New fluorous ionic liquids function as surfactants in conventional room-temperature ionic liquids

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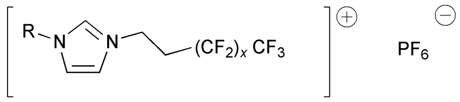
Ionic liquids formulated from imidazole cations with appended fluorous tails function as surfactants when added to conventional ionic liquids, facilitating the emulsification of fluoroalkanes with IL phases.

The development of less-polluting, 'neoteric' solvents is a key element in an emerging agenda for sustainable industrial development.[1] The alternatives receiving the most attention as neoteric solvents are ionic liquids (ILs), supercritical CO_2 (sc-CO_2), supercritical/near-critical H_2O, and perfluorocarbons.[2] Despite the intense interest in them, much of the basic chemistry of ionic liquids remains to be explored. Indeed, an understanding of this basic chemistry is of vital importance to the development of ionic liquids for 'green' applications.[1,3]

The thrust of our work with ionic liquids is the design and synthesis of salts composed of ions that incorporate structural or functional features that imbue them with particular properties.[1*d*,4] In a recent paper, we reported the synthesis of the first imidazolium ion with a long fluorous 'ponytail', with which we formulated a low-melting salt, *cf.*, a fluorous ionic liquid.[5,6] Our observation of the formation of a liquid crystalline phase by this structurally complex, fluorinated IL led us to speculate that the fluorocarbon tails of such ionic-liquid component cations associate. We subsequently reasoned that this property might be exploited to address a question of fundamental importance with regard to ionic liquid chemistry—the capacity of a designed, IL-based surfactant to alter the properties of a more conventional IL phase. Further, we deemed it feasible to capitalize upon such compounds to achieve a result of potential utility in biphasic systems—the use of the surfactant to promote and stabilize dispersions of a fluorous phase into an ionic liquid, two ordinarily immiscible neoteric solvent types. Note that Brennecke, Johnson and Rogers have all recently demonstrated the potential importance of biphasic systems in which both solvent components were neoteric materials.[7]

Here, we report the synthesis of four new fluorinated ionic liquids. The new compounds, **1–4**, differ substantially from the handful of known fluorine-containing ionic liquids in that the cation head-group structure is conventional and the fluorous appendage long (Fig. 1).[8,9] All of the new compounds are surfactants that promote the formation and stabilization of dispersions of perfluorocarbons in a conventional ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate, [6-mim]PF_6. Ours is the first report of the action of a fluorous surfactant on an ionic liquid, and only the second report of any surfactant action on or in an ionic liquid solvent.[10,11]



1 R = Me, *x* = 5
2 R = n-Bu, *x* = 5
3 R = Me, *x* = 7
4 R = n-Bu, *x* = 7

Fig. 1 General structure of the new fluorous ionic liquids.

The new fluorous ionic liquids are readily prepared from commercially available starting materials. Using an approach similar to that used to prepare our earlier fluorous IL, the imidazole cores 1-methyl- and 1-butylimidazole are dissolved in toluene, treated with a slight molar deficiency of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane or 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane and heated under reflux overnight. Cooling to rt followed by removal of the solvent *in vacuo* leaves soft, off-white waxes. These iodide salts are readily metathesized in acetone using $AgPF_6$, giving ILs **1–4** in good yields.[12]

Compounds **1–4** manifest several behaviors common to surfactants. Simple capillary-rise measurements reveal that the surface tensions of saturated solutions (0.3 mass percent, ~ 1–4 mmolar) of **1–4** in [6-mim]PF_6 range from 10 to 15% less than the surface tensions of the conventional ionic liquid alone. Further, Ostwald viscosimetry establishes that increases in the viscosity of [6-mim]PF_6 occur upon addition of compounds **1–4**, a behavior common to known surfactants.[13] Still, the most dramatic surfactant behavior manifested by the new ILs is their capacity to act as agents to promote and stabilize dispersions of perfluorohexane in the 'conventional' IL [6-mim]PF_6. In the absence of the new fluorous ILs, the IL and perfluorohexane phases remain well defined. Controlled, timed mechanical agitation of the two-phase system results in the dispersal of droplets of the fluorous phase into the IL, but the droplets are quite large and individually distinguishable. They visibly begin to coalesce back into a bulk phase upon cessation of agitation. When this experiment is repeated using saturated solutions of **1–4** dissolved in [6-mim]PF_6, the dispersions that are formed persist for weeks without visible change.

Transmittance spectroscopy of the dispersions of perfluorohexane in the fluorous/conventional ionic liquid solution *versus* time graphically demonstrates the enhanced stability of those systems (Fig. 2).[14] Without fluorous IL, the initial turbidity of the system as determined by transmittance is slightly more than 40%. When any of the compounds **1–4** is dissolved in the bulk IL phase, the initial transmittance values are all near 10%. The rapid coalescence of the dispersed perfluorohexane droplets is apparent in the system without any

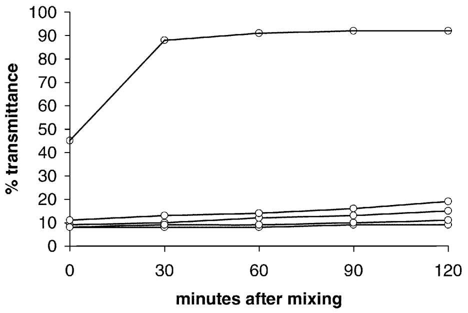


Fig. 2 Transmittance of perfluorohexane dispersions in [6-mim]PF_6 as a function of time with *(top to bottom)* no added fluorous IL; added **2**; added **1**; added **4**; added **3**. The enhanced stability of the dispersions in the presence of the fluorous ILs is apparent.

