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Thermodynamic properties determination of ternary mixture ($NaCl + Na_2HPO_4$ + water) using potentiometric measurements

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ABSTRACT

In this work, the thermodynamic properties of the ternary mixed electrolyte system ($NaCl + Na_2HPO_4$ + water), using the potentiometric method, are reported. The potentiometric measurements were performed on the galvanic cells without liquid junction of the type: Ag–AgCl|NaCl (m_1), Na_2HPO_4 (m_2), H_2O|Na-ISE, over total ionic strengths from (0.0130 to 4.000) $mol \cdot kg^{-1}$ for different series of salt molal ratios r ($r = m_{NaCl}/m_{Na_2HPO_4}$ = 2.5, 5.0, 7.5, and 10.0) and pure NaCl in aqueous system at T = 298.2. The PVC based sodium ion selective electrode (Na-ISE) and Ag–AgCl electrode used in this work were prepared in our laboratory and had a reasonably Nernst response. The activity coefficient results were interpreted based on the Harned rule and Pitzer model. The unknown Pitzer mixing interaction parameters (θ_{ClHPO_4}, $\psi_{NaClHPO_4}$) were evaluated for the ternary system studied according to Pitzer graphical method .Then, the parameters obtained with the Pitzer model were used to calculate the values of the mean activity coefficients of Na_2HPO_4, the osmotic coefficients, the solvent activity and the excess Gibbs free energy for the whole series of the studied mixed electrolyte system.

1. Introduction

Recently, thermodynamic study of aqueous multicomponent electrolyte solutions has been a growing interest because of their importance in areas such as chemistry, biology, process engineering, desalination and atmospheric processes [1]. In addition, solutions of sodium or potassium dihydrogen and hydrogen phosphates have been used extensively as standard buffer solutions for pH measurements [2–4]. In the face of their importance, study of the thermodynamic properties on the most aqueous mixtures of these phosphate salts especially at higher molalities has not been performed.

To measure the thermodynamic properties in mixed electrolyte solutions, the most common methods involve the isopiestic vapor pressure [5,6], vapor pressure lowering [7,8], the electromotive force (emf) techniques [9,10] and hygrometric method [11]. Among the various methods, electrochemical cells with ion-selective electrodes (ISEs) because of rapidity and relative simplicity to generate experimental data are important. These ISEs are efficient tools for the measurements of thermodynamic properties of electrolyte solutions [12,13].

During the last decades, a series of ion-interaction models for electrolyte solution has been proposed to correlate the experimental data in electrolyte solutions. One of the most famous and useful models is that proposed by Pitzer [14]. This model is relatively simple, and it permits electrolyte calculations with accuracy, especially for values of molality under 6 [12].

In our previous papers, we reported the ability of the solvent polymeric membrane electrode for determination of activity coefficient for binary, ternary and quaternary electrolyte solutions [15–17]. In the present study, the results relating to the thermodynamic properties for the ternary mixture of ($NaCl + Na_2HPO_4$ + water) using the potentiometric method are reported at T = 298.2 K. The potentiometric measurements reported in this work were carried out on a galvanic cell containing a solvent polymeric (PVC) Na-ISE and Ag–AgCl electrodes and using various series of this mixed salt electrolyte system, over the ionic strength ranging from (0.0130 to 4.000)$mol \cdot kg^{-1}$. For this purpose, a series of different primary concentrated mixed electrolyte solutions, each one characterized by its molal salt ratio ($r = m_{NaCl}/m_{Na_2HPO_4}$ = 2.5, 5.0, 7.5, and 10.0) and pure NaCl in aqueous system was used in a standard addition technique, in order to modify the molality of the mixed electrolyte in the experimental cell. The activity coefficient results were interpreted based on the Harned rule and Pitzer model. The unknown Pitzer mixing interaction parameters (θ_{ClHPO_4}, $\psi_{NaClHPO_4}$) were evaluated. The parameters obtained with the Pitzer model were then used to calculate the values of the mean activity coefficients of Na_2HPO_4, the osmotic coefficients, the solvent activity and the excess Gibbs free energy for the whole series of these studied ternary mixed electrolyte system.

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2. Experimental

2.1. Apparatus and reagents

All of the potentiometric measurements were made using a digital multimeter (Martini instruments Mi180) 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 $T = (298.2 \pm 0.1)$ K. Dibutyl phthalate (DBP), potassium tetrakis(p-chlorophenyl) borate (KT_PClPB), high molar mass poly(vinyl chloride) (PVC), tetrahydrofuran (THF), sodium chloride (NaCl), disodium hydrogen phosphate (Na_2HPO_4), and all other reagents used were purchased from chemical companies in table 1 and all of them were of analytical reagent grade. Salt solutions were prepared gravimetrically by the use of a balance with a resolution of 0.1 mg. All primary stock solutions were prepared by mass using doubly distilled water. The stock solution of mixed electrolyte were prepared from sodium chloride and sodium dihydrogen phosphate by adding weighed amounts of solid using an analytical balance (Sartorius GMBH 2842) with a resolution of 0.1 mg, double-distilled water whose specific conductance was less than $2.0 \cdot 10^{-4}\ S \cdot m^{-1}$.

2.2. Preparation of electrodes and data acquisition

The sodium ion-selective electrode was prepared in accordance with the general procedure of PVC membrane construction which has been reported in the previous works [17,18]. Also, the Ag-AgCl wire electrodes were prepared essentially as described elsewhere by electrolysis [19]. The fabricated electrode was initially conditioned for 48 h in 0.01 $mol \cdot dm^{-3}$ NaCl electrolyte solution. Both the Na-ISE and Ag–AgCl electrodes were calibrated against a saturated calomel reference electrode before use in a (1 to 10^{-4}) $mol \cdot dm^{-3}$ concentration range of pure solution of NaCl, and showed a good Nernst slope (s) and linear relation (R^2).

