

Prediction of the surface tension, surface concentration, and the relative Gibbs adsorption isotherm of binary liquid systems

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Abstract

Calculation results for surface tension, surface concentration, and the relative Gibbs adsorption isotherm of binary systems, as a function of concentration and temperature, were obtained using a formal thermodynamic model, which includes the activity coefficients for both, the bulk and the surface layer. To take into account the non-ideality of the liquid bulk as well as that of the surface layer, the UNIFAC group contribution activity coefficient model, with binary interaction parameters derived from vapor–liquid equilibrium data and reported previously in the open literature, is also used. The calculation method used to derive the mixture surface tension and surface concentration, makes an analogy between pressure and vapor concentration from a traditional isothermal liquid–vapor bubble point calculation and the surface tension and surface concentration, as used here. Values for the surface tension of 31 binary systems, at different temperatures, covering the full concentration range, which makes a total of 105 different binary systems, were estimated. Simultaneously, values for the surface concentration for the same binary systems were also calculated, which in turn were used to derive values of the relative Gibbs adsorption isotherm, employing a new scheme proposed in this work. The binary systems included in this study, have representatives from different chemical species which include polar, non-polar, and associating compounds. The average relative percent error obtained from the comparison of experimental and calculated surface tension values for the 790 points considered was 2.88%, which leads to establish that the model, together with the calculation scheme here proposed are accurate to reproduce the concentration and temperature dependence of the surface tension.

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1. Introduction

Surface tension is one of the most interesting thermophysical properties due to its influence on many of the naturally occurring phenomena as well as in many industrial applications.

Surface phenomena have high industrial importance, e.g. many reactions occur over the surface of a catalyst, and this fact makes heterogeneous catalysis to be important in many industrial applications. Moreover, processes like lubrication, corrosion, adhesion, detergency and reactions in electrochemical cells are also related to surface effects. In fact, liquid–vapor interfaces are critical for the performance of detergents and soaps, also, in chemical engineering separations such as absorp-

tion and distillation, in enhanced oil recovery, and in the performance of biological membranes, to mention just a few examples.

As part of the systematic work on the surface tension of liquids, which has included the experimental determination and correlation, devoted by our research group to pure and mixed compounds of interest to the oil industry [1–3], this work presents a thermodynamic model and a calculation method to estimate and predict mixture surface tension values, as a function of both concentration and temperature.

Several different approaches have been used to predict the surface tension of mixtures which include the use of an equation of state together with the gradient theory [4], the parachor [5], and also activity coefficient models such as Wilson, NRTL, and UNIFAC [6–8].

The model used here to estimate and predict surface tension values for binary systems as a function of concentration and temperature relates the surface concentration of each component

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to the individual activity coefficients (in the liquid bulk phase and surface layer) and to the molar surface area for each of the components [9]. The activity coefficients were evaluated using the UNIFAC group contribution model [10].

The calculation method developed here to estimate and predict mixture surface tension and surface layer concentration is similar to that extensively used for isothermal bubble point calculations [11]. In this respect, an analogy between the bubble point pressure and vapor concentration with surface tension and surface concentration, respectively, has been used. In fact, the problem of representing the thermodynamic equilibrium between the liquid bulk phase and the surface phase is taken as that between liquid bulk and vapor as if the former were the only phases present.

The thermodynamic model and the calculation method have been tested estimating the surface tension for 31 binary systems in the whole concentration range, at different temperatures. Thus, we carried out a comparison between calculated and experimental surface tension data for 105 binaries which gave a total of 790 experimental points. An average relative error of 2.88% was obtained for this comparison.

The binary systems considered are representative of different types of mixtures, including polar + polar, non-polar + non-polar, non-polar + polar, and aqueous systems, at different temperatures, through the whole concentration range. Unfortunately, there are not surface concentration data reported in the literature to compare with the estimated values from the model here used. However, in order to make this quantity useful, a calculation method is also proposed to derive the corresponding relative Gibbs adsorption isotherm, which only uses the concentrations from both, the liquid bulk phase and the surface layer, in contrast to the commonly used approach employing the trend of surface tension as a function of concentration, at a given temperature [12,13].

2. Theory

Most of the fundamental thermodynamic relations used to describe the mixing Gibbs energy function for both the liquid and the surface layer which in turn are used here to derive the equations to calculate the surface concentration are all well documented [9]. Hence, the expressions for the calculation of the surface tension of mixtures, σ , and surface concentration, x_i^σ , are the following. For component 1:

$$x_1^\sigma = \frac{x_1 \gamma_1}{\gamma_1^\sigma} \exp \left[\frac{\Omega_1(\sigma - \sigma_1)}{RT} \right] \quad (1)$$

and for component 2:

$$x_2^\sigma = \frac{x_2 \gamma_2}{\gamma_2^\sigma} \exp \left[\frac{\Omega_2(\sigma - \sigma_2)}{RT} \right] \quad (2)$$

In Eqs. (1) and (2), x_i is the mole fraction of component i , γ the activity coefficient of component i , σ the surface tension of the mixture of concentration x_i , Ω_i is the molar surface area of component i . Quantities with σ as superscript correspond to the surface layer, whereas those without superscript correspond to

the liquid bulk phase and subscripts 1 and 2 correspond to each of the two components of the binary mixture.

The molar surface area for each component is evaluated, using a quantity readily available from literature for most of the substances as is the case of the molar volume at 298.15 K, according to the following relation [6]:

$$\Omega_i = (V_{mi})^{2/3} (N_A)^{1/3} \quad (3)$$

where N_A is Avogadro's constant.

It has to be mentioned that Eqs. (1) and (2) have been used for some other workers to calculate the surface concentration although in a different way with respect to what we propose here.

In fact, in all the previous works the authors solve directly the non-linear set of equations that can be constructed with those given above [7,8]. In this work, an isothermal bubble pressure-like method was used, this is explained later in detail.

It may be observed that Eqs. (1) and (2) do not include adjustable parameters. They only need the application of any available and appropriate model for representing both the surface and liquid bulk activity coefficients.

In this work, the UNIFAC group contribution activity coefficient model has been used due to the availability of a reliable database on interaction parameters for the molecular groups [10,14] of a large number of molecules.

All the parameters in the UNIFAC model used for the calculations here included were those reported and recommended for traditional liquid–vapor calculations.

We have also carried out the calculation of the relative Gibbs adsorption isotherm using the surface concentrations calculated with Eqs. (1) and (2). The relative Gibbs adsorption isotherm has been traditionally calculated using the following formal relation, considering non-ideality in the bulk liquid phase [12,13]:

$$\Gamma_2^{(1)} = -\frac{1}{RT} \frac{d\sigma}{d \ln a_2} \quad (4)$$

In Eq. (4), $\Gamma_2^{(1)}$ is the relative adsorption of component 2 with respect to component 1, being component 1 that with the highest surface tension value.

Eq. (4) is commonly used considering ideality of the bulk liquid phase, the corresponding activity coefficient takes unity as value, in which case, this equation simplifies to the following:

$$\Gamma_2^{(1)} = -\frac{1}{RT} \frac{d\sigma}{d \ln x_2} \quad (5)$$

With Eq. (5), the relative adsorption is calculated knowing the derivative of the surface tension as a function of component 2 bulk liquid phase concentration, and not as a function of the activity of component 2, as is the case with Eq. (4). These approaches are well documented in standard related literature [12,13].

Another approach has been explored for calculating the Gibbs adsorption isotherm, in which this quantity is derived using exclusively concentrations from both the liquid bulk phase and the liquid–vapor interface.

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