Interfacial Properties, Densities, and Contact Angles of Task Specific Ionic Liquids[†]

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Density, surface tension, interfacial tension with water, and contact angles on Teflon and glass surfaces of 21 ionic liquids based on functionalized imidazolium, ammonium, phosphonium, and guanidinium cations combined with several anions, such as chloride, tetrafluoroborate, bis(trifluoromethanesulfonyl)imide, dicyanamide, *p*-toluenesulfonate, and ethylsulfate, were completely measured. The structure−property relationship of the selected ionic liquids was considered in order to predict their potential applications. Particularly relevant were the lower surface tension values (at 293.15 K) observed for tetrahexyldimethylguanidinium dicyanamide, $[(\text{di-h})_2\text{dmg}][\text{DCA}]$ ($21.35 \pm 0.03\ \text{mN}\cdot\text{m}^{-1}$), and trioctylmethylammonium bis(trifluoromethanesulfonyl)imide, $[\text{Aliquat}][\text{NTf}_2]$ ($22.77 \pm 0.05\ \text{mN}\cdot\text{m}^{-1}$), and the remarkably low contact angles on Teflon surfaces of $[(\text{di-h})_2\text{dmg}][\text{DCA}]$ (39.66°) and trihexyltetradecylphosphonium *p*-toluenesulfonate, $[\text{P}_{6,6,6,14}][p\text{-TsO}]$ (39.77°).

Introduction

Ionic liquids (ILs) are a class of peculiar compounds (often called room-temperature liquid salts) having almost negligible vapor pressure.[1] These features have allowed ionic liquids to be used as sustainable reaction media as an alternative to volatile organic solvents (VOCs).[2−4] The possibility of multiple combinations ($\sim 10^8$)[5] of cations and anions creates the possibility that ILs can be used in a broad range of applications such as solar cells,[6] analytical applications,[7] extractions,[8] surfactants,[7] anticorrosion[7] and antimicrobial[9] coatings, and liquid membranes.[10]

The measurement of different physicochemical properties of ILs is essential to evaluate the applicability of such compounds. Density is one of the most relevant properties, as it is related to the mass and volume of each atom of the compound and the intermolecular interactions between components of the ionic liquid and plays an essential role in extractions, design of energetic compounds,[11] and flotation fluids used in inertial instruments.[12] Surface tension is another important property related to density[13] and is fundamental to the design of multiphasic systems,[14] in the process of solubilization of gases,[15] and in electron transfer in electrochemical and solar cells.[16] Additionally, surface tension can be used to estimate other physicochemical properties such as volume expansivity, critical temperature, and polarity.[17] Recently, surface tensions of several ILs have been reported, in particular for those having imidazolium,[14,15,18] phosphonium,[15] and ammonium[15] cations combined with chloride, bromide, tetrafluoroborate, hexafluorophosphate, bis(trifluoromethanesulfonyl)imide, and triflate anions. Functionalized imidazolium, phosphonium, ammonium, and guanidinium cation-based ILs, including examples with dicyanamide and *p*-toluenesulfonate anions, were selected for our studies.

Through the Young equation (eq 1), the liquid−vapor surface tension γ_{LV} is linked with the contact angle θ:

$$\gamma_{\text{SV}} = \gamma_{\text{SL}} + \gamma_{\text{LV}} \cos \theta \qquad (1)$$

Thus, γ_{LV} is related by the contact angle θ to γ_{SV} and γ_{SL}, the solid−vapor and solid−liquid surface tensions, respectively. The contact angle is a measure of the wettability of a surface or the wetting capacity of a liquid. Wetting capacity is important in many different applications, such as liquid surface coating,[19] flotation, and chemical reactions at solid−liquid interfaces.[20] Through contact angle measurements, ILs have been considered as probe fluids for characterizing solid surfaces of different compositions and textures.[21] ILs have also been used as self-assembled layers in order to tune, for example, the wettability of gold[22] and polyimide[23] surfaces.

Poly(tetrafluoroethylene) (PTFE) Teflon is an organofluoride polymer in current wide use. The structure of Teflon differs from the usual organic compounds because the carbons are linked to electronegative fluorine atoms, and consequently, the carbon atoms present a positive partial charge that minimizes interactions of Teflon with common organic compounds.[24] Hence, wetting a Teflon surface can be a challenge. Previously, attempts were made to wet Teflon AF 1600 with ionic liquids in an electrowetting study, but only moderate results were obtained.[25] Attempts to wet Teflon by modifying its surface have been made using synchrotron radiation[26] and UV photooxidation.[27] Additionally gas pressure has been employed in order to tune Teflon wettability.[28] Here, we present a detailed study of density, surface tension, interfacial tension with water, and static contact angles with glass and Teflon using various ionic liquids based on the ions shown in Figure 1.

