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Reversible Switching of Amphiphilic Self-assemblies Between Micelles and Microemulsions by a Thermal Stimulus

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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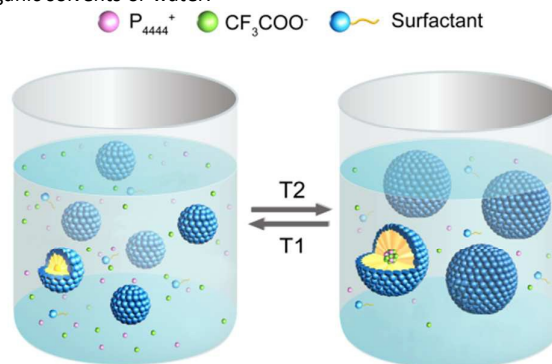
The ionic liquid (IL), tetrabutylphosphonium trifluoroacetate ([P₄₄₄₄][CF₃COO]), showed a low critical solution temperature (LCST)-type phase transition in water. Using this temperature-sensitive IL and Triton X-100/H₂O system, the reversible transformation between micelles and microemulsions was thus realized by a thermal stimulus for the first time.

The properties and functions of amphiphilic self-assemblies depend strongly on their microstructures, such as micelles, vesicles, liquid crystals, emulsions or microemulsions.¹ The amphiphilic self-assemblies have been widely used in numbers of industrial applications, such as environmental science, oil recovery, food industry, and mineral processing.² There has been growing interest in reversible structural transitions of self-assemblies and temperature is often used as a trigger.³ The transition from a higher ordered state to a lower ordered one or a disordered one has been observed, such as the transition from vesicles to micelles on increasing temperature,^{3a-c} the switching between micelles and liquid crystals,^{3d} as well as microemulsions and liquid crystals.^{3e} Moreover, the structural transitions of self-assemblies of block polymers in ionic liquids (ILs) have been investigated by Lodge and Watanabe et al.⁴ For instance, the reversible micellization and sol-gel transition of ABA triblock copolymer solutions in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) triggered by a photostimulus is described.^{4a} Also, they found that a PEO-b-P(AzoMA-r-NIPAm) diblock copolymer exhibited low-temperature micelle and high-temperature unimer transition in [bmim][PF₆].^{4b}

Micelles and microemulsions are liquid dispersions formed by amphiphilic molecules. A typical micelle in aqueous solution is an

aggregate with the hydrophilic heads in contact with surrounding water, sequestering the hydrophobic tails in the centre. So, in micellar dispersions the aggregates are made of surfactants only. Microemulsions are clear, thermodynamically stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. In comparison with micelles, microemulsions are much larger as they have liquid cores. The reversible structural transition between micelles and microemulsions seems unfeasible as water and oil are essentially awfully immiscible in traditional systems.

ILs are organic salts designed to melt below 100 °C, in particular at room temperature, which have characteristic properties such as negligible volatility and nonflammability.⁵ ILs are versatile as they can be designed for a special purpose, which makes them highly desirable in many processes of industrial importance. Of particular interest is the self-assembly of amphiphilic molecules in contact with ILs thereby forming aggregates such as micelles⁶ and vesicles.⁷ Besides, microemulsions have been created by using ILs to replace organic solvents or water.⁸



Scheme 1 A schematic representation of the reversible phase transition behavior between micelles and microemulsions induced by temperature.

Herein, we present for the first time a temperature-induced reversible structural transition between micelles and microemulsions by using a temperature-sensitive IL and Triton X-100/H₂O system. The IL, tetrabutylphosphonium trifluoroacetate ([P₄₄₄₄][CF₃COO]) was reported to exhibit a temperature-sensitive

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[‡] Electronic Supplementary Information (ESI) available: Materials, characterization, and additional data. See DOI: 10.1039/x0xx00000x

phase behavior in water.⁹ In contrast to most substances whose solubility increased with heating, $[P_{4444}][CF_3COO]$ was miscible with water on cooling but became insoluble on heating. This unusual phase behavior was classified as a lower critical solution temperature (LCST)-type phase transition. Temperature can be used as a trigger to switch single phase to double phase “on” and “off”. In the presence of suitable amphiphilic molecules, the reversible transition between micelles and microemulsions becomes reality (Scheme 1).

