



Investigation on the interactions between hydrophobic anions of ionic liquids and Triton X-114 micelles in aqueous solutions



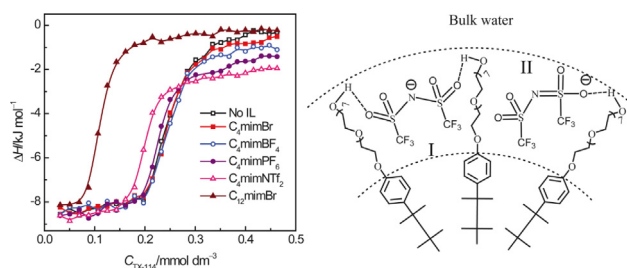
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HIGHLIGHTS

- Hydrophobic anions of ionic liquids can interact with TX-114 micelles.
- The hydrophobic anions are located at the head group area of TX-114 micelles.
- The anion of ionic liquid affects the hydration of the ethylene oxide groups.

GRAPHICAL ABSTRACT



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ABSTRACT

The interactions between hydrophobic anions of ionic liquids (ILs) and Triton X-114 (TX-114) micelles were studied in this work. The 1-alkyl-3-methylimidazolium based ILs with the anions bromide (Br^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) and bis(trifluoromethylsulfonyl)imide (NTf_2^-) were selected to study their effects on physicochemical properties of the TX-114 micellar solution. Both the hydrophilic ILs with long alkyl (e.g., $C_{12}mimBr$) and hydrophobic ILs (e.g., $C_4mimNTf_2$) significantly influenced the aggregate size and increased the absolute value of zeta potential as well as the cloud point. However, $C_4mimNTf_2$ changed the critical micellar concentration (CMC) and the aggregation number much less whereas made the micellization enthalpy decrease more obviously than $C_{12}mimBr$ did. It was suggested that the hydrophobic IL anions (PF_6^- , NTf_2^-) are located at the head group area of TX-114 micelles and interact with the ethylene oxide groups of TX-114 molecules. This work gives a further understanding of the interactions between IL cation/anion and micelles.

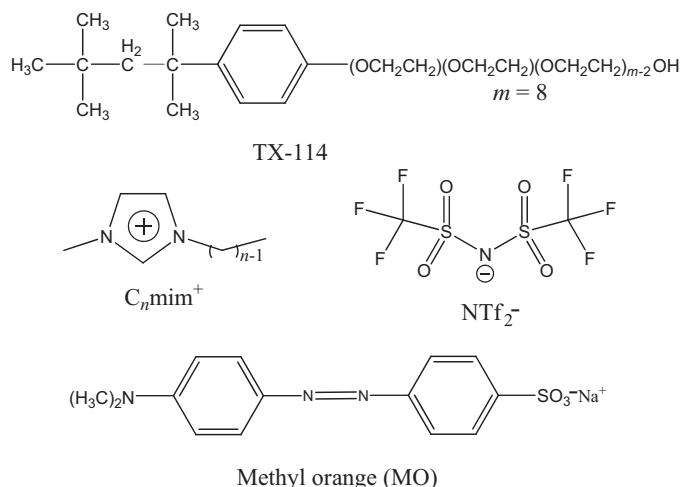
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1. Introduction

Ionic liquids (ILs), which are composed of organic cations and organic/inorganic anions, receive much attention because of their unique properties such as low melting points, negligible vapor pressure, non-flammability, etc. They are considered to be potential solvents instead of organic solvents in many applications, e.g., synthesis, catalysis, electrochemistry, and separation [1–3]. In addition, ILs

are regarded as additives in many applications, due to the fact that their hydrophilicity or hydrophobicity can be controlled by changing their cations or anions. Modification of the physicochemical properties of aqueous surfactant solutions in favorable fashion by the addition of an IL has received much attention. An IL may demonstrate a unique role in altering the properties of aqueous surfactant solutions. For example, we recently reported a method improving the cloud point extraction of uranyl ions using Triton X-114 (TX-114) micellar solutions by the addition of ILs with a common used anion bis(trifluoromethylsulfonyl)imide (NTf_2^- , Scheme 1) [4]. The extraction efficiency increased significantly upon the addition of NTf_2^- based ILs when using neutral extractant tri-octylphosphine

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Scheme 1. Structures of TX-114, C_nmim^+ , NTf_2^- , and methyl orange (MO).

oxide (TOPO), and the extraction efficiency kept high at both nearly neutral and high acidity. Furthermore, the addition of IL increased the separation factor of UO_2^{2+} and La^{3+} , which implied that a soft template for UO_2^{2+} was established upon the addition of NTf_2^- based ILs [4]. The IL anion NTf_2^- plays an important role in the improvement of the extraction. However, the mechanism of the interaction between NTf_2^- and TX-114 micelles is not clear yet.

