Surface study of binary mixtures containing chlorinated and oxygenated compounds

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ABSTRACT

We report in this work, experimental surface tensions for binary mixtures of isomeric chlorobutanes with butyl ethyl ether or diisopropyl ether from $T = 283.15$ K to 303.15 K measured with a drop volume tensiometer. The surface tension data have been correlated with a Redlich–Kister type equation. More information about the surface behaviour can be obtained combining these results with previously reported VLE measurements to calculate the excess surface composition of ether in the mixture. Finally, the results have been compared to the predictions obtained using a group contribution method.

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1. Introduction

In the last few years, our research group has been carrying out a comprehensive thermodynamic study about mixtures formed by chlorobutanes and ethers [1–4] in order to go deeply into the effect of energetic and structural factors in their behaviour. Moreover, the study of ether mixtures is important since oxygenated compounds are added to improve the octane rating and the pollution-reducing capability of gasoline [5–10].

The main aim of this work is to study the surface behaviour of mixtures formed by several haloalkanes and several ethers. For this purpose, we have used surface tension and several derived properties to get the molecular information related to the surface behaviour and the adsorption phenomenon that is carried out during the mixture process.

The study of the surface behaviour of a mixture has been used so to get information about the molecular adsorption process of the components of a mixture [11–14]. It is also well known that surface tension of a substance can be related to the extent of the intermolecular interactions of the molecules of the substance: molecules tend to stay in the bulk of the system due to the increase of their energy when they are in the surface. The more and stronger intermolecular interactions between molecules, the steeper is the tendency and higher values of surface tension the substance presents. Furthermore, if a mixture is under study instead of a pure substance, there is a different distribution of the molecules in the surface, and an adsorption phenomenon appears.

The distribution of the molecules in the surface can be quantified through surface excess concentration. Exploring the behaviour of surface tension and the excess surface concentration of a mixture, information about the extent of weakening of the intermolecular properties of the pure components due to the mixture process and the formation of new ones between the different components of the mixture can be obtained as well as how the adsorption process has been carried out and the amount of molecules of each component migrated to the surface. Due to the nature of the compounds this study will also give some insights into the dipole–dipole intermolecular interaction between of the compounds of the mixture and the specific donor–acceptor interactions between the chlorine and oxygen atoms.

This work reports experimental results of surface tensions for some binary mixtures containing an isomeric chlorobutane: 1-chlorobutane, 2-chlorobutane, 2-methyl-1-chloropropane or 2-methyl-2-chloropropane and butyl ethyl ether or diisopropyl ether measured with a drop volume tensiometer in the temperature range (283.15–313.15) K. Combining the surface tension values with vapor–liquid equilibrium results excess surface concentrations were also calculated in the temperature range (288.15–308.15) K.

Finally, using our experimental data we have checked the accuracy in the prediction of surface tensions of a group-contribution method [15]. This method combines the Sprow and Prausnitz model for the description of surface tensions of liquid mixtures [16] with a group contribution method for the calculation of activity coefficients [17]. This method has been used to predict the surface behaviour of binary and multicomponent mixtures with satisfactory results [18–24].

As far as we know, there are not references in the literature about the surface tensions for these systems.

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Table 1
Surface tension, σ, of the pure compounds and comparison with literature data at $T = 298.15$ K.

Compound	σ/mN·m^{-1} at T/K							
	283.15	288.15	293.15	298.15		303.15	308.15	313.15
	exptl	exptl	exptl	exptl	lit	exptl	exptl	exptl
1-Chlorobutane	24.83	24.34	23.74	23.29	23.10 [a]	22.69	22.16	21.55
2- Chlorobutane	23.79	23.01	22.29	21.83		21.18	20.43	19.43
1-Chloro-2-methylpropane	23.83	22.99	22.31	21.80	21.40 [a]	21.08	20.23	19.23
2-Chloro-2-methylpropane	20.75	20.10	19.62	18.92		18.45	17.82	16.98
Butyl ethyl ether	21.95	21.43	20.96	20.42	20.25 [b]	19.92	19.44	18.98
Diisopropyl ether	18.51	18.12	17.74	17.34	17.31 [c]	16.97	16.58	16.16

[a] Ref. [27].
[b] Ref. [28].
[c] Ref. [6].

2. Experimental section

The chemicals employed were 1-chlorobutane, 2-chlorobutane, 2-methyl-2-chloropropane, butyl ethyl ether and diisopropyl ether (mass fraction > 0.99) obtained from Aldrich and 2-methyl-1-chloropropane (mass fraction > 0.99) provided by Fluka. No additional purification has been carried out.