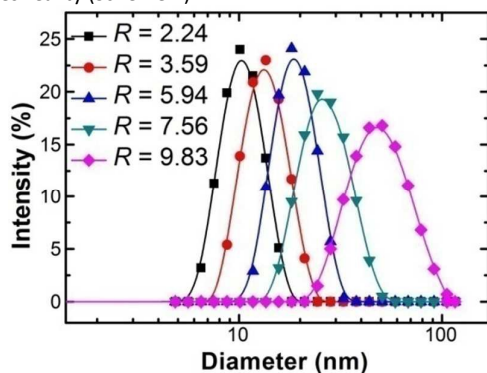


Fig. 1 Sizes and size distributions of the $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ ($[P_{4444}][CF_3COO]/H_2O$, 1:4, w/w) assemblies at different R values ($R = [P_{4444}][CF_3COO]/Triton\ X-100$ molar ratio) at 40 °C.

According to the $[P_{4444}][CF_3COO]/H_2O$ binary phase diagram with temperature (Fig. S1) and the $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ ternary phase diagram at 40 and 50 °C (Fig. S2), the temperature used here was 40 °C, in order to assure that $[P_{4444}][CF_3COO]$ and H_2O were immiscible by themselves but microheterogeneous in the presence of Triton X-100. To prove the formation of microemulsions, dynamic light scattering (DLS) was used to study the swelling behavior of $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ ternary system. The $[P_{4444}][CF_3COO]/H_2O$ weight ratio was fixed at 1:4, but the content of Triton X-100 was changed, which was usually denoted by the $[P_{4444}][CF_3COO]/Triton\ X-100$ molar ratio, R , a parameter to reflect the microemulsion size. As shown in Fig. 1, the droplet sizes of the $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ assemblies increased from 10.1, 13.5, 18.2, 24.4, to 50.7 nm with increasing R from 2.24, 3.59, 5.94, 7.56, to 9.83. This regular swelling behavior was consistent with the volume of dispersed nanodomains being directly proportional to the amount of added inner phase, which was common to many traditional droplet microemulsions,¹⁰ suggesting the formation of $[P_{4444}][CF_3COO]$ -in- H_2O microemulsions. To confirm the swelling behavior, we increased R value through adding $[P_{4444}][CF_3COO]$ at a fixed $H_2O/Triton\ X-100$ weight ratio (10:1) (Fig. S4). A similar result was observed, further suggesting that the ternary system possessed the characteristic swelling behaviour of microemulsions at 40 °C.

However, when temperature was decreased down to 20 °C, that is, $[P_{4444}][CF_3COO]$ and H_2O were miscible, the size of the $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ assembly was 6.7 nm at $R = 4.29$ and was only increased to 9.5 nm when R reached up to 9.48 (Fig. S5). Obviously, this size was much smaller than that of microemulsions formed at 40 °C. Considering that $[P_{4444}][CF_3COO]$ was miscible with water at 20 °C, Triton X-100 may form micelles and $[P_{4444}][CF_3COO]$ molecules were mainly dissolved in the

surrounding water phase. A slight increase in size was possibly due to the interaction between the IL and IL-philic polyoxyethylene (POE) units of Triton X-100.¹¹ To prove the formation of micelles, the surface tension measurement of the homogeneous solution as a function of Triton X-100 concentration at 20 °C was performed (Fig. S6). The surface tension gradually decreased with increasing the concentration of Triton X-100, indicating that Triton X-100 was adsorbed at the air/solution interface. The initial decrease of the surface tension was followed by an abrupt change in the slope of the surface tension versus Triton X-100 concentration. After the breaking point, the surface tension no longer changed obviously, suggesting the formation of micelles in the homogeneous mixture where the break point corresponded to a critical micellar concentration, which was about 0.24 mmol/L.

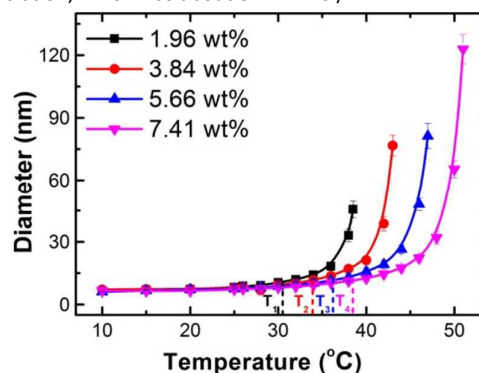


Fig. 2 Temperature dependence of the average sizes of the $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ ($[P_{4444}][CF_3COO]/H_2O$, 1:4, w/w) assemblies at different Triton X-100 contents.

