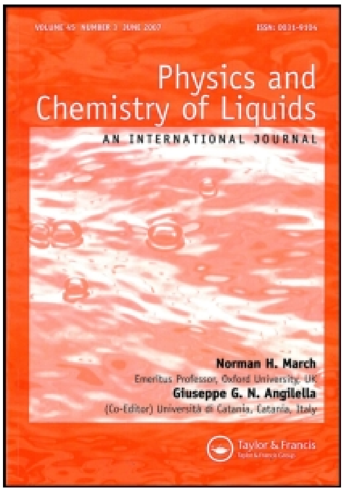

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# Surface tension and density of binary mixtures of monoalcohols, water and acetonitrile: equation of correlation of the surface tension

R. Belda Maximino[a]
[a] Faculty of Pharmacy, Department of Earth Physics and Thermodynamics, University of Valencia, Burjassot, Valencia, Spain

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# Surface tension and density of binary mixtures of monoalcohols, water and acetonitrile: equation of correlation of the surface tension

R. Belda Maximino*

*Faculty of Pharmacy, Department of Earth Physics and Thermodynamics, University of Valencia, Burjassot, Valencia, Spain*

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Measurements of the surface tension ($\sigma$) and density ($\rho$) of binary mixtures of monoalcohols, water and acetonitrile at 298.15 K and at atmospheric pressure, as a function of mole fraction ($x$) have been made. The experimental values of the deviation of surface tension and the excess of molar volume ($\Delta\sigma$, $V^E$) have been correlated by the Redlich–Kister equation. An empirical correlation equation is presented for the study of the surface tension of these mixtures, and comparisons are made of the experimental values of surface tension *versus* those obtained with the correlation equation and with other models of correlation. Finally, with the purpose of corroborating the validity of the correlation equation, the latter is applied to other reference binary mixtures.

**Keywords:** surface tension; binary mixtures; monoalcohols; water; acetonitrile; correlation equation

## 1. Introduction

Alcohols, either alone or in solutions (water, acetonitrile), are very widely used in the chemical, pharmaceutical and cosmetic industries, etc. [1–7].

In relation to the physico-chemical properties of these systems, surface tension and density should be mentioned, among others. Knowledge of both magnitudes is important in order to understand the molecular interactions among the components of the mixtures, and thus optimise their application to processes such as heat transfer, mass transfer, distillation, solubility, absorption, etc. [8–21].

The surface tension of liquids is determined by cohesion forces among their molecules, as a result of which the theoretical description of surface tension is complex. Over the years, a number of theoretical, empirical and semi-empirical models have been developed that are not always applicable to all types of mixtures [22].

In the present article, with the purpose of continuing and expanding the study of the physico-chemical properties of the systems (monoalcohols + water) [23] and [24], a description is made of the experimental results of surface tension ($\sigma$) and density ($\rho$) of binary mixtures of monoalcohols, water and acetonitrile at 298.15 K and at atmospheric pressure.

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*Email: rafael.belda-maximino@uv.es

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A correlation equation is presented for studying the surface tension of these mixtures, and comparisons are made of the experimental values of surface tension *versus* those calculated by means of the following empirical and theoretical equations. Finally, with the purpose of corroborating the validity of the correlation equation, the latter is applied to other reference binary mixtures.

## 2. Correlation equations and model

The present study describes three correlation equations. The first is based on the linear behaviour of the binary mixtures

$$\sigma = x_1 \cdot \sigma_1 + x_2 \cdot \sigma_2, \tag{1}$$

where $\sigma$ is the surface tension of the mixture, $\sigma_1$ and $\sigma_2$ the surface tensions of the pure components, and $x_1$, $x_2$ are the mole fractions of the components of the mixture. By expressing $x_1$ as a function of $x_2$, we have:

$$\sigma = \sigma_1 - (\sigma_1 - \sigma_2) \cdot x_2, \tag{2}$$

in which a correcting factor is introduced associated to the mole fraction $x_2$, to yield the following expression:

$$\sigma = \sigma_1 - (\sigma_1 - \sigma_2) \cdot x_2 \cdot \left( \frac{1 + m_1 \cdot (1 - x_2)}{1 + m_2 \cdot (1 - x_2)} \right), \tag{3}$$

which satisfies the conditions of the experiment, i.e., if:

$$x_2 = 0 \rightarrow \sigma = \sigma_1,$$

$$x_2 = 1 \rightarrow \sigma = \sigma_2,$$

and where $m_1$ and $m_2$ are parameters to be fitted. When $m_1 = m_2 = 0$ the equation respond to linear behaviour.

