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Mean Activity Coefficients of KCl in KCl + $K_2B_4O_7$ + H_2O Ternary System at 298.15 K Determined by Potential Difference Measurements

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Abstract The mean activity coefficients of KCl in the KCl + $K_2B_4O_7$ + H_2O ternary systems were determined at total ionic strength ranging from (0.0100 to 1.0000) mol·kg^{-1} at 298.15 K by potential difference measurements from the electrochemical cell without liquid junction: K-ISE|KCl $(m_1), K_2B_4O_7(m_2)|$ Cl-ISE. The mean activity coefficients of KCl were measured at different ionic strength fractions, y_B, of $K_2B_4O_7$ (with $y_B = 0.8, 0.6, 0.4, 0.2,$ and 0.0). The experimental results showed that K-ISE and Cl-ISE in this work had good Nernstian responses, and the mean activity coefficients of KCl in KCl + $K_2B_4O_7$ + H_2O mixtures were calculated using the Nernst equation. Mixing interaction parameters of $\theta_{Cl^-\cdot B_4O_5(OH)_4^{2-}}$ and $\psi_{K^+\cdot Cl^-\cdot B_4O_5(OH)_4^{2-}}$ in Pitzer's equation were evaluated from the present measurements of the mean activity coefficients of KCl. In addition, the osmotic coefficients, water activity, and the excess Gibbs energy of this system were calculated by Pitzer's equations.

Keywords Activity coefficients · Potential difference · Ion selective electrode · KCl + $K_2B_4O_7$ + H_2O system

1 Introduction

Electrolyte solutions commonly found in nature are a medium for many organic and inorganic reactions and are widely used in desalination, brine development, and hydrometallurgy. Thus, there is considerable interest in the thermodynamic properties of

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electrolyte solutions [1–3]. The activity coefficients of electrolytes are important in thermodynamics, since they reflect the extent of deviations between the real solution and an ideal solution [4–6].

There are many methods to measure activity coefficients in electrolyte solutions, including: gas–liquid chromatography, kinetics, dilute solution colligative method, conductivity, solubility, freezing point depression, equal pressure method, and potential difference measurements [7, 8]. The emergence of ion–selective electrodes is undoubtedly an important advance in potential analysis. These have a wide range of linear response, high sensitivity, good selectivity, high analysis speed and measurements are easy to automate, providing continuous measurement and control, so they have caught people's attention [9–11].

Sodium, potassium, magnesium, chloride, bromine and boron resources are widely distributed in seawater, underground brines and salt lake brines [12]. Therefore, the study of the thermodynamic properties of salt–water systems is necessary. Research reports about activity coefficients calculated using the Pitzer equation are increasing common; for example, Millero et al. [13, 14] measured and calculated the solubilities of oxygen in aqueous solutions of KCl, K_2SO_4, and $CaCl_2$ as a function of concentration and temperature, and determined the dissociation of TRIS in NaCl solutions using the Pitzer equations. Roy et al. [15–17] studied the activity coefficients of HCl + $GdCl_3$ + H_2O system from 278 to 328 K and the thermodynamics of the system HCl + $SmCl_3$ + H_2O with the application of Harned's rule and the Pitzer equations, and the thermodynamics of the HBr + $NiBr_2$ + H_2O system from 278 to 328 K were determined. Sirbu et al. [18], Galleguilos et al. [19, 20] and White et al. [21] studied the activity coefficients of NaCl + Na_2SO_4 + H_2O, KI + KNO_3 + H_2O, and NaCl + Na_2CO_3 + H_2O. Li et al. [22] determined the mean activity coefficients of NaCl and KCl in the NaCl + KCl + H_2O system at 308.15 K.

In our previous work we studied mean activity coefficients of KBr in the KBr + $K_2B_4O_7$ + H_2O and KBr + K_2SO_4 + H_2O ternary system [23, 24] and NaBr in the NaBr + $Na_2B_4O_7$ + H_2O system [25] at 298.15 K by potential difference measurements; we also studied multi–temperature phase diagrams in a series of sub–system of the NaCl + NaBr + Na_2SO_4 + $Na_2B_4O_7$ + KCl + KBr + K_2SO_4 + $K_2B_4O_7$ + H_2O system for salt–water system, that is, NaCl + Na_2SO_4 + $Na_2B_4O_7$ + KCl + K_2SO_4 + $K_2B_4O_7$ + H_2O at 323 K and 298 K [26, 27]; $Na_2B_4O_7$ + Na_2SO_4 + NaCl + H_2O at 323 K [28]; NaBr + Na_2SO_4 + KBr + K_2SO_4 + H_2O at 323 K [29]; and NaBr + Na_2SO_4 + H_2O at 323 K [30]. Pitzer's equations can be used to calculate the thermodynamic properties for brines, so we determined the thermodynamic properties of the salt–water system to predict the thermodynamic equilibrium for brine resources.

