



Thermodynamic investigation of $\text{RbF} + \text{Rb}_2\text{SO}_4 + \text{H}_2\text{O}$ and $\text{CsF} + \text{Cs}_2\text{SO}_4 + \text{H}_2\text{O}$ ternary systems by potentiometric method at 298.2 K

Xiaoting Huang, Shu'ni Li^{**}, Quanguo Zhai, Yucheng Jiang, Mancheng Hu^{*}

Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, Shaanxi, 710062, PR China

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ABSTRACT

In this paper, the potentiometric method was carried out to investigate the thermodynamic properties of the $\text{RbF} + \text{Rb}_2\text{SO}_4 + \text{H}_2\text{O}$ and $\text{CsF} + \text{Cs}_2\text{SO}_4 + \text{H}_2\text{O}$ ternary systems over total ionic strengths from (0.01–0.70) $\text{mol} \cdot \text{kg}^{-1}$ for different ionic strength fractions y_B of $\text{Rb}_2\text{SO}_4/\text{Cs}_2\text{SO}_4$ with $y_B = 0.00, 0.30, 0.60$ and 0.90 , at 298.2 K. The Harned model and the Pitzer model were used to correlate the experimental data. The Harned coefficients and the Pitzer mixing parameters were evaluated by multiple linear regression technique. Moreover, the mean ionic activity coefficients of RbF/CsF and $\text{Rb}_2\text{SO}_4/\text{Cs}_2\text{SO}_4$, the osmotic coefficients, and the excess Gibbs energies of the studied systems were calculated, respectively.

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1. Introduction

Thermodynamic properties of the electrolyte solutions, such as activity coefficients, osmotic coefficients and so on, play an important role in the exploitation and utilization of the resources containing electrolytes. In addition, the determination of thermodynamic properties is also of essence in the theoretical developments on the thermodynamic models [1,2]. In the past decades, a series of thermodynamic models have been proposed to predict thermodynamic properties of the aqueous systems. Among them, the Pitzer model is one of the most famous and useful one [3–6]. The most common methods to determine thermodynamic properties of the aqueous solutions involve hygrometric method [7–9], isopiestic method [10–12] and potentiometric method [13–19]. The potentiometric method presents advantages of high speed, simplicity and accuracy in comparison with the other foregoing techniques. Researchers focused on the thermodynamic properties of mixed electrolyte systems containing alkaline and

alkaline earth metal salts by potentiometric technique. Usually, the mean ionic activity coefficients and the individual activity coefficients were reported to analyze the ion-ion and ion-water (solvent) interactions in the solution. In recent years, the mean ionic activity coefficients of the ternary mixed-electrolyte systems $\text{NaCl} + \text{Na}_2\text{Succinate} + \text{H}_2\text{O}$ [13], $\text{NaCl} + \text{MgCl}_2 + \text{H}_2\text{O}$ [14], $\text{NaCl} + \text{CaCl}_2 + \text{H}_2\text{O}$ [15], $\text{NaCl} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ [16], $\text{NaCl} + \text{NaBF}_4 + \text{H}_2\text{O}$ [17], $\text{KCl} + \text{MgCl}_2 + \text{H}_2\text{O}$ [18], $\text{MgCl}_2 + \text{MgSO}_4 + \text{H}_2\text{O}$ [19] were reported by different researchers. Although it is thought that the individual activity coefficients are not readily available from measurements because their calculation requires an extra-thermodynamic assumption due to the difficulty in estimating liquid junction potentials [20]. Some authors obtained the individual activity coefficients through measurement or calculation. Hurlen et al. [21] studied the ion activity of alkaline-earth chlorides in aqueous solutions. Wilczek-Vera et al. [22,23] reported an in-depth study of the interrelation between the junction potential and the activity of individual ions and performed the theoretical investigation on the activity of individual ions. In our previous work, the thermodynamic properties of systems containing the rare-alkali metal Rb and Cs, such as the systems $\text{CsCl} + \text{Cs}_2\text{SO}_4/\text{MgCl}_2/\text{CaCl}_2 + \text{H}_2\text{O}$ [24–26], $\text{RbF} + \text{urea}/\text{formamide} + \text{H}_2\text{O}$ [27], and so on, were studied by potentiometric

* Corresponding author.

** Corresponding author.

E-mail addresses: lishuni@snnu.edu.cn (S. Li), hmch@snnu.edu.cn (M. Hu).

method at 298.2 K. As an extension of our series work, herein, we carried out the investigation on RbF + Rb₂SO₄ + H₂O and CsF + Cs₂SO₄ + H₂O ternary systems. The experimental data were correlated using the Harned model and the Pitzer model. Meanwhile, the mean ionic activity coefficients of RbF/CsF and Rb₂SO₄/Cs₂SO₄, the osmotic coefficients, and the excess Gibbs energies of the studied systems were also obtained.

2. Experimental section

2.1. Materials

The analytical grade samples (mass fraction >99%) were supplied by Shanghai China Lithium Industrial Co., Ltd. Details about the chemicals used in this study were summarized in Table 1. RbF, Rb₂SO₄, CsF and Cs₂SO₄ were dried in vacuum for 24 h at $T = 393.2$ K and stored in a desiccator before use. The specific conductance of double distilled-deionized water for this research was approximately $(1.0\text{--}1.2) \times 10^{-4} \text{ S m}^{-1}$. Stock aqueous solutions of the mixed electrolyte were prepared by weight.

