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Ion-Responsive Behavior of Ionic-Liquid Surfactant Aggregates with Applications in Controlled Release and Emulsification

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We propose a simple but efficient, rapid, and quantitative ion-responsive micelle system based on counter-anion exchange of a surfactant with an imidazolium unit. The ion-exchange reaction results in the amphiphilic-to-hydrophobic transition of the imidazolium salt, leading to the destruction of the micelles, which has been successfully applied to controlled release and emulsification. The proposed design offers a novel alternative stimulus to control these smart physical aggregates besides pH, temperature and light—with extra advantages. Our finding greatly benefits both fundamental research and industry.

Introduction

Room-temperature ionic liquids (ILs) have been the subject of significant research owing to their high fluidity, ionic conductivity, thermal stability and broad liquid-state temperature range.[1–3] These distinguishing properties can be customized by rational selection of substituents, for design of task-specific functionalized materials.[4–8] Reported applications include using ILs as environmentally benign reaction solvents and separation agents and in electrochemical and biopolymer systems and molecular self-assemblies.[9–18]

Certain amphiphilic ILs, such as those containing 1-alkyl-3-methylimidazolium cations ($[C_nMIM]^+$), can form aggregates similar to cationic surfactant micelles[19–21] with potential application in areas such as controlled release, drug delivery, nanosynthesis, cleaning, and petroleum recovery in oil fields.[22,23] However, aggregates which provide a desired function in one stage of a process may not be useful, or may even hinder, in subsequent stages. Consequently, systems affording controllable formation and breakage of amphiphilic aggregates may be of significant value, and many innovative methods have been developed around control variables such as pH,[24–29] temperature,[30–35] light[36–38] and reversible reaction.[39] For example, Jiang et al. presented light-breakable polymer micelles;[38] Goodwin et al. designed pH-responsive micellar systems assembled from linear-dendritic block copolymers for controlled release;[37] Hamamoto et al. reported temperature-responsive micelles for catalytic applications;[30] and Liu et al. developed switchable surfactants using CO_2 and air as triggers;[39] Han and co-workers investigated the controlling of micelles and reverse micelles by compressed CO_2.[40,41] Active research continues, in search of practical, sensitive, rapid and quantitative methods for forming and breaking amphiphilic aggregates.

It is known that IL surface wettability can be affected by the identity of the counter-anion, which can be facilely exchanged in solution,[42–46] suggesting that anion exchange may be an effective control parameter for on-demand breakage of IL aggregates, which, to the best of our knowledge, has not been previously reported. Therefore, in this report, the ion-responsive aggregation behaviour of a model amphiphilic IL, 1-methyl-3-dodecyl imidazolium bromide (C_{12}MIMBr), was investigated. Dye-containing aggregates were observed to break upon exchange of Br^- for PF_6^-, as measured by change in dye fluorescence upon release into solution. The process was observed to be efficient, rapid and quantitative, and examples are given of potential application to controlled release and emulsification.

Results and Discussion

Ion-Exchange-Triggered Precipitation of C_{12}MIMBr

Figure 1a shows a solution with Nile Red (6 μM) encapsulated in C_{12}MIMBr (10 mM) micelles, with corresponding fluorescence emission spectrum shown in Figure 1b (curve **1**). Upon addition of 1 equiv of PF_6^- (relative to C_{12}MIMBr), the formerly transparent, light-pink solution instantly became turbid, with pinkish-white material settling in a colorless supernatant. The total loss of fluorescence in the supernatant (curve **4**) indicated that Nile Red was no longer in a hydrophobic environment, suggesting significant micellar disruption.[38] In control experiments where 1 equiv of Cl^- or Br^- was added, only a small loss of fluorescence was observed (curves **2** and **3**), and there was no visible precipitation. ^{1}H NMR spectra of 10 mM C_{12}MIMBr solution in D_2O (without Nile Red) before and after adding 1 equiv of PF_6^- are shown in Figure 2a and 2b, respectively. Loss of all peaks after adding PF_6^- indicates the disappearance

