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ARTICLE TYPE

## Study of miniemulsion formulation containing 1-octyl-3-methylimidazolium hexafluorophosphate for application in low-emitting coating products

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Room temperature ionic liquids (RTILs) are non-volatile organic salts and some of them with low melting point may replace conventional coalescing agents in waterborne coating. Thus prevent volatile organic compounds (VOCs) emission caused by coalescing agents. The formation of waterborne coating containing RTILs can be achieved by encapsulation of RTILs inside latexes via miniemulsion polymerization. Achieving stable miniemulsion is a crucial step for further polymerization. In this study, 1-octyl-3-methylimidazolium hexafluorophosphate (C<sub>8</sub>mimPF<sub>6</sub>) was chosen, and various factors which might affect droplet size and its stability were investigated. These included surfactant type, surfactant concentration, and C<sub>8</sub>mimPF<sub>6</sub> concentration. It has been found that the presence of a small amount of C<sub>8</sub>mimPF<sub>6</sub> coupled with the surfactant would offer marked effects on droplet size reduction and the droplet stability. Such effect may reach the maximum within 1~5 wt% C<sub>8</sub>mimPF<sub>6</sub>. Above the critical concentration, adding more C<sub>8</sub>mimPF<sub>6</sub> to the oil phase may cause larger initial droplet size as well as weaken the droplet stability. Such observations were consistent with the zeta potential measurement for miniemulsions prepared under similar conditions.

### 20 Introduction

As legislations about restrictions on volatile organic compounds (VOCs) become more stringent, there has been a trend moving away from solvent-borne coating towards waterborne coating. For waterborne coating, water is used as solvent for dispersion water-reducible resins or latex resins, pigment, filler, and other additives. Though the substitution of organic solvent for water reduces the main VOCs emissions caused by the solvent-borne coating, VOCs derived from organic additives or solvent in waterborne coatings cannot be ignored. For example, Texanol is a coalescing agent used in latex coating to reduce the glass transition temperature (T<sub>g</sub>), thus enhances film formation at a lower temperature. After film formation, Texanol slowly diffused out of the film and evaporated as VOCs,<sup>1</sup> and released “a weak, but mildly unpleasant odour that can persist for days beyond the initial application”.<sup>2</sup>

In order to overcome the VOCs caused by organic solvent, room temperature ionic liquids (RTILs) which are composed of a bulky organic cation and an inorganic anion can be good substitutions. RTILs exhibit a liquid state around room conditions and show unique properties such as chemical, thermal, electrochemical stability, non-volatility, ionic conductance.<sup>3</sup> Hence they are often viewed as “green solvents” in place of conventional organic solvents.<sup>4</sup> RTILs have been found practical applications in the aspects of catalysis, organic/inorganic synthesis, extraction processes, and polymer science.<sup>5-8</sup> In the

aspect of polymer science, RTILs with low melting point have been used as effective plasticizers to reduce T<sub>g</sub> of polymer, thus they could be used as coalescing agents for the reduction of film forming temperature. Scott et al. found that 1-butyl-3-methylimidazolium hexafluorophosphate (C<sub>4</sub>mimPF<sub>6</sub>) could act as a plasticizer for polymer reaction of poly(methyl methacrylate) (PMMA). In which it exhibited a linear drop in glass transition temperature as compared with the one without C<sub>4</sub>mimPF<sub>6</sub>.<sup>9</sup> Mok et al. further studied the compositions of PMMA and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C<sub>2</sub>mimTFSI) from 10 wt % polymer to pure polymer.<sup>10</sup> Two glass transition peaks on DSC curves which represented RTILs and PMMA, respectively at intermediate weight ratio were observed, and T<sub>g</sub> of PMMA linearly reduced from 133 °C to -7 °C as the concentration of PMMA decreased from 100 wt% to 35 wt%. Oh et al. found that RTILs not only acted as plasticizers for the compositions of single-walled carbon nanotube (SWCNT) and polydimethylsiloxane (PDMS), but also promoted the exfoliation and dispersion of SWCNT in PDMS.<sup>11</sup>

With the functions of both reducing T<sub>g</sub> and non-volatility, RTILs may replace the conventional coalescing agents to enhance film formation with minimum evaporation, thus VOCs emission can be significantly reduced. The final film product, consisting of polymer/RTILs composite has superior thermal stability and improved mechanical strength as compared with the one without RTILs. In addition, RTILs may play other roles such as enhancing the ionic conductivity of the film.<sup>12-14</sup> Susan et al. synthesized polymer electrolytes via the polymerization of MMA

in C<sub>2</sub>mimTFSI, in the present of a cross-linker. They obtained self-standing, flexible, and transparent films with ionic conductivity reaching a value close to 10<sup>-2</sup> S·cm<sup>-1</sup>.<sup>13</sup> This conductivity widens the application of RTILs in antistatic coating.<sup>15, 16</sup> RTILs also show effectiveness as anti-biofouling agents, which could be used in marine antifouling coatings.<sup>17</sup> These various functions of RTILs enable them to be “super additives”, hence having high potential to be used in coating products.

Furthermore, RTILs may be desirable components which suit various properties of solvent. For example, RTILs may be hydrophobic to overcome existing problem of low water resistance of coating film. However, hydrophobic RTILs cannot be dispersed directly into water phase; instead, it would be encapsulated inside latexes. Normally, latex coating is prepared by emulsion polymerization which cannot encapsulate RTILs due to its micelle nucleation mechanism. In miniemulsion, relatively stable oil droplets, ranging from 50 to 500 nm in diameter, can be dispersed in water phase. Since most of the surfactant is adsorbed on the surface of droplets, polymerization conducts primarily by the droplet nucleation mechanism. For droplet nucleation mechanism, monomers are polymerized directly inside droplets rather than transferring from droplets to micelles. Thus the final latexes originating from droplets would allow hydrophobic compounds presenting in original droplets to be encapsulated by polymers in the final latexes. The encapsulation of hydrophobic compounds, such as Miglyol 812, castor oil, and n-heptane by miniemulsion polymerization had been reported.<sup>18-20</sup> Thus it is possible to use miniemulsion polymerization to encapsulate RTILs.

To the best of our knowledge, no such work has been done regarding to the encapsulation of RTILs by miniemulsion polymerization. The processes are divided into two steps: (i) initial formation of miniemulsion; (ii) polymerization process. Our study focused on the first step, producing a stable miniemulsion. In this study, considering the factors, i.e. low melting point and low solubility in water, required by coalescence agent for film water resistance, 1-octyl-3-methylimidazolium hexafluorophosphate (C<sub>8</sub>mimPF<sub>6</sub>) with a melting point of -82°C and a solubility of 2.26 g·l<sup>-1</sup> in water was chosen as the target RTILs.<sup>21, 22</sup> Systematically studying various factors, including surfactant type, surfactant concentration, C<sub>8</sub>mimPF<sub>6</sub> concentration on the droplet size and stability of miniemulsion would be carried out.