2.2. Apparatus and procedure

An electrochemical cell without a liquid junction was set up with a Rb/Cs ion-selective electrode (ISE) as the working electrode and a F-ISE as the reference electrode. Both electrodes were activated and calibrated before measuring the potential difference of the cells:

- (a) Rb/Cs – ISE|RbF/CsF(m_{A0})|F – ISE
 (b) Rb/Cs – ISE|Rb₂SO₄/Cs₂SO₄(m_{B0})|F – ISE
 (c) Rb/Cs – ISE|RbF/CsF(m_A), Rb₂SO₄/Cs₂SO₄(m_B)|F – ISE

where m_{A0} and m_A are the molalities of RbF/CsF in pure water and in the mixed solution, while m_{B0} and m_B are the molalities of Rb₂SO₄/Cs₂SO₄ in pure water and in the mixed solution, respectively. Firstly, the cell (a) was performed to calculate the Nernst response of the electrode pair. Secondly, the cell (b) was used to determine the selectivity coefficient of the electrode pair. Finally, the cell (c) was applied for the mixed electrolyte solution with a series of different ionic strength fractions (y_B) of Rb₂SO₄/Cs₂SO₄.

All measurements were carried out in a double-walled glass vessel with the temperature control of 298.2 K (within an uncertainty of ± 0.2 K) by circulating water. All the samples weighed on an analytical balance (Mettler Toledo-AL204, Switzerland) with an accuracy of ± 0.0001 g. The electromotive force (EMF) measurements were achieved using a pH/mV meter (Orion-868, USA), and the uncertainty of the value of potential in the experiment is ± 0.1 mV. To ensure the stability of the electrodes, the whole experiment process was performed within 1.5 h.

3. Results and discussion

3.1. Calibration of the electrode pair Rb/Cs-ISE and F-ISE

The Nernst equation of the cell (a) is:

$$E_a = E_0 + 2k \ln(m_{A0}\gamma_{\pm A0}) \quad (1)$$

where E_a and E_0 are the EMF readings and the standard potential of the cell (a), respectively. $k = RT/F$ indicates the Nernst theoretical slope, and R , T , and F represent the universal gas constant, absolute temperature, and Faraday constant, respectively. m_{A0} is the molality of RbF/CsF in pure water and $\gamma_{\pm A0}$ is the mean ionic activity coefficient of RbF/CsF in pure water. The values of $\gamma_{\pm A0}$ are obtained through Pitzer equation [28]. The Pitzer ionic interaction parameters of RbF/CsF in pure water [29] were listed in Table 2. E_a and m_{A0} were listed in Table 3. The relation between E_a and $\ln a_{A0}$ (the activity of RbF/CsF in pure water) was shown in Fig. 1. Through linear regression, the values of E_0 , k , the standard deviation of the fitting (σ), and the determination coefficient (R^2) were calculated and given in Table 4. The obtained values of k for the two systems are very close to the theoretical one of 25.69 mV of the Nernst slope. Therefore, it can be concluded that the electrode pairs used in this study have a good Nernst response and can be used for the electromotive measurements in this work.

3.2. Determination of F-ISE selectivity coefficient

In fact, the ion-selective electrode is permselective, it has selectivity toward other ions in the solution. Thus, in this work, the selectivity coefficients of the F-ISE for SO₄²⁻ ion should be determined because of the presence of SO₄²⁻ in the mixed solutions. Using the cell (b), the range of m_B was selected from 0.01 mol kg⁻¹ to 0.70 mol kg⁻¹ to measure the selective coefficient K^{Pot} . The selective coefficient K^{Pot} was calculated based on the following equation:

$$K^{\text{Pot}} = [\exp(E_b - E_0)/k] / [2(m_{B0}\gamma_{\pm B0})^{3/2}] \quad (2)$$

where K^{Pot} indicates the selectivity coefficient of the F-ISE for SO₄²⁻ ion. E_b stands for the EMF value of cell (b). $\gamma_{\pm B0}$ represents the mean activity coefficient of Rb₂SO₄/Cs₂SO₄ as single salts in pure water at 298.2 K. The calculated results of K^{Pot} are much smaller than $1.0 \cdot 10^{-4}$.

3.3. Experimental mean activity coefficients of RbF/CsF in the mixed electrolyte solutions

The cell (c) was used to determine the EMF values of the RbF + Rb₂SO₄ + H₂O and CsF + Cs₂SO₄ + H₂O ternary systems at 298.2 K and at different ionic strength $I = m_A + 3m_B$ and ionic strength fraction $y_B = 3m_B/(m_A + 3m_B)$. The Nernst equation of the

Table 2
Values of the Pitzer parameters for RbF, CsF, Rb₂SO₄ and Cs₂SO₄ at 298.2 K.

Electrolyte	$\beta^{(0)}$ Kg·mol ⁻¹	$\beta^{(1)}$ Kg·mol ⁻¹	C° kg ² ·mol ⁻²	m_{max} mol·kg ⁻¹	σ
RbF [29]	0.1141	0.2842	-0.0105	3.5	0.002
CsF [29]	0.1306	0.2570	-0.0043	3.2	0.002
Rb ₂ SO ₄ [31]	0.09123	0.77863	-0.01282	1.500	0.00097
Cs ₂ SO ₄ [31]	0.14174	0.69456	-0.02686	1.831	0.00113

Table 1
The source, purity and purifying method of chemicals for this research.

Chemical name	Source	Purity (mass fraction)	Purification method
RbF	Shanghai China Lithium Industrial Co., Ltd.	>0.99	None
Rb ₂ SO ₄	Shanghai China Lithium Industrial Co., Ltd.	>0.99	None
CsF	Shanghai China Lithium Industrial Co., Ltd.	>0.99	None
Cs ₂ SO ₄	Shanghai China Lithium Industrial Co., Ltd.	>0.99	None

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