So far, mean activity coefficients of KCl in the KCl + $K_2B_4O_7$ + H_2O ternary system at 308.15 K by potential difference measurements have been reported by our group [31], but no report has been found on thermodynamic properties of the KCl + $K_2B_4O_7$ + H_2O ternary system at 298.15 K. Therefore, in this paper, the activity coefficients of KCl in KCl + $K_2B_4O_7$ + H_2O ternary system were determined by potential difference measurement at 298.15 K and in the range 0.0100 to 1.0000 mol·kg^{-1} total ionic strength, and the Pitzer's ion interaction parameters $\theta_{\mathrm{Cl^-\cdot B_4O_5(OH)_4^{2-}}}$ and $\varphi_{\mathrm{K^+\cdot Cl^-\cdot B_4O_5(OH)_4^{2-}}}$ were evaluated from the activity coefficients of KCl in the KCl + $K_2B_4O_7$ + H_2O ternary system. Then the osmotic coefficients, water activity, and excess Gibbs energies of this system were calculated.

2 Experimental Section

The water for experiments was deionized water, with a conductivity less than 1×10^{-4} S·m^{-1}. Prior to use, the G.R. grade $K_2B_4O_7{\cdot}4H_2O$ (mass fraction % >99.5) from Tianjin Kemiou Chemical Reagent Co., Ltd. and KCl salts (mass fraction % >99.5) from Tianjin Guangfu Fine Chemical Research Institute, were placed in an oven under 393 K for 2 h.

Experimental apparatus were as follows: AL104 electronic balance (Mettler–Toledo Group, the smallest error value 0.0001 g); Pxsj-216 ion meter (Leici Precision Scientific Instrument Co., Ltd., accuracy ±0.1 mV); Bilon-HW-05 thermostatic circulating water bath (Beijing Bi-Lang Co., Ltd., accuracy ±0.1 K); JB-1 stirrer (Leici Precision Scientific Instrument Co., Ltd., with automatic speed adjustment); 232-01 calomel reference electrode (Leici Precision Scientific Instrument Co., Ltd.); 401 potassium ion selective electrode (Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd.); PCl-1-01 chloride ion selective electrode (Leici Precision Scientific Instrument Co., Ltd.); 50 mL flasks and other conventional laboratory glass.

3 Method

The K-ISE was soaked for 30 min in 10^{-2} mol·L^{-1} KCl aqueous solution and washed with deionized water to a blank potential around −160 mV. The Cl-ISE was soaked activation for 2 h in 10^{-3} mol·L^{-1} NaCl aqueous solution. The reference electrode was a double–junction saturated calomel electrode with the salt bridge filled with G.R. grade saturated solution of potassium chloride and the outer salt bridge filled with 0.1 mol·L^{-1} lithium acetate solution. During the measurements, we used the same ion-selective electrodes. First, the potential difference of each single salt was determined so the electrode response slope of each electrode and the electrode constant were obtained. The salt composition with KCl single cell without liquid junction was:

$$\text{K-ISE}|\text{KCl}(m_0)|\text{Cl-ISE} \tag{a}$$

whose potential value was:

$$E_a = E^{0\prime} + k\ln a_+ a_- = E^{0\prime} + k\ln a_{0\pm\text{KCl}} = E^{0\prime} + 2k\ln m_0\gamma_{0\pm\text{KCl}} \tag{1}$$

where a_+, a_-, $a_{0\pm\text{KCl}}$, m_0 and $\gamma_{0\pm\text{KCl}}$, respectively, represent a single positive ion activity, negative ion activity, mean activity, molality, and activity coefficient, E_a indicates the galvanic potential difference, $E^{0\prime}$ indicates the standard potential, and k indicates the electrode response slope.

For the mixed salt, the cell without liquid junction was:

$$\text{K-ISE}|\text{KCl}\ (m_1),\ K_2B_4O_7(m_2),\ H_2O|\text{Cl-ISE} \tag{b}$$

whose potential value is:

$$E_b = E^{0\prime} + k\ln a_{K^+}{\cdot}a_{Cl^-} = E^{0\prime} + k\ln m_1(m_1 + 2m_2)\gamma^2_{\pm\text{KCl}} \tag{2}$$

where m_1 and m_2, respectively, represent the molality of KCl and $K_2B_4O_7$ in mixed solution, a_{K^+} and a_{Cl^-}, respectively, represent the activity of K^+ and Cl^-, $\gamma_{\pm\text{KCl}}$ expresses the mean activity coefficient of KCl.

The method and procedure is as follows: the total ionic strength I ($I = m_1 + 3m_2$) ranges from (0.0100 to 1.0000) mol·kg^{-1}; ionic strength fractions y_B, $y_B = 3m_2/(m_1 + 3m_2)$ of $K_2B_4O_7$ are 0.8, 0.6, 0.4, 0.2, and 0.0. The appropriate masses of KCl and $K_2B_4O_7$ were weighed into a beaker and dissolved in 30 mL of deionized water, with stirring, before being placed into the thermostated cell.

