

Series approach to modeling of amino acid and electrolyte mixtures in the aqueous media



Maryam Alamdari Shendi^a, Zohreh Karimzadeh^{b,*}, Rahman Salamat-Ahangari^a

^a Chemistry Group, Faculty of Basic Science, Azarbaijan Shahid Madani University, Tabriz, Iran

^b Department of Chemistry, Shahid Beheshti University, G.C., Evin-Tehran, Iran

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ABSTRACT

In this work, the electrolyte, amino acid and water solutions are modeled using activity coefficient (AC) approach. Two different models, modified Pitzer ion interaction equation proposed by Esteso (PE) and the Pitzer–Simonson–Clegg model (PSC) are used in their original and modified forms to correlate the activity coefficient and osmotic coefficient data for binary and ternary systems containing water, amino acid/peptide and electrolytes. The considered aqueous systems contain one of the eight amino acids: alanine, glycine, serine, threonine, β -alanine, methionine, α -amino n-butyric acid and α -amino butyric acid. Also, glycyglycine is used as one peptide. The salts are NaCl, NaBr, NaNO₃, KCl and KBr.

The results obtained from the studied models are compared to those of experimental data. The comparison shows that the PE model can correlate the experimental AC data of ternary systems more accurate than the other PSC. The equations are tested against the large number (30) of available experimental data sets.

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1. Introduction

Amino acids are molecules containing an amine group, a carboxylic acid group and a side chain. Amino acids are widely used in biotechnology applications and they are the building blocks for very important biological macromolecules. They are chosen as model substances because their phase behaviors represent similarities with more complex molecules, such as small peptides, antibiotics and drugs [1]. Determination of the electrolyte and amino acid thermodynamic properties in aqueous solutions is necessary in understanding and handling the nature of various ionic interactions, industrial and biological processes [1].

The modeling of amino acid thermodynamic properties in aqueous and non-aqueous solutions has been the subject of many studies. Some authors investigated the amino acids in aqueous and non-aqueous mixtures [2–20].

A survey of literature confirms that a limited study in activity coefficient (AC) modeling is available, in regard with water, electrolyte and amino acids mixtures. Kirkwood [3] in a pioneering study investigated the interaction between amino acid and ions. But this model has a qualitative approach to investigate the behavior of the water, electrolyte and amino acids at low concentrations.

A perturbed hard-sphere thermodynamic model with an electrostatic term has been developed by Khoshkbarchi and Vera [4] to correlate the activity coefficient of amino acids in aqueous electrolyte solutions. In this model, the amino acid molecules and ions were considered as hard spheres with embedded dipole moments and as hard spheres with embedded charges respectively. Kamali and Modarress fitted the activity coefficients of glycine in aqueous electrolyte solutions to a virial expansion model [5]. Study of amino acid solubility in aqueous electrolyte solutions at temperatures other than 298.15 K using the Pitzer–Simonson–Clegg equation was performed by Ferreira et al. [6,7]. Fiol and coworkers [8] studied the α -alanine in NaCl based on the Pitzer, Scatchard and a simpler modification of the Debye–Hückel equation.

Activity coefficients were measured for different electrolyte and amino acid concentrations and fitted to a virial expansion by Khoshkbarchi and coworkers [9–15]. The activity coefficient modeling of mixtures containing NaBr, glycine, K₃PO₄, water and NaBr, DL-valine, K₃PO₄, water were performed by Modarress et al. [16,17]. An equation based on modification of Pitzer ion interaction model was proposed to correlate thermodynamic properties, like mean ion activity coefficients, volumes and compressibilities of amino acids in electrolyte solutions by Saritha and coworkers [18]. Sadowski et al. measured and modeled aqueous electrolyte and amino acid solutions with ePC-SAFT equation [19]. Application of the McMillan–Mayer theory of solutions through virial expansion of transfer Gibbs energies was used by Kurhe et al. [20] to

* Corresponding author.