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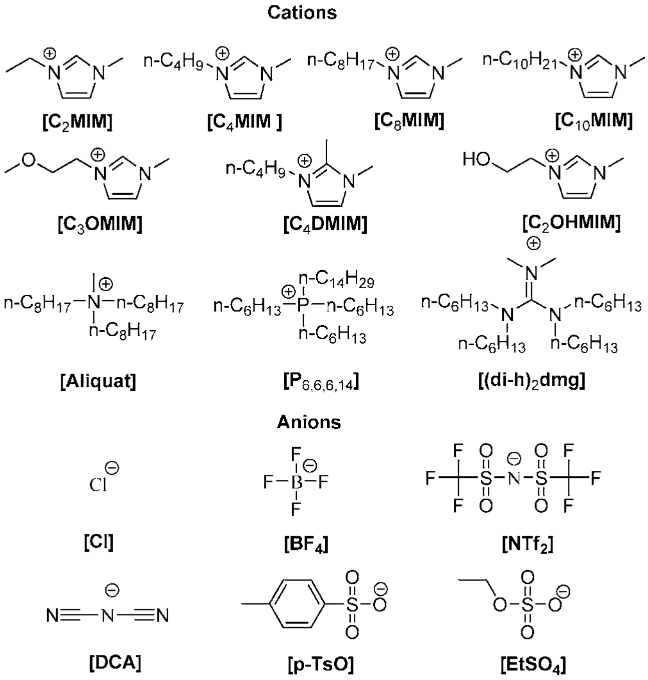

Figure 1. Structures of cations and anions selected for studies.

Experimental Section

Chemicals. All of the commercial reagents were used as supplied (Sigma-Aldrich). The ILs 1-ethyl-3-methy-imidazolium ethylsulfate [C$_2$MIM][EtSO$_4$], 1-butyl-3-methylimidazolium tetrafluoroborate [C$_4$MIM][BF$_4$], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C$_4$MIM][NTf$_2$], 1-butyl-3-methylimidazolium dicyanamide [C$_4$MIM][DCA], 1-methyl-3-octylimidazolium chloride [C$_8$MIM][Cl], 1-methyl-3-octylimidazolium tetrafluoroborate [C$_8$MIM][BF$_4$], 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide [C$_8$MIM][NTf$_2$], 1-methyl-3-octylimidazolium dicyanamide [C$_8$MIM][DCA], 1-decyl-3-methylimidazolium tetrafluoroborate [C$_{10}$MIM][BF$_4$], 1-decyl-3-methylimidazolium dicyanamide [C$_{10}$MIM][DCA], 1-(2-methoxyethyl)-3-methylimidazolium tetrafluoroborate [C$_3$OMIM][BF$_4$], 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [C$_4$DMIM][NTf$_2$], and 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide [C$_2$OHMIM][DCA] were supplied by Solchemar. Trioctylmethylammonium chloride [Aliquat][Cl] was obtained from Sigma-Aldrich, while trihexyltetradecylphosphonium chloride [P$_{6,6,6,14}$][Cl] and trihexyltetradecylphosphonium dicyanamide [P$_{6,6,6,14}$][DCA] with 96 % purity were obtained from Cytec. Trioctylmethylammonium bis(trifluormethylsulfonyl)imide [Aliquat][NTf$_2$],[29] trioctylmethylammonium dicyanamide [Aliquat][DCA],[29] *N,N,N′,N′*-tetrahexyl-*N″,N″*-dimethylguanidinium dicyanamide [(di-h)$_2$dmg][DCA][29] and *N,N,N′,N″*-tetrahexyl-*N″,N″*-dimethylguanidinium chloride [(di-h)$_2$dmg][Cl][30] were prepared according to published procedures. Trihexyltetradecylphosphonium *p*-toluenesulfonate [P$_{6,6,6,14}$][*p*-TsO] was prepared from [P$_{6,6,6,14}$][Cl] by anion exchange with 1.5 equiv of sodium *p*-toluenesulfonate in dichloromethane (DCM) at room temperature. After 24 h, the IL was separated by filtration and dried in vacuum. The final compound was obtained as a yellow viscous oil and then characterized by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.86 (12H, m), 1.24−1.26 (32H, m), 1.43 (16H, m), 2.23−2.30 (11H, m), 7.09 (2H, d, $J = 7.8$ Hz), 7.76 (2H, d, $J = 7.8$ Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 13.89 and 14.07 (rotamers), 18.70 and 19.17 (rotamers), 21.23, 21.81, 22.31, and 22.64 (rotamers), 28.95, 29.30, and 29.61 (rotamers), 30.33, 30.47, 30.66, and 30.80 (rotamers), 31.05, 31.87, 126.06, 128.38, 138.88, 143.84.