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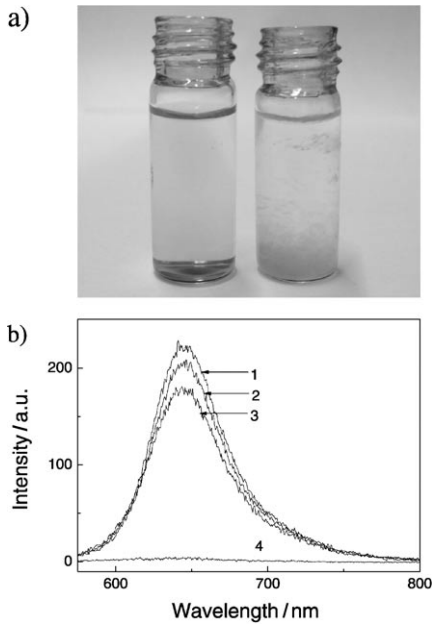


Figure 1. a) Aqueous 10 mM C_{12}MIMBr solution containing Nile Red in micelles (left); after addition of 1 equiv $NaPF_6$ (right). b) Fluorescence emission spectra of C_{12}MIMBr solutions containing Nile Red before (**1**) and after addition of 1 equiv of NaCl (**2**), NaBr (**3**) and $NaPF_6$ (**4**), where the concentration of Nile Red is 6 μM.

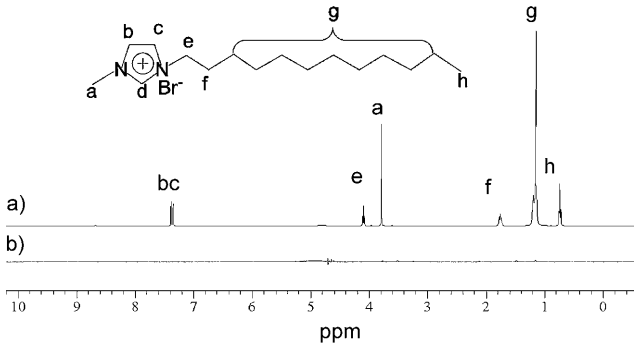
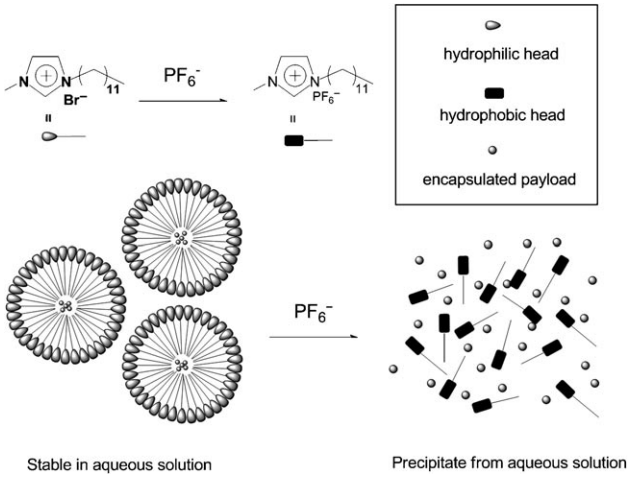


Figure 2. ^{1}H NMR spectra of a) 10 mM C_{12}MIMBr solution in D_2O; b) supernatant after adding 1 equiv $NaPF_6$.

of alkylimidazolium salts from solution. The white precipitate from the NMR samples was isolated by filtration, dried, and examined by X-ray photoelectron spectroscopy (XPS). Figure 3 shows that P and F were present in the precipitate, while Br was absent. These results together indicate that anion exchange from Br^- to PF_6^- completely removes $C_{12}MIM^+$ from the aqueous solution, with corresponding precipitation of Nile Red (Scheme 1).



Scheme 1. Anion exchange to PF_6^- and resulting micelle collapse. For clarity, the payload is drawn together in the center of the micelles; actually it is probably randomly distributed between the hydrophobic parts of the surfactant inside the micelles.