The second of the equations [25] is:

$$\sigma = \sigma_1 \cdot x_1^3 + a_1 \cdot x_1^2 \cdot x_2 + a_2 \cdot x_1 \cdot x_2^2 + \sigma_2 \cdot x_2^3, \tag{4}$$

which also satisfies the conditions of the experimental setting and where $a_1$ and $a_2$ are the parameters to fitting.

The third of the equations [26] is:

$$\sigma = \sigma_1 - (\sigma_1 - \sigma_2) \cdot x_2 - \left( \frac{A}{2RT} \right) \cdot (\sigma_1 - \sigma_2)^2 \cdot x_2 \cdot (1 - x_2), \tag{5}$$

where $A$ is the partial surface area of the mixture in centimetre square per gram mole, given by the expressions:

$$A = \left( \frac{A_1 + A_2}{2} \right) \quad \text{and} \quad A_i = (V_i)^{2/3} \cdot (N_0)^{1/3},$$

where $V_i$ is the molar volume of the pure component $i$, and $N_0$ is the Avogadro number.

In all cases, we used as estimation criterion the standard deviation $S$, defined by:

$$S = \sqrt{\frac{\sum_{i=1}^{n}\left\{\sigma_{\text{exp}} - \sigma_{\text{cal}}\right\}_i^2}{n-k}}, \tag{6}$$

where $n$ is the number of points of the sample and $k$ the number of parameters of the fitting equation.

## 3. Experimental section

The substances used in the mixtures were: methanol, ethanol, 1-propanol and acetonitrile, supplied by Aldrich, with a mass purity of $>$99.5% in all cases. Water used was distilled and deionised.

The mass of the mixtures was measured using a Mettler AT201 balance (repeatability $\pm 1 \times 10^{-5}$ g), and the uncertainty in the mole fraction was estimated to be $<10^{-4}$.

The measurements of the densities of the pure components and the binary mixtures was carried out using an Anton-Paar densitometer (model DMA 4500) with an uncertainly of $\pm 10^{-5}$ g cm$^{-3}$. The temperature of the measuring cell was maintained at 298.15 ± 0.01 K using a Grant thermostatic water bath.

The surface tensions of the pure liquids and their corresponding mixtures were measured with a thermostatted (within ±0.05 K) drop volume tensiometer (LAUDA TVT1) with an uncertainty of $10^{-2}$ mN m$^{-1}$. The detailed instrument design and experimental procedure have been described elsewhere [8].

Binary mixtures were prepared and distributed into three airtight containers. The measurements (in triplicate) in all cases showed deviation uncertainties of $<$1%.

## 4. Results and discussion

Table 1 shows the results of the experimental measurements of surface tension and density of the pure components, and are compared with literature values.

The experimental results for surface tension ($\sigma$) and density ($\rho$) of the mixtures at 298.15 K and at atmospheric pressure, as a function of the mole fraction ($x_2$) are shown in Table 2.

The deviation of surface tension was defined by:

$$\Delta\sigma = \sigma - x_1 \cdot \sigma_1 - x_2 \cdot \sigma_2. \tag{7}$$

The excess molar volume $V^{\mathrm{E}}$ is defined by:

$$V^{\mathrm{E}} = \frac{M_1 \cdot x_1 + M_2 \cdot x_2}{\rho} - \frac{M_1 \cdot x_1}{\rho_1} - \frac{M_2 \cdot x_2}{\rho_2}, \tag{8}$$

where $M_1$, $M_2$, $\rho_1$ and $\rho_2$ are the molecular weights and densities of the pure components, respectively.

Table 1. Surface tension and density of the pure components at 298.15 K and at atmospheric pressure.

| Compound | $\sigma$ (mN m$^{-1}$) This work | $\sigma$ (mN m$^{-1}$) Literature | $\rho$ (g cm$^{-3}$) This work | $\rho$ (g cm$^{-3}$) Literature |
|---|---|---|---|---|
| Water | 72.08 | 71.97 [17]<br>71.8 [18] | 0.99702 | 0.99704 [7]<br>0.9970 [11]<br>0.997048 [12] |
| Acetonitrile | 28.64 | 28.75 [19]<br>28.59 [20] | 0.77673 | 0.77663 [15]<br>0.7821 [16] |
| Methanol | 22.14 | 22.50 [19]<br>22.95 [21] | 0.78658 | 0.7872 [14]<br>0.7866 [11]<br>0.78635 [12] |
| Ethanol | 21.72 | 21.8 [19]<br>21.82 [21] | 0.78513 | 0.78493 [7]<br>0.7851 [11]<br>0.7873 [14] |
| 1-Propanol | 23.37 | 23.34 [19]<br>23.31 [21] | 0.79958 | 0.8020 [14]<br>0.799353 [12] |

Table 2. Surface tension and density for the indicated mixtures at 298.15 K and at atmospheric pressure.