Methods. Density Measurements. The density measurements were done using two different strategies according to the quantity of the samples. For samples available in volumes greater than 1100 μL, a micropycnometer calibrated with heptane was used. The volume of the micropycnometer (1081 μL at 293.15 K) was validated by comparison with measurements of density for [C$_4$MIM][BF$_4$] (1.2069 g·cm^{-3} at 293.15 K).[31] Samples with volumes less than 1100 μL were measured by an indirect method using a micropycnometer. The method was validated by measuring the density of [C$_4$MIM][NTf$_2$] at 293.15 K (1.44 g·cm^{-3} at 293.15 K)[32] in the presence of heptane as the liquid used to complete the volume of the micropycnometer. Expanded uncertainty was calculated for all of the measurements at the 95 % confidence level.

Surface Tension Measurements. Surface tensions were obtained in a surface tension and contact angle meter (KSV Instruments model CAM 100). The pendant drop method was used for all of the measurements at 293.15 K. Previously, the method was validated by measuring the surface tension of [C$_8$MIM][NTf$_2$] (31.93 mN·m^{-1} at 293.15 K)[33] as a reference from literature. The final surface tension for each compound was obtained as a average of five independent measurements. Then the data were treated by CAM 2008 software.

Measurements of Interfacial Tension with Water. In order to obtain interfacial tensions, the same equipment and method as described previously was used. All of the ILs selected were previously saturated with water by stirring an IL + water mixture with a volume fraction of 0.5 for 24 h. After that period, the water phase was removed, and the remaining ILs were used to perform the corresponding measurements. The analyzed drops were formed at the bottom of a syringe inside a water recipient. The method used was validated by measuring the interfacial tension of 1-octanol (8.5 mN·m^{-1} at 293.15 K). The interfacial tension value for each studied compound was obtained as average of five independent measurements (at 293.15 K). Then the data were treated by CAM 2008 software.

Contact Angle Measurements. The contact angle for each selected compound was obtained as the average of five independent measurements as described previously. Two surfaces of different polarity were studied: PTFE Teflon and SiO$_2$ glass surfaces. The teflon surface was washed with water and acetone prior to each measurement. The SiO$_2$ glass surface was washed with water and detergent followed by an acetone wash. Finally, the glass surface was treated with 6 mol·L^{-1} aqueous nitric acid solution for 10 min and then washed with water.

Results and Discussion

ILs with *N*-alkylmethylimidazolium ([C$_n$MIM], $n = 2, 4, 8, 10$), 1-butyl-2,3-dimethylimidazolium ([C$_4$DMIM]), ether- and alcohol-functionalized imidazolium ([C$_3$OMIM] and [C$_2$OHIM]), trioctylmethylammonium ([Aliquat]), trihexyltetradecylphosphonium ([P$_{6,6,6,14}$]), and guanidinium ([(di-h)$_2$dmg]) cationic cores were studied. These cations were combined with chloride ([Cl]), tetrafluoroborate ([BF$_4$]), bis(trifluoromethanesulfonyl)imide ([NTf$_2$]), dicyanamide ([DCA]), *p*-toluenesulfonate ([*p*-TsO]), and ethylsulfate anions ([EtSO$_4$]), as described in Figure 1.

All of the ILs used in these studies were purified by vacuum using a moderate temperature (80 °C) and stirring. The selected ILs were used after the control of initial water and halogen content to below 150 and 50 ppm, respectively