Before determining the activity coefficients in the mixture, the potential difference of cell (a) was measured so as to determine the standard potential difference $E^{0\prime}$ and practical response slope k. Here $k = RT/F$ represents the theoretical Nernst slope. The R, F, and T are the gas constant, Faraday constant, and absolute temperature, respectively. Then the potential difference of cell (b) with different ionic strengths was measured, varying the concentration from low to high.

During measurements, the experimental solution was kept at 298.15 ± 0.1 K until the potential difference was stable to ±0.1 mV for 30 min.

For ionic activity coefficients the corresponding relations are:

$$(\gamma_{\pm \mathrm{KCl}})^2 = \gamma_{\mathrm{K}^+} \cdot \gamma_{\mathrm{Cl}^-} \tag{3}$$

$$\left\{\gamma_{\pm \mathrm{K_2B_4O_5(OH)_4}}\right\}^3 = (\gamma_{\mathrm{K}^+})^2 \cdot \gamma_{\mathrm{B_4O_5(OH)_4^{2-}}} \tag{4}$$

$$\begin{aligned} \ln\gamma_{\mathrm{K}^+} = {} & F + m_{\mathrm{Cl}}\left(2B_{\mathrm{K,Cl}} + ZC_{\mathrm{K,Cl}}\right) + m_{\mathrm{B_4O_5(OH)_4}}\left(2B_{\mathrm{K,B_4O_5(OH)_4}} + ZC_{\mathrm{K,B_4O_5(OH)_4}}\right) \\ & + m_{\mathrm{K}} m_{\mathrm{Cl}} C_{\mathrm{K,Cl}} + m_{\mathrm{K}} m_{\mathrm{B_4O_5(OH)_4}} C_{\mathrm{K,B_4O_5(OH)_4}} \\ & + m_{\mathrm{Cl}} m_{\mathrm{B_4O_5(OH)_4}} \psi_{K,\mathrm{Cl,B_4O_5(OH)_4}} \end{aligned} \tag{5}$$

$$\begin{aligned} \ln\gamma_{\mathrm{Cl}^-} = {} & F + m_{\mathrm{K}}\left(2B_{\mathrm{K,Cl}} + ZC_{\mathrm{K,Cl}}\right) + m_{\mathrm{K}} m_{\mathrm{Cl}} C_{\mathrm{K,Cl}} + m_{\mathrm{K}} m_{\mathrm{B_4O_5(OH)_4}} C_{\mathrm{K,B_4O_5(OH)_4}} \\ & + m_{\mathrm{B_4O_5(OH)_4}}\left(2\Phi_{\mathrm{Cl,B_4O_5(OH)_4}} + m_{\mathrm{K}} \psi_{\mathrm{K,Cl,B_4O_5(OH)_4}}\right) \end{aligned} \tag{6}$$

and

$$\begin{aligned} \ln\gamma_{\mathrm{B_4O_5(OH)_4^{2-}}} = {} & 4F + m_{\mathrm{K}}\left(B_{\mathrm{K,B_4O_5(OH)_4}} + ZC_{\mathrm{K,B_4O_5(OH)_4}}\right) + 2m_{\mathrm{K}} m_{\mathrm{Cl}} C_{\mathrm{K,Cl}} \\ & + 2m_{\mathrm{K}} m_{\mathrm{B_4O_5(OH)_4}} C_{\mathrm{K,B_4O_5(OH)_4}} + m_{\mathrm{Cl}}\left(2\Phi_{\mathrm{Cl,B_4O_5(OH)_4}} + m_{\mathrm{K}} \psi_{\mathrm{K,Cl,B_4O_5(OH)_4}}\right) \end{aligned} \tag{7}$$

where,

$$\begin{aligned} F = {} & -A^{\phi}\left[\frac{I^{1/2}}{(1 + bI^{1/2})} + (2/b)ln\left(1 + bI^{1/2}\right)\right] + m_{\mathrm{K}} m_{\mathrm{Cl}} B'_{\mathrm{K,Cl}} \\ & + m_{\mathrm{K}} m_{\mathrm{B_4O_5(OH)_4}} B'_{\mathrm{K,B_4O_5(OH)_4}} \\ & + m_{\mathrm{Cl}} m_{\mathrm{B_4O_5(OH)_4}} \Phi'_{\mathrm{Cl,B_4O_5(OH)_4}} \end{aligned} \tag{8}$$

where I is the ionic strength, the constants $b = 1.2$ mol$^{-1/2}$·kg$^{1/2}$, and $A^{\phi} = 0.391475$ mol$^{-1/2}$·kg$^{1/2}$ is the value of the Debye–Hückel limiting–law slope for an aqueous solution at $T = 298.15$ K [32, 33]. Values of the Pitzer parameters $\beta^{(0)}_{\mathrm{M,X}}$, $\beta^{(1)}_{\mathrm{M,X}}$ and C^{ϕ}_{MX} for KCl and $K_2B_4O_5(OH)_4$ at 298.15 K are from references [34, 35].

