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Potentiometric determination of the thermodynamic properties for the ternary system ($KCl + KNO_3 + H_2O$) at $T = 298.15$ K

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ABSTRACT

In this work, the potentiometric measurements were performed for the ternary ($KCl + KNO_3 + H_2O$) systems on the galvanic cell of the type: Ag|AgCl|KCl (m_1), KNO_3 (m_2), H_2O|K-ISE over total ionic strengths from (0.001 to 3.000) $mol \cdot kg^{-1}$ for different series of salt molal ratios r ($r = m_1/m_2 = 0.20$, 1.0, 5.0, 10.0, and 20.0). The electrodes used in this work were prepared in our laboratory and had a reasonably good Nernst response. The activity coefficients data were interpreted by using Pitzer model. The unknown Pitzer mixing interaction parameters have been evaluated for the system under investigation ($\theta_{Cl,NO_3} = 0.0186$, $\psi_{KClNO_3} = -0.0066$). Then, the parameters obtained were used to calculate the values of the mean activity coefficients of KNO_3, the osmotic coefficients, the solvent activity, the surface tension, and the excess Gibbs free energies for the whole series of the studied mixed electrolyte systems.

1. Introduction

Study of the thermodynamic properties of aqueous mixed electrolyte solutions at high ionic strengths are of great practical interest in the fields of chemical industry [1], process engineering [2], desalination [3] atmospheric processes [4], development of salt lakes and oceans, and biological or geological processes [5]. In order to facilitate the use of mixed electrolytes in these processes, it is desirable to know accurately the thermodynamic properties of aqueous multi-component systems. In the last decades, a series of ion-interaction models for electrolyte solution have been proposed to predict activity coefficient of each solute and osmotic coefficient of aqueous systems. One of the most famous and useful models is that proposed by Pitzer [6–8]. This model is relatively simple, and it performs electrolyte calculations with accuracy, especially for concentrations under 6 molal. For application of the Pitzer model to electrolyte solutions, there are the numbers of adjustable parameters that must be correlated with experimental data. To measure the experimental thermodynamic properties in mixed electrolyte solutions, the most common methods are the isopiestic vapor pressure [9,10], hygrometry [11,12], and potentiometric techniques [13,14]. The potentiometric method using ion-selective electrodes presents advantages such as rapidity and relative simplicity to generate experimental data in comparison with the other foregoing techniques [8,15]. It can be noted that ion-selective electrodes are not only valuable for analytical use, but also may be employed in determining thermodynamic properties.

In this research, the results relating to the thermodynamic properties for the ternary solutions of $[(1-y)KCl + yKNO_3](aq)$ ($y = m_{KNO_3}/I$) using the potentiometric method are reported at $T = 298.15$ K. To the author's knowledge, study of the ($KCl + KNO_3 + H_2O$) mixed electrolyte system have been performed by isopiestic vapor pressure measurements [16,17]. Besides, electromotive force (emf) measurements have been carried out on the above system at the four total ionic strengths $mol \cdot kg^{-1}$ [18]. However, we have performed to investigate the emf measurements on the system ($KCl + KNO_3 + H_2O$) over the entire range of total ionic strengths with $I = 0.001$, 0.01, 0.05, 0.1, 0.25, 0.5, 1.0, 1.5, 1.75, 2.0, 2.25, 2.5, 2.75, and 3.0 $mol \cdot kg^{-1}$ for a wide series of KNO_3 ionic strength fractions (y) from 0 to 0.83. In addition, the results reported in this research have been incorporated the extra thermodynamic properties such as the solvent activity, the excess Gibbs free energies, and surface tension by modified model for the whole series of the studied mixed electrolyte systems. This paper is the continuation of the research on binary [19–21] and ternary electrolyte solutions with a common chloride ion [22,23]. The potentiometric measurements were carried out on a galvanic cell without liquid junction containing a new solvent polymeric (PVC) K-ISE and Ag–AgCl electrodes by using various series of this mixed salt electrolyte system. For this purpose, a series of different primary concentrated mixed electrolyte solutions, each one characterized by its molal salt ratio ($r = m_{KCl}/m_{KNO_3} = 0.20, 1.0, 5.0, 10.0,$ and 20.0) were used in a standard addition technique, in order to modify the molality of