Table 1. Densities of Ionic Liquids and Representative Organic Compounds

	ρ/g·cm^{-3}			100 ARD^{g}	
compound^{a}	exptl^{b,c}	lit.^{c}	Ye and Shreeve^{c}	lit.	Ye and Shreeve
[C$_2$MIM][EtSO$_4$]	1.242 ± 0.001^{d}	1.240^{17}	–	0.16	–
[C$_4$MIM][BF$_4$]	1.212 ± 0.002^{d} $(1.217 \pm 0.006)^{e}$	1.207^{31}	1.209	0.41	0.25
[C$_4$MIM][NTf$_2$]	$(1.452 \pm 0.006)^{e}$	1.439^{36}	1.433	–	1.33
[C$_4$MIM][DCA]	1.066 ± 0.005^{d}	1.058^{37}	–	–	–
[C$_8$MIM][Cl]	0.971 ± 0.003^{d}	1.010^{38}	0.965	−3.86	0.62
[C$_8$MIM][BF$_4$]	1.110 ± 0.002^{d} $(1.115 \pm 0.023)^{e}$	1.109^{31}	1.107	0.09	0.27
[C$_8$MIM][NTf$_2$]	1.340 ± 0.001^{d}	1.320^{f,32}	1.320	–	1.52
[C$_8$MIM][DCA]	1.013 ± 0.001^{d}	(1.020)^{29}	–	–	–
[C$_{10}$MIM][BF$_4$]	1.076 ± 0.004^{d}	(1.040)^{38}	1.075	–	0.09
[C$_{10}$MIM][DCA]	1.003 ± 0.002^{d}	(1.010)^{29}	–	–	–
[C$_3$OMIM][BF$_4$]	1.306 ± 0.003^{d}	(1.260)^{39}	–	–	–
[C$_4$DMIM][NTf$_2$]	1.425 ± 0.012^{d}	1.440^{31}	1.381	−1.04	3.18
[C$_2$OHMIM][DCA]	1.179 ± 0.001^{d}	–	–	–	–
[Aliquat][Cl]	0.891 ± 0.003^{d} $(0.896 \pm 0.009)^{e}$	0.890^{40}	–	0.11	–
[Aliquat][NTf$_2$]	–	1.110^{f,32}	–	–	–
[Aliquat][DCA]	$(0.890\pm 0.001)^{e}$	(0.900)^{29}	–	–	–
[P$_{6,6,6,14}$][Cl]	0.918 ± 0.003^{d}	(0.883)^{15}	0.867	–	5.88
[P$_{6,6,6,14}$][DCA]	–	0.900^{37}	–	–	–
[P$_{6,6,6,14}$][p-TsO]	$(1.003 \pm 0.011)^{e}$	–	–	–	–
[(di-h)$_2$dmg][Cl]	$(0.943 \pm 0.025)^{e}$	0.900^{f,30}	–	–	–
[(di-h)$_2$dmg][DCA]	–	(0.930)^{29}	–	–	–
1-octanol	0.831 ± 0.001^{d}	0.820^{41}	–	1.34	–
water	1.013 ± 0.002^{d}	1.000^{40}	–	1.30	–
DCM	1.327 ± 0.004^{d}	1.330^{40}	–	−0.23	–
heptane	–	0.680^{40}	–	–	–
octane	–	0.710^{40}	–	–	–
decane	–	0.740^{40}	–	–	–
EG	1.121 ± 0.003^{d}	1.115^{42}	–	0.54	–

[a] DCM, dichloromethane; EG, ethylene glycol. [b] Expanded uncertainty with a 95 % confidence level is given. [c] At 293.15 K (298.15 K), unless otherwise noted. [d] Obtained by the direct method using a micropycnometer. [e] Obtained by the indirect method using a micropycnometer. [f] Obtained at room temperature. [g] Average relative deviation. Precision is on the order of 10^{-3} g·cm^{-3}. Accuracy is on the order of 10^{-2} g·cm^{-3}.

Density. The experimental density values collected in this work and from the literature (at 293.15 K) are summarized in Table 1. The respective average relative deviation (ARD) between the experimental and literature-reported data was calculated in order to evaluate the accuracy of our measurements. Additionally, the Ye and Shreeve model[11] for estimating the densities of the studied ILs was used and also compared against our experimental data.

The range of densities for the selected ILs is 0.891 ± 0.003 g·cm^{-3} ([Aliquat][Cl]) to 1.452 ± 0.006 g·cm^{-3} ([C$_4$MIM][NTf$_2$]). As noted previously,[34] the density of imidazolium ILs decreases with increasing alkyl chain size ([C$_4$MIM][BF$_4$] > [C$_8$MIM][BF$_4$] > [C$_{10}$MIM][BF$_4$]); the same trend was observed for the [DCA] and [NTf$_2$] series. The presence of 2-methyl substitution on the imidazolium cation is not significant ([C$_4$DMIM][NTf$_2$] $\approx$ [C$_4$MIM][NTf$_2$]).

Considering different cationic families, [Aliquat][Cl] has a lower density (0.891 g·cm^{-3}) than [P$_{6,6,6,14}$][Cl] (0.918 g·cm^{-3}) and guanidinium [(di-h)$_2$dmg][Cl] (0.943 g·cm^{-3}). The selected anion also leads to different density values according to the order [Cl] < [DCA] < [*p*-TsO] < [EtSO$_4$] < [BF$_4$] < [NTf$_2$], where the fluorinated anions have higher densities despite their very low intermolecular forces.

Very good correlation between the experimental and literature data was observed using the ARD values, as shown in Figure 2. The expanded uncertainty with a 95 % confidence level was on the order of 10^{-3} g·cm^{-3}, with the highest uncertainties associated with measurements obtained by the indirect method using a micropycnometer, as expected.

The Ye and Shreeve model for estimating the densities of some selected ILs gave results in agreement with our experimental measurements.

Surface Tension. Surface tensions of selected ionic liquids and some representative organic solvents are given in Table 2. In regard to the structure–surface tension relationship, as in previous studies,[14,18] a decrease in surface tension with increasing alkyl chain length was observed, in particular for the case of imidazolium-based ILs ([C$_4$MIM][BF$_4$] > [C$_8$MIM][BF$_4$] > [C$_{10}$MIM][BF$_4$]; the same trend was observed for the [DCA] and [NTf$_2$] series). Different functional groups also lead to different surface tensions relative to equivalent *N*-alkyl units: in particular, [C$_3$OMIM][BF$_4$] has a lower surface tension (35.31 mN·m^{-1}) than [C$_4$MIM][BF$_4$] (44.28 mN·m^{-1}). [C$_2$OHMIM][DCA] has the highest surface tension (45.75 mN·m^{-1}) among the ILs studied. This compound illustrates the effect that hydrogen-bond-forming species, such as alcohols, lead to high surface tensions.