| $x_2$ | $\sigma$ (mN m$^{-1}$) | $\rho$ (g cm$^{-3}$) | $x_2$ | $\sigma$ (mN m$^{-1}$) | $\rho$ (g cm$^{-3}$) |
|---|---|---|---|---|---|
| Water (1) ± methanol (2) | | | Water (1) ± ethanol (2) | | |
| 0.0000 | 72.08 | 0.99702 | 0.0000 | 72.08 | 0.99702 |
| 0.0272 | 63.52 | 0.99013 | 0.0143 | 60.68 | 0.99072 |
| 0.0588 | 56.21 | 0.98221 | 0.0372 | 50.33 | 0.98075 |
| 0.0942 | 50.52 | 0.97347 | 0.0995 | 38.22 | 0.96002 |
| 0.1433 | 44.98 | 0.96154 | 0.2007 | 31.28 | 0.93121 |
| 0.1942 | 41.45 | 0.94942 | 0.2988 | 28.28 | 0.90628 |
| 0.2727 | 37.12 | 0.93121 | 0.3996 | 26.48 | 0.88347 |
| 0.3601 | 33.35 | 0.91160 | 0.5009 | 25.25 | 0.86225 |
| 0.4576 | 29.96 | 0.89049 | 0.5993 | 24.36 | 0.84405 |
| 0.5676 | 27.48 | 0.86763 | 0.7004 | 23.63 | 0.82751 |
| 0.6923 | 25.64 | 0.84287 | 0.7991 | 23.04 | 0.81298 |
| 0.8351 | 24.06 | 0.81593 | 0.9007 | 22.52 | 0.79927 |
| 1.0000 | 22.14 | 0.78658 | 1.0000 | 21.72 | 0.78513 |
| Water (1) ± 1-propanol (2) | | | Water (1) ± acetonitrile (2) | | |
| 0.0000 | 72.08 | 0.99702 | 0.0000 | 72.08 | 0.99702 |
| 0.0477 | 64.26 | 0.97251 | 0.0133 | 62.18 | 0.99107 |
| 0.1110 | 54.19 | 0.94501 | 0.0327 | 53.10 | 0.98359 |
| 0.1924 | 42.31 | 0.91617 | 0.0732 | 45.09 | 0.96654 |
| 0.2703 | 29.28 | 0.89380 | 0.1546 | 38.71 | 0.93563 |
| 0.3459 | 25.64 | 0.87582 | 0.2264 | 34.27 | 0.91236 |
| 0.3999 | 25.52 | 0.86480 | 0.3007 | 32.64 | 0.89032 |
| 0.4999 | 25.41 | 0.84762 | 0.3969 | 31.34 | 0.86605 |
| 0.5882 | 25.23 | 0.83523 | 0.5060 | 30.41 | 0.84254 |
| 0.6897 | 24.20 | 0.82355 | 0.6371 | 29.69 | 0.81907 |
| 0.7874 | 23.85 | 0.81435 | 0.7980 | 29.11 | 0.79648 |
| 0.8861 | 23.57 | 0.80671 | 0.8929 | 28.87 | 0.78596 |
| 1.0000 | 23.32 | 0.79958 | 1.0000 | 28.64 | 0.77673 |

(*continued*)

Table 2. Continued.

| $x_2$ | $\sigma$ (mN m$^{-1}$) | $\rho$ (g cm$^{-3}$) | $x_2$ | $\sigma$ (mN m$^{-1}$) | $\rho$ (g cm$^{-3}$) |
|---|---|---|---|---|---|
| Acetonitrile (1) ± methanol (2) | | | Acetonitrile (1) ± ethanol (2) | | |
| 0.0000 | 28.64 | 0.77673 | 0.0000 | 28.64 | 0.77673 |
| 0.0934 | 28.35 | 0.77774 | 0.0704 | 27.99 | 0.77719 |
| 0.1514 | 28.17 | 0.77851 | 0.1325 | 27.46 | 0.77766 |
| 0.2296 | 27.85 | 0.77961 | 0.2005 | 26.90 | 0.77825 |
| 0.2950 | 27.52 | 0.78052 | 0.2961 | 26.13 | 0.77920 |
| 0.3648 | 27.11 | 0.78147 | 0.3762 | 25.51 | 0.78005 |
| 0.4267 | 26.72 | 0.78228 | 0.4438 | 25.02 | 0.78082 |
| 0.5163 | 26.10 | 0.78342 | 0.5092 | 24.56 | 0.78153 |
| 0.6391 | 25.19 | 0.78490 | 0.6004 | 23.97 | 0.78252 |
| 0.7215 | 24.55 | 0.78590 | 0.7054 | 23.33 | 0.78354 |
| 0.8014 | 23.91 | 0.78670 | 0.8009 | 22.79 | 0.78430 |
| 0.9125 | 22.94 | 0.78718 | 0.9031 | 22.21 | 0.78486 |
| 1.0000 | 22.14 | 0.78658 | 1.0000 | 21.72 | 0.78513 |
| Acetonitrile (1) ± 1-propanol (2) | | | | | |
| 0.0000 | 28.64 | 0.77673 | | | |
| 0.0713 | 27.89 | 0.77848 | | | |
| 0.1414 | 27.24 | 0.78029 | | | |
| 0.2296 | 26.54 | 0.78255 | | | |
| 0.2950 | 26.08 | 0.78426 | | | |
| 0.3648 | 25.64 | 0.78606 | | | |
| 0.4367 | 25.25 | 0.78792 | | | |
| 0.5163 | 24.87 | 0.78988 | | | |
| 0.6091 | 24.49 | 0.79207 | | | |
| 0.7215 | 24.10 | 0.79451 | | | |
| 0.8014 | 23.84 | 0.79609 | | | |
| 0.9125 | 23.54 | 0.79810 | | | |
| 1.0000 | 23.37 | 0.79958 | | | |

