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Calculation of activity and solubility of amino acids in aqueous solution by cubic-plus-association equation of state

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ABSTRACT

Cubic plus association equation of state was applied for the first time to calculate various thermodynamic properties such as activity coefficient, solubility, density, and vapor pressure of aqueous solution of amino acids. Pure compound parameters of CPA EOS were fitted to the activity coefficient of amino acids in aqueous solution. In order to calculate the monomer fractions of amino acids and water in a binary solution of these molecules, a novel 3rd degree linear equation was proposed. The model also has been used to correlate the solubility of amino acids in different temperatures, and the values of Δh and Δs were obtained through the calculation of solubility in water. In addition, a group contribution method was applied to estimate the critical temperature. CPA in contrast with the other equation of states (e.g. SAFT EOS) that previously used to correlate thermodynamic properties of amino acids has the advantage of simplicity. Moreover, the results showed good agreement with the experimental data.

1. Introduction

Recent advances in biotechnology lead to development of producing bio chemicals in a wide variety of applications for chemical and food industries. The separation and purification of the bio products are the most important steps in their productions. The precise estimation of some thermodynamic properties such as activity coefficient is requisite for the design of the separation process. Amino acids are simple biomolecules which contain both an amino group and a carboxylic acid group. Because of the unusual properties of these compounds, many studies have been performed to have a better understanding of their behavior. Thus, it was desirable to calculate the solubility and activity coefficient of these components in aqueous solution. In order to describe phase behavior of amino acid solutions there are two main types of models: excess Gibbs energy models (G^E), and equation of state (EOS). Gupta and Heidemann [1], Pinho et al. [2], Chen et al. [3], Nass [4], Xu et al. [5] and Pazuki et al. [6] applied G^E models, including modified UNIFAC, original UNIFAC, electrolyte NRTL, Wilson and modified Wilson.

Recently, EOS models such as SAFT, have drawn more attention to the calculation of thermodynamic properties of amino acid aqueous solutions. Held et al. [7], Fuchs et al. [8], Cameretti and Sadowski [9] studied thermodynamic properties of amino acids in aqueous solutions by PC-SAFT. Also, some authors used PC-SAFT or other models based on the perturbation theory to calculate activity coefficient and solubility of amino acids in aqueous solution [10], [11]. The results of these equations, especially ones involving an association part, represent the superiority of them to describe the phase behavior of amino acid aqueous solutions. With regard to these achievements, cubic plus association equation of state would seem to be a better alternative for thermodynamic modeling of the amino acid solution, because of its association part and simplicity. It should be mentioned that although amino acids possess large dipole moments, but many studies have proven that the contribution of dipole-dipole interaction in the EOS does not lead to a better result [7].

In this work, the phase equilibrium of glycine, l-alanine, dl-alanine, l-valine, dl-valine, l-leucine, and l-proline were investigated with the CPA EOS for the first time. The 5 adjustable parameters of the CPA were regressed with the activity coefficient of amino acids in aqueous solution data at 298.15 K. In this study, a 3rd degree linear equation was proposed which would make possible the calculation of monomer fractions in our binary systems without using the numerical methods. Then, this equation was validated by comparing modeling results and experimental data. Also, the

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solubility of these amino acids was calculated at different temperatures and the values of Δh and Δs parameters were obtained, as well. To improve the accuracy of the results, a temperature dependent binary interaction parameter k_{ij}, had to be introduced. To simplify the model, dipole-dipole interactions between species were also neglected in this work. The results showed significant ability of the CPA equation of state for calculation of thermodynamic properties of the amino acid aqueous solutions.

2. The model

The cubic plus association equation of state is a fusion of two parts: the physical part is represented by Soave-Redlich-Kwong (SRK) and the association part is taken from SAFT [12]. The expression for mixture in term of P is:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \rho\frac{\partial \ln g}{\partial \rho}\right) \times \sum_i x_i \sum_{A_i}(1 - X_{A_i}) \quad (1)$$

Where $a(T)$ is the energy parameter, b is the co-volume parameter, ρ is the molar density and x_i is the mole fraction of component i in the mixture. X_{Ai} is the mole fraction of molecule i not bonded at site A (i.e. the monomer fraction). More detailed explanations of CPA have been provided in the literature [12]. In this work, the following temperature dependent expression is considered for binary interaction parameter (k_{ij}):

$$k_{ij}(T) = k_{ij,298.15K} + k_{ij,T}(T - 298.15K) \quad (2)$$

This procedure is applied in some of previous studies [7,13] and is appropriate to correlate the solubility data in different temperatures.

