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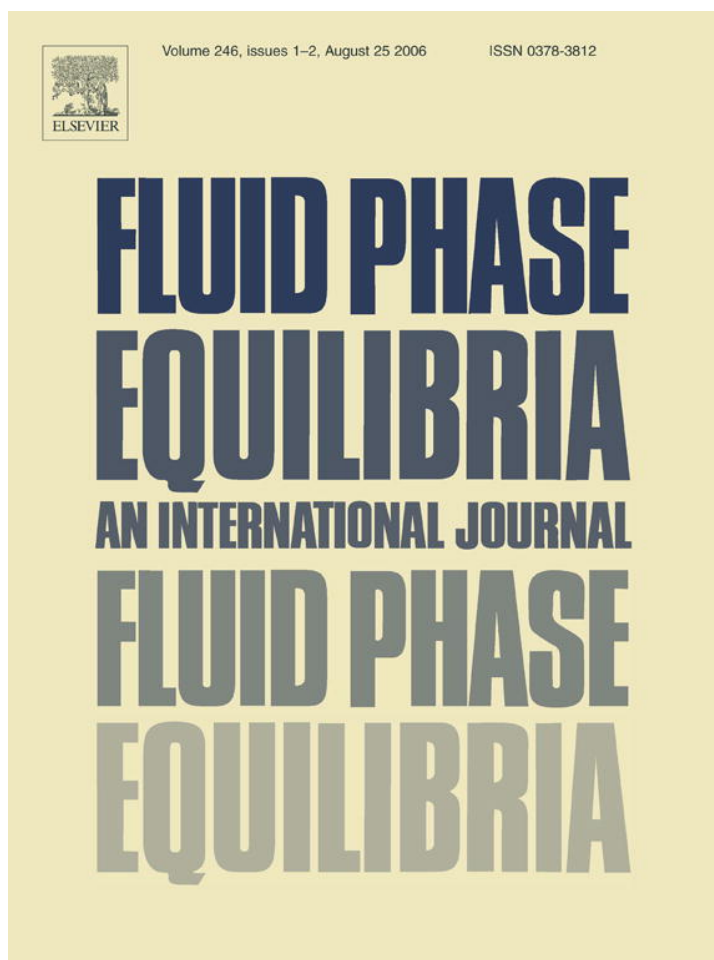


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Prediction of the surface tension, surface concentration, and the relative Gibbs adsorption isotherm of binary liquid systems

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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, adherency, 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.

The derivation of the equation for this approach starts with the use of the Gibbs–Duhem relation applied to a bulk liquid phase of a binary system at a given temperature and pressure. After some algebraic manipulation, including the use of the isochemical potential condition for the bulk liquid phase and the interface, it is possible to arrive to the following equation [15]:

$$-\frac{d\sigma}{d\mu_2} = \frac{1}{A} \left(N_2^\sigma - N_1^\sigma \frac{N_2}{N_1} \right) \quad (6)$$

The left-hand side of Eq. (6) can be identified with the Gibbs adsorption isotherm, in which case it is re-written as:

$$\Gamma_2^{(1)} = \frac{1}{A} \left(N_2^\sigma - N_1^\sigma \frac{N_2}{N_1} \right) \quad (7)$$

Considering that the molar surface area for both components is the same in the bulk liquid phase and in the interface, and translating the individual amount of substance to mole fraction, the following equation is obtained:

$$\Gamma_2^{(1)} = \frac{1}{x_1^\sigma \Omega_1 + x_2^\sigma \Omega_2} \left(\frac{x_2^\sigma x_1 - x_1^\sigma x_2}{x_1} \right) \quad (8)$$

In Eq. (8) the relative Gibbs adsorption isotherm is expressed in terms of the bulk liquid phase and liquid–vapor interface concentrations. The latter are derived together with the mixture surface tension as explained above, and the molar surface areas are calculated using Eq. (3). It is then possible to calculate the relative Gibbs adsorption isotherm using one of the three approaches shown here, Eqs. (4), (5), and (8).

3. Calculation methods

The algorithm developed here to carry out the calculations to estimate simultaneously surface tension and surface concentrations is similar to that used for an isothermal bubble point [11] for systems showing vapor–liquid equilibria, where a physical equilibrium constant relating liquid and vapor phases is introduced. In an analogous way, an equilibrium constant relating the bulk liquid phase and the liquid–vapor interface is introduced here according to:

$$K_i^\sigma = \frac{x_i^\sigma}{x_i} \quad (9)$$

The following constraint is also included,

$$x_1^\sigma + x_2^\sigma = 1 \quad (10)$$

Thus, the following relation also holds:

$$\sum x_i K_i^\sigma = 1 \quad (11)$$

We present in Table 1 a summary of the analogies between an isothermal bubble point and the present surface tension calculations.

Eq. (11) is considered in the convergence criteria during the search for the best values for the mixture surface tension σ and the molar surface concentration x_i^σ , using the double loop iterative process, respectively.

Table 1

Comparison between isothermal bubble point and multicomponent surface tension calculations

Algorithm for isothermal bubble point calculation	Algorithm for isothermal surface tension calculation
Unknown variables: y_i and p	Unknown variables: x_i^σ and σ
Known variables: x_i and T	Known variables: x_i and T
Equilibrium constant: $K_i = y_i/x_i$	Equilibrium constant: $K_i^\sigma = x_i^\sigma/x_i$
Use fugacity coefficients: ϕ_i	Use activity coefficients: γ_i and γ_i^σ
Constraint: $\sum y_i = 1$	Constraint: $\sum x_i^\sigma = 1$
The phases are liquid and vapor	The phases are the bulk liquid and we consider the interface as a second phase

The objective function used to derive the surface tension for the mixture, during the inner iterative process in the bubble pressure-like algorithm used, takes the following form:

$$f(\sigma) = \frac{x_1 \gamma_1}{\gamma_1^\sigma} \exp \left[\frac{\Omega_1(\sigma - \sigma_1)}{RT} \right] + \frac{x_2 \gamma_2}{\gamma_2^\sigma} \times \exp \left[\frac{\Omega_2(\sigma - \sigma_2)}{RT} \right] - 1 = 0 \quad (12)$$

Activity coefficient values for the two components in both the bulk liquid phase and the liquid–vapor interface are calculated using the UNIFAC model together with binary group interaction parameters from Gmehling et al. [10].

