Communication

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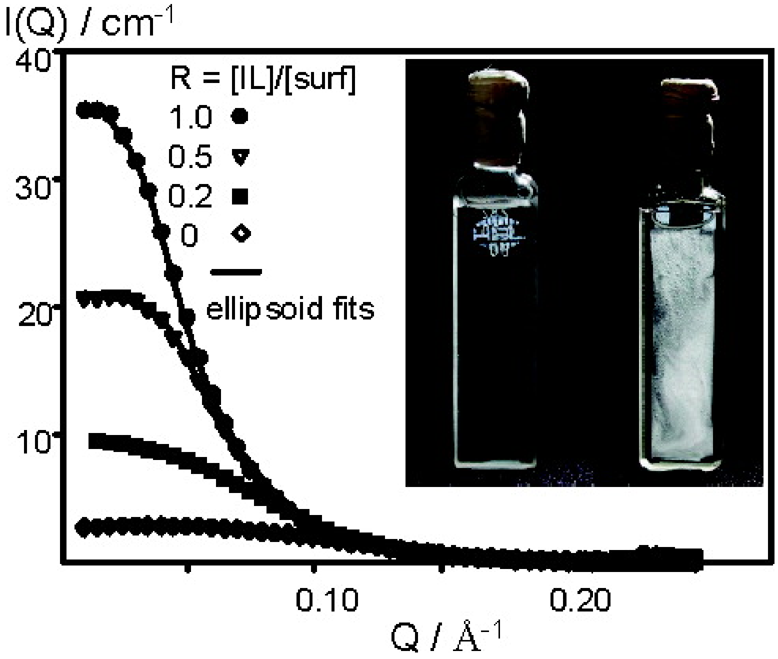

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Ionic Liquid-in-Oil Microemulsions

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Room temperature ionic liquids (ILs) are an interesting class of tunable, designer solvents with essentially zero volatility. ILs are composed of sterically mismatched ions[1,2] that hinder crystal formation; molecular structure can be used to tune physicochemical properties. An example IL employed here is 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] (referred to as IL). Solvation properties of ILs are comparable with those of highly polar solvents, and they have already found use in synthesis and catalytic reactions.[2] Despite these features, solubility limitations for apolar solutes remain, which could be overcome by incorporation of hydrocarbon domains provided by normal micelles or formation of ionic liquid-in-oil (IL-O) microemulsions. The significance is that nanostructured surfactant assemblies would provide hydrophobic or hydrophilic nanodomains, thereby expanding potential uses of ILs as reaction and separation or extraction media.

Interestingly, claims have been recently made of formation of IL-O microemulsions in mixtures of [bmim][BF_4] and cyclohexane, stabilized by the nonionic surfactant T-X100.[3] Light scattering (LS) data from these systems indicate droplet sizes on the order of 0.1 μm; this is generally regarded as outside the range for microemulsions, which typically have nanometer-sized liquid domains. Owing to the higher resolution compared to LS, contrast variation small-angle neutron scattering (SANS) is the ideal method to detect nanodroplet formation in such IL-O systems. Therefore, SANS provides prima face evidence for the presence of compartmentalized liquid nanodomains,[4] for example, four which are recognized as the essential structural units in true microemulsions. Here are reported the first SANS experiments on [bmim][BF_4]-in-cyclohexane IL-O microemulsions, which clearly demonstrate the formation of surfactant-stabilized dispersed nanodroplets with IL cores. The SANS data have been treated in terms of an ellipsoid form factor, showing a regular increase in droplet volume as micelles are progressively swollen with added IL, behavior consistent with "classic" water-in-oil (w/o) microemulsions.[4]

In related fields, Binks et al. have reported the formation of IL emulsions, stabilized solely by adsorbed silica particles.[5] Other reports have indicated possible micellization of some certain common surfactants in ILs,[6,7] based on surface tension and dye probe measurements. Owing to the inevitable presence of trace contaminants in ILs, the techniques typically employed to detect aggregation, such as surface tension (!) and fluorescence of probe dyes, are notoriously difficult to use reliably. Numerous observations of liquid crystalline mesophase formation with pure concentrated ILs have been made,[2] suggesting properties akin to concentrated surfactant phases. In addition, neutron reflectivity has been employed to examine the surface structure of a model pure IL,[8] suggesting a high degree of interfacial ordering.

