# Novel microemulsions: ionic liquid-in-ionic liquid

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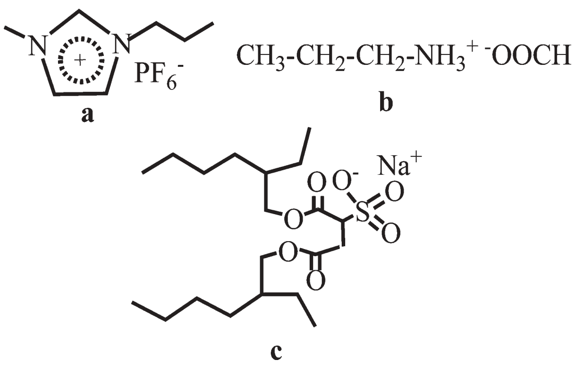
**The hydrophobic IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]) can be dispersed in hydrophilic IL propylammonium formate (PAF) with the aid of surfactant AOT, and [bmim][PF$_6$]-in-PAF microemulsions are formed.**

Microemulsions are thermodynamically stable media formed by two or more immiscible liquids which are stabilized by surfactants. These microheterogeneous systems can solubilize both polar and nonpolar substances, and they have been extensively applied in many fields, such as in chemical reactions, material science, separation science, and in the pharmaceutical industry.[1] Water is one of the most commonly used solvents and the microemulsions with an aqueous continuous phase or dispersed phase have been studied extensively. In recent years, some nonaqueous microemulsions, in which water is replaced by nonaqueous solvents, have attracted much interest because of some unique features.[2] They have been applied to cosmetics, semiconductors, solar energy conversion, microcolloids and chemical reactions.[3] They are particularly more attractive when water should be avoided.

Ionic liquids (ILs)[4] are receiving much attention as a class of neoteric nonaqueous solvents. They have some unusual properties, such as negligible vapor pressure, a wide electrochemical window, nonflammability, high thermal stability, and wide liquid range. Moreover, ILs can be functionalized by designing different cations and anions. Study on microemulsions with an IL as a component has become an attractive topic.[5–9] The evidence of dry micelle formation of several traditional surfactants in IL media has appeared in the literature.[5] In our recent work,[6] we demonstrated that 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]) could form polar nanosized droplets dispersed in a cyclohexane continuous phase, and Eastoe *et al.*[7] investigated the structure of the system by small-angle neutron scattering (SANS), which showed a regular increase in droplet volume as micelles were progressively swollen with added [bmim][BF$_4$]. In addition, we have also shown that at suitable conditions the 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$])–TX-100–water system could form microemulsions.[8] Following the discoveries of novel microemulsions, the mechanism of formation of microemulsions containing an IL with the electropositive imidazolium ring have been explored using spectroscopy techniques,[9] and the application of this kind of microemulsion in material preparation has also been attempted.[10] However, up to now, the studied microemulsion systems contain one or more volatile components that are not IL.



**Scheme 1** Structure of [bmim][PF$_6$], a; PAF, b; and AOT, c.

It is very interesting to create microemulsions in which all the components are non-volatile, and the microemulsions have desirable functions. The non-volatile, designable nature of ILs makes it possible to prepare this kind of microemulsion. Herein we report the first work studying IL-in-IL microemulsions. It is shown that the hydrophobic IL [bmim][PF$_6$] (Scheme 1a)[11] can be dispersed in hydrophilic IL propylammonium formate (PAF) (Scheme 1b)[12] with the aid of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (Scheme 1c), and [bmim][PF$_6$]-in-PAF microemulsions are formed.

Phase behavior measurement† (a) is essential to study microemulsions. In this work, anionic surfactant AOT was used as the surfactant. The ternary phase diagram of the [bmim][PF$_6$]–AOT–PAF system determined at 30 °C by direct observation is illustrated in Fig. 1. The miscibility of hydrophobic IL [bmim][PF$_6$] and hydrophilic IL PAF is very poor. For example, our experiment showed that the solubility of [bmim][PF$_6$] in PAF was less than 0.1 wt% in ambient conditions. Anionic surfactant AOT is not soluble in [bmim][PF$_6$], while it is soluble in PAF. Phase behavior studies show that AOT can promote the miscibility of [bmim][PF$_6$] and PAF in a PAF-rich region, and a single phase region is observed in the ternary phase diagram, in which the