Further, the precipitation was rapid, occurring within 1~2 seconds after addition of PF_6^- (Figure 4), comparatively much faster than other micelle-breaking methods mentioned above.[29,38] For example, breaking pH-, thermo- or light-sensi-

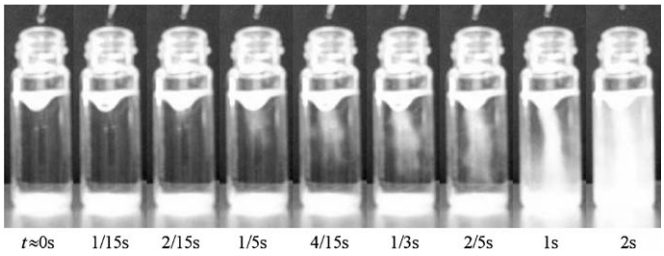


Figure 4. High-speed photographs showing precipitation after adding 12 μL of 3.75 M $NaPF_6$ to 15 mL of a 10 mM aqueous solution of C_{12}MIMBr (for a final PF_6^- concentration of 3 mM, that is, 0.3 equiv relative to C_{12}MIMBr) with mild agitation (vial height 6 cm.)

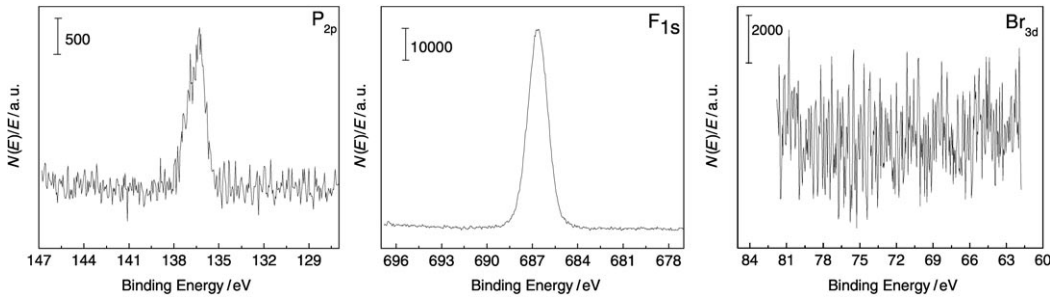


Figure 3. XP spectra of P_{2p}, F_{1s}, and Br_{3d} for a precipitate generated by adding 1 equiv $NaPF_6$ to the solution in Figure 2a.

tive aggregates requires timescales on the order of ~1–100 h.[29,33,37] Even simple salt-induced micelle collapse, where electrostatic repulsion between ionized surfactant head groups is screened by increasing concentrations of counter-ions, requires relatively long time. For example, Ma et al. have reported a minimum period of 30 min to destroy copolymer micelles with 2 M NaCl.[47,48]

Potential Applications in Controlled Release

To explore potential applications for controlled release of micellar payloads, differing amounts of PF_6^- were added to each of a series of otherwise identical Nile-Red-loaded C_{12}MIMBr micelle solutions, and the Nile Red fluorescence emission intensity was recorded (Figure 5). Fluorescence intensity decreased

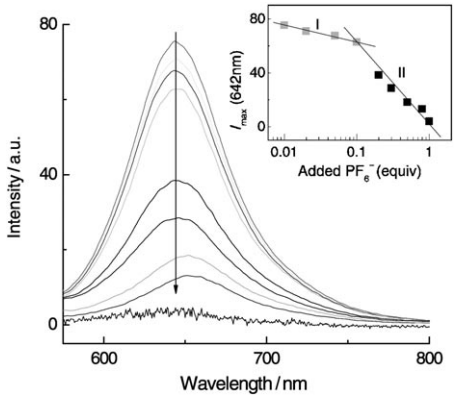


Figure 5. Decrease in Nile Red fluorescence intensity with increasing amount of PF_6^- added to the C_{12}MIMBr micelle solution. The staring concentration of micelles and loaded Nile Red was 10 mM and 6 μM, respectively. Inset: semi-logarithmic relationship between PF_6^- concentration and peak fluorescence intensity at 642 nm.