For the {(1 − y_B) KCl + y_B $K_2B_4O_7$} (aq) system, the osmotic coefficient equation is:

$$\begin{aligned}\phi = 1 + \left(\frac{2}{m_{\mathrm{K}} + m_{\mathrm{Cl}} + m_{\mathrm{B_4O_5(OH)_4}}}\right)\Bigg[\left(\frac{-A^{\phi}I^{3/2}}{1 + bI^{1/2}}\right) + m_{\mathrm{K}}m_{\mathrm{Cl}}\left(B^{\phi}_{\mathrm{K,Cl}} + ZC_{\mathrm{K,Cl}}\right) \\ + m_{\mathrm{K}}m_{\mathrm{B_4O_5(OH)_4}}\left(B^{\phi}_{\mathrm{K,B_4O_5(OH)_4}} + ZC_{\mathrm{K,B_4O_5(OH)_4}}\right) \\ + m_{\mathrm{Cl}}m_{\mathrm{B_4O_5(OH)_4}}\left\{\Phi^{\phi}_{\mathrm{Cl,B_4O_5(OH)_4}} + m_{\mathrm{K}}\psi_{\mathrm{K,Cl,B_4O_5(OH)_4}}\right\}\Bigg]\end{aligned} \tag{9}$$

where Z is given by: $Z = m_{\mathrm{K}} + m_{\mathrm{Cl}} + 2m_{\mathrm{B_4O_7}}$; and $m_{\mathrm{K}} = m_1 + 2m_2$; $m_{\mathrm{Cl}} = m_1$; $m_{\mathrm{B_4O_7}} = m_2$.

The quantities $B^{\phi}_{\mathrm{M,X}}$; $B_{\mathrm{M,X}}$ C_{MX}; and $\mathrm{B}'_{\mathrm{M,X}}$ are defined with the following dependences on ionic strength:

$$B^{\phi}_{\mathrm{M,X}} = \beta^{(0)}_{\mathrm{M,X}} + \beta^{(1)}_{\mathrm{M,X}}\exp\left(-\alpha I^{1/2}\right) \tag{10}$$

$$B_{\mathrm{M,X}} = \beta^{(0)}_{\mathrm{M,X}} + 2\beta^{(1)}_{\mathrm{M,X}}\left\{\frac{\left[1 - \left(1 + \alpha I^{1/2}\right)\exp\left(-\alpha I^{1/2}\right)\right]}{\alpha^2 I}\right\} \tag{11}$$

$$C_{\mathrm{MX}} = \frac{C^{\phi}_{\mathrm{MX}}}{\left(2|\mathrm{Z_M Z_X}|^{1/2}\right)} \tag{12}$$

$$B'_{\mathrm{M,X}} = \frac{\beta^{(1)}_{\mathrm{M,X}}\left\{-\frac{2\left[1-\left(1+\alpha I^{\frac{1}{2}}+\frac{\alpha^2 I}{2}\right)\exp\left(-\alpha I^{\frac{1}{2}}\right)\right]}{\alpha^2 I}\right\}}{I} \tag{13}$$

where M denotes K^+ and X denotes Cl^- or $\mathrm{B_4O_5(OH)_4^{2-}}$; Z_{M} and Z_{X} are the valences of ions M and X. These mixing functions are related to the mixing parameters by:

$$\Phi^{\phi}_{\mathrm{Cl,B_4O_5(OH)_4}} = \theta_{\mathrm{Cl,B_4O_5(OH)_4}} + {}^{\mathrm{E}}\theta_{\mathrm{Cl,B_4O_5(OH)_4}} + I^{\mathrm{E}}\theta'_{\mathrm{Cl,B_4O_5(OH)_4}} \tag{14}$$

$$\Phi_{\mathrm{Cl,B_4O_5(OH)_4}} = \theta_{\mathrm{Cl,B_4O_5(OH)_4}} + {}^{\mathrm{E}}\theta_{\mathrm{Cl,B_4O_5(OH)_4}} \tag{15}$$

and

Table 1 The values for potential difference E_{a}, activity logarithm $\ln a_{0\pm\mathrm{KCl}}$, and mean ionic activity coefficient $\gamma_{0\pm\mathrm{KCl}}$ of KCl in aqueous solutions for different KCl molalities m_0 at 298.15 K

$\frac{m_0}{\mathrm{mol{\cdot}kg^{-1}}}$	$\gamma_{0\pm\mathrm{KCl}}$	$\ln a_{0\pm\mathrm{KCl}}$	$\frac{E_{\mathrm{a}}}{\mathrm{mV}}$
0.0014	0.9510	−13.2609	−99.6
0.0049	0.8884	−10.8928	−36.5
0.0099	0.8528	−9.5511	0.7
0.0498	0.7720	−6.5175	77.1
0.1000	0.7371	−5.2150	110.3
0.2001	0.7024	−3.9239	143.1
0.4980	0.6569	−2.2349	184.5
0.9991	0.6220	−0.9512	213.0
1.9994	0.5874	0.3214	243.1
3.0006	0.5671	1.0630	260.0