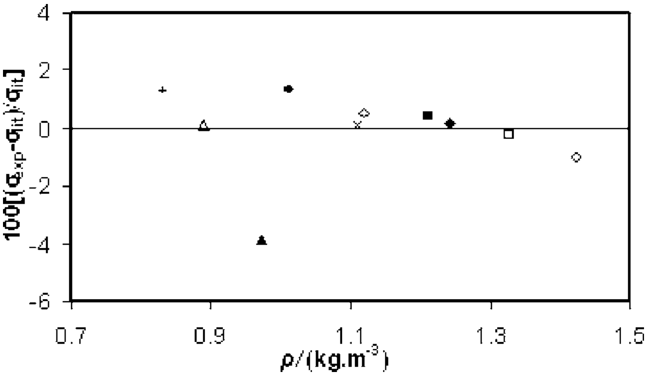

Figure 2. Average relative deviation between the experimental density data from this work and values reported in the literature. Legend: ○, [C$_4$DMIM][NTf$_2$]; ◆ [C$_2$MIM][EtSO$_4$]; ×, [C$_8$MIM][BF$_4$]; △, [Aliquat][BF$_4$]; ●, water; □, DCM; +, 1-octanol; ◇, EG; ■, [C$_4$MIM][BF$_4$]; ▲, [C$_8$MIM][Cl].

Water is an extreme example of a hydrogen-bonded compound with a very high surface tension (72.9 mN·m^{-1}). It was

Table 2. Surface Tensions of Ionic Liquids and Representative Organic Compounds

	γ_{LV}/mN·m^{-1}	
compound[a]	exptl[b,c]	lit.[c]
[C$_2$MIM][EtSO$_4$][d]	46.13 ± 0.22	47.39[43]
[C$_4$MIM][BF$_4$][e]	44.28 ± 0.03	44.81[18]
[C$_4$MIM][NTf$_2$][f]	(38.37 ± 0.01)	(37.50)[44]
[C$_4$MIM][DCA]	38.14 ± 0.05	−
[C$_8$MIM][Cl]	26.20 ± 0.16	(31.90)[45]
[C$_8$MIM][BF$_4$]	33.22 ± 0.01	(32.70)[46]
[C$_8$MIM][NTf$_2$][g]	30.55 ± 0.06	31.93[33]
[C$_8$MIM][DCA]	36.86 ± 0.05	−
[C$_{10}$MIM][BF$_4$]	23.65 ± 0.11	−
[C$_{10}$MIM][DCA]	31.15 ± 0.01	−
[C$_3$OMIM][BF$_4$]	35.31 ± 0.04	−
[C$_4$DMIM][NTf$_2$]	26.66 ± 0.03	−
[C$_2$OHMIM][DCA]	45.75 ± 0.09	−
[Aliquat][Cl]	26.44 ± 0.01	28.00[h,47]
[Aliquat][NTf$_2$]	22.77 ± 0.05	29.06[i,15]
[Aliquat][DCA]	28.80 ± 0.02	−
[P$_{6,6,6,14}$][Cl]	30.70 ± 0.06	33.62[j,15]
[P$_{6,6,6,14}$][DCA]	30.99 ± 0.13	34.85[k,15]
[P$_{6,6,6,14}$][*p*-TsO]	23.20 ± 0.16	−
[(di-h)$_2$dmg][Cl]	28.95 ± 0.12	−
[(di-h)$_2$dmg][DCA]	21.35 ± 0.03	−
1-octanol	−	27.50[48]
water	−	72.9[49]
AcOEt	−	(23.39)[47]
DCM	−	27.84[47]
heptane	−	(19.66)[47]
octane	−	21.62[47]
decane	−	(23.89)[47]

[a] AcOEt, ethyl acetate; DCM, dichloromethane. [b] Expanded uncertainty with a 95 % confidence level is also given. [c] Measured by the pendant drop method at 293.15 K (298.15 K), unless otherwise noted. [d] ARD is −2.66 %. [e] ARD is −1.18 %. [f] ARD is 2.32 %. [g] ARD is −4.32 %. [h] Measured at room temperature. [i] Measured at 299.46 K. [j] Measured at 297.99 K. [k] Measured at 299.35 K. Precision is on the order of 10^{-2} mN·m^{-1}. Accuracy is on the order of 10^{0} mN·m^{-1}.