with increasing PF_6^- concentration, as Nile Red progressively partitioned from hydrophobic micellar interiors to the aqueous exterior, indicating increasing disruption of micelles with increasing PF_6^- concentration. The relationship between the maximum fluorescence intensity at 642 nm and the logarithm of added PF_6^- amount showed two distinct linear regions (Figure 5 inset). Recently, Yoshii and co-workers reported results of a molecular dynamics study of free energy of micelle formation for sodium dodecyl sulphate, wherein $\Delta\mu_{n+1}$, the free energy change for adding one surfactant molecule to spherical micelles of size *n*, was higher at small *n* and lower for larger *n*, indicating that addition of each successive surfactant molecule affords more overall stabilization when micelles are smaller.[49] Interpreting their results for sequential extraction of surfactant molecules from a micelle, it can be proposed that loss of a surfactant molecule causes less overall destabilization when micelles are larger. The data shown in Figure 5 inset, can be interpreted in this context (see Scheme 2), where for $\leq$0.1 equiv of added PF_6^-, conversion of C_{12}MIMBr to C_{12}MIMPF_6 (with subsequent extraction from micelles and desolubilization) caused little overall micelle disruption. In this case (Stage I), the micelles remained *meta*-stable and minimal Nile Red partitioning to aqueous resulted in only ~15% reduction in fluorescence intensity. However, at >0.1 equiv of added PF_6^- (Stage II), micelle disassociation increased significantly, with corresponding release of encapsulated Nile Red, as C_{12}MIMPF_6 formed and precipitated. In Stage II, fluorescence intensity fell off more sharply, to essentially zero at 1 equiv of added PF_6^-, where ion-exchange to insoluble C_{12}MIMPF_6 was complete. These observations are in general accord with the results of Yoshii.[49]

Potential Applications in Oil Transportation

Transporting viscous oils through pipelines in an emulsified state can be useful when the emulsion is less viscous than the oil itself, though at the terminus the emulsion must be broken to recover the oil.[50] To investigate applicability of C_{12}MIMBr for stabilizing, and C_{12}MIM PF_6 for subsequently breaking oil–water emulsions, 95 mg of C_{12}MIMBr was added to a vial containing 6 mL of 2:1 (v/v) cyclohexane:water and the mixture was shaken thoroughly, yielding a milk-white emulsion (Figure 6b). The resulting emulsion showed little evidence of separation until after ~1 hour, at which point a clear lower liquid phase began to appear (Figure 6c). However, after 50 h, the emulsion still occupied ~80% of the liquid volume (Figure 6d). In contrast, adding 1 equiv of $NaPF_6$ to a freshly shaken emulsion resulted in complete separation into two liquid layers

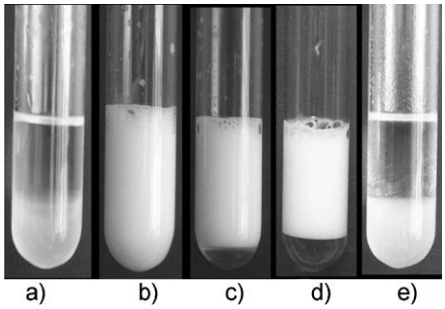
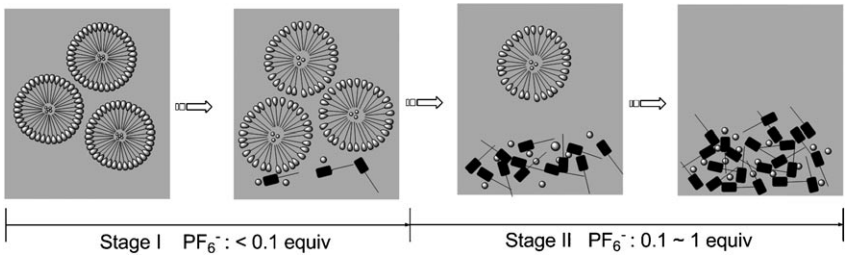


Figure 6. a) 2:1 (v/v) cyclohexane/water; b) with C_{12}MIMBr, shaken 3 min; C_{12}MIMBr-induced emulsion after 1 hour (c) and 50 h (d); e) approximately 2 min after adding 1 equiv $NaPF_6$ to (b).