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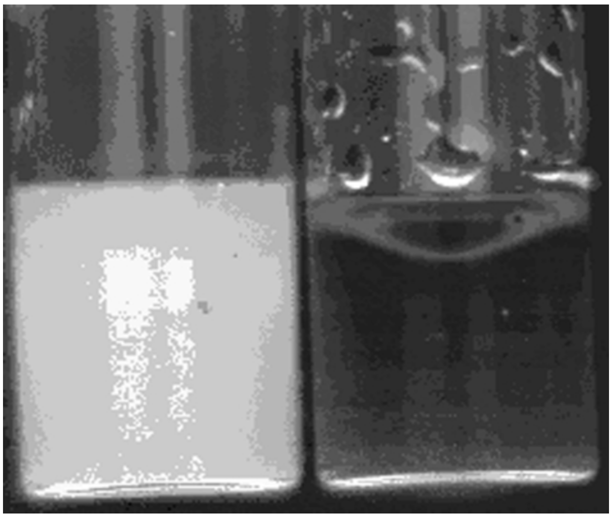

Fig. 3 Solution of **3**/[6-mim]PF_6 with emulsified perfluorohexane *(left)* and a mixture of [6-mim]PF_6–perfluorohexane *(right)*, both with added thymol blue. Note the turbidity of the stabilized emulsion, which has been aged one week, in contrast to the phase separation apparent in the system without FIL, aged five minutes. Also note the more efficient wetting of the container surface by the system containing fluorous IL.

fluorous IL, the transmittance of the system rising to 85% after 30 minutes. After similar time intervals, all four dispersions with added fluorous IL remain below 15% transmittance. This marked disparity persists with time. Over a four-hour interval, the transmittance of the IL–perfluorohexane mixture rises to 92%, while the transmittance values of the dispersions containing fluorous ILs range between 12 and 28%. This stability persists for extended time periods, dispersions of perfluorohexane and [6-mim]PF_6 with added **3** enduring for several weeks. Over periods of time greater than a month, the dispersions gradually decay with the formation of flocs.

In an effort to explore putative changes in the solvent environment arising from the presence of dissolved fluorous salt, we exploited a recent discovery by Rogers that, dissolved in conventional IL phases, thymol blue functions as an effective visual probe of such differences.[15] Systems containing [6-mim]PF_6–perfluorohexane and **3**–[6-mim]PF_6–perfluorohexane were prepared in identical fashion, solid thymol blue being added to each after the initial IL phases had been pre-equilibrated with pH 7.2 buffer. The mixtures were mechanically agitated for 15 min during which time the thymol blue dissolved. Upon dissolution of the thymol blue, the [6-mim]PF_6–perfluorohexane suspension became red, the color remaining in the IL phase as the two component liquids coalesced back into bulk phases. In the case of the **3**–[6-mim]PF_6–perfluorohexane mixture, a persistent suspension was formed which was brilliant yellow (Fig. 3). The yellow coloration was also observed in a mixture of **3** and [6-mim]PF_6 in the absence of perfluorohexane, indicating that the presence of the fluorous IL solute in the conventional IL phase is responsible for the observed difference in color. The effect does not appear to be linked to an electron-withdrawing effect of the fluorous appendage upon the imidazolium ion. Proton NMR spectra of **1**–**4** reveal that the chemical shifts of the imidazole ring C-2 protons—the most acidic within the cation structure—are similar to those of non-fluorinated ILs, suggesting that they are not rendered more acidic by the fluorous appendage.[16]† However, the presence of the fluorous appendage is likely to alter the capacity of the conventional IL to hold trace quantities of water, and the effect of such variations in water content within the IL phase on the behavior of the dye is unknown. Consequently, the basis of the difference in the color, whether pH based, solvatochromic, *etc*. is unclear. Studies to address this issue and other facets of the chemistry of fluorous ionic liquids are in progress, and will be reported in due course.

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Notes and references

† ^{1}H-NMR (CD_3CN), δ. **1**: 2.81 (m, 2H, $\text{-C}H_2\text{CF}_2\text{-}$), 3.83 (s, 3H, N-$CH_3$), 4.50 (t, 2H, N-$CH_2CH_2$-), 7.37 (m, 1H, CH), 7.45 (m, 1H, CH), 8.50 (s, 1H, N-CH-N). **2**: 0.89 (t, 3H, $\text{CH}_2\text{C}H_3$), 1.34 (m, 2H, $\text{CH}_2\text{C}H_2\text{CH}_3$), 2.00 (m, 2H, $\text{C}H_2\text{CH}_2\text{CH}_3$), 2.80 (m, 2H, -$CH_2CF_2$-) 4.11 (m, N-$CH_2$-), 4.48 (m, N-$CH_2$-), 7.40 (m, 1H, CH), 7.44 (m, 1H, CH), 8.51 (s, 1H, N-CH-N). **3**: 2.81 (m, 2H, $\text{-C}H_2\text{CF}_2\text{-}$), 3.83 (s, 3H, N-$CH_3$), 4.50 (t, 2H, $\text{N-C}H_2\text{CH}_2\text{-}$), 7.36 (m, 1H, CH), 7.45 (m, 1H, CH), 8.48 (s, 1H, N-CH-N). **4**: 0.91 (t, 3H, $\text{CH}_2\text{C}H_3$), 1.34 (m, 2H, $\text{CH}_2\text{C}H_2\text{CH}_3$), 2.02 (m, 2H, $\text{C}H_2\text{CH}_2\text{CH}_3$), 2.80 (m, 2H, $\text{-C}H_2\text{CF}_2\text{-}$) 4.10 (m, N-$CH_2$-), 4.50 (m, N-$CH_2$-), 7.39 (m, 1H, CH), 7.44 (m, 1H, CH), 8.46 (s, 1H, N-CH-N).

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