Table 3. Interfacial Tensions of Some Ionic Liquids and Representative Organic Compounds in Water

	γ_{12}/mN·m^{-1}	
compound[a]	exptl[b,c]	lit.[c]
[C$_4$MIM][NTf$_2$]	15.15 ± 0.25	−
[C$_8$MIM][NTf$_2$]	22.81 ± 0.11	−
[C$_4$DMIM][NTf$_2$]	17.04 ± 0.66	−
[Aliquat][Cl]	3.66 ± 0.18	−
[P$_{6,6,6,14}$][Cl]	6.11 ± 0.07	−
toluene	−	36.1[47]
TEA	−	0.1[47]
AcOEt	−	6.8[47]
DCM	−	28.3[47]
1-octanol	8.30 ± 0.24	8.5[d,47]
hexane	−	51.1[47]
heptane	−	50.2[47]
octane	−	50.8[47]
decane	−	51.2[47]
1-heptanal	−	13.7[47]

[a] TEA, triethylamine; AcOEt, ethyl acetate; DCM, dichloromethane. [b] Expanded uncertainty with a 95 % confidence level is also given. [c] Measured by the pendant drop method at 293.15 K. [d] ARD between the exptl and lit. values is 3.53 %. Precision is on the order of 10^{-2} mN·m^{-1}.

also observed that the presence of a methyl group at the 2-position of the imidazolium ring ([C$_4$DMIM][NTf$_2$]) leads to a decrease in the surface tension (26.66 mN·m^{-1} at 293.15 K) relative to that of the imidazolium without substitution at the 2-position ([C$_4$MIM][NTf$_2$], 38.37 mN·m^{-1} at 298.15 K). The acidic hydrogen-bond-forming C2 proton might be crucial to this behavior. Comparing the surface tension values for different cationic cores, we observed that by the choice of the anion it is possible to obtain the lowest surface tensions: ([(di-h)$_2$dmg][DCA], 21.35 mN·m^{-1}; [C$_{10}$MIM][BF$_4$], 23.65 mN·m^{-1}; [Aliquat][NTf$_2$], 22.77 mN·m^{-1}; [P$_{6,6,6,14}$][*p*-TsO], 23.20 mN·m^{-1}). It was also observed that the [*p*-TsO] anion is a good candidate for depressing the surface tension ([P$_{6,6,6,14}$][*p*-TsO] < [P$_{6,6,6,14}$][Cl] < [P$_{6,6,6,14}$] [DCA]). In general, the surface tensions of the ILs are much smaller than that of water and higher than those of most volatile organic solvents (Table 2); [(di-h)$_2$dmg][DCA], [P$_{6,6,6,14}$][*p*-TsO], [Aliquat][NTf$_2$], and [C$_{10}$MIM][BF$_4$] were exceptions in these observations (in comparison to organic solvents).

In the case of the surface tension measurements, the expanded uncertainty with a 95 % of confidence was on the order of 10^{-2} g·cm^{-3}.

Interfacial Tension with Water. Interfacial tensions of some ILs and organic compounds with water are shown in Table 3. All of the selected compounds were previously saturated with water by stirring for 24 h. For these studies, the pendant drop method was validated using 1-octanol as the reference [8.30 ± 0.24 mN·m^{-1} (exptl) vs 8.5 mN·m^{-1} (lit.)].

Water-immiscible ILs based on [Cl] and [NTf$_2$] anions were selected. [Aliquat][Cl] (3.66 mN·m^{-1}) and [P$_{6,6,6,14}$][Cl] (6.11 mN·m^{-1}) as more polar ionic liquids have the lowest interfacial tensions. The more hydrophobic [NTf$_2$] anion showed higher interfacial tensions with increasing alkyl chain length of the imidazolium cation unit: *n*-octyl ([C$_8$MIM][NTf$_2$]) > *n*-butyl ([C$_4$MIM][NTf$_2$]). Upon methyl substitution at C2 of the imidazolium ring, an increase in interfacial tension was also observed ([C$_4$DMIM][NTf$_2$] > [C$_4$MIM][NTf$_2$]). This behavior can be attributed to the hydrogen-bond-forming acidic C2 proton, which might facilitate stronger interactions with water molecules.

The experimental interfacial tensions in the case of NTf$_2$-based ILs are much smaller than those of alkanes but higher than those of some reference volatile organic solvents. In the case of ILs, the interfacial tension with water is lower than the respective surface tension. The opposite behavior is observed for alkanes.[35] In the case of the experimental interfacial tensions with water, the expanded uncertainty with a 95 % confidence level was on the order of 10^{-2} g·cm^{-3}.

Contact Angle Measurements. Tables 4 and 5 show static contact angles of some ILs with PTFE Teflon and SiO$_2$ glass surfaces, respectively. The glass surface commonly is easier to wet, while in the case of the Teflon surface, wetting can be a cumbersome challenge. For the Teflon surface, the values found for the selected ILs range from 88.19° for [C$_3$OMIM][BF$_4$] to 39.77° for [P$_{6,6,6,14}$][*p*-TsO].