In order to detect the phase transition between micelles and microemulsions by changing the temperature, the sizes of the $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ assemblies at a series of temperature were measured by DLS (Fig. 2). As the addition of Triton X-100 would affect the critical temperature of $[P_{4444}][CF_3COO]$ in aqueous solutions, the samples at different Triton X-100 contents were also investigated (Fig. 2). In the low temperature range, the average sizes remained almost unchanged, which was followed by a dramatic increase when temperature was successively increased to a certain extent. This result suggests that the microstructure of aggregates is changed from micelles to microemulsions by a temperature stimulus. $[P_{4444}][CF_3COO]$ molecules are relatively hydrophobic at high temperature and will try to avoid contacting with water, and thus enter the interior of micelles as possibly as they can. This solubilization process is realized by droplet exchange (i.e. by fusion and fission of the droplets) rapidly. The turning point of temperature from micelles to microemulsions is defined as T_n and $T_1 < T_2 < T_3 < T_4$ when the Triton X-100 contents are 1.96, 3.84, 5.66, and 7.41 wt%, respectively. The reason is that the addition of Triton X-100 suppresses the phase transition of $[P_{4444}][CF_3COO]/H_2O$, resulting in the increased LCST with increasing the Triton X-100 content. This transition triggered by temperature stimulus was reversible since the microemulsions formed at high temperature could transit back to micelles when temperature was decreased. (Fig. S7)

The conductivity is a powerful tool to reflect the microstructure information and microstructural change of aggregates. Fig. 3 shows

the conductivity versus temperature curves of the $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ assemblies at different Triton X-100 contents. The conductivity gradually increased with increasing temperature, followed by an obvious change in the slope of the conductivity versus temperature. After the breaking point (denoted as T_n), the conductivity increased relatively slowly, indicating that the microstructure of aggregates was changed from micelles to microemulsions when temperature was increased to a certain extent. T_1-T_4 are 30, 34, 36, and 38 °C when the Triton X-100 contents are 1.96, 3.84, 5.66, and 7.41 wt%, respectively, according with those obtained by DLS. The slow increase in conductivity after the phase transition is attributed to the fact that highly conductive ions ($[P_{4444}]^+$ and $[CF_3COO]^-$) are associated into $[P_{4444}][CF_3COO]$ ion pairs and thus form microemulsions. The latter is known to have a lower conductivity than its aqueous solution.

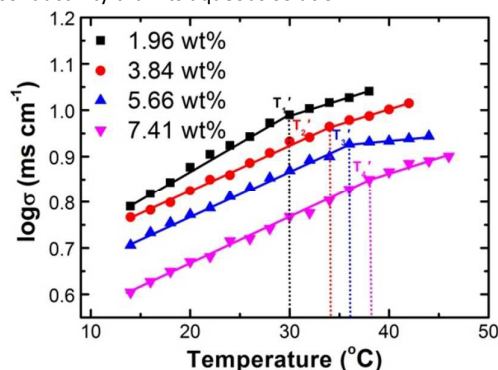


Fig. 3 Temperature dependence of the conductivities of the $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ ($[P_{4444}][CF_3COO]/H_2O$, 1:4, w/w) assemblies at different Triton X-100 contents.

Freeze-fracture transmission electron microscopy (FF-TEM) can provide a direct image of the aggregates in a liquid sample. The morphologies of the $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ (1:4:0.3, w/w) assemblies at different temperatures were examined with FF-TEM (Fig. S8). A representative image at 20 °C shows a spherical structure with a diameter of about 10 nm, in accordance with the DLS result. At 40 °C a tendency toward aggregation of the small droplets into a cluster structure can be observed, which was reported to be a universal phenomenon in IL-containing microemulsions.¹² The average size is about 30 nm, close to that obtained by DLS. Thus, FF-TEM also provides a powerful proof that the reversible transformation between micelles and microemulsions is realized by a thermal stimulus.

The phase transition behavior of $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ ternary system with temperature was further investigated by small-angle X-ray scattering (SAXS) technique. Fig. 4 shows the 1D SAXS curves of the particles in $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ ternary system at different temperatures. In the Guinier region of each SAXS curve, the self-assembly droplet size increases with increasing temperature. The radii of gyration (R_g) of the droplets at 25, 35, 45, and 50 °C were obtained (Table S1). Gnom program was used to calculate the pair distance distribution function (PDDF), $p(r)$, which is the real-space coordinate associated with $I(q)$ and connected via the Fourier transformation:^{13,14}

$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin qr}{qr} dr$$

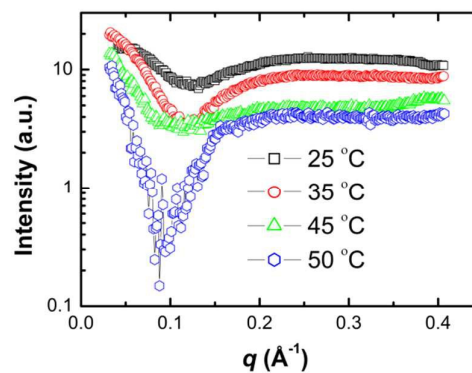


Fig. 4 SAXS intensity curves of the particles in $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ (1:4:0.3, w/w) ternary system at different temperatures.