## Materials and methods

### Chemicals

Methyl methacrylate (MMA, CP), sodium dodecyl sulfate (SDS, CP), sodium dodecyl sulfonate (SDSO, CP), and sodium dodecyl benzene sulfonate (SDBS, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hexadecane (HD, 98%) was from Aladdin Industrial Inc. 1-octyl-3-methylimidazolium hexafluorophosphate (C<sub>8</sub>mimPF<sub>6</sub>, 99%) was supplied by Shanghai Cheng Jie Chemical Co., Ltd. Ultra-pure water with a resistivity of 18.2 MΩ·cm<sup>-1</sup> was used in all experiments.

### Preparation of miniemulsion

Oil in water miniemulsion (O/W) was prepared with a volume

ratio of oil to water phase equal to 3 to 7. The oil phase contained 5 wt% HD, the remaining 95 wt% containing C<sub>8</sub>mimPF<sub>6</sub> and MMA. Both C<sub>8</sub>mimPF<sub>6</sub> and hexadecane are infinitely miscible in methyl methacrylate. After HD and C<sub>8</sub>mimPF<sub>6</sub> were fully dissolved into MMA, the oil phase was added into water phase which contained different types and concentrations of surfactants in a 100 ml plastic container. The total volume of the mixture was 50 mL and kept at 40 °C. Ultrasound probe was then placed one centimeter below the surface of the mixture in the middle of the container. The output power of sonicator (Xinzhong Scientz II) was set as 95 W. After homogenizing the mixture for 6 minute in a state of 1 second on and 1 second off, miniemulsion was prepared.

## Characterization

### The stability of miniemulsion

The stability of miniemulsion was determined by centrifugation at 5000 rpm for 2 hours (TDZ5-WS, Xiangyi Instruments). Method was adopted based on literature.<sup>23, 24</sup> The miniemulsion was then separated into two layers. The top layer was oil phase, and the bottom layer was miniemulsion phase. The oil phase was removed by pipette and weighted.

### Droplet size measurement

The droplet sizes and distributions of miniemulsion with different aging time were measured using the laser diffraction method (Mastersizer 3000, Malvern Inc). This technique has been widely accepted as a tool to evaluate droplet size.<sup>25, 26</sup> The sample was diluted with water solution to meet the requirement of obscuration. The diluted water solution was saturated with surfactant (used in the miniemulsion preparation) and monomers to prevent coalescence during sample measurement.<sup>27</sup> All measurements were repeated for three times.

### Viscosity measurement

The viscosities of water phases and oil phase were measured using the rotational Rheometer with cone-and-plate system (Kinexus Pro+, Malvern Inc). The cone was with a diameter of 60 mm and a cone angle of 1°. Measurement was conducted with the shear rate ranging from 10 s<sup>-1</sup> to 1000 s<sup>-1</sup> at 40°C. The final viscosity was the average value of viscosities with different shear rate.

### Interfacial tension measurement

The interfacial tension between oil phase and water phase was measured using the Du Noüy ring method (BZY-2tensiometer, Hengping Instruments). Since above a certain concentration, surfactant cannot be dissolved in water phase at the storage temperature, 20°C, the measurement was carried out at 40 °C. Measurements were repeated for three times.

### Zeta potential measurement

The Zeta potentials of the miniemulsion were measured using trace laser dopper electrophoresis method (ZetasizerNano ZS, Malvern Inc) at 20 °C. The miniemulsion was injected into high concentration sample cell without dilution. Measurements were repeated for three times.

## Results and discussion

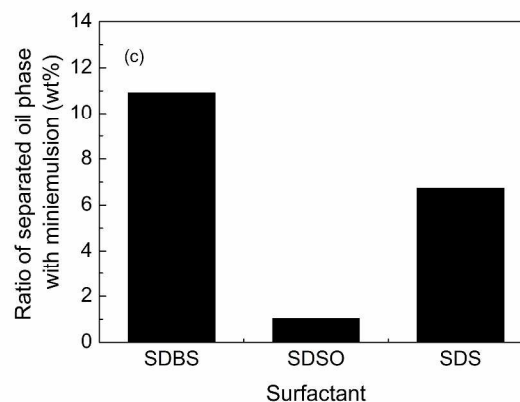
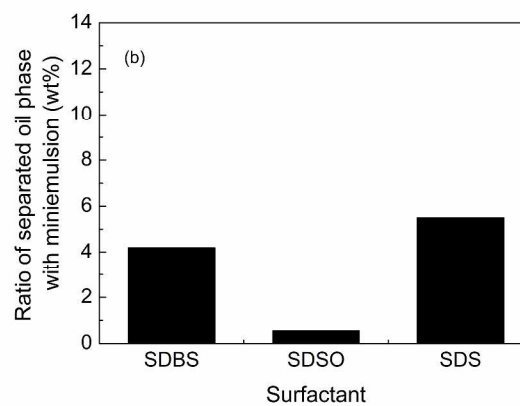
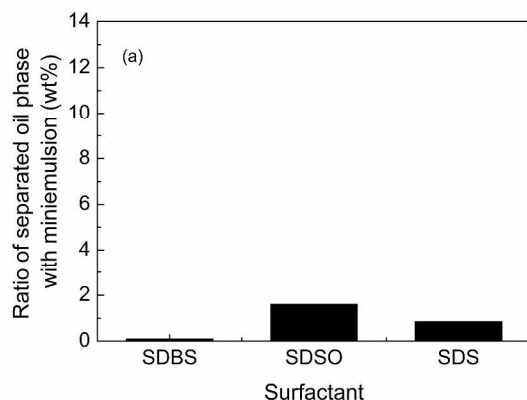
In this section, the effects of surfactant type, surfactant concentration, and C<sub>8</sub>mimPF<sub>6</sub> concentration on droplet size and stability of miniemulsion were investigated.