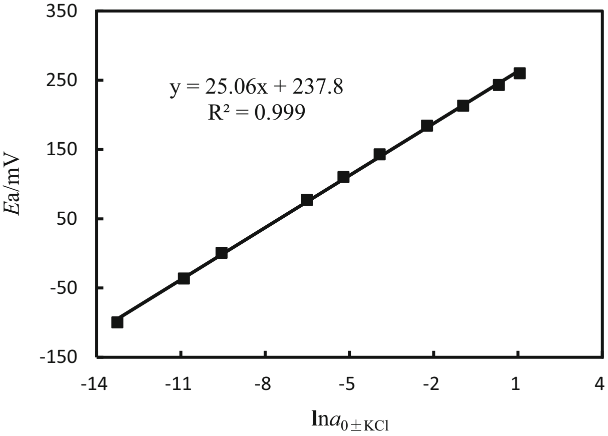

Fig. 1 The response curve of K − ISE | KCl (m_0), H_2O | Cl − ISE galvanic cell versus ln {KCl activity} at 298.15 K

$$\Phi'_{\mathrm{Cl,B_4O_5(OH)_4}} = {}^{\mathrm{E}}\theta'_{\mathrm{Cl,B_4O_5(OH)_4}} \tag{16}$$

where the superscript E applied to a function identifies it as an electrostatic contribution that does not depend on a specific characteristic of the pair of ions (other than their charges). The quantity ${}^{\mathrm{E}}\theta_{\mathrm{Cl,B_4O_5(OH)_4}}$ and its ionic strength derivative ${}^{\mathrm{E}}\theta'_{\mathrm{Cl,B_4O_5(OH)_4}}$ can be calculated, and their values depend only the total ionic strength I and the valences of the ions of like sign, in this case Z_{Cl} and $Z_{\mathrm{B_4O_5(OH)_4}}$. The equations are the following forms:

$${}^{\mathrm{E}}\theta_{\mathrm{Cl,B_4O_5(OH)_4}} = \left(\frac{Z_{\mathrm{Cl}}Z_{\mathrm{B_4O_5(OH)_4}}}{4I}\right)\left[\mathrm{J}\left(\chi_{\mathrm{Cl,B_4O_5(OH)_4}}\right) - \frac{J\left(\chi_{\mathrm{Cl,Cl}}\right)}{2} - \frac{J\left(\chi_{\mathrm{B_4O_5(OH)_4,B_4O_5(OH)_4}}\right)}{2}\right] \tag{17}$$

$$\begin{aligned}{}^{\mathrm{E}}\theta'_{\mathrm{Cl,B_4O_5(OH)_4}} &= -\left(\frac{{}^{\mathrm{E}}\theta_{\mathrm{Cl,}B_4O_5\mathrm{(OH)_4}}}{I}\right) + \left(\frac{Z_{\mathrm{Cl}}Z_{\mathrm{B_4O_5(OH)_4}}}{8I^2}\right)\\ &\quad * \left[\chi_{\mathrm{Cl,B_4O_5(OH)_4}}J'\left(\chi_{\mathrm{Cl,B_4O_5(OH)_4}}\right) - \frac{\chi_{\mathrm{Cl,Cl}}J'\left(\chi_{\mathrm{Cl,Cl}}\right)}{2}\right.\\ &\quad \left. - \frac{\chi_{\mathrm{B_4O_5(OH)_4,B_4O_5(OH)_4}}J'\left(\chi_{\mathrm{B_4O_5(OH)_4,B_4O_5(OH)_4}}\right)}{2}\right]\end{aligned} \tag{18}$$

where

$$\chi_{\mathrm{Cl,B_4O_5(OH)_4}} = 6Z_{\mathrm{Cl}}Z_{\mathrm{B_4O_5(OH)_4}}A^{\phi}I^{1/2} \tag{19}$$

Table 2 The standard potential, $E^{0\prime}$, and the electrode response slope, k, of the galvanic cell K-ISE|KCl (m_0), H_2O| Cl-ISE at 298.15 K

$E^{0\prime}$/mV	k	R^2
237.8	25.06	0.999

Table 3 The values for the total ionic strengths I, stoichiometric ionic strength fraction of $K_2B_4O_7$ y_B, molality of KCl and $K_2B_4O_7$ m_1, m_2, respectively, potential difference E_b, and mean activity coefficient of KCl $\gamma_{\pm KCl}$ in the KCl + $K_2B_4O_7$ + H_2O ternary system at 298.15 K