A structure−contact angle on Teflon relationship was evaluated using longer-alkyl-chain imidazolium cation units. In this context, [C$_8$MIM][NTf$_2$] has a considerably lower contact angle (49.58°) than [C$_4$MIM][NTf$_2$] (66.25°). This observation illustrates the importance of dispersive interactions in the definition of the contact angle with Teflon.[50] In regard to methyl substitution at the imidazolium C2 unit, [C$_4$DMIM][NTF$_2$] has a contact angle (70.62°) similar to that of the corresponding [C$_4$MIM][NTf$_2$] (66.25°). An increase in IL polarity allows higher contact angles on Teflon, as shown for [C$_3$OMIM][BF$_4$] (88.19°). It is already known that Teflon is a surface where dispersive interactions are much more relevant than polar interactions[50] in order to wet this surface. Guanidinium-based ILs presented the lowest contact angles in comparison with imidazolium-, ammonium-, and phosphonium-based ILs ([(di-h)$_2$dmg][DCA] < [Aliquat][DCA] < [P$_{6,6,6,14}$][DCA] < [C$_4$MIM][DCA]), as illustrated in Figure 3. One of the possi-

Table 4. Contact Angles of Some Ionic Liquids and Representative Compounds on a PTFE Teflon Surface

	θ/deg	
compound[a]	exptl[b]	lit.
[C_4MIM][BF_4]	80.51 ± 0.79	–
[C_4MIM][NTf_2]	66.25 ± 0.09	–
[C_4MIM][DCA]	81.71 ± 0.26	–
[C_8MIM][Cl]	47.11 ± 0.26	–
[C_8MIM][NTf_2]	49.58 ± 0.21	–
[C_3OMIM][BF_4]	88.19 ± 0.21	–
[C_4DMIM][NTf_2]	70.62 ± 0.34	–
[Aliquat][Cl]	56.53 ± 0.42	–
[Aliquat][NTf_2]	46.20 ± 0.48	–
[Aliquat][DCA]	63.28 ± 0.39	–
[$P_{6,6,6,14}$][Cl]	64.18 ± 0.49	–
[$P_{6,6,6,14}$][DCA]	68.95 ± 0.20	–
[$P_{6,6,6,14}$][p-TsO]	39.77 ± 0.14	–
[(di-h)$_2$dmg][Cl]	58.96 ± 0.06	–
[(di-h)$_2$dmg][DCA]	39.66 ± 0.71	–
water	–	122 (adv)[50]
		94 (rec)[50]
EG	–	93 (adv)[50]
		64 (rec)[50]
DMF	–	79 (adv)[50]
		48 (rec)[50]
Pyr	–	72 (adv)[50]
		54 (rec)[50]
heptane	–	10.3[51]
octane	–	21.1[51]
nonane	–	28.3[51]
decane	–	32.7[51]

[a] EG, ethylene glycol; DMF, dimethylformamide; Pyr, pyridine. [b] Expanded uncertainty with a 95 % confidence level is also given. Precision is on the order of 10^{-2} deg.

Table 5. Contact Angles of Some Ionic Liquids and Representative Compounds on a SiO_2 Glass Surface

	θ/deg	
compound[a]	exptl[b]	lit.
[C_2MIM][$EtSO_4$]	29.38 ± 0.65	–
[C_4MIM][BF_4]	38.27 ± 0.22	–
[C_8MIM][BF_4]	13.08 ± 0.14	–
[C_8MIM][NTf_2]	22.84 ± 0.23	–
[C_3OMIM][BF_4]	42.38 ± 0.27	–
[C_2OHMIM][DCA]	26.45 ± 0.29	–
[(di-h)$_2$dmg][Cl]	18.84 ± 0.10	–
water	–	<10.0[52]
DCM	–	14.4[51]
heptane	–	<10.0[51]

[a] DCM, dichloromethane. [b] Expanded uncertainty with a 95 % confidence level is also given. Precision is on the order of 10^{-2} deg.

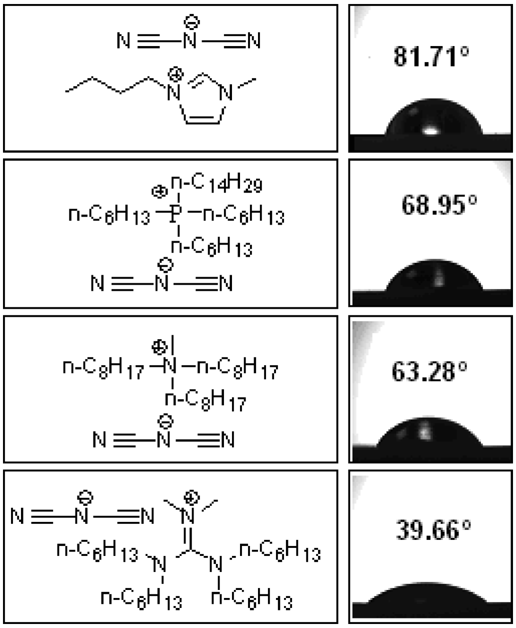

Figure 3. Effect of the cation on the contact angle of the IL with Teflon.