In order to solve Eq. (12) the Newton–Raphson method [16] is used during the iterative process to obtain the mixture surface tension value; the $n+1$ approximation for σ is evaluated according to the following expression:

$$\sigma^{n+1} = \sigma^n - \frac{f(\sigma^n)}{f'(\sigma^n)} \quad (13)$$

The explicit form of Eq. (13) can be obtained from Eq. (12). The Newton–Raphson method needs a first approximation for σ^0 to initiate the iterative process for finding the best value of the mixture surface tension hence, in this work the following relation has been used:

$$\sigma^0 = x_1 \sigma_1 + x_2 \sigma_2 \quad (14)$$

For the calculation of the relative Gibbs adsorption isotherm, two (Eqs. (4) and (5)) of the three possibilities (Eqs. (4), (5), and (8)) require the availability of surface tension information as a function of concentration to obtain the surface tension derivative as a function of the activity of one of the components of the binary mixture, or as a function of the corresponding bulk liquid phase concentration. When using Eq. (8), the only information required is that corresponding to bulk liquid and surface layer concentration and the corresponding molar surface areas.

Surface tension data for pure components, σ_i , in Eqs. (1) and (2) are taken from the open literature.

4. Results and discussion

In order to test the model and the calculation method proposed, we have calculated the surface tension for 31 different

Table 2

Systems considered in the comparison of experimental and calculated surface tension values

Type of system	Pairs	Binary systems	Points
Non-polar + non-polar	8	33	231
Polar + polar	10	23	182
Non-polar + polar	7	27	193
Aqueous systems	6	22	184
Total	31	105	790

binary systems in the full concentration range, at different temperatures. The capability of the model was established by comparing experimental and calculated surface tension values. The total number of experimental points used in this comparison was 790. The type of systems considered in this work include: polar + non-polar, polar + polar, non-polar + non-polar and aqueous binary systems of glycols and organic acids.

Table 2 gives a summary of the type of binaries considered, as well as the number of experimental points. The number of binary systems is greater than the number of pairs because, for some pairs, different temperatures were considered for the studied systems.

Table 3 summarizes the results obtained from the comparison between experimental and calculated surface tension values for the 31 systems considered, at different temperatures.

From Table 3 it is possible to observe that at least 45% of the binary systems included in this study show an average relative error of less than 2%, and 88% of the same binary systems show an average relative error below 6%, the maximum relative error occurs for the binary propionic acid + water at 298.15 K with a value of 13.0%. It is observed that there is a tendency of the average relative error to increase as the temperature increases for some of the studied systems.

Considering some of the results reported in previous works where UNIFAC was also used for the calculation of activity coefficients, we found that the mean absolute percentage error for four systems different from the ones considered in this work is between 5% and 8% [7], whereas Tojo-Suárez et al. [8] show deviations between experimental and predicted surface tensions for 25 binary systems in the range 2.60–5.42% depending on the approach used for the determination of molar surface areas.

As an example of the type of information obtained during the calculation of the mixture surface tension and surface concentration, Table 4 shows the corresponding results for the binary system x_1 benzene + $(1 - x_1)$ nitrobenzene, at 293.15 and 303.15 K. The different columns of this table show: component 1 bulk liquid phase concentration, bulk activity coefficients for components 1 and 2, component 1 surface concentration, surface activity coefficients for components 1 and 2, experimental and calculated mixture surface tension values and the point to point relative error, respectively. The experimental values taken from the literature correspond to bulk liquid concentration and mixture surface tension values; for this system, these values are reported by Suri and Ramakrishna [17]. The remaining values included in Table 4 correspond to those obtained with the proposed method, i.e. activity coefficients for both components of

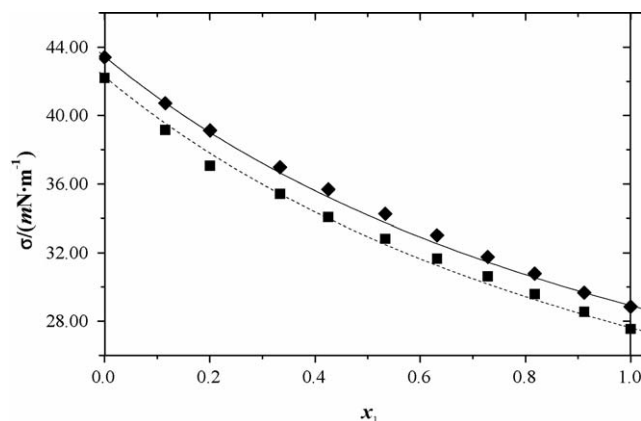


Fig. 1. Comparison of calculated (lines) and experimental (symbols) surface tension values, σ , as a function of mole fraction, x_1 , for the system x_1 benzene + $(1 - x_1)$ nitrobenzene ((\diamond) 293.15 K, (\blacksquare) 303.15 K).

the binary system in the bulk liquid phase and the liquid–vapor interface, which are evaluated using the UNIFAC activity coefficient model [10], and the predicted mixture surface tension values. The overall absolute mean relative error (%) for the 18 mixture points is 0.83, which is within the experimental error of the literature values.

Tables 5–7 shows the same type of results as above for other three binary systems that can be considered as representative of the different types of systems included in this work.

For the binary of *n*-hexadecane with *n*-eicosane the overall absolute mean relative deviation in (%) is 0.29 for the 28 points used for the comparison. For the system x_1 *n*-pentane + $(1 - x_1)$ butanenitrile the error was 1.96 for the 14 points considered, and for the system x_1 *iso*-butanol + $(1 - x_1)$ *n*-decanol, this value was 1.87 for eight points used in the comparison.

Figs. 1–4 show graphically the comparison between experimental and calculated values for the systems mentioned above. In these figures the symbols are used to represent the experimental values and lines represent the calculated surface tension values.

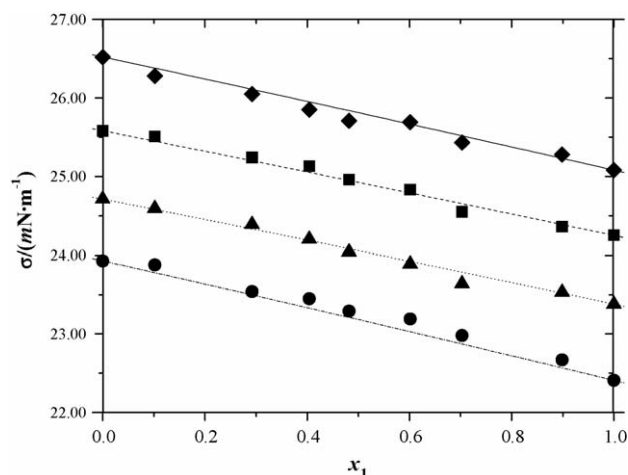


Fig. 2. Comparison of calculated (lines) and experimental (symbols) surface tension values, σ , as a function of mole fraction, x_1 , for the system x_1 *n*-hexadecane + $(1 - x_1)$ *n*-eicosane ((\diamond) 323.15 K, (\blacksquare) 333.15 K, (\blacktriangle) 343.15 K, (\bullet) 353.15 K).