3. Calculation of thermodynamic properties

To determine the vapor pressure of amino acid solutions, the equilibrium condition between vapor and liquid phase has to be considered:

$$f_i^l = f_i^v \quad (3)$$

Where f_i^l and f_i^v are the fugacity of component i in the liquid and vapor phase, respectively. Since the amino acids are highly non-volatile, this equilibrium condition is only used for the water. The activity coefficient of solute i can be estimated from fugacity coefficient as follow:

$$\gamma_i = \frac{\phi_i(T, P, x_i)}{\phi_i^{\infty}(T, P, x_i \to 0)} \quad (4)$$

Where ϕ_i is the fugacity coefficient of amino acid and ϕ_i^{∞} is the fugacity coefficient of the same component at infinite dilution in water. These values are directly calculated with the CPA.

The activity coefficient of water is defined as:

$$\gamma_w = \frac{\phi_w(T, P, x_w)}{\phi_w(T, P, x_w \to 1)} \quad (5)$$

To calculate the solubility of amino acids in the water, the equilibrium condition between the solid and liquid phase should be considered:

$$f_i^s = \gamma_i x_i f_i^0 \quad (6)$$

In which the solid phase be designated by superscript s. Also, x_i is the solubility (mole fraction) of the solute in the solvent, γ_i is the activity coefficient of amino acid in liquid phase and f_i^0 is the standard state fugacity.

From the definition of fugacity, the ratio f_i^s/f_i^0 can be related to the Gibbs energy of the dissolution process through the following relation:

$$\Delta g = \Delta h - T\Delta s = -RT \ln\frac{f_i^s}{f_i^0} \quad (7)$$

Where Δs and Δh are defined as the changes in molar entropy and enthalpy of amino acid from the standard state to the solid state. Combining Eq. (6) and Eq. (7) lead to:

$$x_i\gamma_i = \exp\left(\frac{\Delta s}{R} - \frac{\Delta h}{RT}\right) \quad (8)$$

Using Eq. (8) the temperature dependence of solubility can be obtained.

4. Parameter estimation

CPA has five pure component parameters for the associating compounds; including three accounts for the physical contribution (a_0, b, c_1) and two accounts for associating contribution ($\varepsilon^{A_iB_j}$ and $\beta^{A_iB_j}$). These parameters typically adjust to experimental pure vapor pressure and liquid density data. However, these pure component data cannot be used for evaluating the parameters of CPA, because of the solid state of amino acids used in this work. In this study, these parameters were fitted to experimental data of activity coefficient of amino acids in aqueous solutions at 298.15 K, using the following objective function:

$$OF = \sum_{i=1}^{N_p}\left(\gamma_i^{cal} - \gamma_i^{\exp}\right)^2 \quad (9)$$

Kassab et al. [14], and park et al. [15] assumed that the amino acid molecules behave as neutral zwitterionic molecules with one proton donor and two acceptors. In this study, we followed the approach of held et al. [7] and considered amino acids to have one proton donor site (carboxylic group) and one proton acceptor site (amino group) per molecule that implies the 2B scheme. In this work, the 4C scheme was chosen for the water and the pure component parameters of CPA for water were taken from Kontogeorgis et al. [16] (Table 1).

Fig. 1 illustrated the molecules of amino acid and water and also the association sites of these molecules. In order to reduce the number of adjustable parameters both association site types were considered to have the same amount of association parameters (the energy and volume association parameters). In order to calculate the monomer fractions of amino acid (component 2) and water (component 1), there are four non-linear equations with four variables that must be simultaneously solved typically using numerical methods such as Newton-Raphson or Jacobian:

$$X_{A_2} = \frac{1}{1 + \rho\left(x_2 X_{B_2}\Delta^{a.a} + 2x_1 X_{C_1}\Delta^{CR}\right)} \quad (10)$$

Table 1
CPA pure component of water [16].

Component	a_0	$b(\times 10^5)$	c_1	ε	β
Water	0.12277	1.4515	0.67359	16,655	0.0692