The interactions between IL cation/anion and micelles in aqueous solutions have been widely researched [5–31]. For example, Pandey and co-workers found that the hydrophilic ILs 1-alkyl-3-methylimidazolium tetrafluoroborate (C_nmimBF_4) and the hydrophobic ILs 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_6) induced remarkable changes in the properties of the micelles of nonionic surfactant Triton X-100 (TX-100), anionic surfactant sodium dodecyl sulfate (SDS) and zwitterionic surfactant *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (SB-12) [6–13]. In these studies, the interaction between an IL cation with long alkyl chain and micelles has attracted much attention. An IL cation with long alkyl chain can align itself along with surfactant molecules within the micelles. Zhang et al. reported that $\text{C}_{12}\text{mimBF}_4$ and TX-100 can form mixed micelles in aqueous solutions through H-bonding and hydrophobic interaction [21]. The IL anion with long alkyl chain can also interact with micelles. Sarkar's group studied the effect of ILs on the properties of micellar solutions using solvation and rotational relaxation measurements [24–29]. The presence of a long alkyl chain on the anion of IL can induce the alignment of anion along the tail part of surfactants, which is responsible for the dramatic change in the physicochemical properties of micellar solutions [25].

The interactions between IL cation/anion and surfactants are very complicated, including electrostatic, H-bonding, dipole-induced dipole and hydrophobic interactions. In fact, the interactions between ILs and the micelles formed by nonionic surfactants are very similar to those between ILs and cyclodextrins (CDs). In the study of the interaction between imidazolium based ILs and CDs, we confirmed that the alkyl chain on the imidazolium ring but not the imidazolium ring itself enter into the cavity of β -CD [32,33]. Similarly, in the interaction between $\text{C}_{12}\text{mim}^+$ and the TX-100 micelles, the alkyl chain of $\text{C}_{12}\text{mim}^+$ penetrates into the hydrophobic core of the micelles interacting with the hydrophobic chain and phenyl ring of TX-100, while the imidazolium ring only interacts with the EO groups of TX-100 [21]. On the other hand, the hydrophobic IL anions also exhibit very strong interactions with β -CD. In the interaction between short alkyl substituted IL ($\text{C}_4\text{mimNTf}_2$ and C_4mimPF_6) and β -CD, it is mainly the anion

(NTf_2^- and PF_6^-) but not the cation C_4mim^+ that enters into the cavity of β -CD [32,33]. As to the interaction between C_4mimPF_6 and TX-100 micelles, Pandey and co-workers suggested that it was C_4mim^+ but not PF_6^- partitioning into the micelles [7]. However, considering the similarity to the interactions between ILs and CDs, we believe that there should exist interactions between hydrophobic IL anions (e.g., NTf_2^- and PF_6^-) and micelles, although the anions contain no alkyl chain. To the best of our knowledge, the interactions between hydrophobic anions of ILs and micelles have not received due attention.

In this work, we attempt to investigate the interactions between imidazolium based ILs with different anions (Br^- , BF_4^- , PF_6^- and NTf_2^-) and TX-114 micelles. We speculate that hydrophobic IL anions (PF_6^- and NTf_2^-) can interact with the TX-114 micelles, and the more hydrophobic the IL anion is, the more strongly it would interact with the micelles. This work will be helpful for the understanding of the interactions between IL cation/anion and micelles. Furthermore, the study on the interaction of NTf_2^- with TX-114 micelles will be helpful for the explanation of the improvement of the cloud point extraction of uranyl ions using TX-114 micellar solutions upon the addition of NTf_2^- based ILs [4].

2. Materials and methods

2.1. Materials

TX-114 obtained from Alfa Aesar was used as received. C_nmimBr ($n=4, 6, 8, 10, 12$), C_4mimBF_4 and C_4mimPF_6 (>99%) were purchased from Lanzhou Institute of Chemical Physics, China. $\text{C}_n\text{mimNTf}_2$ ($n=2, 4, 6, 8$) were synthesized via metathetical reaction, according to the literature [34]. Pyrene (spectrographic grade, Fluka) and benzophenone (BP) of AR grade were used as received. D_2O (99.9%, Beijing Chemical Reagents Company) was used as solvent in ^{19}F NMR measurements. All other chemicals were analytical grade and used without further purification.

2.2. Methods

2.2.1. Dynamic light scattering (DLS) measurements

DLS measurements of the aqueous TX-114 solutions on the addition of ILs were performed on a Malvern Nano ZS90 instrument (Malvern Instruments, UK) at 293.2 K and at a scattering angle of 90° . A He–Ne laser with a power of 4 mW was used as a light source. In our experiments, the concentration of the IL in the aqueous solution is 1 mmol dm^{-3} , so we added 1 mmol dm^{-3} of NaCl to shield the effect of the electric field. The intensity autocorrelation functions were analyzed using the Malvern General Purpose method provided by Malvern, which is a conserved and reliable method. The apparent hydrodynamic radius was calculated by the Dispersion Technology Software provided by Malvern. Each DLS experiment was repeated in triplicate and the results were presented as an average.

2.2.2. Zeta potential measurements

Zeta potential experiments were performed on the Malvern Nano ZS90 instrument on the techniques of Laser Doppler Electrophoresis. The electrophoretic mobility U_E was measured and the zeta potential was calculated by the Dispersion Technology Software provided by Malvern according to Henry equation:

$$U_E = \frac{2\varepsilon z f(ka)}{3\eta} \quad (1)$$

where z , ε and $f(ka)$ are the zeta potential, the dielectric constant and the Henry's function. For the electrophoretic determinations of zeta potential made in aqueous media and moderate electrolyte concentration, $f(ka)$ is 1.5.