### Effect of surfactant type on stability of miniemulsion

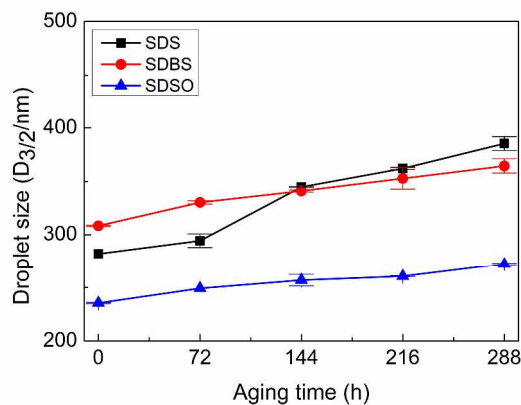
The choice of surfactant has great influence on making a stable miniemulsion. A useful parameter to determine the suitability of surfactant is the Hydrophile-lipophile balance (HLB) value proposed by Griffin.<sup>28</sup> If the HLB value of the surfactant used fits the HLB value of the required oil phase, the produced droplets with the surfactant would be stable. In colloidal science, HLB values ranging from 8 to 18 would favor the formation of O/W emulsion.<sup>29</sup> In this study, two types of anionic surfactants with the HLB values in the range for O/W emulsion were chosen: SDBS (HLB=12.3 obtained by calculation) and SDBS (HLB=10.6).<sup>30</sup> A widely used anionic surfactant, SDS, was also chosen even though its HLB value is 40, which is out of the normal range for O/W emulsion.<sup>30</sup> The surfactant concentration in water phase was kept at 30 mM and the oil phase contained 10 wt% C<sub>8</sub>mimPF<sub>6</sub>, 85 wt% MMA and 5 wt% HD.

It is known that the instability of droplets in miniemulsion is mainly caused by coalescence and Ostwald-ripening.<sup>31</sup> Coalescence is the process that two droplets collide with each other to form one bigger droplet. Ostwald-ripening is the process that monomers diffuse from smaller droplets to larger ones due to the higher chemical potential of smaller ones. Both cases lead to an increase in droplets size, and ultimately macro-phase separation into oil phase occurs due to the gravitational force. The instability process will be accelerated via centrifugation. Thus the oil phase may be separated within hours rather than days or weeks of storage.<sup>23</sup> Centrifugation method was employed to investigate the instability of miniemulsion. The amount of oil phase appearing on the top layer is a good indication for the tendency of instability. The larger the oil phase weight, the more unstable the miniemulsion will be.

Fig. 1 shows the influence of surfactant types on oil phase weight of miniemulsions after centrifugation at different concentration (0 wt%, 10 wt% and 20 wt%) of C<sub>8</sub>mimPF<sub>6</sub>. Without C<sub>8</sub>mimPF<sub>6</sub>, SDBS has the least oil phase weight whilst in the presence of C<sub>8</sub>mimPF<sub>6</sub>, SDBS has the least oil phase weight compared with other two miniemulsions stabilized by SDS or SDBS. Since our formula developed is aiming to use RTILs to reduce glass transition temperature, T<sub>g</sub>, which is one of the key properties in coating products. It is clear SDBS, which offers better performance on stability in the presence of RTILs would be a more suitable surfactant among the three surfactants.



**Fig. 1** Mass ratio of separated oil phase with miniemulsion containing different concentration of C<sub>8</sub>mimPF<sub>6</sub> and surfactants. (a) 0 wt% C<sub>8</sub>mimPF<sub>6</sub>; (b) 10 wt% C<sub>8</sub>mimPF<sub>6</sub>; (c) 20 wt% C<sub>8</sub>mimPF<sub>6</sub>.



**Fig. 2** Variation of droplet sizes as a function of time for miniemulsions containing 10 wt% C<sub>8</sub>mimPF<sub>6</sub> stabilized with different surfactants upon aging at 20°C

The instability of miniemulsion was also studied by measuring the average mean droplet size, D<sub>3/2</sub> at different storage time for various miniemulsions for fixed concentration of C<sub>8</sub>mimPF<sub>6</sub> (10 wt%). Fig. 2 shows variation of droplet sizes as a function of time for miniemulsions stabilized with different surfactants upon aging at 20 °C. The droplet size of miniemulsion stabilized by SDS increases at a rapid rate especially after 72 h storage. The



miniemulsion stabilized by SDBS increases slightly from the initial 308 nm to 364 nm after 288 h, while the miniemulsion stabilized by SDSO, the increase of droplet size is minimum from initial 235 nm to 272 nm after 288 h. The increase of droplet size with aging time gives an intuitive judgment of instability of miniemulsion. Based on Fig. 2, the stabilities of miniemulsions from high to low were ranked as: miniemulsion SDSO > miniemulsion SDBS > miniemulsion SDS. The result shows consistency with the result of centrifugation (Fig. 1). The miniemulsion containing SDSO gave smaller droplet size with better stability. Thus SDSO was identified as the most suitable surfactant for stabilizing oil phase containing C<sub>8</sub>mimPF<sub>6</sub>.

In this work, to prevent Ostwald-ripening in a relatively short time, a common type of co-stabiliser, HD was added in oil phase. Assuming Ostwald-ripening did occur, by making an initial calculation on the Ostwald-ripening rate based on Lifshitz-Slyozov-Wagner (LSW) theory:

$$w = \frac{d(d_m^3)}{d(t)} = \frac{8D\sigma CV_m}{9RT} \quad (\text{Equation 1})$$

, where  $w$  is the Ostwald-ripening rate for single component species ( $\text{cm}^3 \cdot \text{s}^{-1}$ ),  $d_m$  is the average oil droplet diameter (cm),  $t$  is the storage time (s),  $D$  is the diffusion coefficient of oil molecules in water ( $\text{cm}^2 \cdot \text{s}^{-1}$ ),  $\sigma$  is the interfacial tension at the oil-water interface ( $\text{mN} \cdot \text{m}^{-1}$ ),  $C$  is the water solubility of the bulk oil ( $\text{mL} \cdot \text{mL}^{-1}$ ),  $V_m$  is the molar volume of oil ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ),  $T$  is the absolute temperature (K), and  $R$  is the gas constant.<sup>32</sup> In the absence of HD, the Ostwald-ripening rate of MMA,  $w$ , was estimated as  $3.97 \cdot 10^{-14} \text{ cm}^3 \cdot \text{s}^{-1}$ .<sup>32</sup> Rearrange equation 1, the diameter of droplet size at time  $t$  may be expressed as:

$$d_m(t) = \sqrt[3]{wt + (d_m(0))^3} \quad (\text{Equation 2})$$

, taking the initial droplet size  $d_m(0)$  as 235.3 nm which was the initial size of miniemulsion containing SDSO shown in Fig. 2. The new droplet size after 1 minute  $d_m(60)$  could be estimated as 1338 nm. This is about 5 times larger than the one obtained after 12 days storage in our measurement shown in Fig. 2. Clearly, Ostwald-ripening rate theory does not fit our experimental results which further proved that presence of HD did prevent the Ostwald-ripening. Thus the increase in droplet size of miniemulsions obtained in this work may be mainly caused by coalescence as the droplet size increased.