For each mixture, the deviation of surface tension $\Delta\sigma$ and the $V^E$ were fitted by the equation of Redlich–Kister [27]:

$$Y = x_1 \cdot x_2 \sum_{i=1}^{n} A_i \cdot (x_1 - x_2)^{i-1}, \tag{9}$$

where $Y = \Delta\sigma$ or $V^E$.

The coefficients $A_i$ of these fits are shown in Tables 3 and 4, and have been used to obtain the fitting curves, which are shown as a continuous line in Figures 1 and 2. For increased clarity, each have been divided into two: Figure 1(a), (b) and Figure 2(a), (b).

### 4.1. *Excess molar volumes*

Figure 1 shows the values of $V^E$ to be negative for the mixtures of water + (methanol, ethanol, 1-propanol, acetonitrile) and (acetonitrile + methanol), and positive for the mixture of (acetonitrile + 1-propanol), while the mixture of (acetonitrile + ethanol) shows both positive and negative values.

Table 3. Redlich–Kister coefficients $A_i$ and standard deviations $S$ of Equations (9) and (6) for $V^E$ in the investigated system.

| | $V^E_M$ (cm$^3$ mol$^{-1}$) | | | | |
|---|---|---|---|---|---|
| System | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $S$ |
| Water + methanol | −1.57120 | 0.34441 | −0.11292 | −0.27296 | 0.0179 |
| Water + ethanol | −4.89340 | 0.92075 | −0.33934 | −2.14530 | 0.0263 |
| Water + 1-propanol | −2.74390 | 1.01730 | −1.18840 | 0.67261 | 0.0110 |
| Water + acetonitrile | −1.81830 | 1.56250 | 0.03971 | 0.42113 | 0.0393 |
| Acetonitrile + methanol | −0.52469 | −0.27150 | −0.21941 | −0.41391 | 0.0062 |
| Acetonitrile + ethanol | −0.08284 | −0.40344 | −0.03175 | 0.06262 | 0.0381 |
| Acetonitrile + 1-propanol | 0.21277 | −0.35310 | 0.08809 | 0.10761 | 0.0153 |

Table 4. Redlich–Kister coefficients $A_i$ and standard deviations $S$ of Equations (9) and (6) for $\Delta\sigma$ in the investigated system.

| | $\Delta\sigma$ (mN m$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| System | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $A_5$ | $S$ |
| Water + methanol | −74.9190 | 43.1810 | −0.2624 | 71.8010 | −117.9700 | 0.0041 |
| Water + ethanol | −87.4420 | 38.8820 | −20.0610 | 249.6400 | −269.1200 | 0.1042 |
| Water + 1-propanol | −89.9460 | 59.5550 | −52.6780 | 205.2900 | −203.5100 | 0.0482 |
| Water + acetonitrile | −81.3940 | 32.0790 | 3.4851 | 226.4100 | −271.4200 | 0.1243 |
| Acetonitrile + methanol | 3.2766 | −1.1622 | 1.2629 | 0.9622 | −1.7695 | 0.0075 |
| Acetonitrile + ethanol | −2.2271 | 0.1904 | 0.7889 | −0.0010 | −1.1475 | 0.0092 |
| Acetonitrile + 1-propanol | −4.2316 | 1.4302 | −0.2252 | −0.3799 | −0.5023 | 0.0042 |