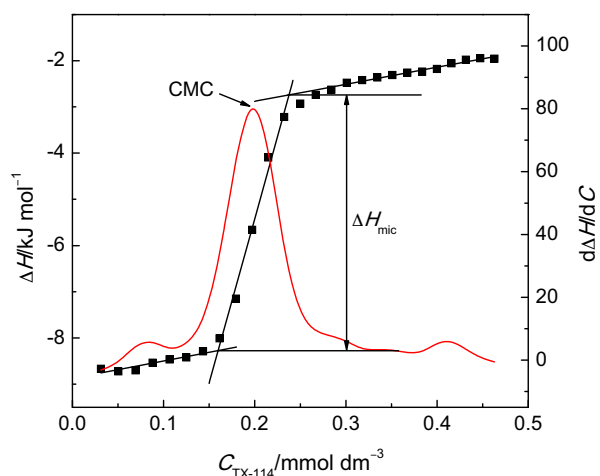


Fig. 1. Typical data obtained from ITC experiments performed with 2 mmol dm⁻³ of TX-114 aqueous solution titrated to 5 mmol dm⁻³ of C₄mimNTf₂.

2.2.3. Cloud point measurements

The determination of cloud point was based on the variation of the UV–vis absorbance as temperature was elevated, according to the method in the literature [35,36]. UV–vis absorption spectra were measured on a U-3010 (Hitachi, Japan) spectrophotometer.

2.2.4. ¹⁹F NMR

¹⁹F NMR spectra of ILs (1 mmol dm⁻³) dissolved in D₂O in the presence of TX-114 (10 mmol dm⁻³) were recorded on a Bruker AV400 MHz NMR spectrometer.

2.2.5. Isothermal titration calorimetry (ITC)

ITC was carried out on a Nano ITC 2G (TA, USA). The CMC and micellization enthalpy (ΔH_{mic}) of TX-114 were simultaneously determined by ITC method in the absence and presence of ILs. In an ITC experiment, the TX-114 solution (2 mmol dm⁻³) in the syringe was injected in a total of 31 drops by each of 8 μ L into the measuring cell filled with the aqueous solution of a specific IL (5 mmol dm⁻³). The temperature was controlled at 293.2 K. The rotational speed of the stirrer was 250 min⁻¹ and the equilibrium time between two injections was set at 450 s for the signal to return to the baseline. The dilution heat of water to the corresponding IL solution was determined in a separate run and was subtracted from the determined heat flow. Fig. 1 shows the typical data obtained from an ITC experiment, and the ΔH_{mic} value is indicated by the three fitting lines. The CMC is defined as the concentration at which the first derivative of the sigmoidal curve reaches a maximum. The uncertainties for both CMC and ΔH_{mic} are less than $\pm 5\%$.

In the titration of an IL solution (10 mmol dm⁻³) to the TX-114 solution (10 mmol dm⁻³) at 293.2 K, a total of 25 drops by each of 10 μ L were injected into the measuring cell with an equilibrium time of 500 s. The dilution heat of IL solution to water was also determined and subtracted.

2.2.6. Aggregation number determination

The aggregation number of surfactant (N_{agg}) for the aqueous TX-114 micelles in the presence of ILs was obtained by observing the fluorescence quenching behavior of pyrene by BP at 293.2 K, depicted as the following equation [37]:

$$\ln \left(\frac{I_0}{I_Q} \right) = \frac{N_{agg}}{C_{TX-114} - CMC} C_{BP} \quad (2)$$

where I_0 and I_Q are the fluorescence intensities of pyrene in the absence and presence of the quencher BP, respectively; C_{TX-114} and C_{BP} are the concentrations of TX-114 and BP in aqueous solution,

Table 1

Peak radii of the aggregate size (R_{peak}), zeta potential and cloud point of TX-114 (10 mmol dm⁻³) aqueous solutions upon the addition of 1 mmol dm⁻³ of ILs.

IL	R_{peak} (nm)	Zeta potential (mV)	CP (K)
No IL	32	-1 ± 2	296.7
C ₄ mimBr	32	1 ± 1	297.1
C ₆ mimBr	31	-1 ± 2	301.1
C ₈ mimBr	26	3 ± 5	312.9
C ₁₀ mimBr	12	29 ± 2	323.3
C ₁₂ mimBr	4.2	47 ± 1	341.0
C ₄ mimBF ₄	31	1 ± 1	297.3
C ₄ mimPF ₆	23	-15 ± 1	310.1
C ₂ mimNTf ₂	9.0	-37 ± 5	331.0
C ₄ mimNTf ₂	9.2	-36 ± 5	329.5
C ₆ mimNTf ₂	9.7	-40 ± 2	323.0
C ₈ mimNTf ₂	20	-27 ± 3	309.2

respectively. Fluorescence spectra were recorded on an FL-4500 (Hitachi, Japan) spectrophotometer. Fresh sample solutions were used in the fluorescence measurements. Stock solutions of pyrene and BP were prepared in methanol. The concentrations of pyrene, TX-114, and IL were 10⁻³, 10, and 5 mmol dm⁻³, respectively, and that of the quencher BP was varied from 0 to 0.1 mmol dm⁻³ in the determination of the aggregation number. Notably, in all the experiments of this work, the concentrations of ILs are all lower than their CMC values in aqueous solutions. The CMC values of imidazolium based ILs have been detected in a previous work [38]. Therefore, there is no micellization of IL itself, and Eq. (2) is still valid.