$\frac{I}{\text{mol·kg}^{-1}}$	y_B	$\frac{m_1}{\text{mol·kg}^{-1}}$	$\frac{m_2}{\text{mol·kg}^{-1}}$	$\frac{E_b}{\text{mV}}$	$\gamma_{\pm KCl}$
0.0053	0.7974	0.0011	0.0014	−73.2	0.988
0.0049	0.6267	0.0018	0.0010	−61.1	0.963
0.0048	0.4029	0.0029	0.0006	−49.7	0.936
0.0050	0.1944	0.0041	0.0003	−39.1	0.910
0.0051	0.0000	0.0051	0.0000	−32.8	0.888
0.0100	0.7981	0.0020	0.0027	−46.0	0.906
0.0100	0.6035	0.0040	0.0020	−27.3	0.894
0.0098	0.3976	0.0059	0.0013	−16.7	0.882
0.0100	0.1988	0.0080	0.0007	−7.3	0.866
0.0100	0.0000	0.0100	0.0000	−1.3	0.851
0.0500	0.8040	0.0098	0.0134	27.8	0.800
0.0495	0.6038	0.0196	0.0100	46.8	0.794
0.0503	0.4039	0.0300	0.0068	59.4	0.787
0.0502	0.1969	0.0403	0.0033	68.3	0.782
0.0498	0.0000	0.0498	0.0000	74.7	0.776
0.1003	0.7977	0.0203	0.0267	59.8	0.742
0.1003	0.5982	0.0403	0.0200	79.0	0.740
0.1004	0.3997	0.0603	0.0134	90.9	0.737
0.0996	0.1996	0.0798	0.0066	99.5	0.735
0.0998	0.0000	0.0998	0.0000	106.8	0.734
0.1992	0.8006	0.0397	0.0532	90.3	0.692
0.1996	0.6008	0.0797	0.0400	110.3	0.697
0.1995	0.4002	0.1196	0.0266	122.6	0.698
0.1994	0.2000	0.1595	0.0133	131.7	0.699
0.1997	0.0000	0.1997	0.0000	139.3	0.701
0.4979	0.8000	0.0996	0.1328	129.0	0.598
0.4985	0.6001	0.1994	0.0997	149.8	0.613
0.4984	0.4001	0.2990	0.0665	163.0	0.626
0.4991	0.2001	0.3992	0.0333	173.2	0.639
0.4998	0.0000	0.4998	0.0000	181.7	0.653
0.9889	0.7999	0.1979	0.2637	159.3	0.551
0.9932	0.6001	0.3972	0.1987	180.7	0.570
0.9937	0.3995	0.5967	0.1323	194.6	0.589
0.9973	0.2000	0.7978	0.0665	205.4	0.608
0.9999	0.0000	0.9999	0.0000	214.4	0.627

$$J(\chi) = \chi\left[4 + 4.581\chi^{-0.7237}\exp\left(-0.0120\chi^{0.528}\right)\right]^{-1} \tag{20}$$

$$\begin{aligned} J'(\chi) = {} & \left[4 + 4.581\chi^{-0.7237}\exp\left(-0.0120\chi^{0.528}\right)\right]^{-1} \\ & + \left[4 + 4.581\chi^{-0.7237}\exp\left(-0.0120\chi^{0.528}\right)\right]^{-2} 4.581\chi \\ & \exp\left(-0.0120\chi^{0.528}\right)\left(0.7237\chi^{-1.7237} + 0.0120 * 0.528\chi^{-0.472}\chi^{-0.7237}\right). \end{aligned} \tag{21}$$

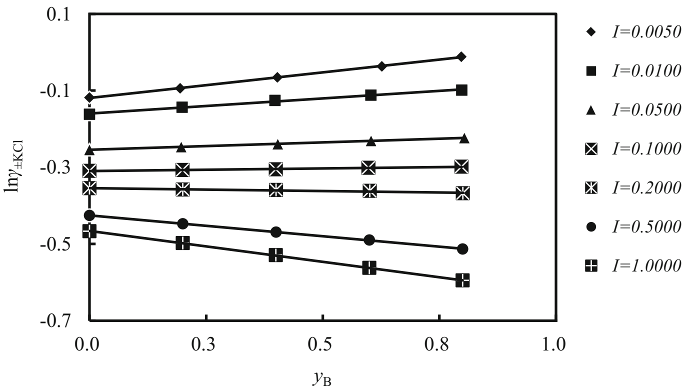

Fig. 2 Plots of the logarithm of the mean activity coefficient $\ln\gamma_{\pm KCl}$ versus stoichiometric ionic strength fraction of $K_2B_4O_7$ y_B at different ionic strengths of the KCl + $K_2B_4O_7$ + H_2O ternary system at 298.15 K

Table 4 Values of the Pitzer parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) for pure KCl and $K_2B_4O_7$ at 298.15 K

Electrolyte	$\frac{\beta^{(0)}}{kg \cdot mol^{-1}}$	$\frac{\beta^{(1)}}{kg \cdot mol^{-1}}$	$\frac{C^{\phi}}{kg^2 \cdot mol^{-2}}$	Ref.
KCl	0.04835	0.2122	−0.00084	[34]
$K_2B_4O_5(OH)_4$	−0.022			[35]