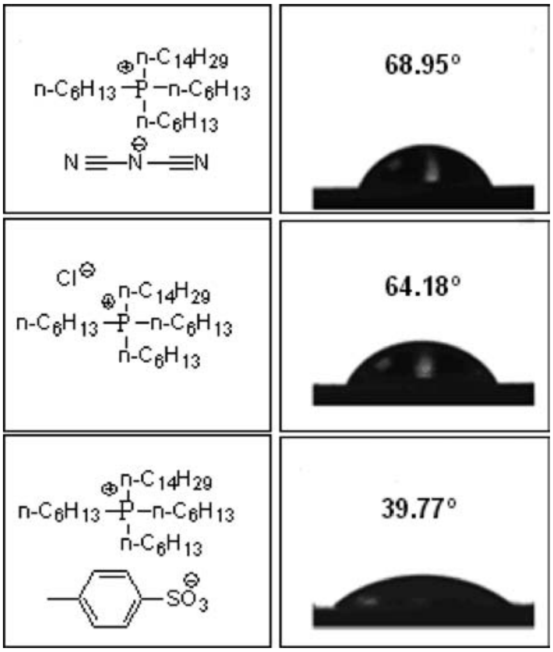

Figure 4. Effect of the anion on the contact angle of the IL with Teflon.

ble reasons for this observation can be related with the planar geometry of guanidinium core where the aligment of hexyl chains of [(di-h)$_2$dmg][DCA] that might play an important role for the final depression of contact angle.

In regard to the effect of the anion, if the cationic core is imidazolium, ammonium, or phosphonium, the order of contact angles is [BF_4] > [DCA] > [Cl] > [NTf_2] > [*p*-TsO]. Figure 4 illustrates the anion effect for the case where the phosphonium cation was mantained and the structure of the anion was changed. Among the selected anions, [*p*-TsO] leads to a lower contact angle (39.77°), probably because of the planarity and electron density of the aromatic ring of the [*p*-TsO] anion. Conversely, for the guanidinium core, the observed order is [Cl] (58.96°) $\gg$ [DCA] (39.66°).

In general, the contact angles of the selected ILs are lower than those of water but higher than those of *n*-alkanes. The ILs [$P_{6,6,6,14}$][*p*-TsO] and [(di-h)$_2$dmg][DCA] have considerably lower contact angles with Teflon than do common organic solvents such as ethylene glycol (EG), dimethylformamide (DMF), and pyridine (Pyr).

In regard to the SiO_2 glass surface, the measured contact angles of the selected ILs are higher than those of water, DCM, and *n*-heptane, except in the case of [C_8MIM][BF_4] (13.08°). Upon analysis and comparison of the differences between the studied ILs, it is possible to observe a decrease in the glass contact angles with increasing size of the alkyl chain of the imidazolium cation unit ([C_4MIM][BF_4] > [C_8MIM][BF_4]) resulting from dispersive interactions with the glass surface.[51] [C_8MIM][BF_4] (13.08°) and [(di-h)$_2$dmg][Cl] (18.84°) are two examples of ionic liquids with lower contact angles with glass.

For all of the experimental contact angles on Teflon and glass, the expanded uncertainty with a 95 % confidence level is on the order of 10^{-1} deg.

Conclusions

On the basis of the results observed here, the adequate combination of cation and anion IL structures is fundamental in order to tune the density and surface tension properties as well as the interfacial tension with water and the potential contact angles on Teflon and glass surfaces. Low-surface-tension ILs ($<24.0\ \mathrm{mN \cdot m^{-1}}$) were found in the case of [(di-h)$_2$dmg][DCA], [$P_{6,6,6,14}$][*p*-TsO], [Aliquat][NTf_2], and [C_{10}MIM][BF_4]. Good candidates for an efficient water/IL biphasic system were found preferently using bis(trifluoromethanesulfonyl)imide anions. The ILs [$P_{6,6,6,14}$][*p*-TsO] and [(di-h)$_2$dmg][DCA] are relevant alternative examples for wetting Teflon (contact angles < 40°). Our experimental density data were found to be in agreement with literature values, and the respective expanded uncertainties with a 95 % confidence level were on the order of 10^{-2} to $10^{-3}\ \mathrm{g \cdot cm^{-3}}$. Finally, several ILs showed attractive interfacial properties and relevant contact angle values that allow them to be considered as novel task-specific ionic liquids (TSILs).

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