Table 3

Results of the comparison between experimental and calculated values of surface tension for 31 binary systems

System	<i>T</i> (K)	Points	Average relative error (%)	Reference
<i>iso</i> -Butanol + decanol	298.15	8	1.88	[20]
<i>sec</i> -Butanol + decanol	298.15	9	1.64	[20]
<i>tert</i> -Butanol + decanol	298.15	8	3.06	[20]
<i>n</i> -Heptane + butanenitrile	293.15	7	1.68	[1]
	303.15	7	2.43	[1]
	313.15	7	1.79	[1]
	323.15	7	2.58	[1]
	333.15	7	2.83	[1]
	343.15	7	3.24	[1]
	263.15	10	2.15	[1]
<i>n</i> -Hexane + butanenitrile	293.15	7	2.93	[1]
	303.15	7	3.34	[1]
	313.15	7	4.37	[1]
	323.15	7	5.67	[1]
	333.15	7	6.79	[1]
	343.15	7	8.41	[1]
	293.15	7	2.06	[1]
<i>n</i> -Pentane + butanenitrile	303.15	7	1.88	[1]
	313.15	7	3.10	[1]
	323.15	7	5.13	[1]
	333.15	7	7.24	[1]
	343.15	7	9.35	[1]
	293.15	6	0.48	[17]
	303.15	6	0.63	[17]
Benzene + 1,4-dioxane	293.15	9	0.83	[17]
	303.15	9	0.89	[17]
Benzene + nitrobenzene	293.15	6	2.36	[17]
	303.15	6	0.41	[17]
Cyclohexane + 1,4-dioxane	293.15	6	7.83	[17]
	303.15	9	4.18	[17]
Cyclohexane + nitrobenzene	293.15	8	0.56	[17]
	303.15	9	1.32	[17]
1,4-Dioxane + nitrobenzene	323.15	7	0.28	[21]
	333.15	7	0.66	[21]
	343.15	7	0.49	[21]
	353.15	7	0.98	[21]
	313.15	7	0.66	[21]
Cyclohexane + <i>n</i> -docosane	323.15	7	0.24	[21]
	333.15	7	0.76	[21]
	343.15	7	0.80	[21]
	353.15	7	1.75	[21]
	323.15	7	0.30	[21]
<i>n</i> -Hexadecane + <i>n</i> -eicosane	333.15	7	0.21	[21]
	343.15	7	0.19	[21]
	353.15	7	0.45	[21]
	323.15	7	0.45	[21]
<i>n</i> -Hexadecane + <i>n</i> -docosane	333.15	7	0.18	[21]
	343.15	7	0.36	[21]
	353.15	7	0.22	[21]
	293.15	6	3.09	[22]
Dichloromethane + carbon disulfide	298.15	7	3.93	[22]
	303.15	8	4.40	[22]
	308.15	8	4.45	[22]
	293.15	7	0.51	[23]
<i>n</i> -Heptane + cyclohexane	303.15	7	1.21	[23]
	313.15	7	0.76	[23]
	323.15	7	1.12	[23]

Table 3 (Continued)

System	<i>T</i> (K)	Points	Average relative error (%)	Reference
Cyclohexane + benzene	293.15	7	2.61	[23]
	303.15	7	2.52	[23]
	313.15	7	2.46	[23]
	323.15	7	3.23	[23]
Cyclohexane + <i>n</i> -dodecane	293.15	7	0.59	[23]
	303.15	7	0.82	[23]
	313.15	7	0.40	[23]
	323.15	7	0.72	[23]
Cyclohexane + <i>n</i> -hexadecane	293.15	7	0.35	[23]
	303.15	7	0.35	[23]
	313.15	7	0.27	[23]
	323.15	7	0.32	[23]
Carbon tetrachloride + ethanenitrile	298.15	7	0.94	[24]
	303.15	6	1.15	[24]
	308.15	7	1.16	[24]
	313.15	8	1.16	[24]
	318.15	8	1.20	[24]
Carbon tetrachloride + carbon disulfide	293.15	8	1.98	[25]
	298.15	8	2.05	[25]
	303.15	8	2.44	[25]
	308.15	8	2.58	[25]
	313.15	8	2.56	[25]
	318.15	8	2.91	[25]
Methanol + glycerol	298.15	9	7.80	[26]
1-Propanol + glycerol	298.15	9	5.33	[26]
Propionic acid + glycerol	298.15	9	4.88	[26]
Ethylenglycol + water	283.15	11	2.65	[27]
	293.15	11	2.99	[27]
	303.15	11	3.60	[27]
	313.15	11	4.18	[27]
	323.15	11	4.24	[27]
1,3-Propylenglycol + water	298.15	5	3.50	[28]
	303.15	5	3.84	[28]
	308.15	5	3.95	[28]
	313.15	5	4.10	[28]
	318.15	5	4.34	[28]
	323.15	5	4.30	[28]
Propylenglycol + water	298.15	6	3.69	[29]
	303.15	7	4.63	[29]
	308.15	6	4.47	[29]
	313.15	7	5.25	[29]
	318.15	6	6.19	[29]
	323.15	7	5.58	[29]
Formic acid + water	298.15	12	6.80	[30]
Propionic acid + water	293.15	12	11.99	[30]
	298.15	12	13.02	[30]
Acetic acid + water	293.15	12	7.25	[30]
	298.15	12	7.75	[30]

$$\text{Average relative error (\%)} = \left[\left(\sum_{i=1}^N (\sigma_i^{\text{exp}} - \sigma_i^{\text{cal}}) / \sigma_i^{\text{exp}} \right) / N \right] \times 100.$$

According to the errors obtained between experimental and calculated surface tension values, the method here proposed to estimate surface tension values for binary systems reproduces very well the experimental behavior shown by the different types of binary systems included in this work.

Taking into account that the test carried out is on both, the model and the calculation method, it is fair to say that the reproducibility of the experimental surface tension behavior with

concentration and temperature, is also strongly related to the availability of values of the binary interaction parameters of the activity coefficient model, which in turn reflect the amount of experimental information used to capture the contribution to the calculation of the thermodynamic properties of a given molecular group.

