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## THERMODYNAMIC PROPERTIES OF THE SYSTEM $\{y\text{NaCl}+(1-y)\text{Na}_2\text{HPO}_4\}(\text{aq})$ AT $T = 298.15$ K BY ELECTROMOTIVE FORCE MEASUREMENTS

D. Ž. Popović<sup>1</sup>, T. G. Ivanović<sup>2</sup>, J. M. Miladinović<sup>3</sup>, Z. P. Miladinović<sup>4</sup>,  
 F.T. Pastor<sup>5</sup> and A. Zlatić<sup>3</sup>

<sup>1</sup> *Innovation Centre Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4,  
 11 001 Belgrade, Serbia (dpopovic@tmf.bg.ac.rs)*

<sup>2</sup> *Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1, 11 030  
 Belgrade, Serbia*

<sup>3</sup> *Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4,  
 11 001 Belgrade, Serbia*

<sup>4</sup> *Institute of General and Physical Chemistry, Studentski trg 12-16,  
 11 000 Belgrade, Serbia*

<sup>5</sup> *Faculty of Chemistry, Studentski trg 12-16, 11 000 Belgrade, Serbia*

### ABSTRACT

The mean ionic activity coefficients of NaCl in a ternary system  $\{y\text{NaCl} + (1 - y)\text{Na}_2\text{HPO}_4\}(\text{aq})$  were determined using electromotive force measurements (EMF) at  $T = 298.15$  K. For EMF measurements, a cell of the type  $\text{Na-ISE} \mid \text{NaCl}(m_{\text{NaCl}}), \text{Na}_2\text{HPO}_4(m_{\text{Na}_2\text{HPO}_4}) \mid \text{Ag} \mid \text{AgCl}$  was employed with NaCl ionic strength fractions  $y = (0.3012; 0.5011; 0.7706)$  in the range of total ionic strength of the solution  $I = (0.0701 - 0.9315) \text{ mol} \cdot \text{kg}^{-1}$ . The Extended Pitzer model was used to analyze experimental data for the mixed electrolyte solution, and good agreement between experimental and calculated values of thermodynamic properties was found with a standard deviation of the fit of  $10^{-3}$  order.

### INTRODUCTION

Many groundwaters and surface waters include phosphorus in the form of protonated orthophosphates  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ . Natural waterways have extremely low quantities of phosphates, however some wastewaters can contain considerably greater concentrations, causing eutrophication. Phosphate soluble salts are widely used in the chemical industry, plant fertilizer, toothpaste, pharmaceuticals, food additives, and within other applications.

Because water solutions can contain salt mixtures, such as NaCl and  $\text{Na}_2\text{HPO}_4$ , a better explanation of their thermodynamic properties is required. Our previous studies of thermodynamic properties with phosphate ions comprised isopiestic measurements [1-10] and electromotive force measurements [11].

The current study focused on the thermodynamic properties of a mixed electrolyte solution  $\{y\text{NaCl} + (1 - y)\text{Na}_2\text{HPO}_4\}(\text{aq})$  at  $T = 298.15$  K utilizing a cell of the type  $\text{Na-ISE} \mid \text{NaCl}(m_{\text{NaCl}}), \text{Na}_2\text{HPO}_4(m_{\text{Na}_2\text{HPO}_4}) \mid \text{Ag} \mid \text{AgCl}$ . The experimental results together with the literature data [12] were analyzed using an Extended Pitzer's model.

### EXPERIMENTAL SECTION

Anhydrous NaCl(cr) and  $\text{Na}_2\text{HPO}_4(\text{cr})$  and doubly-distilled, deionized water were used to make the two stock solutions. The molality of the NaCl(aq) and  $\text{Na}_2\text{HPO}_4(\text{aq})$  stock solutions was  $m = 1.0050 \pm 0.0036 \text{ mol} \cdot \text{kg}^{-1}$  and  $m = 0.3403 \pm 0.0030 \text{ mol} \cdot \text{kg}^{-1}$ , respectively. By mixing appropriate aliquots of the stock solutions, the mixed solutions were formed.