All the other experiments were carried out at 293.2 K unless noted otherwise.

3. Results

3.1. Determination of aggregate size

Fig. 2 represents the variation of the scattering intensity with the radius of micellar aggregates in 10 mmol dm⁻³ of TX-114 aqueous solution containing 1 mmol dm⁻³ of NaCl in the presence of 1 mmol dm⁻³ of ILs. The peak radii of the aggregate size are reported in Table 1. It can be seen that, upon the addition of Br⁻ based ILs, the size is decreased with the alkyl chain lengthening. The peak of the radius of the aggregate size is decreased apparently on the addition of C_nmimNTf₂. Among the added ILs with the same cation C₄mim⁺, the more hydrophobic the IL anion is, the more significantly the IL affects the size of the TX-114 micelles.

3.2. Determination of zeta potential

The results of zeta potential of the aqueous solution of TX-114 (10 mmol dm⁻³) containing 1 mmol dm⁻³ of NaCl in the presence of ILs (1 mmol dm⁻³) are listed in Table 1. The value of zeta potential of the TX-114 aqueous solution is nearly zero. Upon the addition of C_nmimBr, the zeta potential increases with an increase in the alkyl chain length of the ILs. Remarkably, the zeta potential reaches 47 mV in the presence of C₁₂mimBr. Differently, the value of zeta potential is -37 mV upon the addition of C₂mimNTf₂. With the same cation C₄mim⁺, the more hydrophobic the IL anion is, the more significantly the IL decreases the zeta potential of the TX-114 micelles.

3.3. Determination of cloud point

The results of cloud point (CP) of the aqueous solution of TX-114 (10 mmol dm⁻³) in the presence of ILs (1 mmol dm⁻³) are compiled in Table 1. The CP value is 296.7 K in the absence of ILs. Lengthening the alkyl chain of C_nmimBr increases the CP value. For example, the CP value is 341.0 K as C₁₂mimBr is added, much higher than that

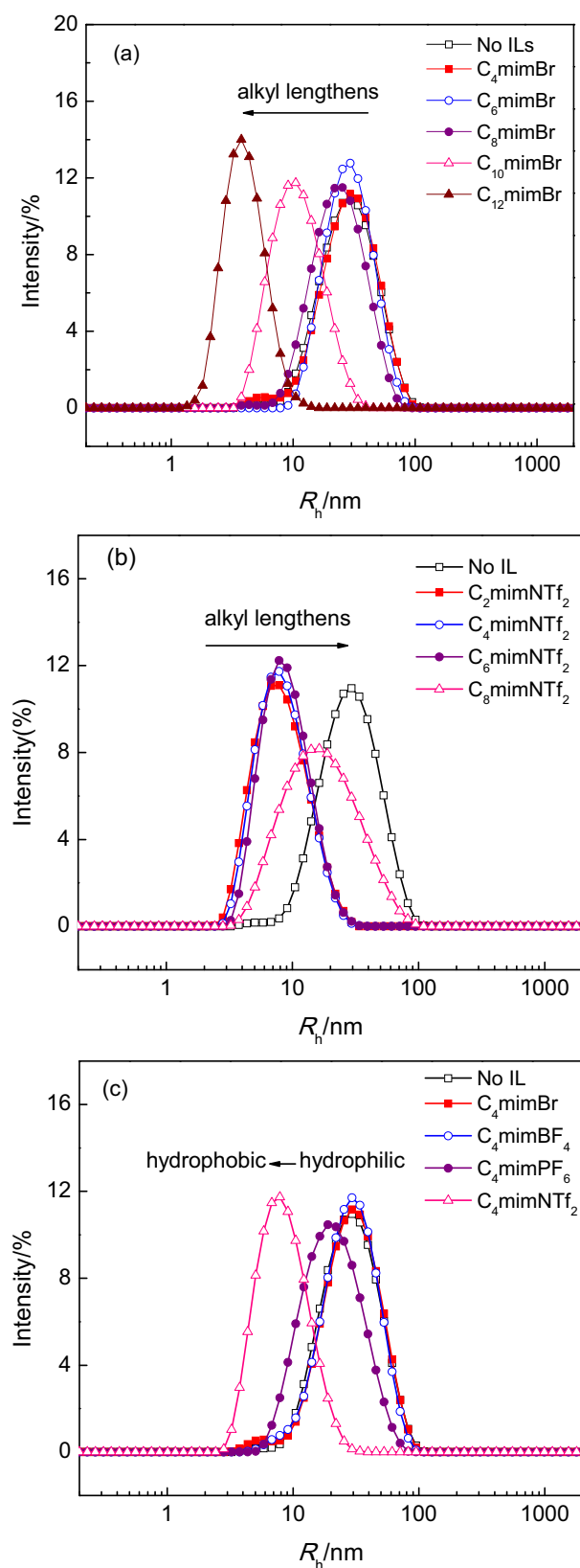


Fig. 2. DLS results of 10 mmol dm^{-3} of TX-114 aqueous solution containing 1 mmol dm^{-3} of NaCl in the absence and presence of 1 mmol dm^{-3} of ILs.