An analysis of the reproducibility of the experimental surface tension information takes us to establish that, when the binary

Table 4

Comparison between experimental and calculated surface tension with Eqs. (1) and (2) for the system x_1 benzene + $(1 - x_1)$ nitrobenzene [17]

x_1	γ_1	γ_2	x_1^σ	γ_1^σ	γ_2^σ	σ^{exp} [17] (mN m ⁻¹)	σ^{cal} (mN m ⁻¹)	Relative error (%)
$T = 293.15$ K								
0.1152	1.3778	1.0042	0.2897	1.2520	1.0292	40.72	40.83	-0.26
0.2003	1.3133	1.0133	0.4616	1.1519	1.0825	39.13	39.05	0.20
0.3335	1.2243	1.0397	0.6526	1.0681	1.1916	36.97	36.60	1.00
0.4254	1.1711	1.0684	0.7407	1.0396	1.2682	35.68	35.16	1.45
0.5333	1.1170	1.1160	0.8153	1.0209	1.3515	34.25	33.70	1.61
0.6320	1.0757	1.1765	0.8664	1.0113	1.4210	33.01	32.53	1.47
0.7285	1.0431	1.2563	0.9068	1.0056	1.4849	31.75	31.49	0.81
0.8177	1.0204	1.3546	0.9393	1.0024	1.5428	30.78	30.60	0.58
0.9117	1.0051	1.4932	0.9709	1.0006	1.6056	29.67	29.70	-0.09
$T = 303.15$ K								
0.1152	1.3692	1.0042	0.2845	1.2494	1.0276	39.15	39.63	-1.23
0.2228	1.2903	1.0164	0.4927	1.1330	1.0943	37.05	37.41	-0.98
0.3335	1.2189	1.0390	0.6449	1.0691	1.1819	35.43	35.40	0.07
0.4374	1.1606	1.0716	0.7438	1.0377	1.2650	34.07	33.78	0.85
0.5333	1.1141	1.1138	0.8101	1.0215	1.3366	32.82	32.47	1.05
0.6320	1.0738	1.1728	0.8625	1.0116	1.4046	31.65	31.29	1.15
0.7285	1.0420	1.2505	0.9042	1.0058	1.4673	30.61	30.24	1.22
0.8217	1.0190	1.3507	0.9391	1.0024	1.5269	29.58	29.29	0.98
0.9118	1.0049	1.4797	0.9702	1.0006	1.5862	28.54	28.41	0.46

Activity coefficients and surface concentrations are also included. Relative error (%) = $[(\sigma^{\text{exp}} - \sigma^{\text{cal}})/\sigma^{\text{exp}}] \times 100$.

Table 5

Comparison between experimental and calculated surface tension with Eqs. (1) and (2) for the system x_1 *n*-hexadecane + $(1 - x_1)$ *n*-eicosane [21]

x_1	γ_1	γ_2	x_1^σ	γ_1^σ	γ_2^σ	σ^{exp} [21] (mN m ⁻¹)	σ^{cal} (mN m ⁻¹)	Relative error (%)
$T = 323.15$ K								
0.1019	0.9828	0.9998	0.1223	0.9835	0.9997	26.28	26.38	-0.37
0.2921	0.9887	0.9983	0.3373	0.9900	0.9977	26.05	26.11	-0.22
0.4041	0.9918	0.9967	0.4561	0.9930	0.9957	25.85	25.95	-0.38
0.4818	0.9936	0.9952	0.5354	0.9948	0.994	25.71	25.84	-0.49
0.6013	0.9961	0.9923	0.6523	0.9970	0.9908	25.69	25.66	0.11
0.7029	0.9978	0.9892	0.7470	0.9984	0.9876	25.43	25.52	-0.33
0.8987	0.9997	0.9813	0.9177	0.9998	0.9804	25.28	25.23	0.20
$T = 333.15$ K								
0.1019	0.9828	0.9998	0.1201	0.9834	0.9997	25.51	25.45	0.24
0.2921	0.9887	0.9983	0.3327	0.9899	0.9978	25.24	25.20	0.15
0.4041	0.9918	0.9967	0.4510	0.9929	0.9958	25.13	25.06	0.30
0.4818	0.9936	0.9952	0.5302	0.9947	0.9941	24.96	24.95	0.03
0.6013	0.9961	0.9923	0.6475	0.9969	0.9910	24.83	24.79	0.15
0.7029	0.9978	0.9892	0.7429	0.9983	0.9878	24.55	24.66	-0.43
0.8987	0.9997	0.9813	0.9160	0.9998	0.9805	24.36	24.39	-0.12
$T = 343.15$ K								
0.1019	0.9828	0.9998	0.1197	0.9834	0.9997	24.59	24.58	0.04
0.2921	0.9887	0.9983	0.3317	0.9899	0.9978	24.39	24.33	0.24
0.4041	0.9918	0.9967	0.4498	0.9929	0.9959	24.20	24.19	0.06
0.4818	0.9936	0.9952	0.5290	0.9947	0.9942	24.04	24.08	-0.17
0.6013	0.9961	0.9923	0.6463	0.9969	0.9910	23.89	23.92	-0.13
0.7029	0.9978	0.9892	0.7419	0.9983	0.9878	23.64	23.79	-0.61
0.8987	0.9997	0.9813	0.9156	0.9998	0.9805	23.53	23.52	0.05
$T = 353.15$ K								
0.1019	0.9828	0.9998	0.1219	0.9835	0.9997	23.88	23.78	0.42
0.2921	0.9887	0.9983	0.3365	0.9900	0.9978	23.54	23.49	0.19
0.4041	0.9918	0.9967	0.4553	0.9930	0.9958	23.45	23.33	0.53
0.4818	0.9936	0.9952	0.5345	0.9948	0.9940	23.29	23.21	0.35
0.6013	0.9961	0.9923	0.6514	0.9970	0.9908	23.19	23.03	0.71
0.7029	0.9978	0.9892	0.7463	0.9983	0.9877	22.98	22.87	0.48
0.8987	0.9997	0.9813	0.9174	0.9998	0.9804	22.67	22.57	0.45

Activity coefficients and surface concentrations are also included. Relative error (%) = $[(\sigma^{\text{exp}} - \sigma^{\text{cal}})/\sigma^{\text{exp}}] \times 100$.