Table 5 Pitzer parameters $\theta_{Cl^- \cdot B_4O_5(OH)_4^{2-}}$ and $\psi_{K^+ \cdot Cl^- \cdot B_4O_5(OH)_4^{2-}}$ for the KCl + $K_2B_4O_7$ + H_2O ternary system at 298.15 K

$\frac{I}{mol \cdot kg^{-1}}$	$\theta_{Cl^- \cdot B_4O_5(OH)_4^{2-}}$	$\psi_{K^+ \cdot Cl^- \cdot B_4O_5(OH)_4^{2-}}$	R^2
0.0050–1.0000	−0.4031	0.8951	0.9733

The excess Gibbs energy (G^E) and activity of water (a_W) are calculated from the following relations:

$$G^E = RT\left[2m_1(1 - \phi + \ln\gamma_{\pm KCl}) + 3m_2\left(1 - \phi + \ln\gamma_{\pm K_2B_4O_5(OH)_4}\right)\right] \quad (22)$$

and

$$a_W = \exp\left[\left(-\frac{18.0513}{1000}\right)(2m_1 + 3m_2)\emptyset\right] \quad (23)$$

4 Results and Discussion

Using the values of m_0 (molality of KCl), E_a (the potential difference value of KCl), and $\gamma_{0\pm KCl}$ (activity coefficients of KCl at 298.15 K), the standard potential $E^{0\prime}$ and the

Table 6 The values for the total ionic strengths I, stoichiometric ionic strength fraction of $K_2B_4O_7$ y_B, mean activity coefficient of $K_2B_4O_7$ $\gamma_{\pm KCl}$, osmotic coefficient ϕ, water activity a_W, and excess Gibbs energy G^E for the KCl + $K_2B_4O_7$ + H_2O ternary system at 298.15 K

$\frac{I}{mol\cdot kg^{-1}}$	y_B	$\frac{\gamma_{\pm K_2B_4O_5(OH)_4}}{mol\cdot kg^{-1}}$	ϕ	a_W	$\frac{G^E}{kJ\cdot mol^{-1}}$
0.0053	0.7974	0.8501	0.9562	0.9999	−0.0014
0.0049	0.6267	0.8559	0.9633	0.9999	−0.0012
0.0048	0.4029	0.8584	0.9694	0.9999	−0.0012
0.0050	0.1944	0.8555	0.9726	0.9998	−0.0013
0.0051	0.0000	0.8554	0.9754	0.9998	−0.0013
0.0100	0.7981	0.8031	0.9408	0.9998	−0.0037
0.0100	0.6035	0.8037	0.9498	0.9998	−0.0036
0.0098	0.3976	0.8061	0.9571	0.9997	−0.0035
0.0100	0.1988	0.8049	0.9620	0.9997	−0.0036
0.0100	0.0000	0.8077	0.9673	0.9997	−0.0036
0.0500	0.8040	0.6370	0.8833	0.9990	−0.0382
0.0495	0.6038	0.6384	0.9013	0.9989	−0.0373
0.0503	0.4039	0.6380	0.9156	0.9987	−0.0376
0.0502	0.1969	0.6414	0.9290	0.9985	−0.0367
0.0498	0.0000	0.6463	0.9404	0.9983	−0.0357
0.1003	0.7977	0.5461	0.8485	0.9982	−0.1037
0.1003	0.5982	0.5467	0.8723	0.9978	−0.1019
0.1004	0.3997	0.5484	0.8923	0.9974	−0.1002
0.0996	0.1996	0.5530	0.9106	0.9971	−0.0966
0.0998	0.0000	0.5575	0.9267	0.9967	−0.0943
0.1992	0.8006	0.4516	0.8075	0.9965	−0.2739
0.1996	0.6008	0.4518	0.8388	0.9958	−0.2690
0.1995	0.4002	0.4540	0.8665	0.9950	−0.2613
0.1994	0.2000	0.4579	0.8911	0.9943	−0.2529
0.1997	0.0000	0.4631	0.9135	0.9934	−0.2436
0.4979	0.8000	0.3299	0.7510	0.9919	−0.9746
0.4985	0.6001	0.3319	0.7978	0.9900	−0.9463
0.4984	0.4001	0.3354	0.8377	0.9880	−0.9094
0.4991	0.2001	0.3402	0.8717	0.9860	−0.8681
0.4998	0.0000	0.3465	0.9004	0.9839	−0.8226
0.9889	0.7999	0.2555	0.7304	0.9845	−2.4445
0.9932	0.6001	0.2649	0.8022	0.9801	−2.3412
0.9937	0.3995	0.2753	0.8532	0.9758	−2.2147
0.9973	0.2000	0.2862	0.8850	0.9718	−2.0997
0.9999	0.0000	0.2979	0.8982	0.9682	−1.9947

electrode response slope k were determined by Eq. 1; these are collected in Table 1 and shown in Fig. 1.