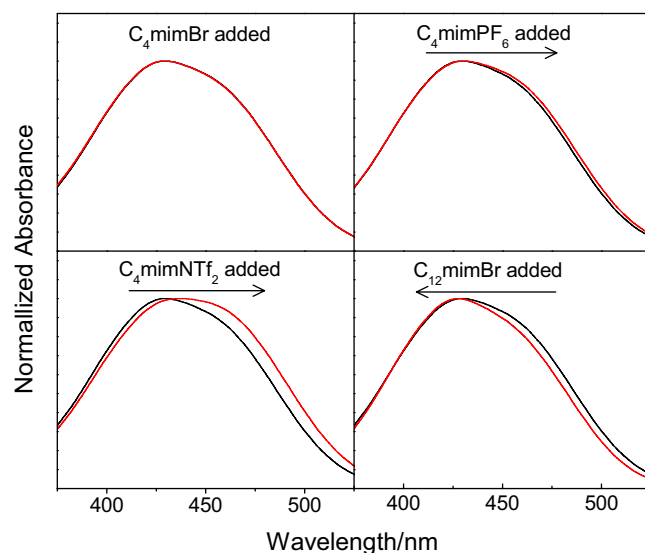


Fig. 3. Spectra of MO within 10 mmol dm^{-3} of TX-114 in the absence and presence of 1 mmol dm^{-3} of different ILs.

in the absence of ILs. Hydrophobic ILs $C_n\text{mimNTf}_2$ increase the CP value remarkably, and lengthening the alkyl chain from C_2 to C_8 reduces the CP value from 331.0 to 309.2 K. $C_4\text{mimPF}_6$ increases the CP value to 310.1 K, while $C_4\text{mimBF}_4$ shows no obvious effect.

3.4. UV absorption of MO in micellar solutions

Fig. 3 illustrates the absorption spectra of MO in 10 mmol dm^{-3} of TX-114 aqueous solution in the absence and presence of 1 mmol dm^{-3} of different ILs. Upon the addition of the $C_4\text{mim}^+$ based ILs, the spectra of MO exhibit red shift with an increase in the IL hydrophobicity. On the contrary, the addition of $C_{12}\text{mimBr}$ gives the spectrum a hypsochromic shift.

The variation of the λ_{max} (maximum of absorbance) value for MO in 10 mmol dm^{-3} of TX-114 aqueous solution as a function of the concentration of IL is shown in Fig. 4. MO dissolved in TX-114 aqueous solution displays a λ_{max} value of 429.5 nm. The short alkyl imidazolium based ILs $C_4\text{mimBr}$ and $C_4\text{mimBF}_4$ show no obvious influence on λ_{max} whereas $C_{12}\text{mimBr}$ causes a decrease of λ_{max} . In contrast, the addition of hydrophobic ILs $C_4\text{mimPF}_6$ or $C_4\text{mimNTf}_2$

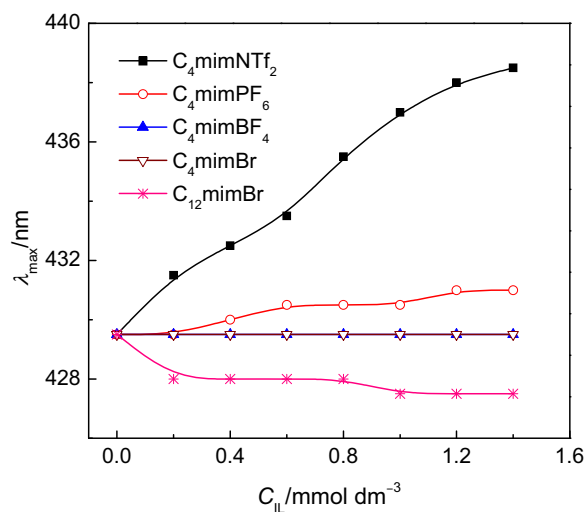


Fig. 4. Variation of λ_{max} of MO within 10 mmol dm^{-3} of TX-114 as different ILs added.

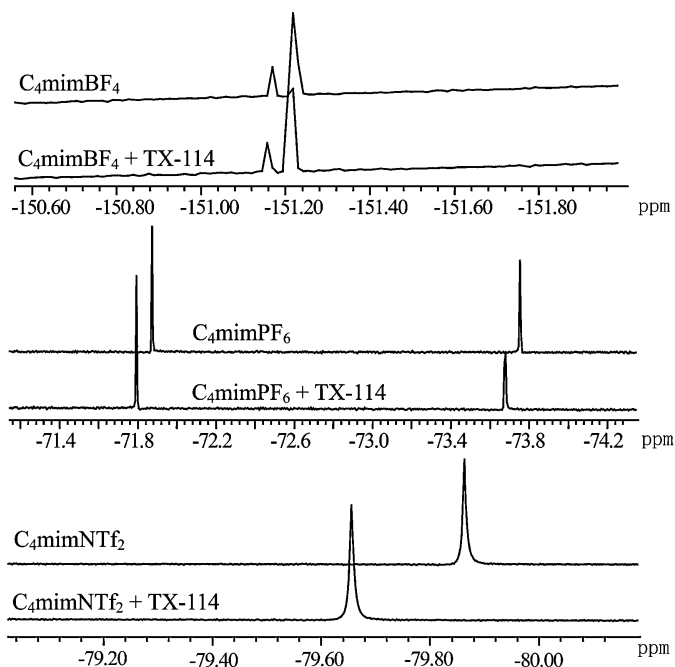


Fig. 5. ^{19}F NMR spectra of 1 mmol dm^{-3} of C_4mimBF_4 , C_4mimPF_6 and $\text{C}_4\text{mimNTf}_2$ in the absence and presence of 10 mmol dm^{-3} of TX-114.

induces an increase of λ_{max} , of which $\text{C}_4\text{mimNTf}_2$ shows a more remarkable effect.