E-mail address: z.karimzadeh@gmail.com (Z. Karimzadeh).

investigate the interactions of amino acid with urea and guanidine hydrochloride in aqueous solutions.

The most frequently and successful model used to describe the thermodynamic properties of aqueous electrolyte solutions is known to be the ion interaction or virial coefficient approach developed by Pitzer and coworkers [21–24]. However, the application of the Pitzer ion-interaction approach to investigate mixture of polar and non-polar species with electrolyte is still scarce [25–27]. Khoshkbarchi showed that Pitzer ion interaction model can accurately correlate the interactions of glycine and NaCl in aqueous solution [26]. But, Estes showed that good fit were obtained for solution consisting of electrolyte and nonelectrolyte if the nonelectrolyte is a non-polar species [28]. Estes and co-workers [29] performed some modifications to the original Pitzer equation to include the dependence of the binary interaction parameters (containing the nonelectrolyte) on the ionic strength and the ion–nonelectrolyte interactions on the nonelectrolyte concentration.

This study demonstrates utility of using the Pitzer–Simonson–Clegg (PSC) and Pitzer–Estes (PE) equation for investigation of electrolyte and amino acid/peptide mixtures in aqueous media. In order to establish a broad systematic investigation of aqueous electrolyte and amino acid solutions, a huge numbers of reliable experimental data are needed. Calculations for activity coefficient and osmotic coefficient of electrolytes and amino acids in water are performed by extensive literature data (30 systems). The electrolytes are KBr, KCl, NaCl, NaBr and NaNO₃. Amino acids are valine, L-valine, alanine, glycine, serine, threonine, methionine, β-alanine, α-amino n-butyric acid and α-amino butyric acid. Fig. 1 shows the structure of amino acids used in this study. Finally the PSC model is compared with the PE equation.

2. Modeling

2.1. Modified Pitzer equation by Estes (PE)

To improve the fitting of experimental data containing polar nonelectrolyte, Estes and co-workers [29] performed some modifications on the original Pitzer equation to include the dependence of the binary interaction parameters (containing the nonelectrolyte) on the ionic strength and the ion–nonelectrolyte interactions on the nonelectrolyte concentration. For electrolyte system containing electrolyte (S=MX), water (W) as solvent and amino acid as nonelectrolyte (A), the PE equation for the activity coefficient of the electrolyte can be written as:

$$\ln \left(\frac{\gamma_S}{\gamma_S^0} \right) = \left(\frac{2}{\nu_S} \right) \chi_{SA} m_A + |z_M z_X| \chi'_{SA} m_S m_A + \left(\frac{2}{\nu_S} \right) \nu_M \nu_X \xi_{ASS} m_S m_A + \omega_{AAS} m_A^2 \quad (1)$$