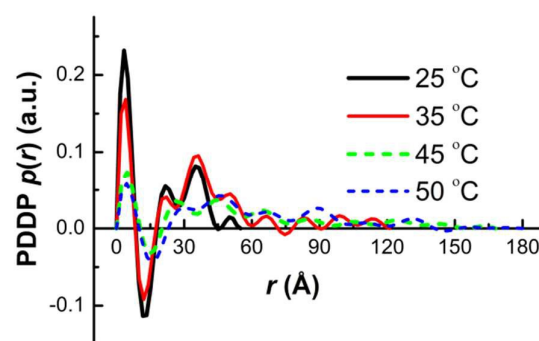


Fig. 5 Pair distance distribution function of the particles in $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ (1:4:0.3, w/w) ternary system at different temperatures.

Fig. 5 shows the $p(r)$ functions of the particles in $[P_{4444}][CF_3COO]/H_2O/Triton\ X-100$ ternary system at different temperatures. From the $p(r)$ functions, the maximum dimensions (D_{max}) of the particles at each temperature were obtained (Table S1). At 25 °C, the $p(r)$ functions of the spherical micelle have three minimums, indicating that the micelle is a multilayer sphere with several density fluctuations from the centre to the shell in the presence of $[P_{4444}][CF_3COO]$, and the density fluctuation of the core part is minus. The $p(r)$ functions of the particle at 35, 45, and 50 °C all show the structural characteristic of unilamellar vesicle,^{15,16} which means that the micelles are swollen by $[P_{4444}][CF_3COO]$ and changed into microemulsion clusters at 35 °C.¹² This is the first time that the cluster structure of IL-containing microemulsions is confirmed by SAXS. With increasing temperature from 25 °C to 35 °C, D_{max} and R_g increased notably from 5.5 and 1.9 nm to 12.1 and 3.5 nm, respectively. A further increase (from 12.1 and 3.5 nm to 16.8 and 4.9 nm, respectively) was also remarkable when the system was heated to 45 °C. However, when the temperature was increased up to 50 °C, D_{max} and R_g just increased slightly to 18.1 and 5.1 nm, respectively. It seems that the system has approached to its extreme status when the temperature is increased up to 50 °C. Actually, this result conforms to the fact that a further increase in temperature (>50 °C) will lead to the phase separation of the system. It can be concluded from the SAXS results that the micelles were swollen to form microemulsions with increasing temperature

as more and more IL molecules entered the interior of the micelles while the microemulsion cluster structure appeared concurrently. Thus, the phase transition from micelles to microemulsions was again confirmed by SAXS measurements.

Here, it is worthy noticing that D_{\max} is much smaller than the size obtained by DLS measurement. DLS and SAXS are both small angle scattering techniques and the vital structural information can be provided by the scattered light due to small contrasting features of samples, however, the type of contrast is different. In SAXS this is an electron density contrast, and for DLS this is a transmittance contrast. This difference means that there is a contrast problem when measuring a sample. For IL-containing microemulsions, we have mentioned above that large-sized microemulsion droplet clusters are prone to appear when microemulsions are swollen to a certain extent.¹² In these clusters, the microemulsion droplets are adhered together and there is not a very distinct interface among the droplets,^{12a} however, the electron density contrast between the surrounding water and surfactant interface can still be detected by SAXS. Therefore, D_{\max} obtained by SAXS is the diameter of microemulsion droplets whereas the size provided by DLS is the hydraulic diameter of self-assemblies, which only gives the structure information of microemulsion clusters, rather than single microemulsion droplet. In fact, the size of IL-containing microemulsions determined by small-angle neutron scattering (SANS) is also much smaller than the DLS result.¹⁰ The reason is similar, but the type of contrast in SANS is a contrast in neutron scattering cross-section.

In summary, the ionic liquid, tetrabutylphosphonium trifluoroacetate ($[P_{4444}][CF_3COO]$) exhibited a lower critical solution temperature (LCST) phase behavior in water. $[P_{4444}][CF_3COO]$ was miscible with water at low temperature but became insoluble at temperature higher than LCST. Based on this unusual phase behavior, microemulsions were created through adding suitable amount of a surfactant (Triton X-100) at high temperature. When temperature was lower than LCST, Triton X-100 molecules aggregated into micelles and $[P_{4444}][CF_3COO]$ was dissolved into the surrounding aqueous water. A reversible phase transition between micelles and microemulsions can be switched by using temperature as a trigger. We consider that this transition may be extended to other nonionic surfactants, including polymeric surfactants.

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (21273235, 21303076, and 11405199).

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