



# Modeling surface tension and interface of (water+methanol), (water+ethanol), (water+1-propanol), and (water+MEG) mixtures



Shahin Khosharay <sup>a,\*</sup>, Sedigheh Tourang <sup>b</sup>, Farhad Tajfar <sup>c</sup>

<sup>a</sup> Iranian Institute of Research & Development in Chemical Industries (IRDICI-ACECR), Tehran, Iran

<sup>b</sup> School of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan, Iran

<sup>c</sup> Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

## ARTICLE INFO

### Article history:

Received 5 July 2017

Received in revised form

19 September 2017

Accepted 20 September 2017

Available online 22 September 2017

### Keywords:

Surface tension

Gradient theory

Chemical potential

Alcohol

Monoethylene glycol

## ABSTRACT

Two models were used to describe the surface tension and interfacial composition of (water + methanol), (water + ethanol), (water+1-propanol), and (water + monoethylene glycol) binary mixtures. The cubic plus association equation of state was applied to compute the composition and molar volume of the phases. The first model was the equality of the chemical potential of components at the interface and the bulk liquid. Four adjustable parameters of this model were determined according to the experimental surface tensions. Then the first model was used to compute the interfacial composition of methanol, ethanol, 1-propanol, and monoethylene glycol. The computed interfacial compositions of ethanol were compared with the available experimental data in the literature. It was found that the first model successfully calculated the interfacial composition of ethanol. The second model was the gradient theory of inhomogeneous interfaces. This model had two adjustable coefficients. These coefficients were regressed based on the experimental surface tensions. The interfacial composition profiles of alcohols and monoethylene glycol were determined. The percentages of the average absolute deviation were 2.59 and 1.75 for the first and the second models, respectively. The results of both models showed that 1-propanol and monoethylene glycol had the highest and lowest absorptions at the interface. However, the second model was more suitable than the first one.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

The surface tension of many binary liquid mixtures is not a linear function of the composition. This non-linearity is usually due to the enrichment of interface with the component, which has a lower surface tension value. Therefore, the knowledge of the interface, including surface tension, profiles of the surface layer, and surface layer thickness is vital. Additionally, the interfacial properties help a researcher to understand the mass and heat transfer across the interface [1,2]. Several approaches have been conducted to compute the surface tension and the composition of the surface layer. Semi-empirical/empirical models [3–6], models based on the classical thermodynamics [7–10], and molecular simulation models [11–14] are the examples of these methods.

The gradient theory of inhomogeneous fluid [15–25] is a popular method of determining the interfacial properties. This theory

can relate the properties of bulk phases to the surface layer by using an appropriate equation of state (EOS) [26,27]. The gradient theory requires two inputs. The first input is the Helmholtz free energy density of the homogeneous fluid. It can be calculated by applying a suitable thermodynamic model. The second input is the influence parameter which can be determined by applying a semi-empirical expression. This theory is applicable for a wide range of fluids and their mixtures, including hydrocarbons [28–31], polar fluids [32,33], polymers and polymer melts [34–37], near-critical interfaces [38–41] and other liquid–liquid interfaces [42,43].

The equality of chemical potentials of components in the liquid and interface is another approach for describing the interface. The previous investigations usually used activity models such as UNI-FAC to describe the surface tension and composition. On the other hand, it is known that the models combining volumetric properties with surface tension can be more successful than the ones using only surface tension information because the properties of the interface are affected by volumetric properties [2]. Khosharay et al. [44,45] conducted the other modeling study. This method used an equation of state to relate the properties of bulk phases to the

\* Corresponding author.

E-mail address: [khosharay@irdci.ac.ir](mailto:khosharay@irdci.ac.ir) (S. Khosharay).

interface. They applied fugacity and equation of state to model the surface layer of binary and ternary liquid mixtures. This model was mainly used for the refrigerant family and the mixtures in which the surface tensions of pure components were relatively close to each other. The partial molar surface areas were supposed to be equal to the molar surface areas of the pure components. This is incompatible with highly non-ideal mixtures such as (water + alcohol). The problems of this assumption were also addressed by Khosharay [46]. The molar surface area is expressed as a function of molar volume [10], so partial molar surface area is a function of partial molar volume. The partial molar volume is different from the molar volume of pure fluid. This is an important concept. Nath [10] applied the Wilson, NRTL, and UNIFAC activity models to describe the non-ideal interfaces such as (Acetone + water) and (1,4-Dioxane + water). He considered different values for the partial molar surface areas and molar surface area of the pure components. He applied some additional equations like Langmuir isotherm because the partial molar volumes cannot be computed by using activity models. Additionally, this model was limited only to one temperature.