The cells for electromotive force measurements were arranged as follows:



where  $m_{\text{NaCl},0}$  and  $m_{\text{Na}_2\text{HPO}_4,0}$  are the stoichiometric molalities of NaCl(aq) and Na<sub>2</sub>HPO<sub>4</sub>(aq), respectively, while  $m_{\text{NaCl}}$  and  $m_{\text{Na}_2\text{HPO}_4}$  are the stoichiometric molalities of NaCl and Na<sub>2</sub>HPO<sub>4</sub> in the mixed solution.

## RESULTS AND DISCUSSION

Calibration of the electrode pair was done in the investigated solutions' ionic strength range from 0.1 to 1 mol·kg<sup>-1</sup> to obtain the corresponding potential,  $E_a$ . Nernst's equation for cell (a) can be given as:

$$E_a = E^0 + k \ln a_{\pm\text{NaCl}} \quad (1)$$

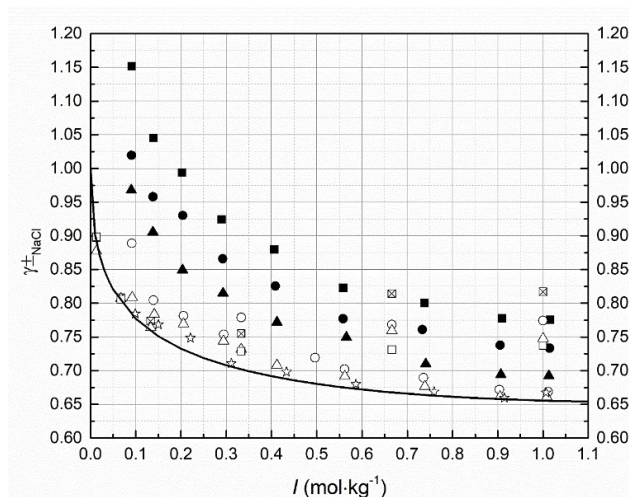
$$E_a = E^0 + k \ln(m_{\text{NaCl},0}^2 \gamma_{\pm\text{NaCl},0}^2) \quad (2)$$

where:  $k$  is the Nernst's slope,  $a_{\pm\text{NaCl}}$  is the activity of the NaCl(aq) solution and  $\gamma_{\pm\text{NaCl},0}$  is the mean ionic activity coefficient of NaCl calculated using the Extended Pitzer's model and Archer's parameters [13].  $E^0$  denotes the standard electrode potential that can be determined by linear regression method, from the relations (1) or (2) and its values is  $E^0 = 23.227$  mV. Linear correlation coefficient for the function  $E_a = f(\ln a_{\pm\text{NaCl}})$  is 0.99934. The cell (c) was employed to determine the values of the mean ionic activity coefficient of NaCl in the mixed solution  $\{y\text{NaCl} + (1-y)\text{Na}_2\text{HPO}_4\}$ (aq) at  $T = 298.15$  K. The mean ionic activity coefficient of NaCl in the mixture and cell arrangement (c) is define as:

$$\ln(\gamma_{\pm\text{NaCl}}) = (E_m - E^0)/2k - 1/2 \ln \{m_{\text{NaCl}} + 2m_{\text{Na}_2\text{HPO}_4}\} \quad (3)$$

where  $\gamma_{\pm\text{NaCl}}$  is the mean ionic activity coefficients of NaCl in the cell (c).

Experimental results of the mean ionic activity coefficient of NaCl in the system  $\{y\text{NaCl} + (1-y)\text{Na}_2\text{HPO}_4\}$ (aq) at  $T = 298.15$  K obtained as a preliminary investigation together with the literature data [12] are presented in Figure 1.



**Figure 1.** Mean ionic activity coefficient of NaCl,  $\gamma_{\pm,NaCl}$ , vs. ionic strength of the system  $\{yNaCl + (1-y)Na_2HPO_4\}$  (aq) at  $T = 298.15$  K: experimental data  $\blacksquare$   $y = 0.3012$ ;  $\bullet$   $y = 0.5011$ ;  $\blacktriangle$   $y = 0.7706$ ; and literature data [12]:  $\boxtimes$   $y = 0.4538$ ;  $\circ$   $y = 0.6385$ ;  $\triangle$   $y = 0.7154$ ;  $\square$   $y = 0.7615$ ; curve calculated values for the pure solution NaCl(aq) at  $y = 1.0$ .