Scheme 2. Illustration of the dissociation of micelles and release of encapsulated payload by adding PF_6^-.

within 2 min, with $C_{12}MIMPF_6$ precipitating (Figure 6e). These observations indicate that the ion-exchange/desolubilization mechanism discussed here might show promise in practical industrial emulsion forming/separating applications, including oil transport. Further investigations of improving the stable time for emulsification such as by selection of proper alkyl-chain of ILs-surfactants, are still needed for the practical applications.

Applying IL surfactants in this type of system promises practical advantages beyond those available from traditional surfactants. For example, downstream resolubilization of precipitated material can significantly impact process viability. For cationic IL surfactants such as $C_{12}MIMX$, PF_6^- salts are soluble in organic solvents (ethanol, acetonitrile, or DMF) and may have potential applications in industry. In contrast, fatty acid sodium salts (*anionic* surfactants) can undergo ion-exchange in aqueous systems, thereby breaking micelles by precipitation (e.g. as calcium salts), but these products often have relatively poor solubility in common solvents like H_2O, ethanol, acetonitrile, and DMF, and can rapidly foul industrial process equipment. Further, the method discussed here is simple, consisting simply of adding commercially available $NaPF_6$, and, because the exchange reaction is rapid and quantitative, the degree of dissociation/desolubilization can be finely controlled via the amount of PF_6^- added. Such precise control is generally not obtainable when using other micelle-breaking stimuli such as pH, light, temperature or gas-reversible reactions, which depend not only on the dose but also depend strongly on time, making them more difficult to simplify and fully manipulate.

IL surfactants offer further unique properties and intriguing possibilities. For example, thanks to facile molecular design of ILs, other units beside imidazolium (e.g. alkylammonium, pyrrolidinium or "greener" cations derived from amino acids[51]) can be integrated into these smart amphiphilic molecules. Other "green" counterions could be used for ion-exchange/desolubilization, as well. For example, compared to PF_6, bis(trifluormethanesulfon)imide and tris(pentafluoroethyl)trifluorophosphate anions do not hydrolyze in aqueous system (i.e. releasing corrosive HF) and are more hydrophobic. Moreover, in this report the $C_{12}MIMPF_6$ generated by switching off aggregates is also an IL (melting point ca. 30-40 °C), which could be recovered and recycled or used in other applications. It should be noted that *N,N'*-dialkylimidazolium hexafluorophosphate salts are a kind of molecular liquid crystal which could be used as an ordered solvent in polymerization and stereochemically controlled organic reactions.[52] In addition, the hexafluorophosphate salt has negligible surface activity and water solubility—a sustainable environmental advantage. Lastly, here the concept of IL surfactants could be facilely extended to amphiphilic IL polymers, offering further potential practical applications.

Conclusions

$C_{12}MIMBr$, a surface-active ionic liquid, was shown to form micelles in aqueous systems (measured CMC = 6.4 mM). Upon exchange of Br^- to PF_6^-, micelles exhibited progressive, and ultimately complete, disaggregation; and a mechanism has been proposed. This phenomenon was rapid, incremental and highly controllable, and feasibility is demonstrated for application to controlled release of hydrophobic dye and formation/destabilization of oil/water emulsions. Ion-exchange-based modulation of micelle structure and surfactant solubility offers an alternative control parameter that may be of significant applicability in both fundamental research (e.g. nanoscience, advanced functional materials) and industrial settings (e.g. controlled release and emulsification).