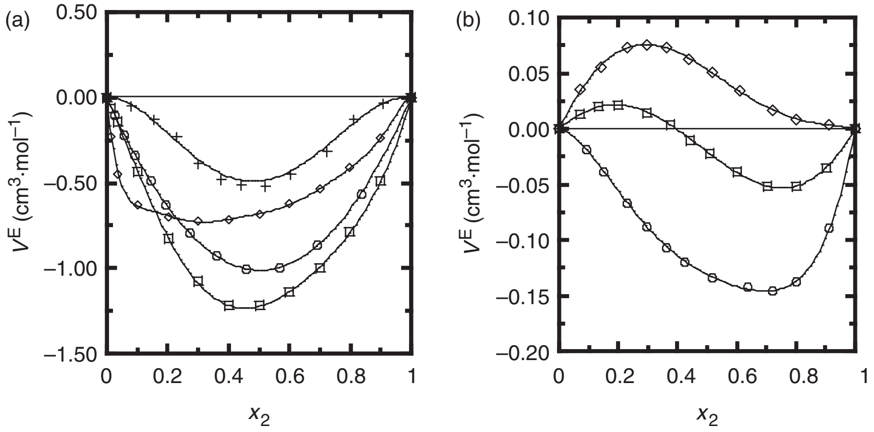

Figure 1. Plot of $V^E$ against mole fraction $x_2$ at 298.15 K and at atmospheric pressure, for the mixtures: (a) water with: ○, methanol; □, ethanol; ◇, 1-propanol; + acetonitrile; and (b) acetonitrile with: ○, methanol; □, ethanol; ◇, 1-propanol. The points are measured, and the lines are calculated from Equation (9), using the parameters in Table 3.

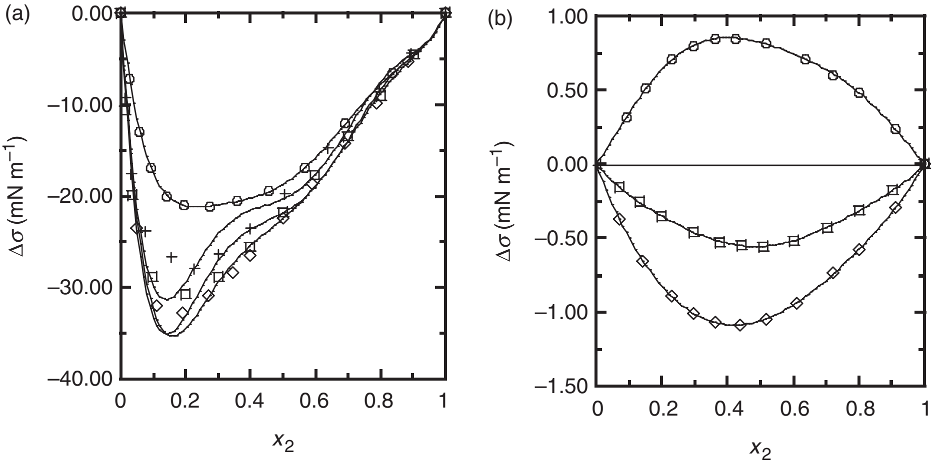

Figure 2. Plot of $\Delta\sigma$ against mole fraction $x_2$ at 298.15 K and at atmospheric pressure, for the mixtures: (a) water with: ○, methanol; □, ethanol; ◇, 1-propanol; +, acetonitrile; and (b) acetonitrile with: ○, methanol; □, ethanol; ◇, 1-propanol. The points are measured, and the lines are calculated from Equation (9), using the parameters in Table 4.

The minimum $V^E$ corresponds to the mixture (water + ethanol) and the maximum $V^E$ to the mixture (acetonitrile + 1-propanol).

The observed $V^E$ values are the resultant of chemical and physical forces and they may be broadly recognised as: (a) specific interactions appearing in the mixture between dissimilar molecules by dipole–dipole; (b) specific interactions appearing in the mixture between dissimilar molecules by electron donor–acceptor complexes; (c) the breaking of liquid order on mixing with the second component; and (d) non-specific physical interactions and unfavourable interactions between unlike molecules. Generally, the first two factors contribute to the diminishing of volume and the latter two factors contribute to the expansion the volume [28]. From Table 2 and Figure 1, it is clear that the volume reduction factors are preponderant for the mixtures water + (methanol, etanol, 1-propanol, acetonitrile) and (acetonotrile + metanol).

The positive values of $V^E$ of the mixture (acetonitrile + 1-propanol) may be explained by the dominance of H bond rupture in 1-propanol over the dipole–dipole interactions between 1-propanol and the acetonitrile molecules, and by the expansion processes that occur in these mixtures.

Comparisons have been made of the experimental values of $V^E$ and those found in the literature [12,24,29]. For the mixtures of (monoalcohols + water), the values are always negative and with similar point distributions – exhibiting minimum values that in all cases are around mole fraction $x_2 = 0.5$. In the case of the mixture (methanol + water), the value is close to $-1\,\mathrm{cm^3\,mol^{-1}}$. In the system (ethanol + water), the value is $-1.2\,\mathrm{cm^3\,mol^{-1}}$ according to our study and [24], *versus* $-1.1\,\mathrm{cm^3\,mol^{-1}}$ according to [12]. The reason for this difference could be the important volatility of ethanol. In the system (1-propanol + water), the values in all cases are close to $-0.7\,\mathrm{cm^3\,mol^{-1}}$.