The surface tension of the pure liquids and their corresponding mixtures were measured with a drop volume tensiometer Lauda TVT-2 [25] with an uncertainty of ± 0.01 mN.m^{-1}. The temperature was kept constant within ± 0.01 K by means of an external Lauda E-200 thermostat. The surface tension, σ, is calculated from the determined drop volume, V, using the following equation:

$$\sigma = \frac{\Delta\rho \cdot g \cdot V}{2\pi \cdot r_{cap} \cdot f} \qquad (1)$$

where $\Delta\rho$ is the density difference of the two adjacent phases, g is the acceleration constant, r_{cap} is the outer radius of the capillary and the function f denotes a correction function necessary to relate the surface tension to the volume of the detached drop [25]. The proper operation of the device was satisfactorily checked by measuring the surface tension of water.

The densities of the pure compounds and mixtures were obtained from interpolation of our previous density measurements [4,26].

The surface tensions of the pure compounds at working temperatures together with literature values at $T = 298.15$ K [6,27,28] are shown in Table 1.

All mixtures were prepared by mass using a Sartorius CP225D precision balance with an uncertainty of $\pm 1 \cdot 10^{-5}$ g, the corresponding uncertainty of the mole fraction calculated is estimated to be better than 10^{-4}.

3. Results and discussion

The surface tension values of all the mixtures studied in this work from $T = 283.15$ K to 313.15 K can be found in the supplementary material. The surface tensions are graphically represented in Figs. 1 to 8.

To correlate the surface tension data, the following equation has been used:

$$\sigma = x_1 \cdot \sigma_1 + x_2 \cdot \sigma_2 + x_1 \cdot x_2 \cdot \sum_{i=0}^{r} \sum_{j=0}^{p} A_{ij}(x_1 - x_2)^i (T - T_0)^j \qquad (2)$$

where x_i and σ_i are the corresponding mole fraction and surface tension of component i, T is the temperature, T_0 is a reference temperature ($T_0 = 283.15$ K), and A_{ij} are adjustable parameters determined by the method of least-squares, these parameters are summarized together with the standard deviations s in Table 2.

The main feature of these systems is that the surface tension deviation, that is the deviation of surface tension behaviour with respect to a lineal composition dependence is negative, although for the system 2-chloro-2-methylpropane + butyl ethyl ether this deviation is slightly positive. There is a significant difference between the systems containing one or another oxygenated compound; the magnitude of this deviation is higher in absolute value for the mixtures containing the ether with lower surface tension, that is diisopropyl ether. On the other hand, among the isomeric chlorobutanes the surface tension deviation is higher in absolute vale for the mixtures formed by 1-chlorobutane, which shows the higher surface tension. With respect to the temperature dependence of the surface tension deviation, its value decrease with temperature except for the mixtures containing 2-chloro-2-methylpropane. It can be also outlined as the presence of negative aneotropes [29], negative surface azeotropy, for some of the mixtures containing diisopropyl ether, at low temperatures for the mixtures containing 1-chlorobutane, 2-chlorobutane or 1-chloro-2-methylpropane and at high temperatures for the mixture involving 2-chloro-2-methylpropane. Information about composition and surface tension of the aneotropes is summarized in Table 3.
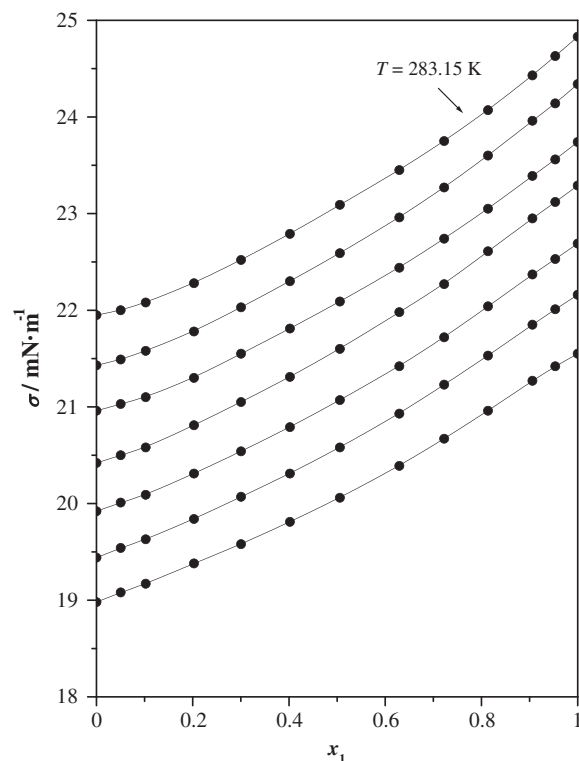

Fig. 1. Surface tensions, σ, of the binary mixture 1-chlorobutane with butyl ethyl ether. Experimental data (●); fitting equation (——).