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Interfacial tensions of pyridinium-based ionic liquids and *n*-alkanes or *n*-alkanols

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ABSTRACT

Interfacial tensions of sixteen systems (pyridinium-based ionic liquid + *n*-alkane or *n*-alkanol) have been measured in the temperature range (283.15–313.15) K and at pressure of 0.1 MPa. The ionic liquids used were: 1-butylpyridinium tetrafluoroborate, 1-butyl-2-methylpyridinium tetrafluoroborate, 1-butyl-3-methylpyridinium tetrafluoroborate, and 1-butyl-4-methylpyridinium tetrafluoroborate. On the other hand, the organic solvents were: *n*-hexane, *n*-octane, *n*-hexanol, and *n*-octanol. The surface tensions of the organic liquids were also measured. The interfacial tensions for the systems involving *n*-alkanes are higher than for the systems containing *n*-alkanols. All the interfacial tensions decrease linearly with temperature. In addition the results have been interpreted using the equation proposed by Girifalco and Good.

1. Introduction

The characteristic and tunable properties of ionic liquids (ILs) allow their use in the chemical industry, as solvents for chemical reactions or separation processes (liquid-liquid extraction). For an effective design of these industrial separations the knowledge of the interfacial tension between the liquid phases plays an important role [1,2]. Moreover, the interfacial tension is a key property to know the structure and the cohesive forces among the molecules in the bulk and also in the interface between two fluids.

There are not many works reporting the interfacial tensions of systems containing ionic liquids and alkanes or alkanols [1,3–9]. The investigated systems include mainly imidazolium-based ionic liquids and as far as we know none of them involve pyridinium-based ionic liquids.

Following our research on thermophysical properties of pyridinium-based ionic liquids [10–13] we report here the interfacial tension of several systems IL-alkane or IL-alkanol at several temperatures (283.15–313.15) K and at atmospheric pressure, 0.1 MPa. The ionic liquids were: 1-butylpyridinium tetrafluoroborate [bpy][BF4], 1-butyl-2-methylpyridinium tetrafluoroborate [b2mpy][BF4], 1-butyl-3-methylpyridinium tetrafluoroborate [b3mpy][BF4], and 1-butyl-4-methylpyridinium tetrafluoroborate [b4mpy][BF4], while the organic solvent were: *n*-hexane, *n*-octane, *n*-hexanol, and *n*-octanol. For the systems involving [b2mpy][BF4] the temperature range was only (303.15–313.15) K due to the high melting point of this IL [11]. The surface tensions for these four organic liquids were also determined in the same temperature range.

The expression proposed by Girifalco and Good [14] in terms of surface tensions of the adjacent phases and an adjustable parameter has been employed to correlate and describe the interfacial tension results of systems containing ILs [1,5–7,15,16]. Here we have also employed this equation to correlate and analyze the interfacial tensions.

2. Experimental section

The information about the pure compounds used in this work is summarized in Table 1. The ionic liquids were dried in vacuum (0.05 kPa) during 24 h in order to minimize the water content. The water content of the liquids was obtained through a Karl-Fischer titration using a Crison KF 1S-2B automatic titrator.

The surface tensions of the n-alkanes and n-alkanols and interfacial tensions of the systems IL/*n*-alkane and IL/*n*-alkanol were measured with an uncertainty of 0.2 $mN \cdot m^{-1}$ using a Lauda TVT-2 drop volume tensiometer [17]. The apparatus was thermostated at ±0.01 K by means of an external Lauda E-200 thermostat. This tensiometer determines the interfacial (surface) tension from the measuring of the volume of a drop detaching from a capillary of known diameter using the following equation:

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

being V the drop volume, $\Delta\rho$ the density difference of the two adjacent phases that can be considered not miscible [18–21], g the acceleration constant, r_{cap} the outer diameter of the capillary and finally f a correction function needed to relate the interfacial (surface) tension to the volume of the detached drop. The proper operation of the tensiometer was

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Table 1
Sample table.

Chemical name	Formula	CAS number	Source	Purification method	Mass fraction purity[a]	Water content/ppm
1-Butylpyridinium tetrafluoroborate	$C_9H_{14}BF_4N$	203389-28-0	Iolitec	Vacuum treatment	0.99	325
1-Butyl-2-methylpyridinium tetrafluoroborate	$C_{10}H_{16}BF_4N$	286453-46-1	Iolitec	Vacuum treatment	0.99	275
1-Butyl-3-methylpyridinium tetrafluoroborate	$C_{10}H_{16}BF_4N$	597581-48-1	Iolitec	Vacuum treatment	0.99	265
1-Butyl-4-methylpyridinium tetrafluoroborate	$C_{10}H_{16}BF_4N$	343952-33-0	Iolitec	Vacuum treatment	0.99	260
n-Hexane	C_6H_{14}	110-54-3	Sigma-Aldrich	None	0.991	210
n-Octane	C_8H_{18}	111-65-9	Sigma-Aldrich	None	0.993	235
n-Hexanol	$C_6H_{14}O$	111-27-3	Sigma-Aldrich	None	0.996	310
n-Octanol	$C_8H_{18}O$	111-87-5	Sigma-Aldrich	None	0.99	320

[a] As stated by the supplier.

checked by measuring the interfacial tension of the system water-*n*-hexane, the agreement between our experimental data and literature ones [22] was found excellent.