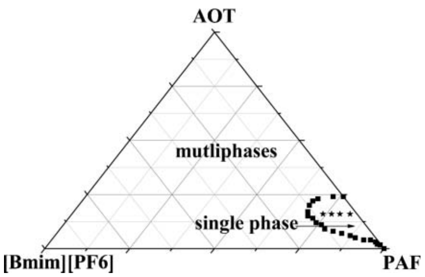


**Fig. 1** Phase diagram of the [bmim][PF$_6$]–AOT–PAF ternary system at 30 °C.

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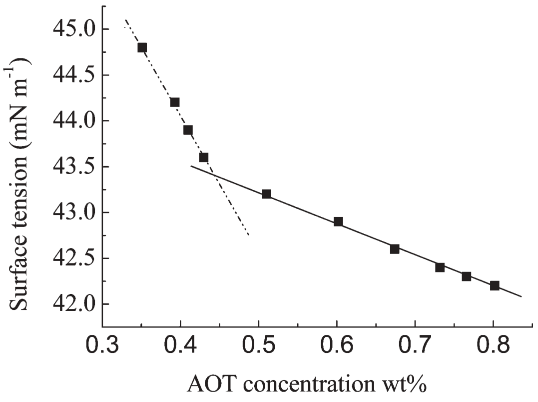

**Fig. 2** Plot of surface tension of PAF as a function of AOT concentration at 30 °C.

microemulsions are formed. Fig. 1 allows us to select conditions to characterize the system further.

Surface tension measurement† (b) is one of the most commonly used methods for studying the formation of aggregates. Fig. 2 shows the surface tension of AOT in PAF solution as a function of AOT concentration. It is known from Fig. 2 that the surface tension of the solution decreases with increasing AOT concentration and the distinct break point appears at 0.44 wt% AOT, indicating the formation of AOT micelles in PAF.

Freeze-fracture electron microscopy (FFEM)† (c) is one of the powerful tools to characterize the size and shape of the aggregates in microemulsions.[13] The micrographs obtained by FFEM technique are illustrated in Fig. 3a–d. The weight fraction of AOT in the microemulsions is kept at 0.16, and the [bmim][$PF_6$]-to-AOT molar ratios (*R*) are 0.2, 0.5, 0.75 and 1.0, respectively. These compositions are marked by the asterisks in Fig. 1. Clearly, the droplets in the microemulsions investigated in this paper are spherical. At the fixed concentration of AOT, the sizes of the droplets increase with *R*, which is similar to other conventional microemulsions.[14] The diameters (averge diameter of 100 droplets) range from about 30 nm to about 100 nm as *R* increases from 0.2 to 1.0. According to the swelling law of microemulsions, the size of the droplets should be a linear function of *R* if the droplets are spherical.[15] Fig. 3e shows dependence of $R_h$ on *R*. Obviously, $R_h$ is a linear function of *R*, *i.e.*, the microemulsions obey swelling law.

We believe that mechanism for the formation of the microemulsions is similar to that of other kinds of microemulsions.[14] [Bmim][$PF_6$] is hydrophobic and PAF is hydrophilic.[11,12] AOT is soluble in PAF and can form micelles with hydrophobic cores and the polar heads extends to PAF continuous phase. [Bmim][$PF_6$] is dispersed in the hydrophobic cores of AOT micelles in the PAF-rich phase, and [bmim][$PF_6$]-in-PAF microemulsions are formed. However, the size of droplets in the IL-in-IL microemulsions is larger than that in conventional microemulsions. The reason for this and the detailed structure of the microemulsions should be studied further.

