.0	0.1000	0.0000	−1.2	0.7679
	0.2	0.0800	0.0067	−8.8	0.7656
	0.4	0.0600	0.0133	−18.3	0.7628
	0.6	0.0400	0.0200	−30.9	0.7589
	0.8	0.0200	0.0267	−51.2	0.7544
0.50	0.0	0.5000	0.0000	72.7	0.6495
	0.2	0.4000	0.0333	64.8	0.6444
	0.4	0.3000	0.0667	55.1	0.6378
	0.6	0.2000	0.1000	41.9	0.6295
	0.8	0.1000	0.1333	21.1	0.6197
1.00	0.0	1.0000	0.0000	104.5	0.6040
	0.2	0.8000	0.0667	96.4	0.5973
	0.4	0.6000	0.1333	86.4	0.5884
	0.6	0.4000	0.2000	73.0	0.5772
	0.8	0.2000	0.2667	51.8	0.5641
2.00	0.0	2.0000	0.0000	137.2	0.5729
	0.2	1.6000	0.1333	128.9	0.5636
	0.4	1.2000	0.2667	118.5	0.5513
	0.6	0.8000	0.4000	104.7	0.5362
	0.8	0.4000	0.5333	83.0	0.5186
2.30	0.0	2.3000	0.0000	144.1	0.5698
	0.2	1.8400	0.1533	135.7	0.5597
	0.4	1.3800	0.3067	125.3	0.5465
	0.6	0.9200	0.4600	111.3	0.5304
	0.8	0.4600	0.6133	89.4	0.5116

Table 3. Parameter Values of the Harned Equation and the rmsd

I/mol·kg^{-1}	ln $\gamma_{\pm A0}$	$10^2\alpha_{AB}$	$10^2\beta_{AB}$	10^3(rmsd)
0.0100	−0.1045	−0.0607	−0.5179	0.3585
0.0500	−0.2042	−0.7893	−0.7321	0.1287
0.1000	−0.2640	−1.1628	−1.3214	0.0783
0.5000	−0.4316	−3.1936	−3.3400	0.0169
1.0000	−0.5028	−6.9009	−2.4744	3.8914
2.0000	−0.5571	−6.7636	−7.0893	0.0170
2.3000	−0.5624	−7.4314	−7.5357	0.0169

ficients of KCl in pure solutions at the same total ionic strength as that of the mixture. The outcomes, listed in Table 3 and shown in Figure 2, indicate that at lower ionic strengths the relationship between ln $\gamma_{\pm A}$ and y_B basically appears to be linear, but it becomes slightly curved when the ionic strength becomes higher ($I > 1.00$ mol·kg^{-1}). From the above results we can conclude that the Harned rule can be applied to describe the title system very well.

(II) Pitzer Model. In this article, we adopted the modified form of the Pitzer equation suggested by Harvie and Weare[9] to fit the experimental data. For the mixed solution studied, after a series of substitutions and rearrangements of related terms, the mean activity coefficients $\gamma_{\pm KCl}$ and $\gamma_{\pm K_2SO_4}$ and the osmotic coefficients Φ can be given as the following equations:

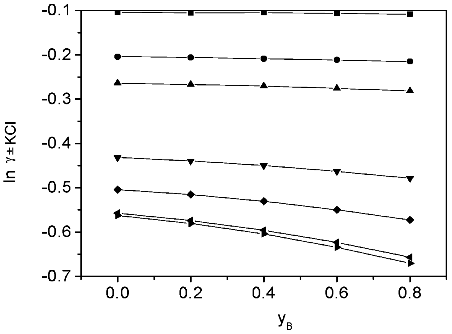

Figure 2. Plot of ln $\gamma_{\pm KCl}$ against y_B in the following mixtures: ■, $I = 0.01$; ●, $I = 0.05$; ▲, $I = 0.10$; ▼, $I = 0.50$; ◆, $I = 1.00$; triangle left solid, $I = 2.00$; triangle right solid, $I = 2.30$.