Several modeling studies [1,14,47–49] were dedicated to model the interface of (water + alcohol) binary mixtures. Only a few studies [1,49] used equations of state; therefore, it is crucial to apply a reliable model based on the equation of state. The (water + methanol), (water + ethanol), (water+1propanol), and (water + monoethylene glycol (MEG)) have been selected for this study. The cubic-plus-association equation of state (CPA EOS) has been used for phase equilibrium calculations. The interfacial properties of these binary mixtures, including surface tension and composition have been studied. Firstly, a model using the equality of the chemical potentials of components at the interface and bulk liquid has been used to determine surface tension and composition. To show the reliability of the model, the gradient theory of fluid interfaces is combined with the proposed expression of influence parameter [44,50–55]. Then the composition profiles have been determined. The performance and results of these two models have also been compared and discussed.

## 2. General features of the model

### 2.1. CPA equation of state

The applied models require the Helmholtz free energy and mole density, so the accurate description of phase behavior is important. Water and alcohols are hydrogen-bonding molecules. Moreover, the hydrogen-bonding interactions exist between the molecules of alcohol and water. Therefore, the self-association of water and alcohols in addition to the cross association have to be considered. Since the CPA equation of state [56–64] allows a researcher to consider the association contribution, the CPA EOS has been selected for this study.

The compressibility factor of the CPA EOS is expressed as a sum of two parts: The Soave-Redlich-Kwong (SRK) EOS that belongs to the physical interactions between molecules, and the Wertheim association theory [56–64] that relates to the self-association and cross association.

$$Z = Z^{phys.} + Z^{assoc.}$$

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

In Eq. (1),  $Z$  is the compressibility factor,  $T$  is the temperature,  $R$  is the ideal gas constant,  $a$  is the energy parameter,  $b$  is the co-volume,  $\rho$  is the density,  $g$  is the simplified version of the radial

distribution function [56–64],  $X_{A_i}$  is the pure component  $i$  mole fraction (not bonded at site  $A$ ), and  $x_i$  is the mole fraction of component  $i$ . Superscripts *phys* and *assoc* shows physical and association contributions, respectively.

The energy parameter  $a$  in the SRK part is computed by using Soave-type temperature dependence:

$$a = a_0 \left[ 1 + c_1 \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (2)$$

In Eq. (2),  $T_c$  is the critical temperature,  $a_0$  and  $c_1$  are adjustable parameters of the CPA EOS. The pure-compound parameters ( $a_0$ ,  $c_1$  and  $b$ ) are typically obtained by curve fitting of the experimental vapor pressure and saturated liquid density data.

$X_{A_i}$  can be calculated by Eq. (3):

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_i X_{B_j} \Delta^{A_i B_j}} \quad (3)$$

In Eq. (3),  $\Delta^{A_i B_j}$  is the association strength.

For self-associating molecules,  $\Delta^{A_i B_j}$  is given by Eq. (4):

$$\Delta^{A_i B_j} = g(\rho) \left[ \exp\left(\frac{\epsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ii} \beta^{A_i B_j} \quad (4)$$

In Eq. (4),  $\epsilon^{A_i B_j}$  and  $\beta^{A_i B_j}$  show the association energy and volume, respectively. The present study uses Elliot combining rule (ECR) to the association sites of two different associating molecules.

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}} \quad (5)$$

The following equation is used for the hard-sphere radial distribution

$$g(\rho) = \frac{1}{1 - 1.9\eta}, \quad \eta = \frac{1}{4} b\rho \quad (6)$$

CPA has five pure-compound parameters. Three parameters are for non-associating compounds ( $a_0$ ,  $b$ , and  $c_1$ ) and two parameters belong to the associating compounds ( $\epsilon^{A_i B_j}$  and  $\beta^{A_i B_j}$ ). The five pure-compound parameters are usually regressed simultaneously based on pure component vapor pressure and liquid density data.

A four-site association scheme (4C) has been selected for water and MEG:

$$X_A = X_B = X_C = X_D = \frac{-1 + \sqrt{1 + 8\rho \Delta^{AC}}}{4\rho \Delta^{AC}} \quad (7)$$

$$\begin{aligned} \Delta^{AA} = \Delta^{AB} = \Delta^{BB} = \Delta^{CC} = \Delta^{CD} = \Delta^{DD} = 0 \\ \Delta^{AC} = \Delta^{AD} = \Delta^{BC} = \Delta^{BD} \neq 0 \end{aligned} \quad (8)$$

Also, 2B scheme is considered for alcohols:

$$X_A = X_B = \frac{-1 + \sqrt{1 + 4\rho \Delta^{AC}}}{2\rho \Delta^{AC}} \quad (9)$$

$$\begin{aligned} \Delta^{AA} = \Delta^{BB} = 0 \\ \Delta^{AB} \neq 0 \end{aligned} \quad (10)$$

Fig. 1 shows types of hydrogen bonding (association schemes) for the applied fluids of this study.

The classical van der Waals mixing rule is used to calculate the vapor-liquid equilibrium according to the following expressions:

Download English Version:

<https://daneshyari.com/en/article/4767862>

Download Persian Version:

<https://daneshyari.com/article/4767862>

[Daneshyari.com](https://daneshyari.com)