Experimental Section

Materials: 1-bromododecane (98%) and 1-methylimidazole (99%) were obtained from Acros. $NaPF_6$ (98%) was obtained from Aldrich. Nile Red was obtained from Fluka. 1-Methylimidazole was distilled before use, and all other reagents were used as received. Aqueous solutions were prepared immediately prior to use, with ultrapure water from a Millipore-Q system (18.2 MΩ cm).

Preparation of $C_{12}MIMBr$: 1-dodecyl-3-methyl imidazolium bromide ($C_{12}MIMBr$) was synthesized by reflux of 1-methylimidazole (3.3 g, 0.04 mol) and 1-bromododecane (5.7 g, 0.06 mol) for about 24 h.[45] The resulting product was purified by crystallization and confirmed by NMR. ^1H NMR (DMSO): $\delta = 9.13$ (s, 1H), 7.76 (s, 1H), 7.71 (s, 1H), 4.15 (t, 2H), 3.85 (s, 3H), 1.77 (m, 2H), 1.24 (s, 18H), 0.85 (t, 3H).

Determining CMC of $C_{12}MIMBr$: Critical micelle concentration (CMC) was determined by measuring variation in fluorescence of Nile Red dye across a series of solutions of increasing $C_{12}MIMBr$ concentration, from 1 mM to 9 mM.[37] Solutions were prepared by adding 1 mL of 60 μM Nile Red in tetrahydrofuran (THF) to each vial, where different amounts of $C_{12}MIMBr$ has been put inside in advance. Then 1 mL of deionized water was added dropwise to the solution under ultrasonication. More deionized water was added to bring the solution to the desired concentration. The solution was equilibrated under sonication for a few hours at room temperature, after which THF was removed via evaporation by heating to 70 °C in a water bath for 3 h. To ensure full micelle loading, Nile Red was in significant excess relative to $C_{12}MIMBr$. During removal of THF, unencapsulated Nile Red precipitated and was later removed by filtration through a 0.22 μm nylon membrane. Subsequently, fluorescence emission spectra were measured at 575–800 nm, with an excitation wavelength of 550 nm. Emission intensity at 642 nm (λ_{max}) was plotted against the log of $C_{12}MIMBr$ concentration, yielding an estimated CMC of 6.4 mM (Figure 7).

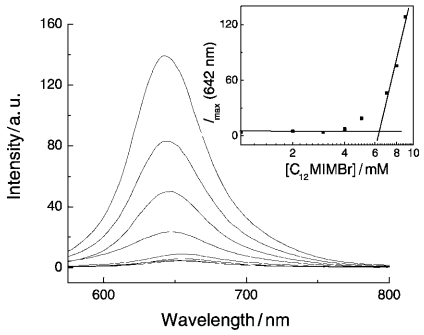


Figure 7. Fluorescence emission spectra of Nile Red ($\lambda_{exc} = 550$ nm) in solutions containing varying concentrations of $C_{12}MIMBr$, where the concentration of Nile Red is 6 μM. Inset: The relationship between maximum emission intensity at 642 nm and the logarithm of $C_{12}MIMBr$ concentration.

Instruments: ^{1}H NMR spectra were obtained using a Varian Unity-400 (400 MHz) NMR spectrometer with tetramethylsilane (TMS) as an internal standard in per-deuterated dimethyl sulfoxide ([D_6]DMSO) or D_2O. Fluorescence experiments were carried out using a Perkin–Elmer LS55 Luminescence spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted using a VG ESCALAB MK II spectrometer (VG Scientific, UK) employing a monochromatic Mg K_α X-ray source ($h\gamma = 1253.6$ eV). Peak positions were internally referenced to the C_{1s} peak at 284.6 eV. Rapid-ion-response photographs were taken with a Kodak DX6340 digital camera at 15 fps.

Acknowledgements

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Keywords: counter-anion exchange · emulsion · ionic liquids · micelles · surfactants

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