



Thermodynamic study of the surface of liquid mixtures containing pyridinium-based ionic liquids and alkanols



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ABSTRACT

Surface tension for seven binary mixtures containing a pyridinium-based ionic liquid (1-propylpyridinium tetrafluoroborate, 1-butylpyridinium tetrafluoroborate, 1-butyl-3-methylpyridinium tetrafluoroborate, or 1-butyl-4-methylpyridinium) and a short chain alkanol (methanol or ethanol) were determined at the temperatures: (293.15, 303.15, 313.15, and 323.15) K. From these data, the surface tension deviations were calculated. These deviations were correlated using a Redlich–Kister polynomial expansion. Moreover, relative adsorptions of alkanol at the (air + liquid) interface were calculated from the Gibbs isotherm.

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1. Introduction

The most common ionic liquids are formed by imidazolium derivative cations combined with different anions such as tetrafluoroborate, bis(trifluoromethylsulfonyl)imide, chloride, hexafluorophosphate or dicyanamide. However, pyridinium-based ionic liquids are receiving an increasing interest during the last decade, since they show good thermal stability and they are less expensive than imidazolium-based compounds [1].

Ionic liquids (ILs) have been nominated “designer solvents”, because there exists an almost unlimited number of potential combinations of cations and anions that could be interesting from an industrial point of view. Moreover, the properties can be modified mixing ionic liquids with organic solvents, thus enabling the mixtures to be used in a broad number of technological processes [2–4]. The study of thermodynamic properties of these mixtures provides useful information in order to correlate composition with their potential applications. In this sense, an important property is the surface tension of the mixtures. The knowledge of the surface composition in a mixture supplies information about cohesive forces between the components; moreover, surface tension values reflect the organisation on the bulk and migration of molecules to the surface [5].

Publications about the surface tension of binary mixtures containing ionic liquids are scarce, some of these papers are briefly

noted below. Rilo *et al.* [6] have determined the surface tension of the ionic liquid family 1-alkyl-3-methyl imidazolium tetrafluoroborate with water and ethanol at $T = 298.15$ K. The analysis of the data shows that at the surface level the behaviour of the mixture containing water or methanol is completely different. Domańska *et al.* [7] have measured the surface tension of binary mixtures of imidazolium and ammonium based ionic liquids with alcohols, or water at $T = 298.15$ K, in order to test the influence of the cation, or anion alkyl chain length on the surface tension. Domańska *et al.* [8] have also investigated the influence of the temperature on the surface behaviour of the mixtures formed by 1-butyl-3-methylimidazolium thiocyanate and alcohols. Oliveira *et al.* [5] have determined the surface tension of binary mixtures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with other ionic liquids with a common anion, namely 1-butyl-2,3-dimethylimidazolium, 3-methyl-1-propylpyridinium, 1-methyl-1-propylpyrrolidinium and 1-methyl-1-propylpiperidinium, at $T = 298.2$ K and atmospheric pressure over the whole range of composition. The surface tension deviation and Gibbs adsorption isotherms were obtained from experimental measurements. Values of surface tension deviations were small, indicating that the IL cation core seems to have a limited influence on the mixtures behaviour. Jiang *et al.* [9] have measured the density and surface tension of the binary mixture constituted for 1-butyl-3-methylimidazolium L-lactate plus water or several alcohols (methanol, ethanol, and 1-butanol) over the whole range of compositions from $T = (298.15$ to $318.15)$ K at atmospheric pressure. From experimental results, these authors have obtained surface tension deviations.

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Values of the surface tension deviation show sigmoid shape for mixtures formed by methanol and ethanol, and negative values for 1-butanol mixtures.

In order to increase the information about the surface tension of binary mixtures containing ionic liquids, we report a comprehensive study of the surface tension of the systems formed by a pyridinium-based ionic liquids (1-propylpyridinium tetrafluoroborate [ppy][BF₄], 1-butylpyridinium tetrafluoroborate [bpy][BF₄], 1-butyl-3-methylpyridinium tetrafluoroborate [b3mpy][BF₄], or 1-butyl-4-methylpyridinium tetrafluoroborate [b4mpy][BF₄]) and two short chain alcohols (methanol or ethanol). These mixtures were studied at atmospheric pressure over the temperature range $T = (293.15 \text{ to } 323.15) \text{ K}$ and over the whole composition range. It is noted that [ppy][BF₄] is not miscible with higher alkanols, on the other hand the system {[bpy][BF₄] + ethanol} presents solubility problems at $T = 293.15 \text{ K}$. The results obtained have been compared in order to establish the influence on the surface behaviour of this kind of systems of both the cation structure of the ionic liquid and the chain length of the alkanol.

2. Experimental

In table 1, the information about the ionic liquids and alkanols used in this work is summarized. To decrease the amount of water as much as possible, the ILs were dried for 24 h stirring under vacuum of about 0.05 kPa. The water content of the liquid was less than 100 ppm as determined by Karl Fischer titration using an automatic titrator Crison KF 1S-2B.

