A model to calculate concentration-dependent surface tension of binary systems

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ABSTRACT

Surface tension for aqueous solutions of 1,2,3-Propanetriol, 2-Propanol, Ethylacetate, Dimethylacetamide, Dimethylformamide and 1-Butanol was measured as functions of composition using the method of Wilhelmy plate at 295.15, 300.15, 305.15, 310.15, and 315.15 K with emphasis on the dilute composition region. In this work, a modified model based on the thermodynamic definition of surface tension using Gibbs free energy was proposed. The well-known Wilson equation was applied to represent the excess Gibbs free energy of the system. Also, a four-parameter surface tension equation for a binary system was used. The accuracy of the model was evaluated using experimental data of 130 binary systems including polar, non-polar, aqueous and non-aqueous solutions reported in the literature and conducted in this work. The prediction performance of the model was compared with the studied models by calculating the mean relative standard deviation between the calculated and experimental values. According to the results, the new model reveals the best prediction among the other models.

1. Introduction

The surface tension is one of the main properties of liquids that reveals useful information about their surface, intermolecular interactions, and energy/mass transfer across the interface [1]. In the industrial processes such as phase transitions, boiling, condensation, absorption and distillation, microscale channel flow and detergents, the surface tension plays a fundamental role. Due to the widespread applications of liquid mixtures in various industrials, prediction of their surface tension is of special importance. The main factors which can affect on surface tension of the solution, are temperature and concentration. At a given temperature, surface tension is often not a linear functions of composition. Many studies suggest that this non-linearity is associated with the surface enrichment of one species in the surface layer. In this regard, the molecules with lower surface tension are generally enriched (or preferentially adsorbed) in the surface area. This process could lead to a substantial difference in compositions between the bulk liquid and the surface regions. There are several factors affecting this complex surface enrichment phenomenon, such as interaction

between molecules, size and orientation and volatility of the molecules in the surface phase [2,3]. Several approaches such as using equation of state together with the gradient theory [4], perturbation theory [5], taking into account the parachor [6], as well as the activity coefficient models [7,8], and other models [9—11] have been used to predict the surface tension of solutions.

Wang-Fu [9] model is based on the local composition theory proposed by Wilson [12]. Their model has been successfully examined for prediction of surface tension of various non-ideal binary and ternary liquid mixtures [13]. The other surface tension model is the Connors and Wright equation [10] which describes the composition dependency of surface tension for aqueous solutions of organic solutes [14,15]. They analyzed literature data on 15 systems and found a well description of their model. Wang—Chen model [11] is another equation to correlate the surface tension data with the composition. This model has been successfully used for correlating surface tension data of binary systems [13].

Based on the thermodynamic definition of surface tension, Chunxi et al. [7] proposed another efficient model. The accuracy of their model has been extensively tested with 124 binary, 13 ternary and three quaternary systems. This model was also able to predict temperature dependence of surface tension. In models Wang-Fu, Connors and Wright, Wang-Chen and Chunxi et al. there are two adjustable parameters.

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In this work a modified model for surface tension based on Wilson activity coefficient model is proposed. By neglecting the simplified assumptions which were assumed previously by Chunxi et al. [7], we derive a new four-parameter equation of surface tension. Then, the proposed model will be examined for aqueous and non-aqueous solutions reported in the literature and also those measured in this work. The predicted results of this model will be compared with those obtained from the previous studied models and discussed.

2. Methodology

For a multi-component liquid mixture (at temperature T and pressure P), the molar Gibbs free energy of the system can be expressed as:

$$g(T,P) = \sum_i x_i \left[g_i^0(T,P) + RT \ln x_i \right] + g^{ex} \tag{1}$$

where x_i and $g_i^0(T,P)$ are the mole fraction and molar Gibbs free energy of component i, respectively, at the system temperature and pressure. Assuming that the excess molar Gibbs energy of the liquid phase, g^{ex}, can be represented by the Wilson equation [12] Eq. (1) could written as follows:

$$g(T,P) = \sum_i x_i \left[g_i^0(T,P) + RT \ln x_i \right] - RT \sum_i x_i \ln \left(\sum_j x_j \Lambda_{ij} \right) \tag{2}$$

where

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp\left(-\frac{U_{ij} - U_{ii}}{RT} \right) \tag{3}$$

and v_i is the molar volume of component i (the value of this parameter is fixed at a constant temperature and pressure) and $U_{ij} - U_{ii}$ is the difference in interaction energy between pairs of molecules i–j and i–i. According to surface thermodynamics, surface tension is defined as the Gibbs free energy required for an increase of unit surface area at constant temperature, pressure and composition (Eq. (4)):

$$\sigma = (\partial G^s / \partial A)_{T,P,\{n_i\}} = (\partial g^s / \partial A)_{T,P,\{x_i\}} \tag{4}$$

