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Application of the SAFT-VR equation of state in estimation of physiochemical properties of amino acid solutions

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ABSTRACT

In the present study, the SAFT-VR equation of state has been utilized to examine the phase behavior of aqueous and aqueous-electrolyte solutions of amino acids and simple peptides. The main distinguishing feature of this model, is taking into account the range of interactions as a variable, in addition to other intrinsic qualities of these biomolecules such as diameter, number of segments per chain, energy of interaction and energy and volume of association. At the first stage of the simulation process, the optimized molecular parameters of water, amino acids and simple peptides are respectively obtained by correlating the experimental data of vapor pressure and activity coefficients. Subsequently, the solubility of amino acids in a wide range of temperature is correlated by means of enthalpy and entropy of dissolvation as the adjustable parameters. Afterwards, influence of pH variation on the solubility of amino acids and the phase behavior of one amino acid in the presence of another are predicted. Regarding the importance of equilibrium vapor pressure of aqueous solutions of amino acids in designing the separation units, activity and vapor pressure of water are also predicted. In the next step, the optimized molecular parameters of electrolytes are calculated by correlating the experimental mean ionic activity coefficient data and consequently the activity coefficients and solubility of amino acids in aqueous-electrolyte solutions are predicted.

1. Introduction

Having undergone major developments, Statistical Association Fluids Theory (SAFT-EoS) [1] has become a successful integrated method which associates the Wertheim's thermodynamic perturbation theory (TPT) [2–7] with new ideas of molecular simulation to study the phase behavior of diverse pure or complex systems. These ideas mostly deal with developing more accurate potential functions [8–12] which best define the dominant interactions in a system and consider steric configuration features such as ring formation [13–16], double bonding [17], isotropic–nematic transition for rod-like molecules [18,19] and bond co-operativity [20].

In the thermodynamic framework of SAFT equation of state, the contributions due to the dispersive energy among hard spheres in the reference fluid, covalent forces which cause chain formation and association energies due to hydrogen bonding between pairs of attractive sites on molecules are the terms that the total free Helmholtz energy is consisted of. The interactions among hard spheres are represented by a perturbation expansion, while the attractive forces are described by means of a radial distribution function. In this approach, the precision of characterization of different systems is highly dependent on the designated potential function. Application of variable-range potentials such as Sutherland, Yukawa and square-well, has led to development of a different version of equations of this type, namely SAFT-VR [21], in which the parameter λ adjusts the range of the attractive potential. This feature brings about accuracy in simulating the behavior of the systems in which long-range interactions are present.

In our previous work [22], the phase behavior and physiochemical properties of aqueous and aqueous-electrolyte solutions of amino acids were studied by adopting the SAFT equation of state in its original form. Although many works have been conducted to investigate aqueous solutions of amino acids, such as studies on the activity coefficients, pH variation and solubility in aqueous solutions [23–25], further investigations, including the study of aqueous-electrolyte solutions, are yet to be done. To fulfill this goal, we have chosen to take advantage of the SAFT-VR equation of state coupled with the Yukawa potential, which has the ability of demonstrating the Coulombic interactions found in electrolyte solutions.

According to the mean spherical approximation (MSA) theory [26–29], the ions resulting from dissociation of salt molecules in water, could be of equal or different sizes. To model long-range interactions due to the presence of ions in aqueous-electrolyte solutions, a simple restricted-primitive MSA approach [29] was applied in our previous works [22,30]. Since this method involves simplifying assumptions, here we make use of a more sophisticated version of MSA, named as non-restricted-primitive MSA [27–29] which considers ions as species of different sizes. Application of the MSA model is due to

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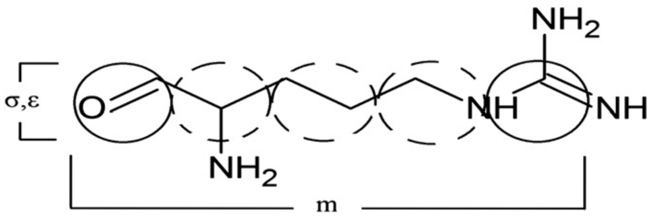

Fig. 1. Approximated chain structure of Arginine.

its compatibility with the SAFT equation of state. In contrary to other models which consider ions as species with no particular size, such as the Debye–Huckel model [29], the ionic particles have a specific diameter in the MSA model.

The following sections of this paper are allocated to description of the thermodynamic framework of SAFT-VR, physiochemical property estimations and the concluding remarks.