The model IL ([*h*-bmim][BF_4]) was prepared and stored as documented elsewhere.[1] Cyclohexane-d_{12} (99.9% D-atom) was obtained from Goss Scientific (U.K.), and the nonionic hydrocarbon surfactant, Triton-X100 (T-X100), was supplied by Aldrich. For phase behavior studies, samples were prepared by weight into sealed vials, as a function of the molar ratio R = [*h*-bmim]/[T-X100]. Samples were thermostated by suspension in a Grant LTD6 circulating bath, and the phase boundaries shown in Figure 1 were located by inspection. In the absence of T-X100, the two components, IL and cyclohexane-d_{12}, are immiscible. Below an added volume fraction of $\phi_{\text{T-X100}} = 0.40$, it was not possible to stabilize a single phase with the ternary mixtures, suggesting a minimum background critical microemulsion concentration (cμc), which is known for w/o microemulsions containing nonionic surfactants.[9] Once established, the single-phase systems display thermoreversible transitions, and phase separations are seen as the boundaries are crossed, demonstrated by the images in Figure 1.

SANS experiments[10] were carried out at the time-of-flight LOQ instrument at ISIS, U.K., where incident wavelengths are $2.2 \leq \lambda \leq 10$ Å (effective Q range of $0.009 \rightarrow 0.249$ Å^{-1}), and on the D22 diffractometer at ILL, Grenoble, France, using a neutron wavelength of $\lambda = 10$ Å (Q range of $0.0024 \rightarrow 0.37$ Å^{-1}). Experiments were carried out on freshly made samples at the two institutes, on two separate occasions, yielding essentially identical $I(Q)$ distributions in the region of Q overlap. Subtraction of the empty cell and a mixed C_6D_{12}−T-X100 background ($\phi_{\text{T-X100}} \sim 0.39$; Supporting Information) accounted for the residual incoherent scattering, generating the SANS curves shown in Figure 2. The data in Figure 2 were all taken at 55 °C; hence, with reference to Figure 1, the samples are all single-phase systems. The $R = 0$ sample represents scattering from IL-free reversed micelles of T-X100. With added IL, there is a regular increase in SANS intensity at a constant level of T-X100 ($\phi_{\text{T-X100}} \sim 0.41$).

Detail on the fitting analysis is described in Supporting Information. The SANS curves were fitted by a model for dilute homogeneous ellipsoidal particles, of semi-minor radius r and aspect ratio l/r;[11] fitted parameters are given in Table 1. The nanodomains appear to become progressively more elongated as the IL is added. Since the neutron scattering length densities of IL and *h*-T-X100 are quite similar, the entire aggregates are contrasted against the cyclohexane-d_{12}−T-X100 mixed background. Therefore, these fitted dimensions represent the IL liquid cores plus the T-X100 stabilizing layer thickness. The inset to Figure 2 shows the microemulsion droplet swelling behavior, in terms of the dependence of ellipsoid volume V on [IL]/[T-X100] mole ratio R. This regular swelling behavior is consistent with the volume of dispersed nanodomains being directly proportional to the amount of added IL, which is

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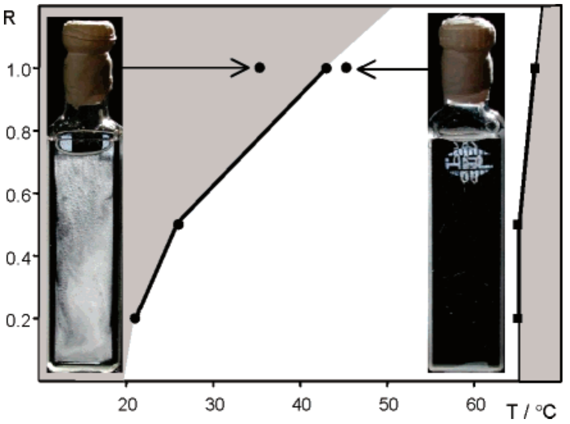

Figure 1. Phase behavior of [*h*-bmim][BF_4] in cyclohexane-d_{12} microemulsions at constant surfactant volume fraction, $\phi_{T-X100} = 0.41$, and various ratios, $R = [IL]/[T\text{-}X100]$. Photographs show an $R = 1.0$ system at 45 °C (single phase) and 35 °C (phase separated), and the locations of these systems are marked.