3.5. ^{19}F NMR study

The ^{19}F NMR spectra of 1 mmol dm^{-3} of C_4mimBF_4 , C_4mimPF_6 and $\text{C}_4\text{mimNTf}_2$ in water and in 10 mmol dm^{-3} of TX-114 aqueous solution are shown in Fig. 5. The signals of C_4mimBF_4 show no obvious variation as TX-114 is added whereas those of C_4mimPF_6 and $\text{C}_4\text{mimNTf}_2$ shift downfield with a value of 0.08 and 0.19 ppm, respectively.

3.6. ITC experiments

ITC is a useful technique for acquiring information of the self-organization of surfactants [39]. From an ITC experiment, one can obtain the CMC value and the micellization enthalpy (ΔH_{mic}) of a surfactant. In this work, we utilized ITC to detect the influence of ILs on these two parameters for the TX-114 micelles. The results of TX-114 aqueous solution titrated to aqueous solution of ILs (5 mmol dm^{-3}) are presented in Fig. 6, and the values of CMC and ΔH_{mic} are listed in Table 2.

Our result for the CMC value of TX-114 is 0.24 mmol dm^{-3} , consisting with those in the literature [40–42]. Addition of $\text{C}_{12}\text{mimBr}$ remarkably decreases the value of CMC to 0.11 mmol dm^{-3} . Compared with $\text{C}_{12}\text{mimBr}$, C_4mimX ($\text{X}=\text{Br}^-$, BF_4^- , PF_6^- and NTf_2^-) generally shows little effect on the variation of the CMC value. The

Table 2
CMC and ΔH_{mic} values of TX-114 in aqueous solutions containing 5 mmol dm^{-3} of ILs.

	CMC (mmol dm^{-3})	ΔH_{mic} (kJ mol^{-1})
No IL	0.24	6.9
C_4mimBr	0.24	6.6
C_4mimBF_4	0.24	6.4
C_4mimPF_6	0.23	5.4
$\text{C}_4\text{mimNTf}_2$	0.20	5.3
$\text{C}_{12}\text{mimBr}$	0.11	7.1

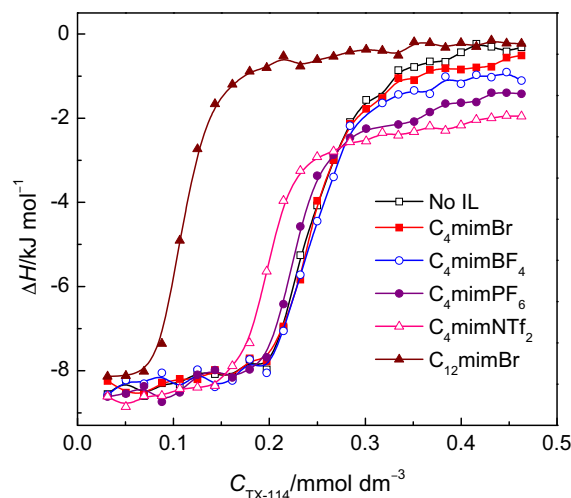


Fig. 6. ITC data for 2 mmol dm^{-3} of TX-114 titration into 5 mmol dm^{-3} of different ILs.

value of ΔH_{mic} is 6.9 kJ mol^{-1} for TX-114 in the absence of ILs, which means that the micellization of TX-114 in water is an endothermic process. Enhancing the hydrophobicity of ILs decreases the micellization enthalpy of TX-114. According to the literature [39], when sigmoidal curves are obtained, they can be divided into three concentration ranges showing successively: (i) the dissociation of the micelles into unimers, (ii) the micellization of the surfactant, and (iii) the dilution of the micelles. One can see that, as the hydrophobicity of ILs increased, the decrease of the micellization enthalpy of TX-114 is attributed to the fact that ILs make the process of the dilution of the TX-114 micelles more exothermic, suggesting an interaction between ILs and the TX-114 micelles. Unlike the striking decrease in CMC, insignificant effect by $\text{C}_{12}\text{mimBr}$ is observed in the dilution of TX-114 micelles.

We subsequently performed titrations of ILs to the aqueous solutions of the TX-114 micelles, in which the concentrations of the ILs and TX-114 surfactant are both 10 mmol dm^{-3} . Fig. 7 shows the total heat as a function of the volume of the titrant. The titration of $\text{C}_{12}\text{mimBr}$ to TX-114 shows negligible heat, whereas an evidently exothermic process is observed in the titration of $\text{C}_4\text{mimNTf}_2$ or C_4mimPF_6 to TX-114, consisting with the result that $\text{C}_4\text{mimNTf}_2$ and C_4mimPF_6 interact with the TX-114 micelles as mentioned