Extended Pitzer's model for the activity coefficient of ions  $Na^+$ (aq) and  $Cl^-$ (aq) in the mixed aqueous solution of NaCl and  $Na_2HPO_4$  has the form:

$$\ln \gamma_{Na^+} = z_{Na^+}^2 F + \left(\frac{m_{Cl^-}}{m^0}\right) (2B_{NaCl} + ZC_{NaCl}^T) + \left(\frac{m_{HPO_4^{2-}}}{m^0}\right) (2B_{Na_2HPO_4} + ZC_{Na_2HPO_4}^T) + \left(\frac{m_{Cl^-}}{m^0}\right) \left(\frac{m_{HPO_4^{2-}}}{m^0}\right) \psi_{Na^+,Cl^-,HPO_4^{2-}} + z_{Na^+} \left[ \left(\frac{m_{Na^+}}{m^0}\right) \left(\frac{m_{Cl^-}}{m^0}\right) C_{NaCl}^T + \left(\frac{m_{Na^+}}{m^0}\right) \left(\frac{m_{HPO_4^{2-}}}{m^0}\right) C_{Na_2HPO_4}^T \right] \quad (4)$$

$$\ln \gamma_{Cl^-} = z_{Cl^-}^2 F + \left(\frac{m_{Na^+}}{m^0}\right) (2B_{NaCl} + ZC_{NaCl}^T) + \left(\frac{m_{HPO_4^{2-}}}{m^0}\right) \left[ 2\theta_{Cl^-,HPO_4^{2-}} + \left(\frac{m_{Na^+}}{m^0}\right) \psi_{Na^+,Cl^-,HPO_4^{2-}} \right] + |z_{Cl^-}| \left[ \left(\frac{m_{Na^+}}{m^0}\right) \left(\frac{m_{Cl^-}}{m^0}\right) C_{NaCl}^T + \left(\frac{m_{Na^+}}{m^0}\right) \left(\frac{m_{HPO_4^{2-}}}{m^0}\right) C_{Na_2HPO_4}^T \right] \quad (5)$$

In the above equations,  $I$  is the ionic strength of the solution and  $m^0$  is the standard molality  $1 \text{ mol} \cdot \text{kg}^{-1}$ ,  $F$  is a specific function,  $B_{NaCl}$  and  $B_{Na_2HPO_4}$  are the second virial and  $C_{NaCl}^T$  and  $C_{Na_2HPO_4}^T$  are the third virial coefficients, function

$$Z = \left(\frac{m_{Na^+}}{m^0}\right) z_{Na^+} + \left(\frac{m_{Cl^-}}{m^0}\right) |z_{Cl^-}| + \left(\frac{m_{HPO_4^{2-}}}{m^0}\right) |z_{HPO_4^{2-}}| \quad (6)$$

and  $\theta_{HPO_4^{2-},Cl^-}$  together with  $\psi_{Na^+,HPO_4^{2-},Cl^-}$  are the empirical mixing parameters.

By treatment of obtained results for mean ionic activity coefficients of NaCl, in the ionic strength range app. from 0.1 to  $1.0 \text{ mol} \cdot \text{kg}^{-1}$  and literature data [12] for the same system by Extended Pitzer's model, one obtain the following values of mixing parameters  $\theta_{HPO_4^{2-},Cl^-}(m^0) = 1.19955$  and  $\psi_{Na^+,HPO_4^{2-},Cl^-} = -0.19825$  with standard deviation of the fit being  $s.d.(\gamma_{\pm}) = 8.7 \cdot 10^{-3}$ . Because chloride and sodium ions have minor influence on solution structure, this comparatively large value of

standard deviation can be explained by the likely development of hydrogen-bonded phosphate dimers or polymers in  $\text{HPO}_4^{2-}$  solutions.

## CONCLUSION

The mean ionic activity coefficients of NaCl in the system  $\{y \text{ NaCl} + (1 - y) \text{ Na}_2\text{HPO}_4\}(\text{aq})$  have been, preliminary determined using a cation-selective electrode at ionic strengths up to  $1 \text{ mol} \cdot \text{kg}^{-1}$ . The obtained results were compared to literature data and treated jointly by the Extended Pitzer's model with standard deviation being  $\text{s.d.}(\gamma_{\pm}) = 8.7 \cdot 10^{-3}$ . These findings suggest that phosphate dimers might form in solution via hydrogen bonding.

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