Table 6

Comparison between experimental and calculated surface tension with Eqs. (1) and (2) for the system x_1 *n*-pentane + $(1 - x_1)$ butanenitrile [1]

x_1	γ_1	γ_2	x_1^σ	γ_1^σ	γ_2^σ	σ^{exp} [1] (mN m ⁻¹)	σ^{cal} (mN m ⁻¹)	Relative error (%)
$T = 293.15$ K								
0.1022	3.1409	1.0109	0.3066	2.1791	1.1120	24.28	25.09	-3.34
0.2046	2.6011	1.0462	0.7614	1.1581	2.4525	22.37	22.32	0.23
0.2995	2.2059	1.1061	0.8807	1.0457	3.9545	20.82	20.21	2.92
0.5015	1.6061	1.3712	0.9302	1.0170	5.1722	18.50	18.13	2.01
0.6026	1.3966	1.6302	0.9394	1.0130	5.4720	17.18	17.67	-2.83
0.7997	1.1162	2.7973	0.9542	1.0077	6.0134	16.85	17.08	-1.34
0.8961	1.0356	4.2743	0.9676	1.0039	6.5893	16.45	16.73	-1.69
$T = 303.15$ K								
0.1022	3.0674	1.0108	0.3002	2.1599	1.1055	23.75	24.03	-1.18
0.2046	2.5453	1.0457	0.7272	1.1915	2.1706	21.86	21.32	2.47
0.2995	2.1630	1.1048	0.8639	1.0548	3.5219	19.87	19.23	3.23
0.5015	1.5827	1.3649	0.9220	1.0196	4.6852	17.90	17.09	4.54
0.6026	1.3801	1.6169	0.9329	1.0148	4.9786	16.55	16.59	-0.26
0.7997	1.1103	2.7294	0.9508	1.0082	5.5315	16.12	15.93	1.15
0.8961	1.0334	4.0927	0.9661	1.0040	6.0915	15.60	15.56	0.27

Activity coefficients and surface concentrations are also included. Relative error (%) = $[(\sigma^{\text{exp}} - \sigma^{\text{cal}})/\sigma^{\text{exp}}] \times 100$.

Table 7

Comparison between experimental and calculated surface tension with Eqs. (1) and (2) for the system x_1 *iso*-butanol + $(1 - x_1)$ *n*-decanol [20]

x_1	γ_1	γ_2	x_1^σ	γ_1^σ	γ_2^σ	σ^{exp} [1] (mN m ⁻¹)	σ^{cal} (mN m ⁻¹)	Relative error (%)
$T = 298.15$ K								
0.1724	1.0612	1.0014	0.2468	1.0544	1.0031	27.72	27.48	0.86
0.2834	1.0511	1.0043	0.3909	1.0412	1.0092	27.38	26.91	1.73
0.4003	1.0403	1.0097	0.5287	1.0287	1.0197	26.77	26.26	1.91
0.5080	1.0306	1.0177	0.6420	1.0190	1.0336	26.25	25.63	2.37
0.5985	1.0226	1.0276	0.7269	1.0123	1.0484	25.67	25.08	2.32
0.6984	1.0145	1.0429	0.8097	1.0067	1.0681	25.01	24.45	2.26
0.7995	1.0074	1.0653	0.8825	1.0029	1.0911	24.28	23.79	2.02
0.8929	1.0024	1.0949	0.9412	1.0008	1.1149	23.54	23.17	1.57

Activity coefficients and surface concentrations are also included. Relative error (%) = $[(\sigma^{\text{exp}} - \sigma^{\text{cal}})/\sigma^{\text{exp}}] \times 100$.

system under study is formed by components of the same chemical nature, and molecular size, the system tends to show a more “ideal” behavior, in which case, the UNIFAC activity coefficient model used in this work allows to reproduce the experimental

surface tension behavior with enough accuracy. This is the case for the systems formed by two alkanes or two alcohols.

It has to be mentioned here that, even when formally there is not a definition of an “ideal” behavior in terms of surface tension,

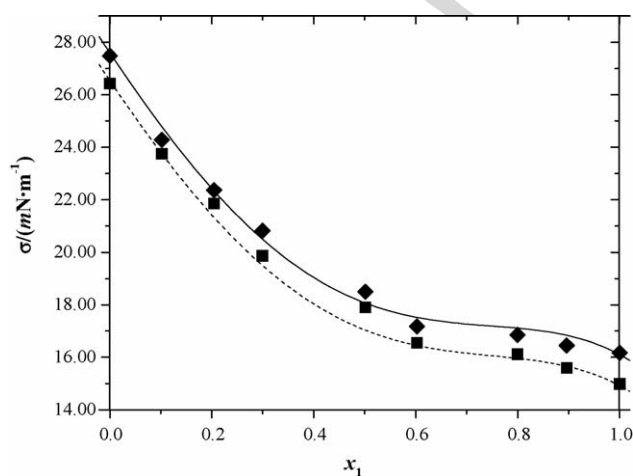


Fig. 3. Comparison of calculated (lines) and experimental (symbols) surface tension values, σ , as a function of mole fraction, x_1 , for the system x_1 *n*-pentane + $(1 - x_1)$ butanenitrile ((♦) 293.15 K, (■) 303.15 K).

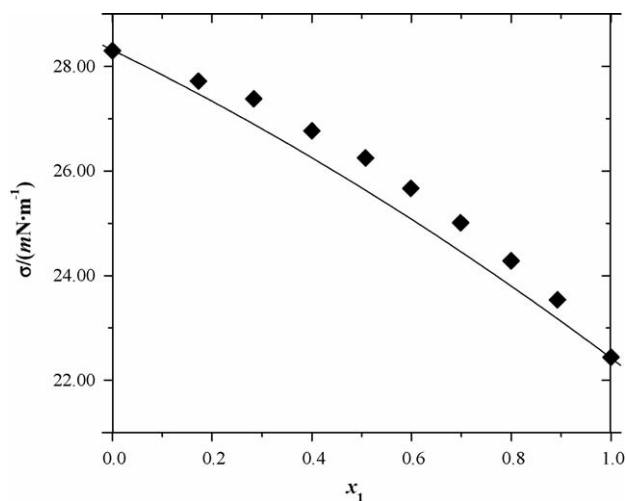


Fig. 4. Comparison of calculated (lines) and experimental (symbols) surface tension values, σ , as a function of mole fraction, x_1 , for the system x_1 *iso*-butanol + $(1 - x_1)$ *n*-decanol ((♦) 298.15 K).