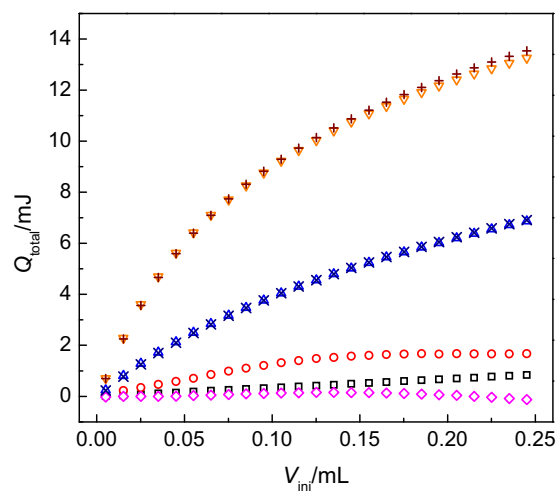


Fig. 7. Total heat as a function of the volume of the titrant during the titration of 10 mmol dm^{-3} of C_4mimBr (\square), C_4mimBF_4 (\circ), C_4mimPF_6 (\triangle), $\text{C}_4\text{mimNTf}_2$ (∇), $\text{C}_{12}\text{mimBr}$ (\diamond), LiNTf_2 ($+$), and KPF_6 (\times) to 10 mmol dm^{-3} of TX-114.

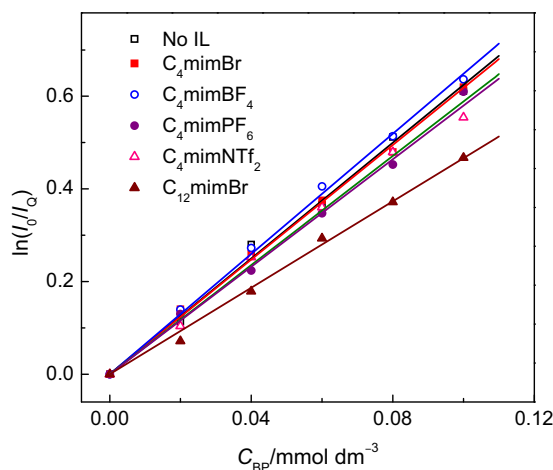


Fig. 8. Plot of $\ln(I_0/I_Q)$ against C_{BP} in 10 mmol dm^{-3} of TX-114 in the presence of different ILs (5 mmol dm^{-3}). The concentration of pyrene is $10^{-6} \text{ mol dm}^{-3}$.

above. For comparison, the titration of LiNTf_2 aqueous solution to TX-114 aqueous solution is also carried out, and the heat released is identical to that of $\text{C}_4\text{mimNTf}_2$ to TX-114. Similar case is also found during the titration of $\text{C}_4\text{mimPF}_6/\text{KPF}_6$ to TX-114.

3.7. Determination of the aggregation number

Fig. 8 shows the plot of $\ln(I_0/I_Q)$ versus C_{BP} in 10 mmol dm^{-3} of TX-114 aqueous solution in the presence of 5 mmol dm^{-3} of ILs. Our result of N_{agg} for TX-114 in the absence of ILs is 62 ± 7 , consisting with that reported in the literature [43]. The detected aggregation numbers of TX-114 upon the addition of C_4mimBr , C_4mimBF_4 , C_4mimPF_6 , $\text{C}_4\text{mimNTf}_2$ and $\text{C}_{12}\text{mimBr}$ are 62 ± 5 , 65 ± 5 , 59 ± 6 , 58 ± 7 and 47 ± 4 , respectively.

4. Discussion

The above results strongly suggest that the hydrophobic IL anions play a key role in the modification of the physicochemical properties of TX-114 micellar solution. The hydrophobic ILs (e.g., $\text{C}_4\text{mimNTf}_2$) do not so evidently influence the CMC and the aggregation number as the hydrophilic ILs with long alkyl chain (e.g., $\text{C}_{12}\text{mimBr}$) do, but obviously affect the aggregate size, zeta potential, cloud point and micellization enthalpy. The hydrophobic IL anions should be responsible for these changes, and thus one can infer that the anions modify the properties of TX-114 micellar solution in a way different from what a long alkyl chain substituted imidazolium cation does.

4.1. Partitioning of hydrophobic IL anions into micelles

The variation of the micellar size upon the addition of $\text{C}_{12}\text{mimBr}$ is attributed to the penetration of $\text{C}_{12}\text{mim}^+$ into the TX-114 micelles, according to the literature [21]. Compared with the effects of C_4mimBr and C_4mimBF_4 on the micellar size, the significant variation of the micellar size upon the addition of C_4mimPF_6 and $\text{C}_4\text{mimNTf}_2$ cannot be attributed to the alignment of C_4mim^+ with TX-114 molecules. Because of the hydrophobicity, NTf_2^- and PF_6^- are very likely to interact with the TX-114 micelles. This is proved by the zeta potential experiment. The negative zeta potential in the presence of $\text{C}_n\text{mimNTf}_2$ and C_4mimPF_6 suggests the partitioning of the hydrophobic anions (NTf_2^- and PF_6^-) into the micelles, while an increase of zeta potential with the addition of long alkyl C_nmimBr indicates the penetration of long alkyl C_nmim^+ into the micelles.