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the mixed electrolyte in the experimental cell. The Pitzer ion-interaction model was used for the experimental results correlation and calculation of activity coefficients [24]. The mean activity coefficients of KNO_3, the osmotic coefficients, the solvent activity, the surface tension and the excess Gibbs free energies were calculated for the whole series of these studied ternary mixed electrolyte systems.

2. Experimental

2.1. Apparatus and reagents

All of the potentiometric measurements were made by using a multimeter (Martini instruments Mi 180) whose resolution was 0.1 mV. The output of the multimeter was connected to a personal computer (AMD) by the RS232 connector for data acquisition. The Mi 5200 software together with Microsoft Excel (Office 2007) software were used for data acquisition and calculations. The solutions were continuously stirred using a magnetic stirrer (Delta Model HM-101) at a slow constant rate to avoid concentration gradients in the test solutions. A Model GFL circulation water bath was used to control the temperature of the test solution at $T = 298.15 \pm 0.1$ K. The conductivity measurements were carried out with a Metrohm 660 conductometer.

Dibutyl phthalate (DBP), sodium tetra phenyl borate (NaTPB), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF), potassium chloride (KCl), potassium nitrate (KNO_3), and all other reagents used were purchased from Merck and Fluka chemical company and all of them were of analytical reagent grade. Prior to use, potassium chloride (KCl) and potassium nitrate (KNO_3) were heated at $T = 393.15$ K in an oven for 5 h, subsequently stored over silica gel in a desiccator. The stock aqueous solution of mixed electrolyte were prepared from potassium chloride and potassium nitrate by adding weighted amounts of solid using an analytical balance (Sartorius GMBH 2842) with accuracy 0.1 mg and double-distilled water whose specific conductance was less than $2.0 \cdot 10^{-4}\ \mathrm{S \cdot m^{-1}}$.

2.2. Preparation of electrodes and data acquisition

The potassium ion-selective electrode was prepared in accordance with the general procedure of PVC membrane construction. An optimized mixture containing of 31 mg of powdered PVC, 58 mg of plasticizer DBP and 8 mg of additive NaTPB was dissolved in 2 ml of dry freshly distilled THF. To this mixture 3 mg of N,N′-(4,4′-ethylene biphenyl) bis(3-methoxy salicylidene-imine (EBSI) as an ionophore which was prepared according to the reported method in the literature [25] was added and mixed very well. The resulting clear mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated at the room temperature. After 2 h the polymer membrane could be easily removed from the plate. Then the transparent PVC membrane was taken up from the plate and attached to the end of a glass tube with a diameter of 1 cm and height of 5 cm by means of PVC–THF viscose solution. The ion-selective membrane was mounted between two solutions: internal electrolyte filling solution and sample solution. From the preliminary experimental tests performed with different concentrations of internal electrolyte filling solution the best results were those obtained with $0.1\ \mathrm{mol \cdot dm^{-3}}$ KCl electrolytes.

The Ag–AgCl wire was used as both internal reference electrodes and chloride selective electrode. The Ag–AgCl wire electrodes were prepared essentially as described previously by electrolysis [26]. The fabricated electrodes were initially conditioned for 48 h in $0.01\ \mathrm{mol \cdot dm^{-3}}$ KCl aqueous electrolyte solution. Both potassium and Ag–AgCl electrodes have been calibrated *versus* a saturated calomel reference electrode before use in 1 to 10^{-4} M concentration range of pure solution of KCl, and showed good Nernst slope (s) and linear relation (R^2), with amounts of $s = 53.3 \pm 0.2$ mV/decade ($R^2 = 0.9999$) and $s = 53.9 \pm 0.2$ ($R^2 = 0.9997$), respectively. Both K-ISE and Ag–AgCl electrodes were conditioned overnight in the appropriate mixed electrolyte system before each series of measurements.