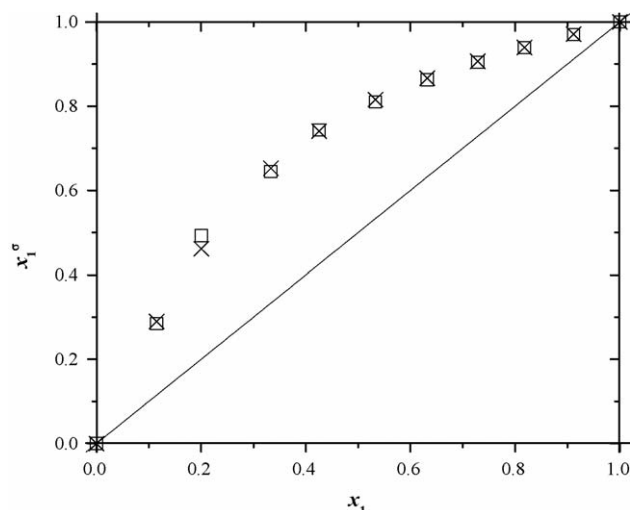


Fig. 5. Calculated concentration of component 1 at the liquid–vapor interface (x_1^σ) as a function of concentration of component 1 at the liquid bulk phase (x_1) for the binary system x_1 benzene + $(1 - x_1)$ nitrobenzene ((\times) 293.15 K, (\square) 303.15 K); (—) reference line at 45° .

we have used the approach of considering an ideal behavior that which connects both pure component surface tension values with a straight line, following the additivity rule given in Eq. (14).

The “ideality” of the surface tension of a given system is also reflected using the surface layer concentration, which is the other quantity estimated simultaneously using the calculation scheme proposed in this work. A plot of the surface concentration versus the bulk liquid concentration gives us the possibility of establishing the non-ideality of a given system by observing the form of the corresponding curve. For almost ideal systems, this curve tends to be a line very close to that a hypothetical ideal system would show, which corresponds to a 45° slope straight line. See for example the curves shown in Figs. 6 and 8 for the two binaries considered for illustration. We can observe for these two systems different curves corresponding to at least two different temperatures, showing the above-mentioned behavior. Similar behavior is observed for the remaining quasi-ideal systems.

For systems formed by components of different chemical nature, behaviors shown in Figs. 5 and 7 would be observed for the curve surface layer versus bulk liquid concentration, tending to separate with respect to the 45° slope line as the non-ideality of the system becomes higher. As an example, in Fig. 7 the corresponding curve for the system n -pentane + butanenitrile is shown for two different temperatures, 298.15 and 303.15 K. The behavior of these curves is similar to that shown by systems with a well-defined surfactant nature (see for example the effect of the addition of a surfactant on the surface tension value of an aqueous solution of alkanolamines in a previous work from our group [18]). At low concentration of n -pentane, values for the surface layer concentration are higher than that corresponding to the bulk liquid concentration, reaching an asymptotic behavior from about 0.4 in bulk liquid concentration. With this observation, it is possible to establish an order for the “ideality” (or “non-ideality”) of the surface tension for the four binary systems shown in Figs. 1–4, according to the following: n -hexadecane + n -

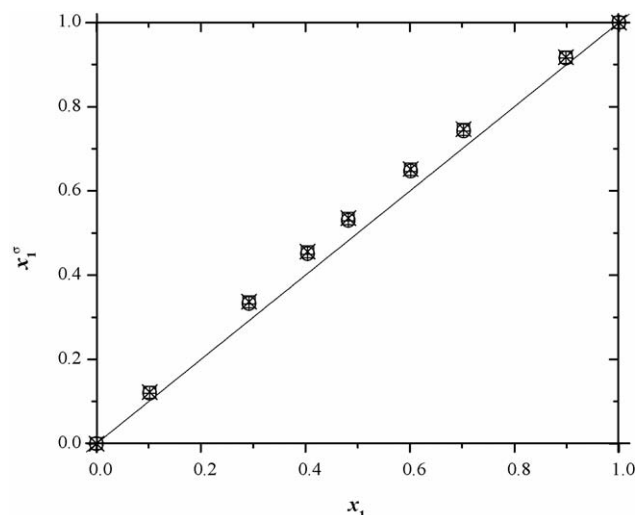


Fig. 6. Calculated concentration of component 1 at the liquid–vapor interface (x_1^σ) as a function of concentration of component 1 at the liquid bulk phase (x_1) for the binary system x_1 n -hexadecane + $(1 - x_1)$ n -eicosane ((\times) 323.15 K, (\square) 333.15 K, (+) 343.15 K, (\circ) 353.15 K); (—) reference line at 45° .

eicosane > *iso*-butanol + decanol > benzene + nitrobenzene > n -pentane + butanenitrile.

The behavior of the curve surface layer concentration versus bulk liquid concentration for all the 31 binary systems included in this study show one of the four types of curves shown in Figs. 5–8, according to the non-ideality of the corresponding binary system.

Estimated values for the surface layer concentration cannot be compared to any experimental value because of the lack of this type of information, since this quantity has not been measured, as far as we know. In spite of the lack of surface layer concentrations, the information obtained from this quantity would be very helpful, mainly if it is related to the macroscopic behavior of mixtures of interest in separation processes. In fact, it is

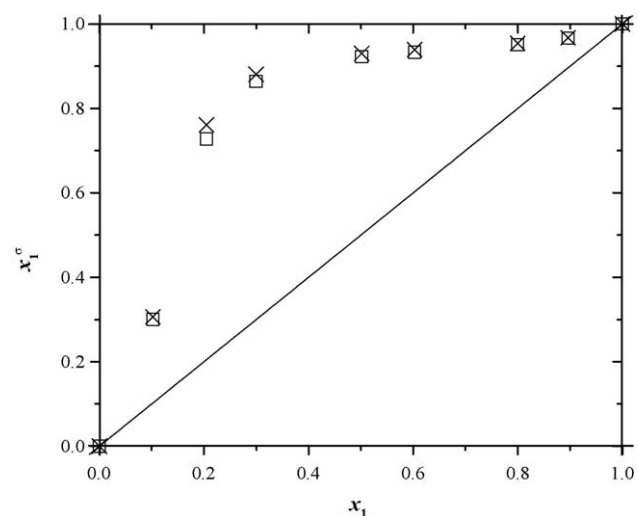


Fig. 7. Calculated concentration of component 1 at the liquid–vapor interface (x_1^σ) as a function of concentration of component 1 at the liquid bulk phase (x_1) for the binary system x_1 n -pentane + $(1 - x_1)$ butanenitrile ((\times) 293.15 K, (\square) 303.15 K); (—) reference line at 45° .