where G^s and g^s are related via $G^s = n_t^s g^s$ and are the total and the molar Gibbs free energy, respectively, in the surface phase. These parameters are functions of temperature, pressure, composition and surface area. In fact, the surface phase is formed of several molecular layers and there is a little knowledge about its phase composition and properties. Hence it is assumed that the concentration and Gibbs free energy in the surface phase are proportional to those in the bulk liquid phase, and Eq. (2) can be an appropriate representation of the Gibbs free energy in the surface phase. The involved approximations might be well adapted by adjustable model parameters for a binary system. By substituting g^s in Eq. (4) with $g(T,P)$ from Eq. (2) and making a simple derivative manipulation on g^s with respect to surface area, A, the following expression for the surface tension of a liquid mixture can be derived:

$$\sigma_m = \sum_i x_i \sigma_i - RT \sum_i \frac{x_i}{\sum_j x_j \Lambda_{ij}} \sum_j x_j \left(\frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} \tag{5}$$

where

$$\left(\frac{\partial \Lambda_{ij}}{\partial A} \right)_{T,P,x} = -\frac{\Lambda_{ij}}{RT} \left(\frac{\partial (U_{ij} - U_{ii})}{\partial A} \right)_{T,P,x} \tag{6}$$

There are four adjustable parameters, in order to correlate surface tension of binary systems i.e $U_{12} - U_{11}$, $U_{21} - U_{22}$, $(\partial(U_{21} - U_{22})/\partial A)_{T,P,x}$ and $(\partial(U_{12} - U_{11})/\partial A)_{T,P,x}$. In order to reduce the number of the adjustable parameters, Chunxi et al. [7] assumed that the cross interaction energy is equal to the arithmetic average of the pure components:

$$U_{ij} = \left(\frac{U_{ij} + U_{jj}}{2} \right) \tag{7}$$

It then follows:

$$(U_{ij} - U_{ii}) = -(U_{ji} - U_{jj}) \tag{8}$$

$$\left(\frac{\partial (U_{ij} - U_{ii})}{\partial A} \right)_{T,P,x} = -\left(\frac{\partial (U_{ji} - U_{jj})}{\partial A} \right)_{T,P,x} \tag{9}$$

According to above assumption, only two adjustable parameters are remained for a binary system, i.e. $U_{12} - U_{11}$ and $(\partial(U_{12} - U_{11})/\partial A)_{T,P,x}$, and Eq. (5) is given by:

$$\sigma = (x_1\sigma_1 + x_2\sigma_2) - \frac{x_1 x_2 RT}{x_2 + x_1 \Lambda_{21}} \left(\frac{\partial \Lambda_{21}}{\partial A} \right) \left[1 - \frac{1}{\Lambda_{21}} \right] \tag{10}$$

The applicability of this equation has been extensively tested with 124 binary, 13 ternary and three quaternary systems. The present model is able to account for the temperature dependence of surface tension of liquid mixtures with good accuracy.

In this paper, in order to achieve more reliable results, we ignored the Chunxi et al. simplified assumptions and the four-parameter equation was used to predict the surface tension. As a result for a binary system, the resultant equation is given by

$$\sigma_m = x_1\sigma_1 + x_2\sigma_2 - RT \left[\frac{x_1 x_2}{x_1 + x_2 \Lambda_{12}} \left(\frac{\partial \Lambda_{12}}{\partial A} \right) \right.$$
$$\left. + \frac{x_1 x_2}{x_2 + x_1 \Lambda_{21}} \left(\frac{\partial \Lambda_{21}}{\partial A} \right) \right] \tag{11}$$

In Eq. (11), introducing a instead of Λ_{12}, c instead of Λ_{21}, b instead of $RT(\partial \Lambda_{12}/\partial A)$, and d instead of $RT(\partial \Lambda_{21}/\partial A)$, the following expression is obtained:

$$\sigma_m = x_1\sigma_1 + x_2\sigma_2 - \left[\frac{x_1 x_2}{x_1 + x_2 a} b + \frac{x_1 x_2}{x_2 + x_1 c} d \right] \tag{12}$$

Hence, there are four adjustable parameters in order to correlate of surface tension of binary systems, i.e. a, b, c and d.

The validity of this equation for correlating the surface tension of binary systems has been extensively tested with our experimental data and 100 other systems reported in the literature, including polar, nonpolar, aqueous, and nonaqueous liquid mixtures. The wide applicability of the present model to different systems will be clearly demonstrated.

3. Experimental method

The materials used in this work are following: 1,2,3-Propanetriol (99 wt%, Dr. Mojallali, Iran), 2-Propanol (99 wt%, Merck), Ethyl-acetate (99 wt%, Merck), Dimethylacetamide (99 wt%, Merck), Dimethylformamide (99 wt%, Merck) and 1-Butanol (99 wt%, Merck). Water was distilled and deionized before use. All aqueous solutions were prepared by weight using an analytical balance (HR-