In the mixture (acetonitrile + methanol), the values are always negative and with similar point distributions – exhibiting a minimum around mole fraction $x_2 = 0.7$ of $-0.16\,\mathrm{cm^3\,mol^{-1}}$. In the mixture (acetonitrile + ethanol) the values are both positive and negative, with similar point distributions and exhibiting a relative maximum at mole fraction $x_2 = 0.2$ of $0.018\,\mathrm{cm^3\,mol^{-1}}$ and a relative minimum at mole fraction $x_2 = 0.8$ of $-0.07\,\mathrm{cm^3\,mol^{-1}}$.

### 4.2. *Excess surface tension*

Figure 2 shows that $(\Delta\sigma)$ is positive for the system (acetonitrile + methanol) and negative for the rest of the mixtures studied.

The mixtures in which $(\Delta\sigma)$ is negative reflect depletion of one of the components, that with the greatest surface tension, which in the systems water + (methanol, ethanol, 1-propanol, acetonitrile) corresponds to water, while in the systems acetonitrile + (methanol, ethanol, 1-propanol) it corresponds to acetonitrile, at the liquid–vapour interface.

In the mixtures of water + (methanol, ethanol, 1-propanol), $(\Delta\sigma)$ becomes more negative as the length of the studied alcohol chain increases. The same occurs with the mixtures of acetonitrile + (ethanol, 1-propanol).

In the mixture (acetonitrile + methanol), $(\Delta\sigma)$ is positive, which indicates enrichment of the component with greater surface tension (corresponding to acetonitrile in this system).

Comparisons have been made of the experimental values of $(\sigma)$ with those of the literature [30–32] – revealing similar point distributions, though in the mixtures (water + ethanol), we found that in the interval $x_2 = (0.2, 0.3)$, the differences exceed by more than $1\,\mathrm{mN\,m^{-1}}$ those reported in [32] and by $0.8\,\mathrm{mN\,m^{-1}}$ those reported in [33]. These discrepancies could be the result of substance loss, since ethanol is very volatile. However, in the system (water + 1-propanol), the differences with respect to [33] and [34] are minimal and less than 1.5%.

Figure 2(a) and the data in Table 4 indicate that for mixtures of water + (methanol, ethanol, 1-propanol, acetonitrile), the fitting of $(\Delta\sigma)$ as a function of mole fraction $(x_2)$ via Equation (9), with five parameters, yields standard deviation values $S$ that exceed 7% on average.

These systems, as most of the cases found in the industrial setting, involve the difficulty posed by non-linear mixture behaviour. As a result, rigorous data must be available, with models capable of providing a reliable estimation of the surface tension behaviour of mixtures.

For this motive and with the purpose of studying correlation the surface tension $\sigma$ of the binary mixtures of monoalcohols, water and acetonitrile as a function of the mole fraction $(x_2)$, Equation (3) is presented and comparisons are made of the experimental surface tension $(\sigma)$ versus the values obtained with Equations (3)–(5).

The results of the fits made with Equations (3)–(5) are provided in Table 5.

From Table 5 it is deduced that out of Equations (3)–(5), the one offering the best results is Equation (3), except in the case of the system (acetonitrile + ethanol), where Equation (4) yields better results than Equation (3). The poorest results correspond to Equation (5).

From the results reported in Table 5, and in order to corroborate the validity of Equation (3), we obtained 23 files from a recent literature review [17,35–38] (Table 6) studying the surface tension of different binary mixtures of liquids at atmospheric pressure and over different temperature ranges. Although the number of files is not extensive, they

Table 5. Coefficients $m_1$, $m_2$ and $a_1$, $a_2$ obtained from the fits of Equations (3) and (4), with the corresponding standard deviations $S$ calculated by Equation (6), including those obtained for Equation (5), for the systems analysed.