Table 8
Relative Gibbs adsorption isotherm calculated with the different approaches discussed in this work for the binary system x_1 *iso*-butanol + $(1 - x_1)$ *n*-decanol, at 298.15 K [20]

x_1	x_1^σ	σ^{exp} (mN m ⁻¹)	$\Gamma_2^{(1)}$ ($\times 10^6$ mol m ⁻²) using Eq. (5)	$\Gamma_2^{(1)}$ ($\times 10^6$ mol m ⁻²) using Eq. (4)	$\Gamma_2^{(1)}$ ($\times 10^6$ mol m ⁻²) using Eq. (8)
0.1724	0.2468	27.72	0.2135	0.2011	0.3537
0.2834	0.3909	27.38	0.4738	0.4855	0.6285
0.4003	0.5287	26.77	0.7963	0.8348	0.9564
0.5080	0.6420	26.25	1.1537	1.2160	1.2865
0.5985	0.7269	25.67	1.5103	1.5910	1.5787
0.6984	0.8097	25.01	1.9807	2.0774	1.9053
0.7995	0.8825	24.28	2.5601	2.6681	2.2273
0.8929	0.9412	23.54	3.2133	3.3296	2.5116

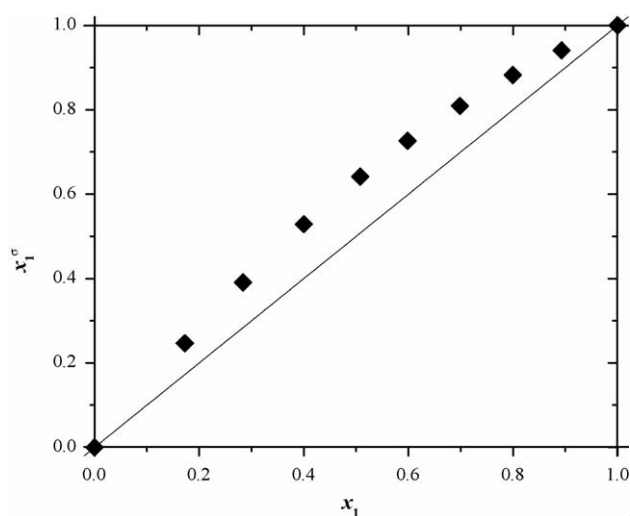


Fig. 8. Calculated concentration of component 1 at the liquid–vapor interface (x_1^σ) as a function of concentration of component 1 at the liquid bulk phase (x_1) for the binary system x_1 *iso*-butanol + $(1 - x_1)$ *n*-decanol (\blacklozenge 298.15 K); (—) reference line at 45°.

well recognized that, for processes which involve mass transfer between liquid and vapor phases, surface tension plays an important role, and according to what we have observed from the surface layer concentration curves, this property is a consequence of the preferential migration of molecules of the different components of a given mixture to the surface layer [19] and eventually to the vapor phase.

A quantity that is also used to infer directly the preferential distribution of the components on the surface layer is the relative Gibbs adsorption isotherm, which can be calculated using one of

the approaches expressed in terms of Eqs. (4) and (5) or Eq. (8), as explained previously. Some results of the Gibbs adsorption isotherm are shown in Tables 8 and 9 for two of the binary systems included in this study.

It has to be mentioned here that, the use of Eq. (4) corresponds to the exact way of calculating the Gibbs adsorption isotherm because the non-ideality of the system under study is incorporated through the derivative of the surface tension with respect to the activity of component 2. Eq. (5) considers ideality of the bulk liquid phase (the activity coefficient of component 2 is considered equal to unity). The use of Eq. (8) incorporates indirectly the non-ideality of the system considering that the concentration of the liquid–vapor interface is obtained through the use an activity coefficient model.

Table 8 includes the $\Gamma_2^{(1)}$ results corresponding to the binary *n*-decanol + *iso*-butanol at 298.15 K. This table gives: the liquid bulk and surface layer concentrations for the component with the highest surface tension (*iso*-butanol), the experimental surface tension value, and the relative Gibbs adsorption isotherm as calculated using Eqs. (4), (5), and (8), respectively.

The calculated values of the relative Gibbs adsorption isotherm using the three different equations show the same overall behavior at a given liquid bulk concentration. This can be attributed to the almost ideal behavior shown by this system which is formed by compounds of the same chemical nature. This can be better observed in Fig. 9 in which the three different curves show almost the same behavior up to a concentration of about 0.7 in mole fraction; above this concentration, the values obtained with Eq. (8) are lower than those obtained with Eqs. (4) and (5).

Table 9
Relative Gibbs adsorption isotherm calculated with the different approaches discussed in this work for the binary system x_1 *n*-pentane + $(1 - x_1)$ butanenitrile, at 293.15 K [1]

x_1	x_1^σ	σ^{exp} (mN m ⁻¹)	$\Gamma_2^{(1)}$ ($\times 10^6$ mol m ⁻²) using Eq. (5)	$\Gamma_2^{(1)}$ ($\times 10^6$ mol m ⁻²) using Eq. (4)	$\Gamma_2^{(1)}$ ($\times 10^6$ mol m ⁻²) using Eq. (8)
0.1001	0.2590	25.01	1.3172	1.2147	0.9596
0.1993	0.7339	23.16	0.8785	2.1995	3.0836
0.3000	0.8382	22.46	0.7333	2.4478	3.4375
0.4989	0.8838	21.49	0.6725	2.5718	3.3869
0.5993	0.8942	21.26	0.6831	2.5936	3.2350
0.8009	0.9217	20.76	0.7353	2.6328	2.6450
0.8950	0.9488	20.51	0.7667	2.6579	2.2158

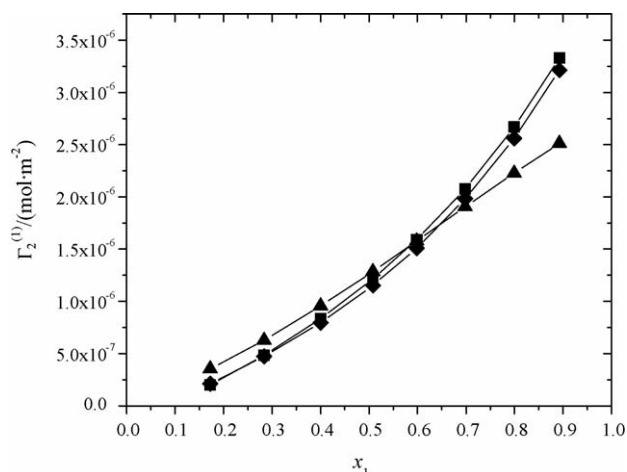


Fig. 9. Relative Gibbs adsorption isotherms as a function of liquid bulk concentration x_1 for the binary system x_1 *iso*-butanol + $(1 - x_1)$ *n*-decanol, at 298.15 K. (■) Eq. (4); (◆) Eq. (5); (▲) Eq. (8).