#### Effect of concentration of surfactant on the droplet size of miniemulsion

Fig. 3 shows the variation of droplet sizes as a function of surfactant concentration for miniemulsions. Different concentrations of SDSO ranging from 10 mM, 20 mM, 30 mM, 40 mM to 50 mM was investigated. The oil phase contained 10 wt% C<sub>8</sub>mimPF<sub>6</sub>, 85 wt% MMA and 5 wt% HD. The droplet size decreases sharply with the increase of surfactant concentration in the lower concentration up to 30 mM. Further increase of surfactant concentration from 30 mM to 50 mM, the change of droplet size becomes less pronounced. Similar observation was reported by Abismail et al. when studied the relationship between droplet size and surfactant concentration at the 130 W output

power of sonicator.<sup>33</sup>

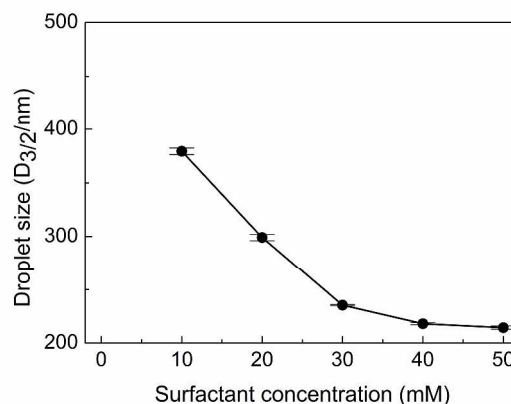


Fig. 3 Variation of droplet sizes as a function of surfactant concentration for miniemulsions containing 10 wt% C<sub>8</sub>mimPF<sub>6</sub> stabilized with SDSO

In order to identify the reason causing different changing rates on droplet size reduction when increasing surfactant (SDSO) concentration, the interfacial tension for different oil water composition was investigated. Results are shown in Fig. 4. It was found that the interfacial tension decreases sharply with an increase in surfactant concentration from 0 to 10 mM, further increase SDSO concentration to 30 mM, results in a slow reduction on interfacial tension. The interfacial tension becomes more stable when the SDSO concentration is above 30 mM. Such observation indicated the change of surface adsorption of surfactant hence surface activity on the interface during the miniemulsion droplet formation process. Below 30 mM, adsorption of SDSO on the oil/water interface did not form a saturated monolayer. Thus when more SDSO were added, they continually adsorbed on the interface result in sharp reduction on the interfacial tension initially. Above 30 mM, a saturated adsorption of SDSO on the interface was obtained. This meant no further surface activity change occur thus the interfacial tension remained stable.

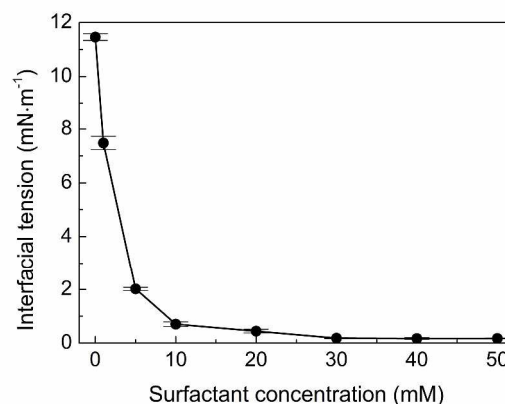


Fig. 4 Variation of interfacial tension as a function of surfactant concentration

Based on the above explanation, it is clear that the principle that gathering initial droplet size and droplet stability is different when changing concentration of surfactant (SDSO) during

ultrasonic homogenization process. In the initial droplet formation process, the droplets were disrupted and coalesced before reaching a dynamic steady state. Landfester et al. reported that within a certain range of surfactant concentration, the droplet size in steady state was determined by the surfactant concentration because smaller droplets created by disruption could only be stable if excess surfactant was left for stabilization, otherwise they would coalesce to form bigger one.<sup>34</sup> Low surfactant concentration would lead to the incompletely covered interface, thus more surfactants were required to prevent smaller droplets from coalescence.<sup>35</sup> These may explain the sharp decline on droplet size shown in Fig. 3.

#### Effect of RTILs concentration on the initial droplet size and stability of miniemulsions

In order to evaluate the role of  $C_8mimPF_6$  in the miniemulsion formulation, the initial droplet sizes for miniemulsions containing different  $C_8mimPF_6$  concentration were investigated. The same surfactant SDSO with fixed concentration in water phase 30 mM was chosen. The oil phase contained different concentrations of  $C_8mimPF_6$  ranging from 0 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt% to 30 wt%. Results are shown in Fig. 5. It is interesting to note that at lower concentration of  $C_8mimPF_6$ , i.e. between 0 and 1 wt%, there are sharp decline on droplets size of the miniemulsions, then droplet size trends to be stable until 5 wt%, whilst beyond this point, droplet size of the miniemulsion tended to increase as the concentration of RTILs increased. The reason causing this unique observation is investigated in later section from three aspects: viscosity, interfacial tension, and zeta potential.

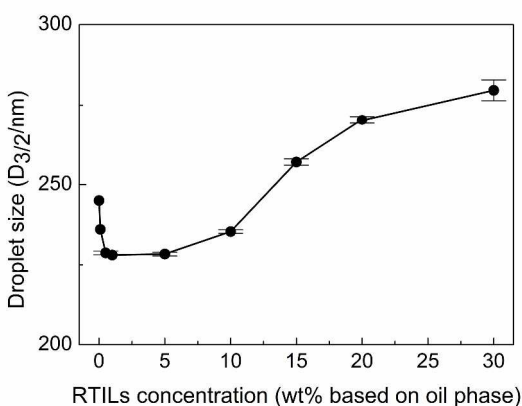


Fig. 5 Variation of droplet sizes as a function of  $C_8mimPF_6$  concentration for miniemulsions stabilized with SDSO

From the open literature, it has been reported that increase of the viscosity of oil phase (dispersed phase) may affect miniemulsion droplet size. This is depends on the viscosity ratio between dispersed phase and continuous phase. Nazarzadeh and Sajjadi studied the viscosity effects of dispersed phase (silicon oil) on droplet size of miniemulsion prepared by ultrasound.<sup>36</sup> They found that the average droplet size sharply decreased as the increase of dispersed/continuous phase ratio, reached a minimum when the viscosity ratio was around 1.0, and then remained constant, followed by a significant increase at viscosity ratio beyond 10.