The surface tension, σ , of the pure compounds and their binary mixtures were measured using a Lauda TVT-2 drop volume tensiometer. This tensiometer determines the property measuring the volume of a drop detaching from a capillary of known diameter. The detailed design and experimental procedure have been described elsewhere [10]. The temperature was kept constant within $\pm 0.01 \text{ K}$ by means of an external Lauda E-200 thermostat. At least 50 drop volume determinations per sample were performed and the results were averaged. Densities of the pure compounds and mixtures at operating temperatures required to calculate surface tension from volume drop determinations have been reported in previous papers [11–13]; these densities were measured using an AntonPaar DMA-5000 vibrating tube densimeter. The uncertainty of the surface tension measurements is $\pm 0.5\%$. The surface tension of the pure compounds together with literature values at $T = 303.15 \text{ K}$ [14–16] are shown in table 2.

3. Results and discussion

The surface tension deviation is a quantity widely used to describe the variation of the surface tension of a liquid mixture with composition, [9,17–21]. Surface tension deviations can be calculated by the expression:

$$\Delta\sigma = \sigma - x_1\sigma_1 - x_2\sigma_2, \quad (1)$$

where σ is the surface tension of the mixture and x_i and σ_i refer to the mole fraction and the surface tension of the component i ,

respectively. These surface tension deviations are graphically represented in figures 1–7. Experimental surface tension together with calculated surface tension deviations for the studied mixtures at working temperatures are given in the Supplementary material.

The surface tension deviations were correlated using the Redlich–Kister equation [22]:

$$\Delta\sigma = x_1x_2 \sum_{i=0}^n A_i(x_1 - x_2)^i, \quad (2)$$

where A_p are adjustable parameters determined by the method of least squares. The values of these parameters are given in table 3 along with the corresponding standard deviation.

As can be observed in the figures, surface tension deviations in the mixtures containing methanol are positive for [bpy][BF₄], [b3mpy][BF₄] and [b4mpy][BF₄]. However they are negative for [ppy][BF₄] over the whole range of composition and they increase when temperature rises. Additionally, the maximum values are slightly shifted towards the rich ionic liquid region for binary mixtures containing [b3mpy][BF₄] or [b4mpy][BF₄], although for [bpy][BF₄] the maximum is shown at $x_1 \approx 0.5$. On the other hand for [ppy][BF₄], the minimum is presented at $x_1 \approx 0.4$. When $\Delta\sigma$ values obtained for the different ionic liquids are compared, it can be seen that the sequence is the following: [b4mpy][BF₄] > [b3mpy][BF₄] > [bpy][BF₄].

Binary mixtures containing ethanol show negative surface tension deviation values in all systems studied and this property decreases in absolute value when temperature increases. Minimum values are slightly displaced towards the rich composition in ethanol. In this case, the absolute values of $\Delta\sigma$ present the sequence: [b4mpy][BF₄] < [b3mpy][BF₄] < [bpy][BF₄].

Before analysing the surface behaviour of the mixtures, it is important to indicate that some properties of the pure ILs were previously investigated in our research group [23–25]. The data obtained in these studies have been used here to facilitate a complete interpretation of the phenomena that occur in the mixture. From previous studies, it can be concluded that [bpy][BF₄] shows stronger self-interactions than [b3mpy][BF₄] and [b4mpy][BF₄]. This behaviour is related with the existence of a methyl group in cations [b3mpy] and [b4mpy] that hinders self-interactions. Surface tension values of pure liquids confirm this tendency, since σ values at all temperatures are greater for [bpy][BF₄] than for [b3mpy][BF₄] or [b4mpy][BF₄]. Moreover, differences between [b3mpy][BF₄] and [b4mpy][BF₄] are scarce, with σ values of [b4mpy][BF₄] slightly higher than those of [b3mpy][BF₄]. Kolbeck et al. [26] found that aliphatic alkyl chains generally dominate the composition at the outer surface of pure ILs, independently of where these chains are attached to the cation. Consequently, the absence of the methyl substituent in [bpy] increases the surface tension of [bpy][BF₄]. The comparison between σ values for [ppy][BF₄] and [bpy][BF₄] shows that the increment of the length of the alkyl chain from propyl to butyl leads to a decrease of the surface tension.

The main component in the surface of a binary liquid mixture is the compound with the lower surface tension [27,28]. In the

TABLE 1
Provenance and purity of the materials studied.

| Chemical name | Source | Initial mass fraction purity | Final mass fraction purity | Analysis method |
|--|---------------|------------------------------|----------------------------|-----------------|
| 1-Propylpyridinium tetrafluoroborate | Iolitec | 0.99 | 0.99 | |
| 1-Butylpyridinium tetrafluoroborate | Iolitec | 0.99 | 0.99 | |
| 1-Butyl-3-methylpyridinium tetrafluoroborate | Iolitec | 0.99 | 0.99 | |
| 1-Butyl-4-methylpyridinium tetrafluoroborate | Iolitec | 0.99 | 0.99 | |
| Methanol | Sigma–Aldrich | 0.998 | 0.998 | GC |
| Ethanol | Acros | 0.998 | 0.998 | GC |

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