

# Mean activity coefficients measurement of sodium chloride and thermodynamic modeling of sodium chloride and polysodium acrylate aqueous mixtures at $T=(298.2$ and $303.2)$ K



Bahram Ghalami-Chooabar\*, Tayyeb Nosrati Fallahkar

Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box 19141, Rasht, Iran

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## ABSTRACT

In this work, thermodynamic properties of the ternary (sodium chloride + polysodium acrylate) aqueous system was investigated using the potentiometric method at  $T=(298.2$  and  $303.2)$  K. Potentiometric measurements were carried out on the galvanic cell with ion-selective electrodes containing a solvent polymeric (PVC) Na-ISE and Ag–AgCl over total molality from 0.0010 to 2.9997 mol kg<sup>-1</sup> for various series of molal ratios ( $r=m_{\text{NaCl}}/m_{\text{NaPA}}=50, 40, 30, 20,$  and/or 15) and NaCl single electrolyte. Modeling of this ternary system was made based on proposed model and mixing interaction parameters ( $\theta_{\text{CIPA}}, \psi_{\text{NaCIPA}}$ ) were evaluated for the studied ternary system according to Pitzer graphical method. These parameters were used to calculate the values of the mean activity coefficients of NaPA, the osmotic coefficients, solvent activity and excess Gibbs free energies of the whole series for under investigation system.

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## 1. Introduction

Polyelectrolytes are described as the class of macromolecules with ionizable groups which are both polymers and electrolytes [1]. In polar solvent, they are dissociated into charged polymer backbones (polyions) and mobile counterions [2,3]. Polyelectrolytes are divided into natural polyelectrolytes such as natural proteins, DNA, RNA, polysaccharides (biopolyelectrolytes) and synthetic polyelectrolytes such as polyacrylic acid, polymethacrylic acid, polystyrene sulfonic acid and their salts [4]. Synthetic polyelectrolytes are used in many fields for instance, in fuel cells [5], dental materials and polymeric drugs [6], as flocculating agents in the petroleum industry and as retention aids in the paper industry [7]. Prediction of activity coefficients of simple electrolytes in polyelectrolyte solutions is needed to describe transport properties of ion-exchange membranes [8]. Besides in biological fluids, biopolyelectrolytes are usually surrounded by a mixture of ions ( $\text{Na}^+, \text{K}^+, \text{Ca}^{+2}, \text{Mg}^{+2}, \text{Cl}^-$ ). Therefore, thermodynamic study of simple electrolyte in polyelectrolyte solutions is of practical and theoretical importance [9]. Due to the wide biological and industrial significance of polyelectrolyte solutions with and without added salt, thermodynamic modeling and experimental study of these systems are needed.

Up to now, spherical and cylindrical approaches have been presented to determine the thermodynamic properties of polyelectrolyte solutions. First, the cylindrical model was independently proposed by Alfrey and Fuoss et al. [10]. This cylindrical model was extended by Dolar and Peterlin [11]. One of the most important models for aqueous solutions of polyelectrolytes that were based on the concept of counterion condensation was presented by Manning [12]. The concept of counterion condensation was caused by strong coulombic interactions between polyion and its counterions introduced for the first time by Imai and Onishi [13]. Manning extended the cylindrical cell model through accounting the effects of presence electrolyte in the aqueous polyelectrolyte solutions. In Manning's theory, the real polyelectrolyte chain was assumed as an infinite long line with a linear charge density. For a charge density greater than the critical value (at infinite dilution in water), a certain fraction of the counterions are condensed in vicinity of the polymer backbone. Furthermore, Manning assumed that the condensed counterions move in a volume near the polyion and the influence of uncondensed mobile ions was treated using the cylindrical version of the Debye–Hückel theory. This model was valid only at infinite dilution. However, Nagvekar and Danner [14] introduced a model for polyelectrolyte solutions at finite concentrations. They expressed the excess Gibbs free energy of system as the sum of long-range and short-range terms. The long-range contribution from the Manning's theory and short-range contribution from the NRTL model were approximated. Jiang et al.

\* Corresponding author. Tel.: +98 1313233262; fax: +98 1313233262.  
E-mail address: [B-Ghalami@guilan.ac.ir](mailto:B-Ghalami@guilan.ac.ir) (B. Ghalami-Chooabar).

[15,16] proposed a molecular-thermodynamic model for polyelectrolyte solution using cavity-correlation functions. Cai et al. [17] developed Jiang et al.'s proposed expressions for the osmotic pressure and activity coefficient of polyelectrolyte solutions. Moreover, Deshkovski et al. [18] solved the nonlinear Poisson–Boltzmann equation for dilute rod like polyelectrolyte. Lammertz et al. [4] proposed a thermodynamic model to express Gibbs energy of aqueous polyelectrolyte solutions and applied it to correlate the experimental data of aqueous polyelectrolyte solutions with and without added salt. In addition, Budkov et al. [19] suggested the Gaussian equivalent representation to determine the thermodynamic and structural properties of polyelectrolyte solutions.

The various experimental methods have been employed to measure the thermodynamic properties of polyelectrolyte solutions. These methods include membrane osmometry (MO) [20,21], differential membrane osmometry (DMO), vapor pressure osmometry (VO) [6], isopiestic measurement (ISO) [22], potentiometric method [23], equilibrium dialysis (EQDIA) [24] and solubility determination [25]. For instance, isopiestic determination of the osmotic coefficients for sodium poly(styrene sulfonate) (NaPSS) and poly(vinyl benzyl trimethyl ammonium chloride) (PVBtMACl) with added sodium chloride was performed by Boyd [26] at  $T=298.2\text{ K}$ . Also the activity of water in aqueous solutions of 10 single polyelectrolytes and sodium chloride at  $T=298.2\text{ K}$  were reported using the isopiestic method by Lammertz et al. [27].