2. Thermodynamic framework

In the SAFT-VR approach [21], the residual Helmholtz energy of an electrolyte-containing mixture, is composed of the contributions due to the dominant interactions existing in the system:

$$\tilde{A}^{res}(T,\rho,x_i)=\tilde{A}^{mono}+\tilde{A}^{chain}+\tilde{A}^{assoc.}+\tilde{A}^{ion}. \tag{1}$$

$\tilde{A}^{mono}$ represents the free Helmholtz energy of monomer segments, $\tilde{A}^{chain}$ represents the energy of chain formation, $\tilde{A}^{assoc.}$ corresponds to the association energy of aggregate chains and $\tilde{A}^{ion}$ signifies the free energy released by long-range electrostatic interactions due to the presence of electrolytes.

2.1. Monomer contribution

On the basis of high-temperature expansion (HTE) approach [31], the intermolecular potential corresponding to dispersion interactions between segments i and j is given by:

$$U(r)=U^{HS}(r,\sigma)-\varepsilon\varphi^{Yukawa}(r,\lambda). \tag{2}$$

U^{HS} signifies the repulsive part:

$$U^{HS}(r,\sigma)=\begin{cases}0 & if \quad r>\sigma\\ \infty & if \quad r<\sigma\end{cases} \tag{3}$$

and φ^{Yukawa} represents the attractive part of the Yukawa potential:

$$\varphi^{Yukawa}=\frac{e^{-\lambda(r/\sigma-1)}}{r/\sigma}. \tag{4}$$

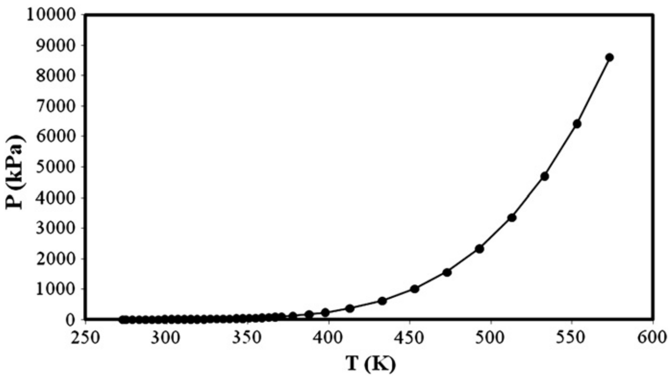

Fig. 2. Experimental saturated vapor pressure data of water (●) in comparison with the SAFT-VR calculations (solid curve).

Hence each monomer features σ as diameter, ε as the well depth of the potential and λ as the effective range of attractive forces. According to the Barker and Henderson perturbation theory [32–34], the second-order perturbation equation of free Helmholtz energy for a mixture of monomer segments is evaluated by [34]:

$$\tilde{A}^{mono}=A^{HS}+\beta A_1+\beta^2A_2. \tag{5}$$

β is the inverse of temperature $\frac{1}{kT}$ and A^{HS} corresponds to the Helmholtz energy of hard spheres, calculated by the Boublik expression [35]. The mean attractive energy A_1 is given by:

$$A_1=\sum_{i=1}^{n}\sum_{j=1}^{n}m_ix_im_jx_jA_1^{ij} \tag{6}$$

where

$$A_1^{ij}=-\beta\rho A_{ij}^{vdW}g_{ij}^{SH}\left(\sigma_{ij};\xi^{eff}(\lambda)\right). \tag{7}$$

A_{ij}^{vdW} is the van der Waals attractive constant, expanded for segments i and j [21,36]:

$$A_{ij}^{vdW}=2\pi\sigma_{ij}^3\varepsilon_{ij}\left(\frac{1}{\lambda_{ij}}+\frac{1}{\lambda_{ij}^2}\right). \tag{8}$$

In Eq. (7), g_{ij}^{HS} is the radial distribution function for a mixture of i and j segments proposed by Carnahan and Starling [37]:

$$g_{ij}^{HS}\left(\sigma_{ij};\xi^{eff}(\lambda)\right)=\frac{1-\xi^{eff}/2}{\left(1-\xi^{eff}\right)^3}. \tag{9}$$

The effective packing fraction is expressed by:

$$\xi^{eff}=c_1\left(\lambda_{ij}\right)\xi_x+c_2\left(\lambda_{ij}\right)\xi_x^2 \tag{10}$$

Table 1
Molecular parameters of pure water.

	$\sigma(A^\circ)$	ε/k	m	$\varepsilon^{assoc.}/k$	$\kappa^{assoc.}$	λ	AAD%		
							Vapor density	Liquid density	Vapor pressure
This work	3.1	251.99	1	1207.1	0.0523	1.24	0.392	1.58	1.94
McCabe and Kiselev[a]	3.036	253.3	1	1366	1.028	1.8			

[a] [43].