In this study, the viscosity of  $C_8mimPF_6$  is 1052 mPa·s at 20°C,<sup>37</sup> and that of MMA is 0.5311 mPa·s at 30°C.<sup>38</sup> The viscosity of water phase is 0.839 mPa·s at 40 °C. The effect of  $C_8mimPF_6$  on viscosity of oil phase cannot be ignored. Fig. 6 shows the variation of viscosity ratio between oil phase and water phase as a function of  $C_8mimPF_6$  concentration in oil phase. The viscosity ratio increases as the increase of  $C_8mimPF_6$  concentration in oil phase and ranges from 0.7 to 2.5. This is well below the critical increasing point (i.e. 10) being observed by Nazarzadeh and Sajjadi,<sup>36</sup> which means the increase of droplet size between 10 wt% and 30 wt% of  $C_8mimPF_6$  may not due to the increase of viscosity. Compared with silicon oil,  $C_8mimPF_6$  can ionize in solution, results in variation of surface charger, which in turn may affect interfacial activity; hence droplet size. These factors may be more important and will be evaluated further in the following section.

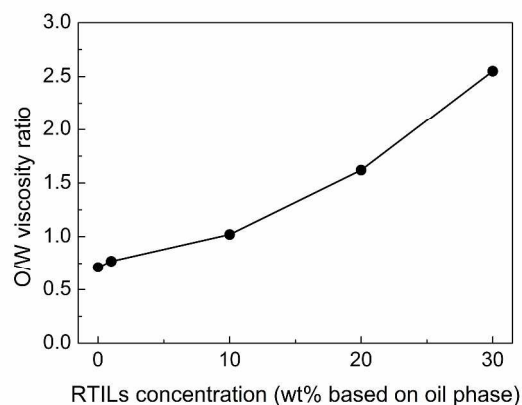


Fig. 6 Variation of viscosity ratio between oil phase and water phase as a function of  $C_8mimPF_6$  concentration

We first examine the storage stability of miniemulsion prepared with the same condition as being investigated initially. The droplet sizes of miniemulsion were continually measured within at 72, 144, 216 and 288 hours. Results are shown in Fig. 7.

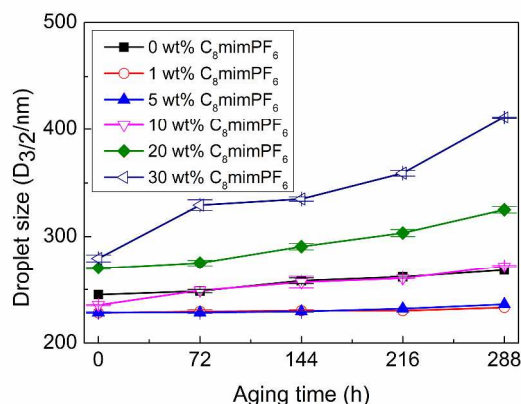


Fig. 7 Variation of droplet sizes as a function of time for miniemulsions containing different  $C_8mimPF_6$  concentration at 20°C

It was observed that the change of droplet sizes of 0 wt%, 1 wt%, 5 wt%, 10 wt%, 20 wt% and 30 wt%  $C_8mimPF_6$  from initial conditions are very different. The droplet sizes of 0 wt%, 1 wt%,

5 wt%, 10 wt%, 20 wt% and 30 wt%  $C_8mimPF_6$  increase from initial size at 245 nm, 228 nm, 228 nm, 235 nm, 270 nm and 280 nm to final size at 268 nm, 233 nm, 236 nm, 272 nm, 325 nm and 411 nm respectively after 288 h storage. The increasing rate of droplet size for 10 wt%, 20 wt% and 30 wt% are much pronounced, which are 15.7%, 20.2% and 47.1% respectively. The tendency suggests that in the presence of  $C_8mimPF_6$  at lower concentration (i.e. less than 10 wt%) the much smaller initial droplet size and better size stability may be obtained. Above certain concentration, e.g. 10 wt%, adding  $C_8mimPF_6$  into oil phase caused instability of the droplet in miniemulsion. Such effect is independent of initial droplet size. For example, the initial droplet size of miniemulsion at 10 wt% is smaller than the one at 0 wt%. However after 288 h storage, the droplet size for 10 wt% is larger than the one obtained at 0 wt%. It is worth of pointing out that O/W viscosity ratio is around 1 at the oil phase containing 10 wt%  $C_8mimPF_6$ , as Fig. 6 shown. The smaller droplet size obtained at 10 wt%  $C_8mimPF_6$  might be attributed as that in a simple shear field, with lower interfacial tension for oil and water phase with similar viscosity; maximum energy transfer may be achieved.<sup>36, 39</sup> In our case, it is possible that the smaller droplet size occurs at 10 wt%  $C_8mimPF_6$  compared to 0 wt%  $C_8mimPF_6$ , partially because the energy transfer efficacy is higher. To gain further insight on variation of droplets size for miniemulsions between 0 wt% and 30 wt%  $C_8mimPF_6$ , further investigation on droplet size distribution, interfacial properties etc are necessary.

Fig. 8 shows droplet size distributions at 0 h and 288 h aging time for miniemulsions containing different  $C_8mimPF_6$  concentrations.