$$\ln \gamma_{\pm KCl} = 2(m_A + m_B)\beta^{(0)}_{KCl} + m_B\beta^{(0)}_{K_2SO_4} + 2(m_A + m_B)g(2\sqrt{I})\beta^{(1)}_{KCl} + m_B g(2\sqrt{I})\beta^{(1)}_{K_2SO_4} + (1.5m_A^2 + 4m_Am_B + 2m_B^2)C^{\phi}_{KCl} + \sqrt{2}/2(m_Am_B + 2m_B^2)C^{\phi}_{K_2SO_4} + m_B\theta + m_B{}^{E}\theta + (1.5m_Am_B + m_B^2)\psi + F \quad (7)$$

$$3 \ln \gamma_{\pm K_2SO_4} = 4(m_A + 2m_B)(m_AC^{\phi}_{KCl} + \sqrt{2}/2m_BC^{\phi}_{K_2SO_4}) + 4m_A\beta^{(0)}_{KCl} + (2m_A + 8m_B)\beta^{(0)}_{K_2SO_4} + \sqrt{2}/2(m_A + 2m_B)^2C^{\phi}_{K_2SO_4} + 4m_Ag(2\sqrt{I})\beta^{(1)}_{KCl} + (2m_A + 8m_B)g(2\sqrt{I})\beta^{(1)}_{K_2SO_4} + 2m_A\theta + 2m_A{}^{E}\theta + (m_A^2 + 6m_Am_B)\psi + 6F \quad (8)$$

$$F = -A_{\phi}\{\sqrt{I}/(1 + 1.2\sqrt{I}) + 2 \ln(1 + 1.2\sqrt{I})/1.2\} + (m_A + 2m_B)g'(2\sqrt{I})(m_A\beta^{(1)}_{KCl} + m_B\beta^{(1)}_{K_2SO_4})/I + 2m_Am_B{}^{E}\theta' \quad (9)$$

where A_{ϕ} denotes the Debye−Huckel parameter for the osmotic function, with its value being 0.392 for an aqueous solution at 298.15 K. All the other symbols have their usual significance[10]

$$\Phi = \{m_A(m_A + 2m_B)\beta^{(0)}_{KCl} + m_B(m_A + 2m_B)\beta^{(0)}_{K_2SO_4} + m_A(m_A + 2m_B)\exp(-2\sqrt{I})\beta^{(1)}_{KCl} + m_B(m_A + 2m_B)\exp(-2\sqrt{I})\beta^{(1)}_{K_2SO_4} + m_A(m_A + 2m_B)^2C^{\phi}_{KCl} + \sqrt{2}/2m_B(m_A + 2m_B)^2C^{\phi}_{K_2SO_4} + 2m_Am_B({}^{E}\theta + \theta + {}^{E}\theta'I) + 2m_Am_B(m_A + 2m_B)\cdot\psi - A_{\phi}I^{1.5}/(1 + 1.2\sqrt{I})\}/(m_A + 1.5m_B) + 1 \quad (10)$$

in which the symbols represent the same meaning as that mentioned above. In these equations, ${}^{E}\theta$ and ${}^{E}\theta'$ stand for the unsymmetrical higher-order electrostatic terms of the Pitzer model, which can be calculated according to the empirical formula[11] suggested by Pitzer.

The Pitzer's mixing interaction parameters (θ_{Cl-SO_4}, ψ_{Cl-SO_4-K}), by taking into account the contribution of

Table 4. Values of the Mixing Interaction Parameters of the Pitzer Equation

				10^3(rmsd)	
	I/mol·kg^{-1}	θ_{Cl-SO_4}	ψ_{Cl-SO_4-K}	$\theta_{Cl-SO_4} \neq \psi_{Cl-SO_4-K} \neq 0$	$\theta_{Cl-SO_4} = \psi_{Cl-SO_4-K} = 0$
emf	0.01−2.3000	0.04481	−0.004165	4.05	7.54
isop[a]	0.01−2.3000	0.0300	−0.0050		

[a] isop: isopiestic method and taken from ref 1.

Table 5. Mean Activity Coefficients of K_2SO_4 in the Mixture, Osmotic Coefficients of the Mixture, and Excess Free Energies of Mixing

I/mol·kg^{-1}	y_B	$\gamma_{\pm K_2SO_4}$	Φ	$\Delta_m G^E$/J·kg^{-1}
0.01	0.0	0.8035	0.9673	0
	0.2	0.8042	0.9622	0.1117
	0.4	0.8068	0.9574	0.1665
	0.6	0.8068	0.9504	0.0743
	0.8	0.8064	0.9419	−0.0607
0.05	0.0	0.6436	0.9404	0
	0.2	0.6466	0.9305	1.2645
	0.4	0.6481	0.9188	1.4156
	0.6	0.6495	0.9056	0.7003
	0.8	0.6501	0.8893	−0.4496
0.10	0.0	0.5597	0.9267	0
	0.2	0.5631	0.9132	3.2252
	0.4	0.5656	0.8981	3.8207
	0.6	0.5667	0.8803	1.8127
	0.8	0.5666	0.8585	−1.2905
0.50	0.0	0.3628	0.9004	0
	0.2	0.3674	0.8754	29.0193
	0.4	0.3701	0.8474	33.4486
	0.6	0.3707	0.8149	16.7629
	0.8	0.3695	0.7754	−7.1652
1.00	0.0	0.2901	0.8982	0
	0.2	0.2949	0.8662	73.6664
	0.4	0.2975	0.8311	84.9905
	0.6	0.2977	0.7902	44.7896
	0.8	0.2955	0.7391	−9.1830
2.00	0.0	0.2328	0.9123	0
	0.2	0.2374	0.8719	186.2611
	0.4	0.2393	0.8296	207.5644
	0.6	0.2386	0.7798	111.7303
	0.8	0.2351	0.7129	1.5779
2.30	0.0	0.2238	0.9188	0
	0.2	0.2282	0.8765	223.5787
	0.4	0.2299	0.8331	244.7459
	0.6	0.2288	0.7817	129.8167
	0.8	0.2250	0.7110	5.2622