| | Equation (3) | | | Equation (4) | | | Equation (5) |
|---|---|---|---|---|---|---|---|
| System | $m_1$ | $m_2$ | $S$ | $a_1$ | $a_2$ | $S$ | $S$ |
| Water + methanol | −0.06656 | −0.87362 | 0.0089 | 17.603 | 106.280 | 0.0659 | 6.0312 |
| Water + ethanol | −0.03990 | −0.95321 | 0.0003 | −37.762 | 118.410 | 0.1608 | 9.7753 |
| Water + 1-propanol | −0.02794 | −0.99011 | 0.0407 | −46.333 | 125.680 | 0.1821 | 11.3748 |
| Water + acetonitrile | 0.00413 | −0.95230 | 0.0120 | −22.553 | 138.640 | 0.1349 | 10.7120 |
| Acetonitrile + methanol | −0.80897 | −0.39491 | 0.0006 | 83.644 | 74.465 | 0.0007 | 0.9284 |
| Acetonitrile + ethanol | 0.12205 | −0.16548 | 0.0004 | 76.626 | 70.111 | 0.0004 | 0.0367 |
| Acetonitrile + 1-propanol | 0.15603 | −0.46180 | 0.0004 | 75.060 | 72.394 | 0.0007 | 0.5069 |

Table 6. Components of the mixtures used in the reference files.

| | Mixture | | |
|---|---|---|---|
| File | Component (1) + Component (2) | $T$ (K) | Ref. |
| 1 | Water + 1,2-butanediol | 298.15 | [17] |
| 2 | Water + 1,3-butanediol | 298.15 | [17] |
| 3 | Water + 1,4-butanediol | 298.15 | [17] |
| 4 | Water + 2,3-butanediol | 298.15 | [17] |
| 5 | Cyclohexane + heptane | 297.82 | [35] |
| 6 | Toluene + propanone | 297.82 | [35] |
| 7 | Cyclohexane + propanone | 297.82 | [35] |
| 8 | $Ar + N_2$ | 83.82 | [36] |
| 9 | $O_2 + N_2$ | 83.82 | [36] |
| 10 | $CH_4$-$N_2$ | 91 | [36] |
| 11 | $CH_4$-CO | 91 | [36] |
| 12 | Etanol + octane | 298.15 | [37] |
| 13 | 1-Propanol + octane | 298.15 | [37] |
| 14 | 1-Butanol + octane | 298.15 | [37] |
| 15 | 1-Pentanol + octane | 298.15 | [37] |
| 16 | 1-Hexanol + octane | 298.15 | [37] |
| 17 | 1-Heptanol + octane | 298.15 | [37] |
| 18 | 1-Octanol + octane | 298.15 | [37] |
| 19 | Tetrahydrofuran + 1-hexanol | 298.15 | [38] |
| 20 | Tetrahydrofuran + 1-heptanol | 298.15 | [38] |
| 21 | 1-Octanol + tetrahydrofuran | 298.15 | [38] |
| 22 | 1-Nonanol + tetrahydrofuran | 298.15 | [38] |
| 23 | 1-Decanol + tetrahydrofuran | 298.15 | [38] |

contain the four different types of distributions $\sigma = f(x_2)$ that may be found in studies of this kind and which are shown in Figure 3 – though for improved clarity the latter has been divided into four parts: Figure 3(a)–(d). The distributions represented in the Figure 3(a)–(d)) have been fitted by Equation (3).

The files indicated in Table 6 have been fitted by means of Equations (3)–(5), and the results of these fits are reported in Table 7. In Table 7, the values $S$ of Equation (5) could not be completed in 16 of the files, due to missing densities of the corresponding mixtures.