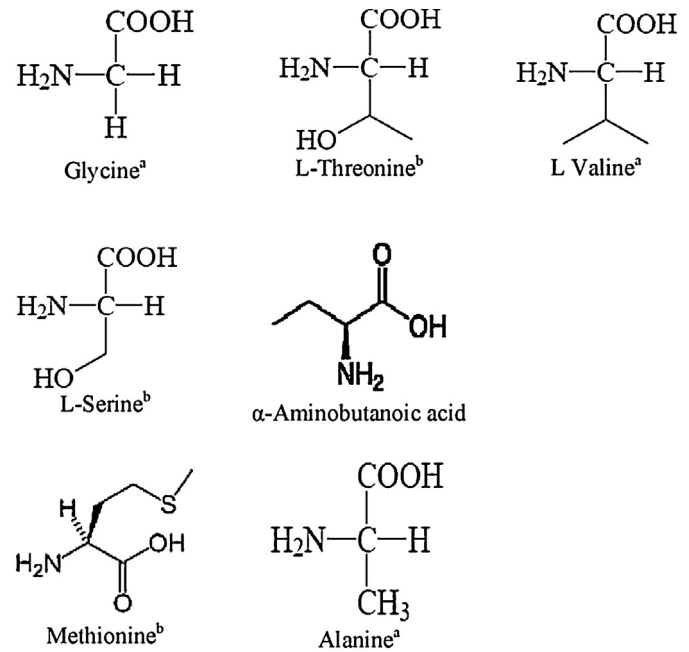
where

$$\ln \gamma_S^0 = |z_M z_X| f^\gamma + m \left(\frac{2\nu_M \nu_X}{\nu} \right) B_S^\gamma + m^2 \left(\frac{2(\nu_M \nu_X)^{1.5}}{\nu} \right) C_S^\gamma \quad (2)$$

$$f^\gamma = -A_\phi \left(\left(\frac{I^{0.5}}{1 + bI^{0.5}} \right) + \left(\frac{2}{b} \right) \ln(1 + bI^{0.5}) \right) \quad (3)$$

$$B_S^\gamma = 2\beta_S^{(0)} + \left(\frac{2\beta_S^{(1)}}{\alpha^2 I} \right) [1 - \exp(-\alpha I^{0.5})(1 + \alpha I^{0.5} - 0.5\alpha^2 I)] \quad (4)$$

$$C_S^\gamma = \left(\frac{3}{2} \right) C^\phi \quad (5)$$



a: Non-polar amino acids (hydrophobic)
b: Polar amino acids (hydrophilic)

Fig. 1. Amino acid structures are used in this study.

$$\chi_{SA} = \chi_{SA}^{(0)} + (\chi_{SA}^{(1,0)} + \chi_{SA}^{(1,1)} m_A) \left(\frac{2}{(\alpha_0 I^{0.5})^2} \right) \times [1 - (1 + \alpha_0 I^{0.5}) \exp(-\alpha_0 I^{0.5})] \quad (6)$$

$$\chi'_{SA} = (\chi_{SA}^{(1,0)} + \chi_{SA}^{(1,1)} m_A) \times \frac{-2/(\alpha_0 I^{0.5})^2 [1 - (1 + \alpha_0 I^{0.5}) + ((\alpha_0 I^{0.5})^2)/2] \exp(-\alpha_0 I^{0.5})}{I} \quad (7)$$

In PE activity coefficient equation for mixture of electrolyte (S), nonelectrolyte (A), and water (W), the terms ξ_{ASS} and ω_{AAS} are the ternary interaction parameters of nonelectrolyte–ion–ion and nonelectrolyte–nonelectrolyte–ion, respectively. In principle, $\chi_{SA}^{(0)}$, $\chi_{SA}^{(1,0)}$, $\chi_{SA}^{(1,1)}$, ξ_{ASS} and ω_{AAS} are the adjustable parameters. In the above equations, z is the charge number of an ion; $\nu = \nu^+ + \nu^-$ is the number of ions dissociated in one unit electrolyte formula; m is the molality of electrolyte (mol kg^{-1}); I is the ionic strength on a molality scale; $\beta^{(0)}$ (kg mol^{-1}), $\beta^{(1)}$ (kg mol^{-1}), $\beta^{(2)}$ (kg mol^{-1}) and C^ϕ (kg mol^{-1})^{0.5} are the parameters of the Pitzer equations and $b = 1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$.

The experimental data are fitted by considering $\alpha_0 = 2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ as a fixed value.

In order to correlate the experimental osmotic coefficient for some systems, equations for mixture of (S+A+W) and (A+W) could be achieved by the method described in [27].

2.2. Pitzer–Simonson–Clegg model (PSC)

Since the virial expansion formalism at very high concentrations, like miscible fused salt, becomes unsatisfactory, Pitzer and Simonson presented a new equation for systems containing ions of symmetrical charge type at very high concentration and for miscible fused salt [30,31]. In this approach, a three suffix Margules

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