higher-order electrostatic terms, were evaluated by using a multiple linear regression technique. In this case, it is assumed that θ_{Cl-SO_4} and ψ_{Cl-SO_4-K} are independent of ionic strength. Table 4 shows the contrast between the results obtained by emf and by isopiestic methods, respectively. It is clear that the obtained Pitzer parameters and the corresponding rmsd's of both the methods agree with each other very well. That further makes clear the consistency of the thermodynamic study by use of these two methods and simultaneously the reliability of the used research method as well as the results.

The activity coefficients of K_2SO_4 and the osmotic coefficients for the mixture at different ionic strengths were calculated by substituting the regressed mixing parameters obtained from this work in the Pitzer equation. These results are together given in Table 5.

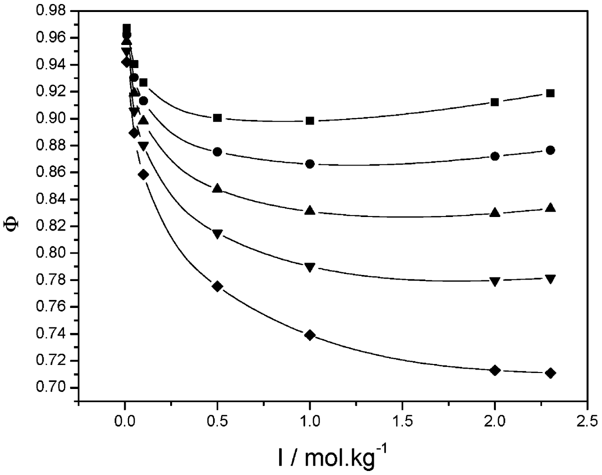

Figure 3. Plot of osmotic coefficient Φ against ionic strength I in the following mixtures: ■, $y_B = 0.0$; ●, $y_B = 0.2$; ▲, $y_B = 0.4$; ▼, $y_B = 0.6$; ◆, $y_B = 0.8$.

As seen from the above results, the Pitzer equation could correlate the experimental data with very small errors, which also tested the stability and suitability of our electrode used during experiments.

5. Excess Free Energy of Mixing for the System KCl and K_2SO_4 and H_2O. The excess free energies of mixing have been calculated by using the following relation:[12]

$$\Delta_m G^E = 2m_A RT\{\ln(\gamma_{\pm A}/\gamma_{\pm A0}) + Y_A(\Phi_A - \Phi)\} + 3m_B RT\{\ln(\gamma_{\pm B}/\gamma_{\pm B0}) + Y_B(\Phi_B - \Phi)\}$$

where $\gamma_{\pm A0}$ and Φ_A, respectively, refer to the mean activity coefficient and the osmotic coefficient of KCl in pure solution at the same total ionic strength as that of the mixture. The Y_A is the mole fraction of KCl in the mixture, and the subscript B symbolizes K_2SO_4. The calculated results are also listed in Table 5. Figure 3 shows the relation between the osmotic coefficients Φ of the mixture and the total ionic strength I of the system.

6. Prediction and Experimental Validation of Mutual Solubility in the Mixture. Predicting the solubility of mixed salts in aqueous solution is one of the most important applications of the Pitzer theoretical model. For the mixed salt system studied, at constant temperature it is assumed that KCl is saturated but K_2SO_4 is not. In such a case, the following dissociation equilibrium equation should exist,

$$KCl(s) \rightleftarrows K^+(aq) + Cl^-(aq)$$

and we thus have the dissociation equilibrium constant equation

$$K_{KCl} = a_{K^+}a_{Cl^-}$$

in which K_{KCl} is the equilibrium constant of the dissociation reaction of KCl(s). As for K_2SO_4, it should be dissociated completely. Consequently, in this aqueous mixture, there should exist the relation