The activity coefficients for KCl in the ternary system ($KCl/KNO_3/H_2O$) were determined from the emf measurements using the following galvanic cells:

$$\mathrm{Ag|AgCl|KCl}(m_A), \mathrm{H_2O|K\text{-}ISE}, \tag{A}$$

$$\mathrm{Ag|AgCl|KCl}(m_1), \mathrm{KNO_3}(m_2), \mathrm{H_2O|K\text{-}ISE}, \tag{B}$$

$$\mathrm{Ag|AgCl|KNO_3}(m_B), \mathrm{H_2O|K\text{-}ISE}. \tag{C}$$

The emf measurements of the galvanic cell (B) were made by using standard addition procedure. For this purpose, the concentrated mixed electrolyte solutions were added into the cell (B) containing a proportion volume of double-distilled water. The standard addition steps were carried out using proper burette and suitable Hamilton syringes (CH-7402 Bonaduz). In each series and for each standard addition step, data collection was performed every 10 s interval and during 15 (for concentrated solutions) to 20 min (for dilute solutions) by using a multimeter (Martini instruments Mi 180) connected to personal computer. As usual, all measurements were performed under stirring conditions and the temperature was kept constant at 298 K (±0.1 K), employing a double-wall container enabling the circulation of thermostated water from a Model GFL circulation.

3. Method

3.1. Pitzer model

The Pitzer ion-interaction model was used for the experimental data correlation and calculation of thermodynamic properties for mixed electrolyte solutions. According to the Pitzer model, the mean molal activity coefficient for KCl ($\gamma_{\pm\mathrm{KCl}}$) in the aqueous mixed electrolyte solution with common cation, $(1-y)\mathrm{KCl} + y\mathrm{KNO_3}$ is written as:

$$\ln\gamma_{\pm\mathrm{KCl}} = \ln\gamma^0_{\pm\mathrm{KCl}} + yI[(B^\phi_{\mathrm{KNO_3}} - B^\phi_{\mathrm{KCl}}) + I(C^\phi_{\mathrm{KNO_3}} - C^\phi_{\mathrm{KCl}})] + yI\left[\theta + \left(1 - \frac{y}{2}\right)I\psi\right], \tag{1}$$

where

$$\ln\gamma^0_{\pm\mathrm{KCl}} = f^\gamma + B^\gamma_{\mathrm{KCl}}I + \frac{3}{2}C^\phi_{\mathrm{KCl}}I^2, \tag{2}$$

$$f^\gamma = -A_\phi\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln\left(1+b\sqrt{I}\right)\right], \tag{3}$$

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\exp\left(-\alpha\sqrt{I}\right), \tag{4}$$

$$B^\gamma_{MX} = 2\beta^{(0)}_{\mathrm{MX}} + \frac{2\beta^{(1)}_{\mathrm{MX}}}{\alpha^2 I}\left[1 - \left(1 + \alpha\sqrt{I} - \frac{\alpha^2}{2}I\right)\exp\left(-\alpha\sqrt{I}\right)\right]. \tag{5}$$

In these equations, A_φ denotes the Debye–Huckel parameter for the osmotic function that its value is $0.3915\ \mathrm{kg^{1/2} \cdot mol^{-1/2}}$ for an aqueous solution at 298.15 K. I and y are the total ionic strength on a molality scale and ionic strength fraction, respectively. MX stands for KCl and KNO_3 in mixture solutions. $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ symbolize the parameters of Pitzer equation for single salt electrolyte solution, were taken from the literature [8] and are presented in table 1. θ and ψ indicate the unknown mixing interaction parameters which should be determined. The other constants have their usual meaning.