Colloids and Surfaces A: Physicochem. Eng. Aspects 467 (2015) 78–88

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

How do temperature and chemical structure affect surface properties of aqueous solutions of carboxylic acids?

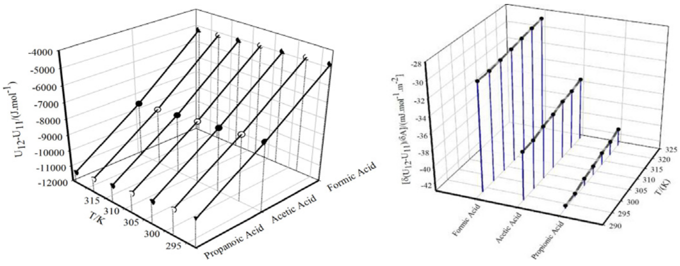
Ahmad Bagheri*, Kolsum Alizadeh

Department of Chemistry, Semnan University, P.O. Box, 35131-19111, Semnan, Iran

HIGHLIGHTS

- The surface properties of binary systems of aqueous–organic acid calculated.
- The activity coefficients of components have been calculated by UNIFAC methods.
- The interaction energy values were calculated by using LWW model.
- The U_{12}–U_{11} value shows same behavior for studied systems with rising temperature.
- The relative Gibbs adsorption increases with increasing the length of carboxylic acid chain.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 August 2014
Received in revised form
13 November 2014
Accepted 17 November 2014
Available online 26 November 2014

Keywords:
Surface tension
Correlation
UNIFAC
Adsorption
Interaction energy

ABSTRACT

Surface properties of binary mixtures of organic acids (formic, acetic, propanoic and butanoic acids) with water have been calculated by surface tension data at various temperatures (293.15–323.15) K. The surface tension data over the whole mole fraction range are correlated by the Li et al. (LWW) model, then the interaction energy between organic acids and water have been calculated with the results of this model. Also, adsorption isotherms of binary aqueous solutions of organic acids are determined using Gibbs adsorption equation with experimental data found in the literature and using the UNIFAC group contribution method. The values of adsorption for mixtures of organic acids/water increases with increasing the alkyl chain length of organic acid at different temperatures. Finally, the results have been discussed in terms of surface concentration and lyophobicity using the extended Langmuir (EL) isotherm. The results provide information on the molecular interactions between unlike molecules that exist at the surface and the bulk.

1. Introduction

The surface tension of a liquid mixture is not a simple function of the surface tension of the pure components, because in a mixture the composition of the interface is not the same as that of the bulk. The deviations of the surface tension of a liquid mixture from linearity reflect changes of structure and cohesive forces during the mixing process. At the interface, there is a migration of the species having the lowest surface tension or free energy per unit area, at the temperature of the system [1–3].

Surface tension data are scarce for liquid mixtures over a wide range of composition and temperature and hence the calculation methods for estimating surface tension and surface properties of multicomponent systems are very necessary. Several different approaches have been used to predict the surface tension of non-ideal liquid mixtures as a function of composition which include

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* Corresponding author. Tel.: +98 02333654057; fax: +98 02333654110.
E-mail addresses: abagheri@semnan.ac.ir, bagheri.alm@gmail.com (A. Bagheri).

http://dx.doi.org/10.1016/j.colsurfa.2014.11.037
0927-7757/

the use of an equation of state together with the specific theory [4–6].

Covering the water surface with the solutes having weaker molecular interactions reduces surface energy observed as surface tension. Generally, the hydrophobic hydration and the surface adsorption are known to occur in binary aqueous–organic systems such as: alcohol–water, organic acid–water and, etc. [7].

The purposes of the present work are to clarify the surface phenomena which occur in aqueous solutions of formic acid, acetic acid, propanoic acid and butanoic acid at various temperatures:

(i) The composition dependence of the surface tension of binary aqueous–organic acid mixtures is described using LWW and FLW models, and then in a new approach, the effect of temperature on the interaction energy values is explained in the binary mixtures [8–12].

(ii) A Langmuir type isotherm model (or the extended Langmuir (EL)) is employed to determine the surface mole fractions from the knowledge of the bulk mole fractions. The results provide information on the molecular interactions between the unlike molecules that exist at the surface and the bulk at various temperatures [13,14].

(iii) The surface adsorption is another parameter that produces some useful information about the surface behavior of mixtures. Adsorption of a component at the phase boundary of a system causes a different concentration in the interfacial layer and the adjoining bulk phases. The relative Gibbs adsorption, $\Gamma_{2,1}$, provides an exact relationship between bulk concentrations, total surface coverage and the surface tension changes produced at liquid interface. To evaluate $\Gamma_{2,1}$, a reliable data set of two parameters, the surface tension, σ, and the activity coefficient of solute (acid), γ_2, is necessary for calculation. In the present study, the UNIFAC group-contribution model was adopted to calculate the activity coefficients because it can be applied to any kind of substances whenever the molecular structure is known [15–18].