Among the various methods, potentiometric method is proper because of rapidity and relative simplicity to generate experimental data in comparison with the other techniques [28]. Electromotive force (emf) measurement was performed by Kwak and co-workers [29] who measured mean activity coefficient of simple electrolyte in aqueous mixtures of potassium chloride–potassium poly(styrene sulfonate), magnesium chloride–magnesium poly(styrene sulfonate) and calcium chloride–calcium poly(styrene sulfonate). Also, the activity coefficients of NaCl in poly(diallyl dimethyl ammonium chloride), poly(anethole sulfonic acid, sodium salt) and polysodium acrylate solutions were reported over ionic strength ranging from 0.01 to  $1\text{ mol kg}^{-1}$  by Yu et al. [30] at  $T=298.2\text{ K}$ .

In this work, thermodynamic properties of sodium chloride and polysodium acrylate (NaPA) aqueous solutions were investigated using the potentiometric method with ion-selective electrodes containing a solvent polymeric (PVC) Na-ISE and Ag–AgCl over total molality from 0.0010 to  $2.9997\text{ mol kg}^{-1}$  for various series of molal ratios ( $r=m_{\text{NaCl}}/m_{\text{NaPA}}=50, 40, 30, 20,$  and/or 15) and NaCl single electrolyte at  $T=(298.2\text{ and }303.2)\text{ K}$ . In the previous works [31,32], we reported ability of self-made electrode to determine thermodynamic properties of the ternary and quaternary electrolyte solutions in according to Pitzer model. In this work, we modified the Pitzer model to determine the thermodynamic properties of electrolyte and polyelectrolyte mixtures and used it to correlate the experimental data. Mixing interaction parameters ( $\theta_{\text{ClPA}}, \psi_{\text{NaClPA}}$ ) were evaluated for the studied ternary system according to Pitzer graphical method. These parameters were used to calculate the values of the mean activity coefficients of NaPA, the osmotic coefficients and excess Gibbs free energies of the whole series for under investigation system.

## 2. Experimental

### 2.1. Apparatus and reagents

All of the potentiometric measurements were made using a digital multimeter (Martini instruments Mi 180) whose resolution was 0.1 mV. The output of the multimeter was connected to a personal computer by the RS232 connector for data acquisition. The Mi 5200

**Table 1**

The company and purity value of compounds used.

| Chemical used                                       | Company        | Purity (%) |
|---|----------------|------------|
| Sodium chloride                                     | Merck          | >99.5      |
| Tetrahydrofuran (THF)                               | Merck          | >99        |
| Dibutyl phthalate                                   | Merck          | >99        |
| Potassium tetrakis ( <i>p</i> -chlorophenyl) borate | Fluka          | >98        |
| Poly(vinyl chloride)                                | BDH Laboratory | 99.6       |
| Polysodium acrylate <sup>a</sup>                    | Sigma-Aldrich  | –          |

<sup>a</sup> Average molecular weight = 1200, refractive index = 1.43, density = 1.32, and concentration = 45 wt.% in H<sub>2</sub>O.

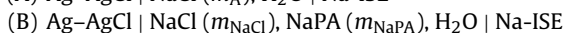
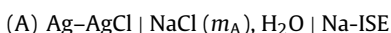
software together with Microsoft Excel (Office 2007) software was used for data acquisition and calculations. The solutions were continuously stirred using a magnetic stirrer (Delta Model HM-101) at a slow constant rate to avoid concentration gradients in the test solutions. A Model GFL circulation water bath was used to control the temperature of the test solution at  $T=298.2 \pm 0.1$  and  $303.2 \pm 0.1\text{ K}$ . Dibutyl phthalate (DBP), potassium tetrakis (*p*-chlorophenyl) borate (KT<sub>4</sub>CIPB), high molar mass poly(vinyl chloride) (PVC), tetrahydrofuran (THF), polysodium acrylate (NaPA), sodium chloride (NaCl) and all other reagents used were purchased from Merck, Fluka and Sigma chemical company and all of them were of analytical reagent grade (Table 1). Salt solutions were gravimetrically prepared 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 solutions of polysodium acrylate and sodium chloride were prepared by adding weighed amounts using an analytical balance A&D with a resolution of 0.1 mg, double-distilled water whose specific conductance was less than  $2.0 \times 10^{-4}\text{ S m}^{-1}$ . The power supply current (MP-3003D) was used to electrolysis the Ag wires.

### 2.2. Preparation of electrodes

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 [33]. Also, the Ag–AgCl wire electrodes were prepared essentially as described elsewhere by electrolysis [34]. The fabricated electrodes were initially conditioned for 48 h in  $0.01\text{ mol dm}^{-3}$  NaCl electrolyte solution. Both the Na-ISE and Ag–AgCl electrodes were calibrated against a saturated calomel reference electrode before use in a  $(1-10^{-4})\text{ mol dm}^{-3}$  concentration range of pure solution of NaCl, and showed a good Nernst slope (*s*) and linear relation ( $R^2$ ).

### 2.3. Potentiometric measurements

The mean activity coefficients for NaCl in the ternary system (NaCl + NaPA + water) were determined from the emf measurements using the following galvanic cells:



Here,  $m_A$  was the molality of NaCl as single salt electrolyte. The  $m_{\text{NaCl}}$  and  $m_{\text{NaPA}}$  were the molalities of NaCl and NaPA in the mixtures, respectively. The emf measurements of the galvanic cell (B) were made using standard addition procedure. For this purpose, the concentrated solutions of polyelectrolyte and sodium chloride

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