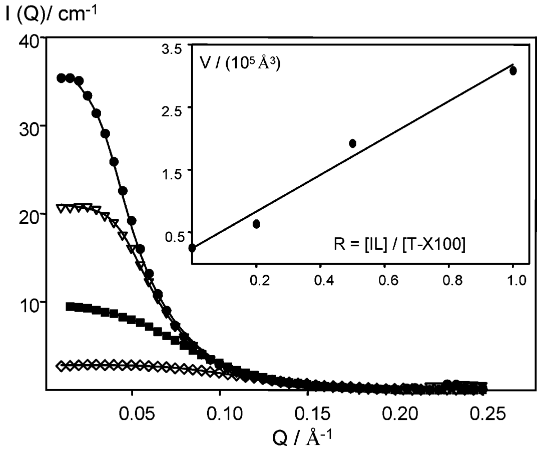

Figure 2. SANS from single-phase [*h*-bmim][BF4] in cyclohexane-d_{12} microemulsions at 55 °C. $R = 0$ (◇), 0.2 (■), 0.5 (▽), and 1.0 (●); $\phi_{T-X100} = 0.41$. The fits shown as lines are to a form factor for homogeneous ellipsoids. Inset shows the micelle swelling behavior in terms of the ellipsoid volume V as a function of added IL.

Table 1. [*h*-bmim][BF_4] in Cyclohexane-d_{12} Microemulsions Studied by SANS at Volume Fraction $\phi_{T-X100} = 0.41^a$

R	ϕ_{IL}	r/Å	l/r
0	0.00	16	1.5
0.2	0.03	19	2.4
0.5	0.06	23	4.0
1.0	0.12	24	5.1

[a] Parameters are fitted to SANS data shown in Figure 2 using a homogeneous ellipsoid form factor of semi-minor radius *r* and aspect ratio *l/r*.[11] T = 55 °C. Uncertainty on *r* is ±2 Å.

common to many droplet microemulsions, for example, AOT-stabilized w/o systems.[4] It should be noted that this ellipsoidal scattering law represents a plausible description, but this does not rule out other possibilities. However, all common form factors were tested,[11] and among these, the ellipsoid model gave the best statistical fits, even compared to polydisperse spherical particles (Supporting Information). On the basis of the fitted particle dimensions and intensity scale factors, estimates for the effective surfactant molecular areas at the IL−solvent interface of between 64 and 95 Å^2 were obtained. These values are similar to those found in typical w/o systems with common surfactants,[4] suggesting that the model of nanodroplet formation is physically reasonable in terms of interfacial coverage by the T-X100 surfactant. This provides further support for the idea that these unusual systems behave akin to common w/o microemulsions.

Therefore, IL-in-oil microemulsions comprising surfactant-stabilized nanodomains of ionic liquids dispersed in organic liquids may be formed. This finding expands the potential of ILs in microheterogeneous systems as possible reaction and separation media. An unusual feature of the systems studied here is the necessity to include high background levels of surfactant T-X100, suggesting that custom IL−philic surfactants should be explored to optimize performance in these new systems.

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Supporting Information Available: Details of SANS data treatment and analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Information on the SANS technique and data processing may be found at http://www.isis.rl.ac.uk/largescale and http://www.ill.fr. Absolute intensities for $I(Q)$ (cm^{-1}) were determined to within ±5% by measuring the incoherent scattering from 1 mM H_2O at ILL, whereas at ISIS, a partially deuterated polymer standard was employed.
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