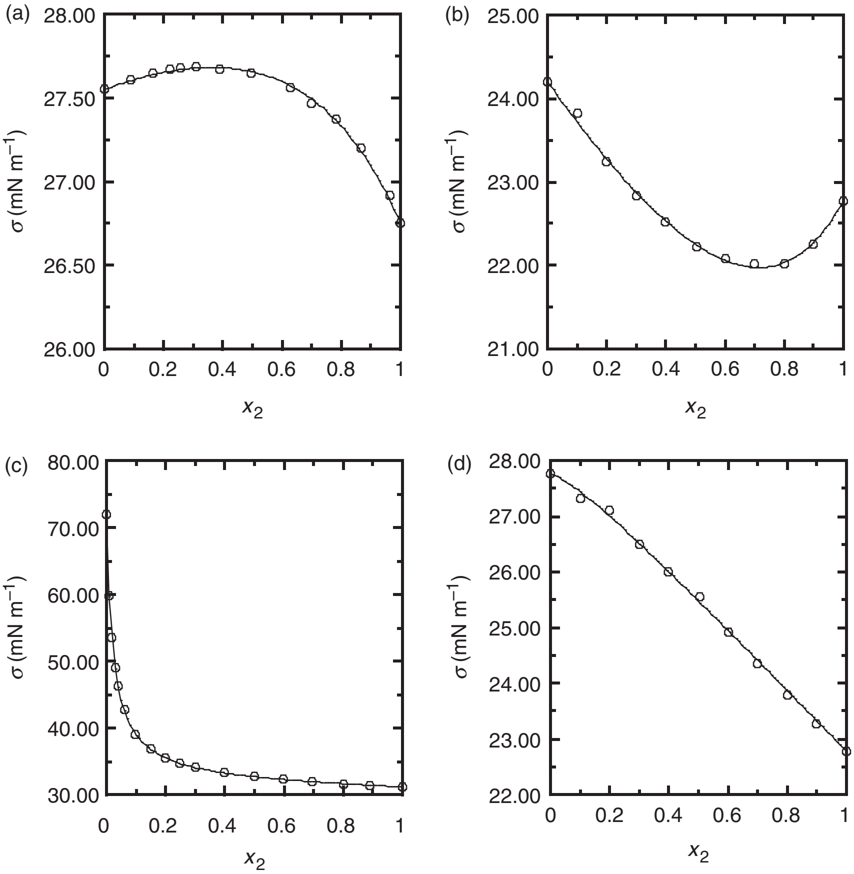

Figure 3. Distribution of points $\sigma = f(x_2)$ corresponding to the files: (a) (1-nonanol + tetrahydrofuran), (b) (cyclohexane + propanone), (c) (water + 1,2-butanediol), (d) (toluene + propanone), fitted by Equation (3).

From Table 7 it is deduced that Equations (3) and (4) yield better results than Equation (5). In turn, it is seen that in 8 of the 23 files analysed, the values of the standard deviation $S$ for Equation (4) are better than for Equation (3). However, the mean values of the deviation standard $\overline{S}$ for Equation (8) are (807% and 4844%) better than for Equations (4) and (5), respectively.

## 5. Conclusions

From the current study it is deduced that the negative values of $V^E$ correspond to the mixtures of water + (methanol, ethanol, 1-propanol, acetonitrile) and (acetonitrile + methanol), while the positive values correspond to the system (acetonitrile + 1-propanol). The mixture (acetonitrile + ethanol) in turn presents both positive and negative values.

The minimum ($V^E$) corresponds to the mixture (water + ethanol), and the maximum to the mixture (acetonitrile + 1-propanol).

Table 7. Standard deviations $S$ calculated by Equation (6), and mean standard deviations $\overline{S}$ for the reference files.

| | $S$ | | |
|---|---|---|---|
| File | Equation (3) | Equation (4) | Equation (5) |
| 1 | 0.0002 | 0.2062 | – |
| 2 | 0.0010 | 0.1127 | – |
| 3 | 0.0043 | 0.0630 | – |
| 4 | 0.0080 | 0.1320 | – |
| 5 | 0.0017 | 0.0015 | – |
| 6 | 0.0026 | 0.0020 | – |
| 7 | 0.0019 | 0.0022 | – |
| 8 | 0.0037 | 0.0063 | – |
| 9 | 0.0016 | 0.0012 | – |
| 10 | 0.0170 | 0.0172 | – |
| 11 | 0.0100 | 0.0097 | – |
| 12 | 0.0010 | 0.0020 | 0.1151 |
| 13 | 0.0007 | 0.0021 | 0.1607 |
| 14 | 0.0010 | 0.0004 | 0.1358 |
| 15 | 0.0019 | 0.0004 | 0.1353 |
| 16 | 0.0012 | 0.0003 | 0.1025 |
| 17 | 0.0008 | 0.0005 | 0.0923 |
| 18 | 0.0007 | 0.0005 | 0.1925 |
| 19 | 0.0005 | 0.0007 | – |
| 20 | 0.0005 | 0.0007 | – |
| 21 | 0.0007 | 0.0009 | – |
| 22 | 0.0005 | 0.0008 | – |
| 23 | 0.0010 | 0.0010 | |
| | | $\bar{S}$ | |
| | 0.0027 | 0.0245 | 0.1335 |

In turn, the values of $(\Delta\sigma)$ are positive for the mixture (acetonitrile + methanol) and negative for the rest of the mixtures analysed.

In the mixtures of water + (methanol, ethanol, 1-propanol), $(\Delta\sigma)$ becomes more negative as the length of the alcohol chain is increased ($C_1{-}C_3$). The same applies to the mixtures of acetonitrile + (ethanol, 1-propanol).

Regarding the study of surface tension, it is shown that for the mixtures of monoalcohols, water and acetonitrile, Equation (3) yields better results for the standard deviation $S$ than Equations (4) and (5), except in the case of the system (acetonitrile + ethanol), where Equation (4) offers better results than Equation (3). In turn, Equation (4) yields better results than Equation (5).

In all the reference files, Equations (3) and (4) yield better results than Equation (5), and in 15 of them Equation (3) offers better results than Equation (4).

In addition, for both the binary mixtures of monoalcohols, water and acetonitrile and for the reference files, Equation (3) yields better results for the mean standard deviation $\overline{S}$ than Equations (4) and (5). Consequently, Equation (3) can be considered an adequate correlation equation for the study of the surface tension of liquid binary mixtures.

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