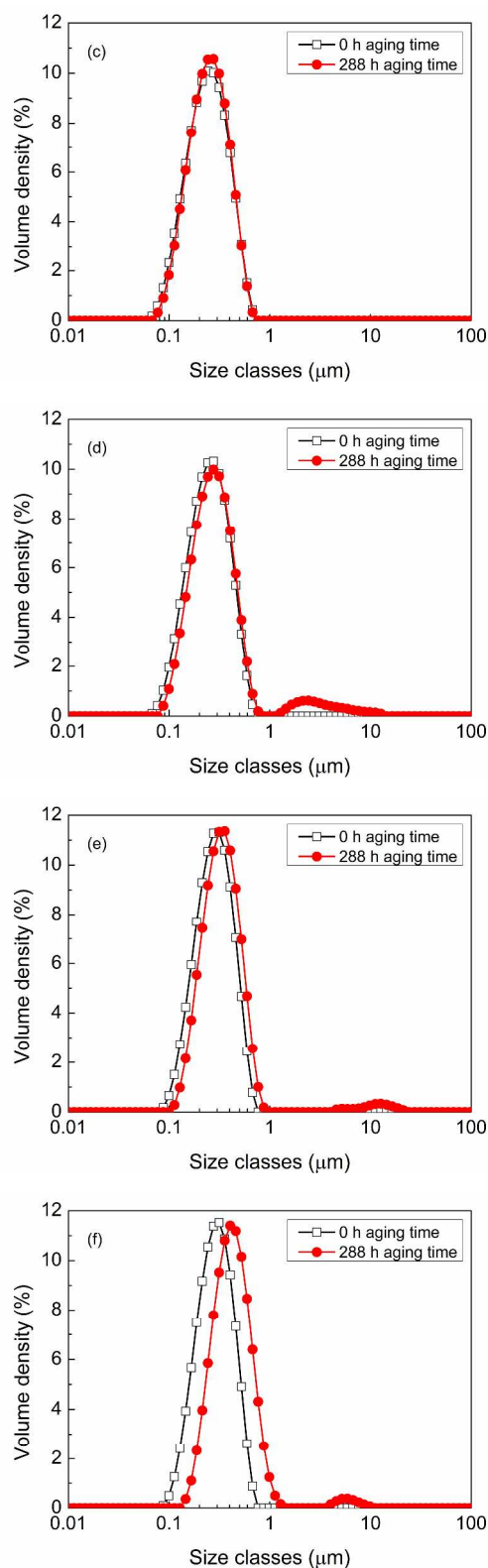
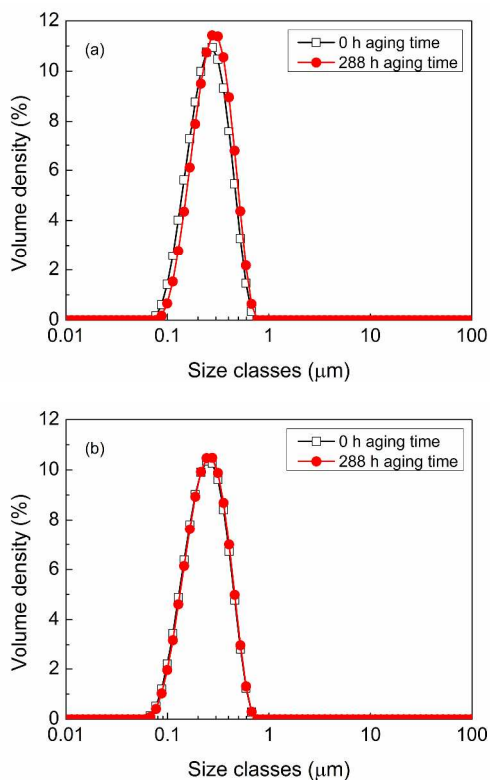
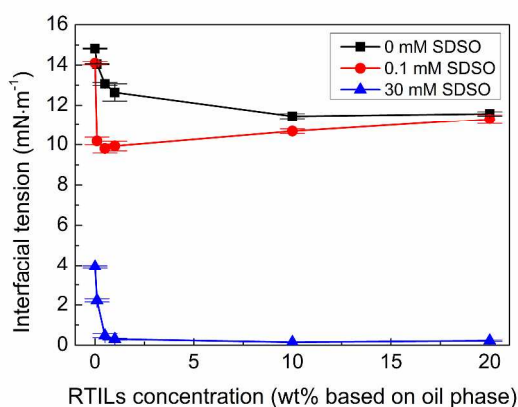


Fig. 8 Droplet size distribution at 0 h and 288 h aging time for miniemulsions containing different concentration of  $C_8mimPF_6$ . (a) 0 wt%; (b) 1 wt%; (c) 5 wt%; (d) 10 wt%; (e) 20 wt%; (f) 30wt%.

There are no obvious changes on distributions for miniemulsions containing 1 wt% and 5wt%  $C_8mimPF_6$  after 288 h storage time. However, further increase of  $C_8mimPF_6$  concentration (above 10 wt%) into oil phase, the larger droplet

distributions appear after 288 h storage. The results are agreed with the droplet size stability shown in Fig. 7. Clearly, above the critical concentration, i.e. 10 wt%  $C_8\text{mimPF}_6$ , the droplets of miniemulsion become unstable. The phenomenon has yet to be reported. It needs further investigation on the underlying mechanism.

In order to interpret the effect of  $C_8\text{mimPF}_6$  concentration on the initial droplet size and stability of miniemulsion, the interfacial tensions between oil and water at different concentrations of  $C_8\text{mimPF}_6$  in oil phase were measured. Fig. 9 shows interfacial tensions for different concentrations of SDSO in water phase as a function of  $C_8\text{mimPF}_6$  concentration in the oil phase ranging from 0 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 10 wt% to 20 wt%. The changes of interfacial tensions for different concentrations of SDSO in water phase, i.e. 0 mM, 0.1 mM, and 30 mM, are compared.



**Fig. 9** Variation of interfacial tensions as a function of  $C_8\text{mimPF}_6$  concentration at 0, 0.1, 30 mM SDSO in water phase

It is interesting to note that in the absence of surfactant SDSO in water phase, the interfacial tension decreases sharply from  $14.82 \text{ mN}\cdot\text{m}^{-1}$  to  $11.46 \text{ mN}\cdot\text{m}^{-1}$  as the concentration of  $C_8\text{mimPF}_6$  increases up to 10 wt%. Similar trends are found for the water phase containing 0.1 mM SDSO and 30 mM SDSO. Especially for liquid containing 30mM SDSO, the interfacial tension changed from  $3.94 \text{ mN}\cdot\text{m}^{-1}$  to  $0.31 \text{ mN}\cdot\text{m}^{-1}$ , which is significant, indicating that the instability of 0 wt%  $C_8\text{mimPF}_6$  compared to 1wt%  $C_8\text{mimPF}_6$  observed in Fig. 7 are mainly attributed to the higher surface energy. This also explained the reduction of droplet size at 1 wt% compared to 0 wt%  $C_8\text{mimPF}_6$  showed in Fig. 5.

To some extent,  $C_8\text{mimPF}_6$  might act as surfactant, hence when bringing oil phase and water phase into contacting point, the  $C_8\text{mimPF}_6$  molecules might accumulate at the interface between water phase and oil phase, thus reduce the interfacial tension. The adsorption process might continue until  $C_8\text{mimPF}_6$  adsorbed on the interface form a saturated monolayer, then no more reduction on interfacial tension in the excess of  $C_8\text{mimPF}_6$ . From Fig. 9, such critical point occurs circa 1 wt% of  $C_8\text{mimPF}_6$ . Similar phenomenon has been observed by Hezave et al. who studied the effect of 1-dodecyl-3-methylimidazolium chloride ( $C_{12}\text{mimCl}$ ) on the interfacial tension between water and crude oil phase.<sup>40</sup> However, unlike what we have studied,  $C_{12}\text{mimCl}$  is hydrophilic and dissolves in the water phase. The interfacial

tension decreased from  $39.98 \text{ mN}\cdot\text{m}^{-1}$  to  $6.84 \text{ mN}\cdot\text{m}^{-1}$  when  $C_{12}\text{mimCl}$  concentration increased from 0 ppm to 5000 ppm. Fitchett et al. studied the change of interfacial tension between water phase and pure RTILs phase for different type of RTILs, i.e. 1-octyl-3-methylimidazolium bis(perfluoromethylsulfonyl)imide ( $C_8\text{mimBMSI}$ ) and 1-dodecyl-3-methylimidazolium bis(perfluoromethylsulfonyl)imide ( $C_{12}\text{mimBMSI}$ ).<sup>41</sup> They found that the interfacial tension reduced from  $11.7 \text{ mN}\cdot\text{m}^{-1}$  to  $10.4 \text{ mN}\cdot\text{m}^{-1}$  when RTILs changed from  $C_8\text{mimBMSI}$  into  $C_{12}\text{mimBMSI}$ . This suggested the dependence of interfacial tension on the cation chain length. The results reported in literatures, together with our result, indicate that cations of RTILs may have certain surface activity function. Such interfacial activity for oil and water can be enhanced as carbon chain length increases.