As shown in Fig. 1, E_a increases linearly with $\ln a_{0\pm KCl}$, ($R^2 = 0.999$) showing that the K-ISE and Cl-ISE have a good linear Nernstian responses and the measured potential difference value is reliable. The electrode constants and the electrode response slope are listed in Table 2.

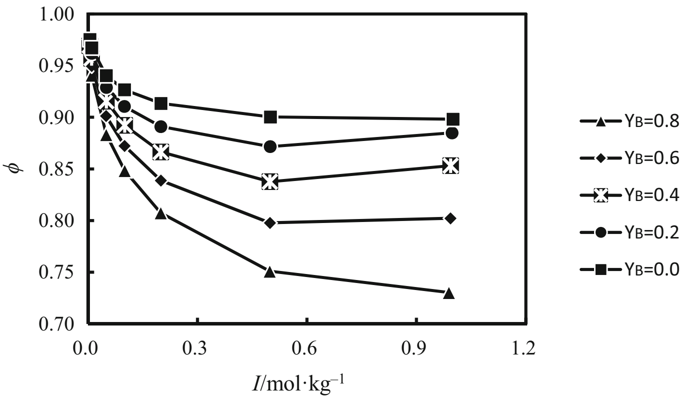

Fig. 3 Plot of the osmotic coefficients ϕ against total ionic strength I of the KCl + $K_2B_4O_7$ + H_2O ternary system at different y_B at 298.15 K

The molal concentrations m_1, m_2 and the potential difference E_b of the mixed solutions are listed in Table 3. From the electrode constants $E^{0'}$, the electrode response slope k and the potential difference E_b, the mean activity coefficient $\gamma_{\pm KCl}$ of mixed solution can be calculated according to Eq. 2, the results are also listed in Table 3. The relationship between the mean activity coefficients $\gamma_{\pm KCl}$ in the mixed solutions and the ionic strength fractions y_B of $K_2B_4O_7$ is shown in Fig. 2.

As can be seen from Table 3, in a mixed solution containing $K_2B_4O_7$, $\ln\gamma_{\pm KCl}$ decreases with increasing I. As shown in Fig. 2, when I is constant, $\ln\gamma_{\pm KCl}$ increases with increase of y_B for I less than 0.1000 mol·kg^{-1} but decrease with increasing y_B for I greater than 0.1000 mol·kg^{-1}.

According to an early experimental study on the phase equilibrium of potassium borate solutions from 298.15 to 323.15 K, we found that potassium tetraborate crystallized in the form of $K_2B_4O_7{\cdot}4H_2O$ from its saturated solution [27]. Therefore, this study treats $K_2B_4O_7{\cdot}4H_2O$ as the structure of $K_2B_4O_5(OH)_4{\cdot}2H_2O$ [36].

Values of the Pitzer parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) for pure KCl and pure $K_2B_4O_7$ are listed in Table 4. According to measured values E_b of the KCl + $K_2B_4O_7$ + H_2O system and the Pitzer model formula, the Pitzer parameters $\theta_{Cl^-{\cdot}B_4O_5(OH)_4^{2-}}$ and $\psi_{K^+{\cdot}Cl^-{\cdot}B_4O_5(OH)_4^{2-}}$ were calculated using the linear regression method (using Matlab) on the basis of Eqs. 2–23. The results are shown in Table 5. The osmotic coefficient, water activity, and excess Gibbs energy results for the KCl + $K_2B_4O_7$ + H_2O ternary system at 298.15 K are listed in Table 6. The relationship of osmotic coefficient and total ionic strength of the KCl + $K_2B_4O_7$ + H_2O ternary system are shown in Fig. 3.

As is shown in Fig. 3, when y_B is constant, the osmotic coefficient ϕ and excess Gibbs energy G^E show a downward trend with the increase of I; when I is constant, they decrease with the increase of y_B, while the water activity a_W increases with increasing y_B.

5 Conclusion

The thermodynamics of the KCl + $K_2B_4O_7$ + H_2O ternary system was studied by the EMF method using K-ISE and Cl-ISE at 298.15 K. The mean activity coefficients of KCl in pure and mixed solution were determined from cells without liquid junction. From the electrode constant and the response slope, the mean activity coefficients of KCl in the $KCl + K_2B_4O_7 + H_2O$ systems were calculated using the Nernst equation. Pitzer ion interaction parameters $\theta_{Cl^-\cdot B_4O_5(OH)_4^{2-}}$ and $\psi_{K^+\cdot Cl^-\cdot B_4O_5(OH)_4^{2-}}$ were calculated by linear regression. The osmotic coefficients ϕ, activity of water a_W and the Gibbs energies G^E of the system were calculated using these mixing parameters and Pitzer equations. The results showed that the Pitzer model can be used to describe this aqueous system satisfactorily. The results of Pitzer model indicate that the present investigations in this work can provide basic thermodynamic reference data for further research applications.

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