The activity coefficients for NaCl in the ternary system ($NaCl/Na_2HPO_4/H_2O$) were determined from the emf measurements using the following galvanic cells:

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

$$\mathrm{Ag|AgCl|Na_2HPO_4}(m_B), \mathrm{H_2O|Na\text{-}ISE}, \tag{B}$$

$$\mathrm{Ag|AgCl|NaCl}(m_1), \mathrm{Na_2HPO_4}(m_2), \mathrm{H_2O|Na\text{-}ISE}. \tag{C}$$

Here m_A and m_B represent the molality of NaCl and Na_2HPO_4 as single salts in mixed solvent respectively. The m_1 and m_2 represent the molality of NaCl and Na_2HPO_4 in the mixture, respectively. The emf measurements of the galvanic cell (C) were made using standard addition procedure. For this purpose, the concentrated mixed electrolyte solutions were added into the cell (C) containing a proportion volume of mixed solvent. 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 10 (for concentrated solutions) to 20 min (for dilute solutions) 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 298.2 K, employing a double-wall container enabling the circulation of thermostatted water from a Model GFL circulation.

TABLE 1
The company and purity value of compounds used.

Chemical used	Company	Mass fraction purity
Sodium chloride	Merck	>0.995
Tetrahydrofuran (THF)	Merck	>0.99
Dibutyl phthalate	Merck	>0.99
Potassium tetrakis(p-chlorophenyl) borate	Fluka	>0.98
Poly (vinyl chloride)	BDH Laboratory	0.996
Disodium hydrogen phosphate	Alfa Aesar	0.99

3. Method

3.1. Thermodynamic 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, $\gamma_\pm$, for NaCl in the aqueous mixed aqueous electrolyte solution, (m_1NaCl + m_2 Na_2HPO_4) is written as:

$$\begin{aligned}\ln \gamma_{\pm\mathrm{NaCl}} = {} & F + 2m_1\beta_1^0 + 2m_1\beta_1^1 \times \frac{1}{2I}[1-(1+2\sqrt{I})e^{-2\sqrt{I}}] + 2m_2\beta_1^0 \\ & + 2m_2\beta_1^1 \times \frac{1}{2I}[1-(1+2\sqrt{I})e^{-2\sqrt{I}}] + m_2\beta_2^0 + m_2\beta_2^1 \\ & \times \frac{1}{2I}[1-(1+2\sqrt{I})e^{-2\sqrt{I}}] + (1.5m_1^2 + 4m_1m_2 + 2m_2^2)C_1^\varphi \\ & + \frac{\sqrt{2}}{2}(m_1m_2 + 2m_2^2)C_2^\varphi + m_2\theta + (m_1m_2 + m_2^2)\psi,\end{aligned} \tag{1}$$

where

$$\begin{aligned}F = {} & -A_\varphi\left[\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2}\ln(1+1.2\sqrt{I})\right] \\ & + (m_1+2m_2)(m_1\beta_1^1 + m_2\beta_2^1)\frac{1}{2I}[-1+(1+2\sqrt{I}+2I)e^{-2\sqrt{I}}].\end{aligned} \tag{2}$$

In these equations, A_φ denotes the Debye–Huckel parameter for the osmotic function that its value is 0.3915 $kg^{1/2} \cdot mol^{-1/2}$ at $T = 298.2$ [12]. The I and m are the total ionic strength on a molality scale and molality of NaCl and Na_2HPO_4 in mixtures, respectively; $\beta^{(0)}$, $\beta^{(1)}$ and C^φ symbolize the parameters of Pitzer equation for single salt electrolyte solution, which were taken from literature [12] and are presented in table 2. The θ and ψ indicate the unknown mixing interaction parameters which should be determined. The other constants have their usual meaning.

The unknown Pitzer mixing interaction parameters ($\theta_{\mathrm{ClHPO_4}}$, $\psi_{\mathrm{NaClHPO_4}}$) were evaluated using the graphical procedure recommended by Pitzer. This procedure defines the quantity of $\Delta\ln\gamma_\pm$ as the difference between the measured mean activity coefficients for the mixture ($\ln\gamma_{\mathrm{exp}}$) and that calculated ($\ln\gamma_{\mathrm{calc}}$) on the basis of $\theta = \psi = 0$ from equation (1). Then this equation is simplified and rearranged to yield

$$\frac{1}{m_{\mathrm{HPO_4}}}\Delta\ln\gamma_{\pm\mathrm{NaCl}} = \theta_{\mathrm{ClHPO_4}} + \frac{1}{2}(m_{\mathrm{Na}} + m_{\mathrm{Cl}})\psi_{\mathrm{NaClHPO_4}}. \tag{3}$$

So a plot of left side of equation (3) *versus* ½($m_{\mathrm{Na}} + m_{\mathrm{Cl}}$) should give θ as the intercept and ψ as the slope. Firstly, from the

TABLE 2
Pitzer parameter values $\beta^{(0)}$, $\beta^{(1)}$ and C^{φ} for single electrolyte of NaCl and Na_2HPO_4.

Electrolyte	$\beta^{(0)}$/ ($kg \cdot mol^{-1}$)	$\beta^{(1)}$/ ($kg \cdot mol^{-1}$)	$C^{(\varphi)}$/ ($kg^2 \cdot mol^{-2}$)	Reference
NaCl	0.0765	0.2664	−0.00127	[12]
Na_2HPO_4	0.0573	1.4655	0.0146	[12]