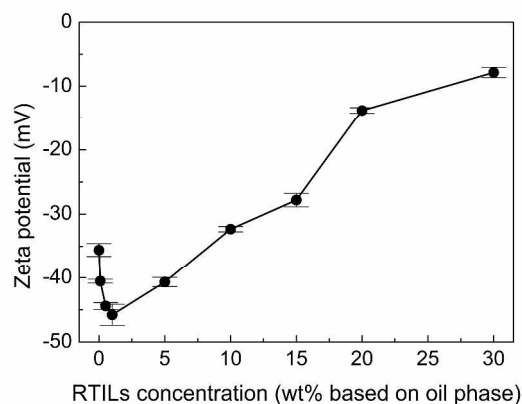
Fig. 9 also shows that in the absence of  $C_8\text{mimPF}_6$ , as SDSO concentration increases from 0 mM to 0.1 mM, there is a limited change on the interfacial tension, e.g. decreases slightly from  $14.82 \text{ mN}\cdot\text{m}^{-1}$  to  $14.09 \text{ mN}\cdot\text{m}^{-1}$ . However, adding just 0.1 wt%  $C_8\text{mimPF}_6$  in the oil phase, the interfacial tension is dramatically reduced from  $14.04 \text{ mN}\cdot\text{m}^{-1}$  to  $10.18 \text{ mN}\cdot\text{m}^{-1}$  as the surfactant concentration increases from 0 mM to 0.1 mM. This suggested that there is strong interaction between SDSO and  $C_8\text{mimPF}_6$  which further reduced their interfacial tension. The main reason might be attributed into two aspects. Firstly, because the imidazolium moiety of  $C_8\text{mimPF}_6$  cation and the sulfonic acid moiety of SDSO anion are hydrophilic, the carbon chains in both  $C_8\text{mimPF}_6$  cation and SDSO anion are hydrophobic, both cations of  $C_8\text{mimPF}_6$  and anions of SDSO accumulated at the interface, with hydrophilic moieties towards the aqueous side and carbon chains towards oil side hence stabilized the interface between oil and water phase. Secondly, there might be an electrostatic attraction between the positively charged imidazolium moiety in  $C_8\text{mimPF}_6$  cations and the negatively charged sulfonic acid moiety in SDSO anions, which could result in a tighter space alignment at the interface to further stabilize the interface. These two joined effects contribute to the significant decrease in the interfacial tension when the concentration of SDSO in water phase increases from 0 to 0.1 mM in the presence of  $C_8\text{mimPF}_6$ . Similar synergistic effect between anionic surfactants and imidazolium cations of  $C_8\text{mimPF}_6$  has been reported in vesicle and micelles formation.<sup>42,43</sup>

The strong interaction between  $C_8\text{mimPF}_6$  and surfactant SDSO mentioned above only occurred at lower concentration of  $C_8\text{mimPF}_6$ . For a fixed concentration of SDSO (30 mM), an increase of  $C_8\text{mimPF}_6$  concentration from 0.5 wt% to 20 wt% causes almost no change on interfacial tension. While at 0.1 mM concentration of SDSO, the interfacial tension even increases. This might be explained by the phenomenon that micelles composed of surfactant and  $C_4\text{mimPF}_6$  in water phase might form and grow when hydrophobic  $C_4\text{mimPF}_6$  dissolved in water phase.<sup>44</sup> In our case, because  $C_8\text{mimPF}_6$  partially dissolved in water ( $2.26 \text{ g}\cdot\text{L}^{-1}$  at  $25^\circ\text{C}$ ),<sup>22</sup> as the concentration of  $C_8\text{mimPF}_6$  in oil phase increases, thus more  $C_8\text{mimPF}_6$  could be dissolved into water phase. In this case, part of  $C_8\text{mimPF}_6$  cations might interact with SDSO anions being adsorbed on the oil/water interface. As a result, the SDSO may be desorbed from oil/water interface to participate in the formation of micelles in water phase, to increase



the interfacial tension. In order to confirm this hypothesis, further investigations are needed.

Zeta potential may indicate the degree of electrostatic repulsion between adjacent, similarly charged particles or droplets in dispersion. The larger the zeta potential value, the higher the electrostatic expulsion, hence results in more stable droplets. Thus the stability of colloidal dispersion being electrically charged can be related to its zeta potential value. Positive or negative zeta potential value indicating the dispersion is positively charged or negatively charged. Thus the absolute value of zeta potential would matter the stability. When the absolute value of zeta potential is low, it means the repulsion between droplets cannot prevent collide, hence the droplets in dispersion will coalesce and flocculate. The droplets with higher zeta potential values indicate that the electric repulsions between droplets are stronger hence can effectively prevent coalescence. Normally, when the absolute value of zeta potential is higher than 30 mV, droplets in dispersion are in a stable state.<sup>45</sup>



**Fig. 10** Variation of zeta potential values of droplet sizes as a function of  $C_8mimPF_6$  concentration

With the above theory as a guideline, a series of measurements on zeta potential was carried out for miniemulsions prepared at different concentration of  $C_8mimPF_6$ , ranging from 0 wt%, 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, and 30 wt%. Results are shown in Fig. 10. Negative zeta potential values are observed for all the miniemulsions which suggested that droplets are negatively charged. The absolute zeta potential value increases from 35.6 mV to 45.8 mV with an increase of  $C_8mimPF_6$  concentration from 0 wt% to 1 wt%. The absolute zeta potential value then decreases from 45.8 mV to 7.8 mV as further increasing the  $C_8mimPF_6$  concentration up to 30 wt%. This result is quite different to the tendency on interfacial tension, which is almost unchanged above 1 wt%  $C_8mimPF_6$  shown in Fig. 9. For miniemulsions containing  $C_8mimPF_6$  at 0 wt% and 10 wt%, the values are all larger than 30 mV. This indicates that the droplet sizes were relatively stable in this region. For miniemulsions containing  $C_8mimPF_6$  at 20 wt%, and 30 wt%, the absolute value of zeta potential are less than 30 mV, which indicating that droplets were unstable in this region. Such observations are consistent with the droplet stability results in shown in Fig. 7, which further suggest that variation of surface charge on interface O/W may be the main reason causing the instability of droplet at higher concentration of  $C_8mimPF_6$ . In this case, the static

interfacial tension value will not be suitable on reflecting interfacial activity.