The example included in Table 9 corresponds to the binary *n*-pentane + butanenitrile at 293.15 K, which is a binary system showing a pronounced difference in chemical nature of the components. Such difference is reflected in the non-ideality of the behavior of different mixture properties, like liquid partial miscibility.

A non-monotonic decay in the mixture surface tension, and of course the high non-ideality of this system is also reflected in the values obtained for the relative Gibbs adsorption isotherm using Eqs. (4), (5), and (8).

The results for this quantity using Eq. (5) are opposite when compared to those obtained with Eqs. (4) and (8), this can be observed with more detail in Fig. 10. This is due to the simplifications in Eq. (5) which considers ideality for both the liquid bulk and the surface layer. Using Eqs. (4) and (8) the calculated relative Gibbs adsorption isotherms are of the same order of magnitude, since both equations consider the non-ideality of the bulk liquid phase and the liquid–vapor interface. The results obtained using Eq. (8) shows a maximum in the relative adsorption for

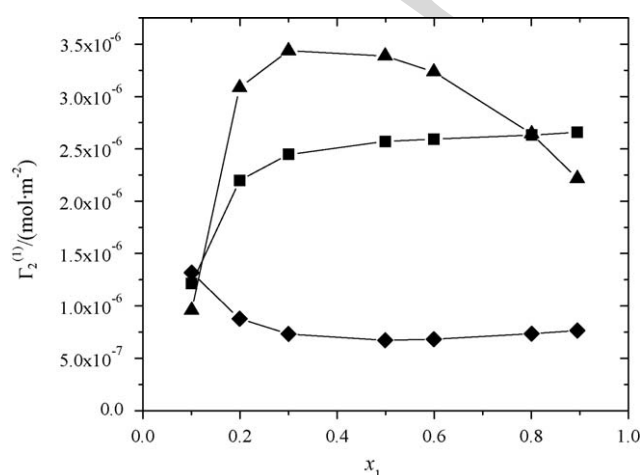


Fig. 10. Relative Gibbs adsorption isotherms as a function of liquid bulk concentration x_1 for the binary system x_1 *n*-pentane + $(1 - x_1)$ butanenitrile, at 293.15 K. (■) Eq. (4); (◆) Eq. (5); (▲) Eq. (8).

n-pentane in the surface layer, which seems to correspond to the saturation limit for this compound in the surface, and then it starts to decrease.

With Eq. (4), the trend of the relative adsorption is like that shown by a surfactant solution, with a rapid increase at low concentration of *n*-pentane, reaching an asymptotic behavior above 0.3 in mole fraction. All this is clearly supported by the observed functionality of the experimental surface tension–mole fraction data [1].

The two examples here included are representatives of binary systems with components of the same chemical (i.e. *n*-decanol + *iso*-butanol), and of different chemical nature (*n*-pentane + butanenitrile).

The remaining binary systems show similar trends to one of the above-mentioned, or intermediate behavior in the relative Gibbs adsorption isotherm as a function of concentration.

It has to be stressed here that the surface concentrations derived simultaneously with the mixture surface tension values are now a way of indicating the preferential surface layer enrichment, as is shown by plotting directly this quantity as a function of the bulk liquid concentration, or using the relative Gibbs adsorption isotherm calculated with Eq. (8).

In a recent work, Mejía et al. [4] showed some results on the calculation of surface tension using an approach based on cubic equations of state and the modified Huron–Vidal mixing rule together with the gradient theory, in which they included results of the prediction of the surface tension of the binary system cyclohexane + benzene for which a relative average error of 1.0% was given without specifying the number of points nor the different temperatures taken for the comparison.

Also for this system, Bahramian and Danesh [31], reported surface tension values calculated using different equations (the Lattice Theory, Buttlar, Parachor, Regular Solution Theory) with which reported an average relative deviation of 1.04%, 1.10%, 1.03% and 0.21%, respectively.

5. Conclusions

We have presented a thermodynamic model and a calculation method to estimate values of surface tension of binary systems together with the concentration of the components at the liquid–vapor interface.

Both, the thermodynamic and activity coefficients models, and the calculation method here proposed are able to reproduce, within experimental uncertainty, the surface tension behavior as a function of concentration and temperature, for different types of binary systems as established by the average relative percent error obtained with the 790 experimental points considered in this study, which was 2.88%.

Furthermore, the calculation scheme developed can be used for the prediction of surface tension values of binary systems, both as a function of concentration and temperature, without the use of any adjustable parameter. It is possible to use this method for a large variety of component combinations of different chemical nature using the UNIFAC activity coefficient model, which represents satisfactorily the activity coefficients for both, the liquid bulk and the surface layer.

Additionally, since the thermodynamic model can be extended to estimate values of surface tension and surface concentration for systems with more than two components, the prediction of the above-mentioned values is now possible for almost any combination of components for which UNIFAC group interaction parameters are available.

Considering that it has been possible estimating surface tension and liquid–vapor surface concentration with high precision using the UNIFAC activity coefficients model with binary interaction parameters from the open literature, which in turn were obtained from experimental vapor–liquid equilibrium data for different molecular groups, we visualize the possibility of carrying out the inverse process, that is, to obtain binary interaction parameters from mixture surface tension measurements, which are far easier, cheaper and faster than liquid–vapor experiments, for new molecular groups, which would be used to estimate now the liquid–vapor equilibrium.

We have taken advantage of the surface concentrations calculated simultaneously with the mixture surface tension values, which are now used to infer the preference of one of the components to be in the surface layer, as it is demonstrated using plots of surface concentration versus liquid bulk concentration or with the aid of the relative Gibbs adsorption isotherm.

Both the model and the calculation method presented are extended in a straightforward manner to multicomponent mixtures, this fact has also been explored and the results will be part of a separate work.

List of symbols

A	surface area
K_i^σ	bulk surface equilibrium constant
N_A	Avogadro's constant
p	pressure
R	universal gas constant
T	temperature
V_{mi}	molar volume of component i
x_i	bulk concentration of liquid phase in mole fraction of component i
x_i^σ	surface concentration in mole fraction of component i

Greek symbols

γ_i	activity coefficient of component i
γ_i^σ	surface activity coefficient of component i
$\Gamma_2^{(1)}$	Gibbs adsorption isotherm of component 2, with respect to component 1
σ	surface tension of a mixture

Subscripts

i	the i th component
1, 2	refers to components 1 and 2 in a binary mixture

Superscript

σ	refers to the liquid–vapor interface
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