Table 6. Predicted and Experimental Results of the Solubility of KCl in the Mixture[a]

S_{cal}/mol·kg^{-1}	KCl	4.8114	4.7539	3.4438	2.4567	1.5707	0.7621	0.0000
	K_2SO_4	0.0000	0.0801	0.1547	0.2172	0.3091	0.4565	0.6912
S_{exp}/mol·kg^{-1}	KCl	4.8114	4.4847	3.4438	2.4567	1.5707	0.7621	0.0000
	K_2SO_4	0.0000	0.0861	0.1547	0.2318	0.3304	0.4635	0.6912

[a] S_{cal}: calculated solubility. S_{exp}: experimental solubility.

$$K_{\mathrm{KCl}} = S(S + m^{2}{}_{\mathrm{K_2SO_4}})\gamma^{2}_{\pm\mathrm{KCl}}$$

where S (unit: mol·kg^{-1}) refers to the solubility of KCl and $m_{\mathrm{K_2SO_4}}$ is the given concentration of K_2SO_4 in the mixture. $\gamma_{\pm\mathrm{KCl}}$ denotes the mean activity coefficient of KCl, which is already expressed as in eq 7. To achieve the solubility S, here the key point is to obtain the accurate value of K_{KCl} at first. Since the Pitzer model can describe the binary system KCl + H_2O with high precision, even up to saturated concentration, we chose relatively accurate solubility data of KCl in water at 298.15 K from the literature[13] to compute the equilibrium constant K_{KCl} by using the Pitzer equation. The selected solubility of KCl in water at 298.15 K and the calculated equilibrium constant K_{KCl} are 4.8114 mol·kg^{-1} and 0.898, respectively. Thereby, after introducing K_{KCl} and $\gamma_{\pm\mathrm{KCl}}$ into the above equation, we can get a function about the unknown variable S. By way of an iterative technique and a computer program, the solubility of KCl can be obtained for a given concentration of K_2SO_4 in the aqueous mixture. Table 6 lists both the calculated and the experimental mutual solubilities.

As seen from the results, it is evident that the predicted solubility agrees satisfactorily with the experimental one, and the Pitzer model can be applied to accurately predict solubility.

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Literature Cited

(1) Pitzer, K. S. *Activity coefficients in electrolyte solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991; p 118.

(2) Pitzer, K. S.; Kim, J. J. Thermodynamics of electrolytes: Activity and osmotic coefficients for mixed electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701−5707.

(3) Sarada, S.; Ananthaswamy, J. Thermodynamic properties of mixed electrolyte solutions: Activity coefficients of KCl in KCl−K_2SO_4−H_2O system at 25, 35 and 45 °C. *J. Electrochem. Soc. India* **1991**, *40*, 19−22.

(4) Christenson, P. G.; Gieskes, J. M. Activity coefficients of KCl in several mixed electrolyte solutions at 25 °C *J. Chem. Eng. Data* **1971**, *16*, 398−400.

(5) Wu, G.-L.; Gao, S.-W. Construction and application of valinomycin potassium electrodes. *Chem. World (Chin.)* **1981**, *10*, 291−293.

(6) Ives, D. J. G.; Janz, G. J. *Reference Electrodes*; Academic Press: New York, 1961; Chapter 4, pp 179−230.

(7) Kim, H. T.; Frederick, W. J. Evaluation of Pitzer Ion Interaction Parameters of Aqueous Electrolytes at 25 °C. 1. Single Salt Parameters. *J. Chem. Eng. Data* **1988**, *33* (2), 177−184.

(8) Harned, H. S.; Owen, B. B. *The physical chemistry of electrolytic solutions*, 2nd ed.; American Chemical Society Monograph Series; 1950; pp 454−479.

(9) Harvie, C. E.; Moller, N.; Weare, J. H. The prediction of mineral solubilities in natural waters: the Na−K−Mg−Ca−H−Cl−SO_4−OH−HCO_3−CO_3−CO_2−H_2O system to high ionic strengths at 25 °C. *Geochim. Cosmochim. Acta* **1984**, *48*, 723−751.

(10) Pitzer, K. S. Thermodynamics of Electrolytes. 1. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77* (2), 268−277.

(11) Pitzer, K. S. Thermodynamics of electrolytes. 5. effects of higher-order electrostatic terms. *J. Solution Chem.* **1975**, *4* (3), 249.

(12) Riley, J. P.; Skirrow, G. *Chemical Oceanography*; Academic Press: London, 1975; pp 104−105.

(13) Ridanovski, A. B. *Solubility Handbook of Salt Aqueous System* (Russian); The Geochemical Press: Moscow, 1961; Vol. 3., p 1405.

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