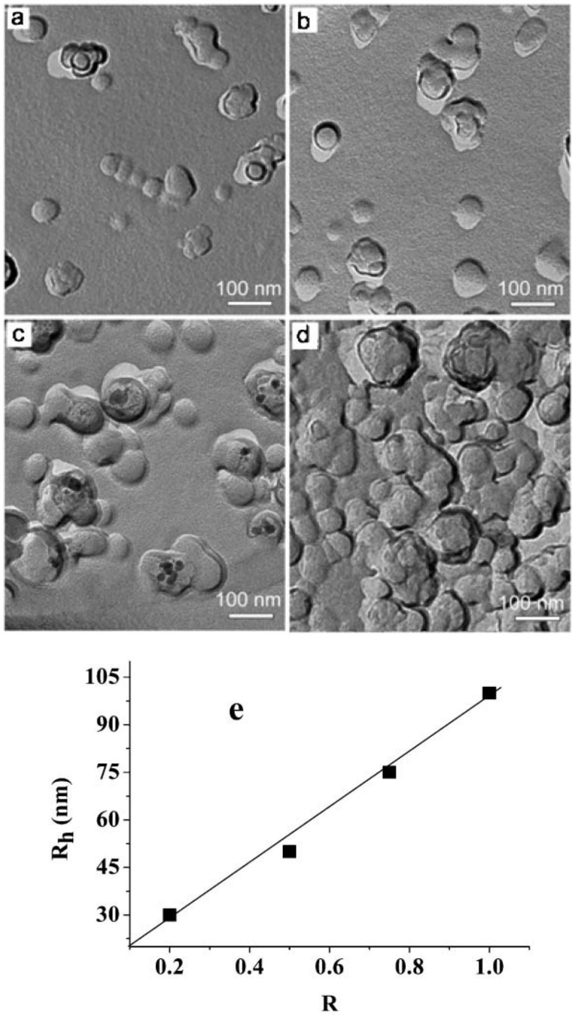

**Fig. 3** a–d. TEM images of FFEM replicas of [bmim][$PF_6$]–AOT–PAF microemulsions. a *R* = 0.2, *b* R = 0.5, c *R* = 0.75 d *R* = 1.0 (weight fraction of AOT is 0.16); e. Dependence of diameter of the droplets ($R_h$) on [bmim][$PF_6$]-to-AOT molar ratio (*R*).

In summary, we report the first work to prepare IL-in-IL microemulsions, and [bmim][$PF_6$]-in-PAF microemulsions have been prepared and characterized. Future research may be directed toward design and preparation of more IL-in-IL microemulsions with different functions. Potential applications may include carrying out chemical reactions and synthesis of organic and inorganic materials using this kind of microemulsion.

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## Notes and references

† Brief experimental procedures: (a) The ternary phase diagrams of [bmim][$PF_6$]/AOT/PAF system at 30 °C were determined by direct observation under the protection of nitrogen. The mixture consisted of hydrophobic IL [bmim][$PF_6$], surfactant AOT and hydrophilic IL PAF. In preparation of the microemulsions, the desired amounts of AOT and PAF were mixed in test tubes, [bmim][$PF_6$] was then added. The phase boundaries were determined by observing the transition from transparency to turbidity. The masses of the components were determined by a DT-100 balance with a resolution of $\pm 0.1$ mg (Shanghai Science Instrument Company). The test tubes were sealed before weighing to avoid absorption of moisture from air; (b) A JYW 200 A Tension Meter (Chengde Instrument Company, China) was used for the surface tension measurements of PAF with and without AOT at 30 °C under the protection of nitrogen. It was based on the principle of detachment of a platinum ring. The surface tension was measured after thorough mixing of the solution. The results were accurate within $\pm 0.1$ mN m$^{-1}$; (c) The procedures for

FFEM study consisted of three steps: freezing of the sample, fracturing and replication, and obtaining the transmission electron microscope (TEM) images. In the experiments, about 4 mL of the sample was placed on a 0.1 mm thick copper disk and covered with a second copper disk. The copper sandwich with the sample was frozen by plunging this sandwich into liquid propane at $-180$ °C (cooling rate was in the order of 3000 K $\mathrm{s}^{-1}$). For fracturing, the samples were clamped under liquid nitrogen inside the vacuum chamber of the freeze-etching apparatus (Balzers/BAL-TE, Liechtenstein) at a temperature of $-140$ °C. Fracturing was achieved by displacing a microtome arm cooled by liquid nitrogen, which had been cooled with liquid nitrogen. The now-exposed fracture face was immediately shadowed unidirectionally by Pt–C deposited at a 45° angle. The replicas were examined by JEOL JEM-2010 TEM.

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