The unique zeta potential behaviour mentioned above might be best explained by Chaumont et al. who studied the interface between water and  $C_8mimPF_6$  by a molecular dynamics simulation.<sup>46</sup> According to the simulation result,  $PF_6^-$  anions were more hydrophilic as compared with  $C_8mim^+$  cations, hence more  $PF_6^-$  anions dispersed in the water phase than  $C_8mim^+$  cations. Thus a small excess of  $C_8mim^+$  cations was kept in the  $C_8mimPF_6$  phase.  $C_8mim^+$  cations might accumulate at the interface and were ordered with their imidazolium moiety towards the water phase and carbon chain towards oil phase. The excessive  $C_8mim^+$  cations accumulated at the O/W interface caused the interface being positively charged. This positively charged interface was experimentally proven by Fitchett et al. who found that the surface charge at the  $C_{10}mimBMSI$ /water interface were positive and had value up to  $27 \mu C \cdot cm^{-2}$ .<sup>41</sup> Based on the points mentioned above, we can deduce that in this study, in the presence of  $C_8mimPF_6$ , the droplets would be positively charged due to adsorption of excessive  $C_8mim^+$  cations on the droplet interface regardless the existence of surfactants. On the other hand, in the presence of SDSO anion in the water phase, the droplet would be negatively charged due to the adsorption of the SDSO anion on the interface. As Fig. 10 shows that in the absence of  $C_8mimPF_6$ , it is no surprise that a large negative zeta potential value has been found. As compared with droplets of 0 wt%  $C_8mimPF_6$ , when adding a small amount of  $C_8mimPF_6$ , more SDSO were adsorbed on the interface due to tightened space alignment at interface, as explained in the early section. Thus the interface became more negatively charged causing an increase on the absolute value of zeta potential. Such interface charge would continuously increase until the adsorption of SDSO at interface was saturated. The point at 1 wt%  $C_8mimPF_6$  (Fig. 9) is a good example. Above this saturation point, as a further increase in  $C_8mimPF_6$  concentration, e.g. 10 wt%, 20 wt% and 30 wt%, no more SDSO would adsorb on the interface, but the amount of  $C_8mimPF_6$  dissolved in water phase might increase, hence more excessive  $C_8mim^+$  cations would be kept in the oil phase as mentioned above and adsorbed on water/oil interface to neutralize the negative interface charge, thus decreased the absolute value of zeta potential. Similar phenomenon that  $C_8mimPF_6$  affected the zeta potential of micelles has also been reported by Rai et al.<sup>47</sup> They found that the solubility of  $C_4mimPF_6$  has been enhanced due to the micelles of SDBS in water phase and the absolute value of zeta potential of negatively charged micelles decreased as the increase of  $C_4mimPF_6$  concentration in water phase. They claimed that such change on zeta potential was caused by the interaction of anionic surfactant with  $C_4mim^+$  cations.

## Conclusions

In this study, a stable miniemulsion containing  $C_8mimPF_6$  in droplets was prepared. Suitable surfactant, sodium dodecyl sulfonate (SDSO), was chosen based on their performance regarding the stability of miniemulsion. When SDSO was used as a surfactant and 10 wt%  $C_8mimPF_6$  was added, initial droplet size sharply decreased as the surfactant concentration increased, which tended to be stable. The droplet size in decreasing region was determined by surfactant concentration. When fixing 30 mM

SDSO, within 1wt% C<sub>8</sub>mimPF<sub>6</sub> concentration, the initial droplet size decreased with the addition of C<sub>8</sub>mimPF<sub>6</sub>, then trended to level off until 5 wt% C<sub>8</sub>mimPF<sub>6</sub>, and miniemulsions became more stable. Above 5 wt% C<sub>8</sub>mimPF<sub>6</sub>, adding more C<sub>8</sub>mimPF<sub>6</sub> to the oil phase causes an increase on initial droplet size and weakens the droplet stability. The existence of C<sub>8</sub>mimPF<sub>6</sub> in droplets had great influence on zeta potential of droplets that affected the stability of miniemulsion. Because the absolute zeta potential values were less than 30 mV for miniemulsions containing 20 wt%, 30 wt% C<sub>8</sub>mimPF<sub>6</sub>, they were unstable during long time storage. The dispersion of the anions of C<sub>8</sub>mimPF<sub>6</sub> towards water were faster than the cations of C<sub>8</sub>mimPF<sub>6</sub>, hence more cations were kept in droplets. The cations neutralized negatively charged surfactant, causing the decrease in the absolute zeta potential value when C<sub>8</sub>mimPF<sub>6</sub> concentration was above 5 wt%. A sharp decrease in O/W interfacial tension indicating anionic surfactant and imidazolium cations had synergistic effects.

### Acknowledgments

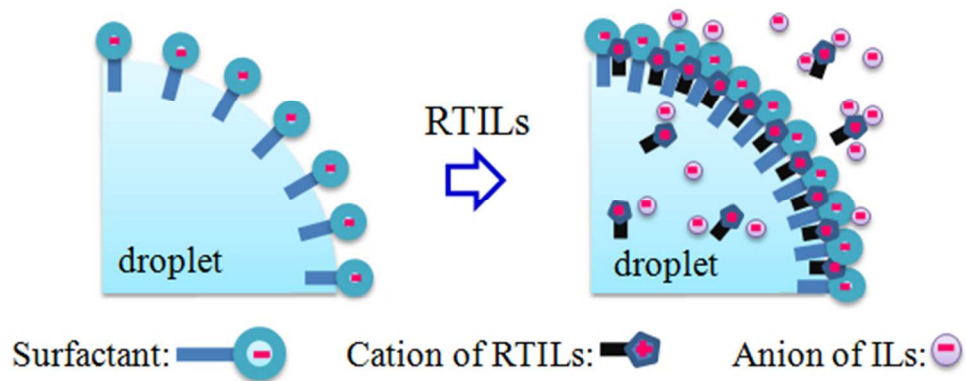
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### Notes and references

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