The densities of *n*-alkanes and *n*-alkanols were measured by means of an Anton Paar DMA-5000 vibrating tube densimeter with an uncertainty of 0.1 $kg \cdot m^{-3}$, these density values are collected in the Supplementary material (Table S1) while the densities of the ILs were taken from our previous papers [10–12].

Surface tensions of the pure compounds at $T = 298.15$ K and at $p = 0.1$ MPa, along with literature values [23–32] are shown in Table 2.

3. Results and discussion

The surface tensions of the pure organic liquids at working temperatures and at pressure of 0.1 MPa can be found in Table S1of the Supplementary material, while the interfacial tensions of the studied systems at the same experimental conditions are presented in Table 3. The surface and interfacial tensions are graphically represented in Figs. 1–5.

Both surface tensions and interfacial tensions, σ, for our systems decrease linearly with temperature, T, so we have correlated these magnitudes using a linear equation:

$$\sigma = A + B \cdot T \tag{2}$$

Table 2
Surface tensions, σ, of the pure liquids at $T = 298.15$ K and at $p = 0.1$ MPa, and comparison with literature values.[a]

Compound	$\sigma^{exp}/(mN \cdot m^{-1})$	$\sigma^{lit}/(mN \cdot m^{-1})$
1-Butylpyridinium tetrafluoroborate	46.64	
1-Butyl-2-methylpyridinium tetrafluoroborate[b]	45.30	
1-Butyl-3-methylpyridinium tetrafluoroborate	44.86	47.1[c]
1-Butyl-4-methylpyridinium tetrafluoroborate	45.42	45.4[d]
n-Hexane	17.92	17.89[e]
		17.91[f]
n-Octane	21.11	21.18[g]
		21.10[h]
n-Hexanol	25.94	25.90[i]
		25.90[j]
n-Octanol	27.14	27.04[k]
		27.13[l]

[a] Standard uncertainties u are $u(T) = 0.01$ K, $u(p) = 0.05$ kPa, and the combined expanded uncertainty U_c is $U_c(\sigma) = 0.2$ $mN \cdot m^{-1}$ with 0.95 level of confidence ($k = 2$).
[b] $T = 303.15$ K.
[c] Ref. [23].
[d] Ref. [24].
[e] Ref. [25].
[f] Ref. [26].
[g] Ref. [27].
[h] Ref. [28].
[i] Ref. [29].
[j] Ref. [30].
[k] Ref. [31].
[l] Ref. [32].

The best linear fitting parameters, A and B, and relative root-mean square deviations, $RMSD_r$, between experimental and correlated values have been collected in Table 4.

$$RMSD_r(\%) = 100\left(\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\sigma_{i,\,exp} - \sigma_{i,corr}}{\sigma_{i,\,exp}}\right)^2\right)^{1/2} \tag{3}$$

Our surface tension values for *n*-alkanes and *n*-alkanols are in good agreement (better than 0.2 $mN \cdot m^{-1}$ in average) with those previously reported [33–36].

Linear alkanes have a significantly lower surface tension than linear alkanols of the same chain length, due mainly of the existence of hydrogen bond in the alkanols that enhances the liquid cohesive forces. Within each group (alkanes and alkanols) a relationship between the σ values and the number of carbons is observed, the surface tension diminishes with the chain length, this effect is less marked in the alkanols. On the other hand, the surface tension decreases with temperature, the temperature coefficients for alkanes are higher in absolute value than for alkanols.

Next, we will briefly discuss the surface tensions of ionic liquids since they will be useful in the discussion of the interfacial tensions of our systems. Obviously the surface tension of ionic liquids is much higher than for alkanes and alkanols due to the strong self-interactions acting in the ionic liquids. An appreciable difference among [bpy] [BF4] and its methylated derivatives can be pointed out, being the surface tension for [bpy] [BF4] higher. Furthermore, it is observed that within the three ionic liquid isomers, the surface tensions follow the sequence [b2mpy] [BF4] > [b4mpy] [BF4] > [b3mpi] [BF4]. Finally, the surface tension of the ionic liquids diminishes with temperature, this decrease is lower for [bpy] [BF4].

For the same IL, the interfacial tension for the systems IL-alkane has values significantly higher than those presented for the systems containing the corresponding alkanol. Within each group it is observed that the highest interfacial tension is presented for the system containing the organic solvent with the longest carbon chain following the sequence: *n*-octane > *n*-hexane > 1-octanol > 1-hexanol. This result is according with the work of Gardas et al. [4]. It is clear that the cohesive forces inside both ILs and alkanols are stronger than the van der Waals forces acting in the alkanes. On the other hand, there is a greater interaction between IL and alkanol than that between IL and alkane molecules at the interface. So, the interfacial tensions for the systems IL-alkanol must be lower than for the systems IL-alkane.

The systems involving [bpy] [BF4] have an interfacial tension higher than the other three ionic liquids. Now, taking into account the three isomers, it is remarkable the higher interfacial tension values of the systems containing [b2mpy] [BF4] compared to those formed by [b3mpy] [BF4] or [b4mpy] [BF4]. The systems involving [b3mpy] [BF4] and [b4mpy] [BF4], have a similar behavior, although the interfacial tension for the systems with the ionic liquid with the methyl group in position 3 is slightly lower than for the ionic liquid with the methyl group in position 4. Finally, comparing the four ionic liquids against the same organic