Surface tension data are scarce for aqueous–organic acid mixtures over a wide range of composition and temperature. In this work, two different sets of experimental data have been selected from the literature (see the supplementary information) [19,20].

2. Theory and methods

2.1. Temperature dependence of the interaction energy in organic acid–water solutions

A few empirical and thermodynamic-based equations are available to correlate the surface tension some of which have recently been proposed and are well founded on a thermodynamic basis.

To explain the surface tension, σ, the proposed model by Fu et al. (FLW), based on the modified Hildebrand–Scott equation, was used [10,21]:

$$\sigma = \sum_{i=1}^{n} \frac{x_i\sigma_i^*}{\sum_{j=1}^{n} x_j f_{ij}} - \sum_{i=1}^{n}\sum_{j=1}^{n} \frac{x_i x_j |\sigma_i^* - \sigma_j^*|}{\sum_{q=1}^{n} x_q f_{iq} \sum_{r=1}^{n} x_r f_{jr}} \tag{1}$$

where the f_{ij}'s are adjustable parameters for the binary systems. This equation was also used to predict the ternary surface tension. For a binary mixture, the above equation reduces to

$$\sigma = \frac{x_1\sigma_1^*}{x_1 + x_2 f_{12}} + \frac{x_2\sigma_2^*}{x_2 + x_1 f_{21}} - \frac{x_1 x_2 |\sigma_1^* - \sigma_2^*|}{(x_1 + x_2 f_{12})(x_2 + x_1 f_{21})} \tag{2}$$

where f_{12} and f_{21} are adjustable parameters for the binary systems and x_i is the mole fraction of the component i in the mixture [22].

The surface tension deviations, $\Delta\sigma$, were determined in order to get information about the type and the strength of the molecular interactions in the binary systems. The calculations of $\Delta\sigma$ were carried out from the well known general equation:

$$\Delta\sigma = \sigma - \sum_{i=1}^{n} x_i\sigma_i^* \tag{3}$$

where σ is the surface tension of the mixture, and σ_i^* is the surface tension of the pure component i at the same temperature and pressure of the mixture, x_i is the mole fraction of the component i and n is the number of components.

The surface tension deviations of the above mentioned binary systems were correlated by two models.

Li et al. (LWW) proposed a two-parameter equation to correlate the surface tension data with the composition in the binary systems which are based on the Wilson equation for the excess Gibbs energy [8,23]:

$$\Delta\sigma = -RT \sum_i \frac{x_i}{\sum_j x_j \Lambda_{ij}} \sum_j x_j \left(\frac{\partial \Lambda_{ij}}{\partial A}\right)_{T,P,X} \tag{4}$$

where

$$\Lambda_{ij} = \exp\left(-\frac{U_{ij} - U_{ii}}{RT}\right), \quad \left(\frac{\partial \Lambda_{ij}}{\partial A}\right)_{T,P,X} = -\frac{\Lambda_{ij}}{RT}\left[\frac{\partial (U_{ij} - U_{ii})}{\partial A}\right]_{T,P,X} \tag{5}$$

In the preceding relations, $U_{ij} - U_{ii}$ is the difference in the interaction energy between molecular pair ij, and the derivative $[\partial(U_{ij} - U_{ii})/\partial A]_{T,P,X}$ reflects the energy change with the increase in surface area. Li et al. [8,22] made the assumption $U_{ij} = (U_{ii} + U_{jj})/2$, decreasing the number of adjustable parameters from four to two for a binary system, i.e., $U_{12} - U_{11}$ and $[\partial(U_{12} - U_{11})/\partial A]_{T,P,x}$; hence, the resultant equation is given by:

$$\Delta\sigma = \frac{x_1 x_2 RT}{x_2 + x\Lambda_{21}} \left(\frac{\partial \Lambda_{21}}{\partial A}\right) \left[1 - \frac{1}{\Lambda_{21}}\right] \tag{6}$$

where $(\partial\Lambda_{21}/\partial A)$ and Λ_{21} are adjustable parameters.

Myers–Scott (MS) proposed an equation to correlate the surface tension deviation data with the composition in the binary systems [9,11,12]:

$$\Delta\sigma = x_i x_j \left[\frac{\sum_{p=0}^{m} B_p (x_i - x_j)^p}{1 + \sum_{l=1}^{m} C_l (x_i - x_j)^l}\right] \tag{7}$$

where B_p and C_l are adjustable parameters.

In this paper, the Levenberg–Marquardt method (as a nonlinear regression algorithm for fitting data) is used to estimate the adjustable parameters.

2.2. Application of the UNIFAC model for calculation of the relative Gibbs adsorption of binary systems

The adsorption process involves the transport of molecules from the bulk solution to the interface, where they form specially oriented molecular layers according to the nature of the two phases. The Gibbs adsorption isotherm for multicomponent systems is an equation used to relate the changes in concentration of a component in contact with a surface with changes in the surface tension. For a binary system containing two components, from the Gibbs