The partitioning of PF_6^- and NTf_2^- into the TX-114 micelles is further demonstrated by the red-shift and the increase of λ_{max} value in UV absorption of MO in the micellar solution. The negative zeta potential due to the partitioning of PF_6^- or NTf_2^- into the micelles is unfavorable for the incorporation of MO because of its ionic nature (see Scheme 1). Smaller amount of MO molecules incorporating in micelles makes its spectrum red-shift and the λ_{max} value increase [44]. On the other hand, the alignment of $\text{C}_{12}\text{mim}^+$ within TX-114 micelles attracts more MO molecules partitioning into the micelles, inducing a blue-shift of the spectrum and a decrease of λ_{max} .

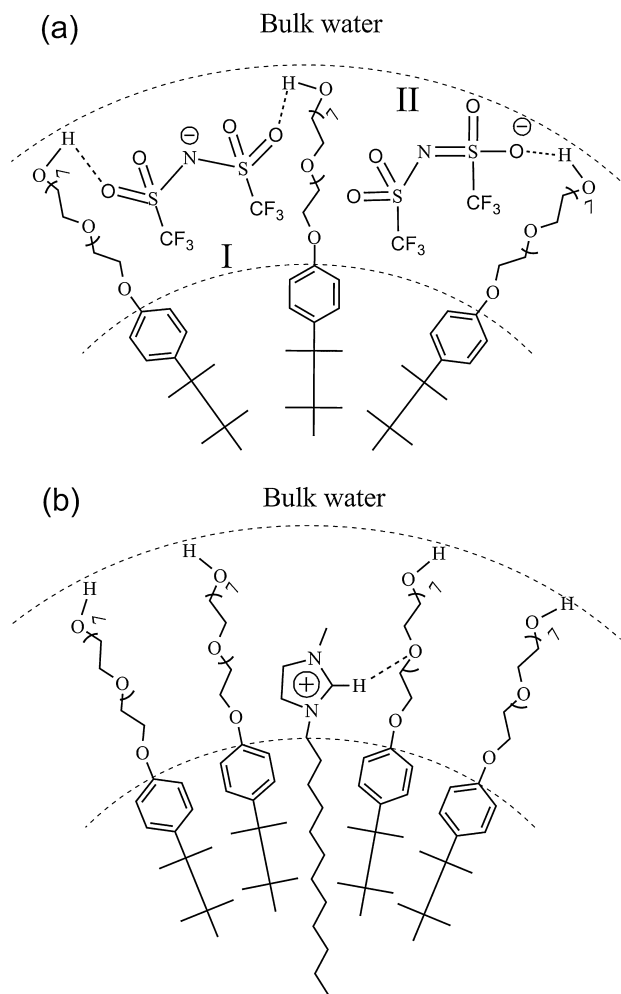
The partitioning of the hydrophobic IL anions into TX-114 micelles is responsible for the increase in the cloud point. Cloud point is a temperature at which the micellar solution becomes turbid due to the reduction of the intermicellar repulsion which are affected by the hydration of the hydrophilic groups of the surfactants and the zeta potential of the micelles [45–47]. Obviously, the positive or negative zeta potential of the TX-114 micelles leads to an increase in the CP value.

4.2. Location of hydrophobic IL anions in micelles

The results of the aggregate size, zeta potential, UV absorbance and cloud point indicate that the IL anions PF_6^- and NTf_2^- are partitioning into the TX-114 micelles. Theoretically, the group with charge is energetically unfavorable to enter into the hydrophobic core of micelles because of easy hydration. For instance, only the alkyl chain of $\text{C}_{12}\text{mim}^+$ interacts with the hydrophobic chain and phenyl ring of the surfactant whereas the imidazolium ring interacts with the EO groups, according to the literature [21]. In the case of NTf_2^- , due to the fact that NTf_2^- contains no long alkyl chain and the mutual phobicity of hydrocarbons and fluorocarbons [48], NTf_2^- should not interact with the aliphatic chain of the TX-114 molecule. Furthermore, the $-\text{CF}_3$ group of NTf_2^- seems to be unfavorable for interacting with the aromatic ring, according to the literature [49]. The location of NTf_2^- at the head group area of the TX-114 micelles is also suggested by the ^{19}F NMR spectra. We performed the ^{19}F NMR of 1 mmol dm^{-3} of $\text{C}_4\text{mimNTf}_2$ in the mixture of D_2O and PEG400 (Fig. S1), and it was found that the chemical shift of the fluorine atoms of NTf_2^- in the TX-114 micellar solution is close to that in the mixture of 40% (v/v) PEG400/ D_2O . Based on the above discussion, one can conclude that NTf_2^- only interacts with the EO groups of TX-114 and is located at the head group area of the TX-114 micelles. This is the reason why the aggregate size, zeta potential and cloud point are altered but the CMC and aggregation number are insignificantly influenced.

4.3. Hydrophobic interaction and H-bonding between hydrophobic IL anions and micelles

It is reasonable to suggest that hydrophobic interaction is the main driving force for the partitioning of hydrophobic IL anions into the TX-114 micelles. As NTf_2^- interacts with the EO groups of TX-114, the hydration/dehydration of EO groups and the dehydration of NTf_2^- contribute to the variation of TX-114 micellization enthalpy or the substantial heat release in the titration of $\text{C}_4\text{mimNTf}_2/\text{LiNTf}_2$ to the TX-114 micellar solution. The dehydration of NTf_2^- gives an endothermic effect whereas the hydration of EO groups gives an exothermic effect. Therefore, the interaction of NTf_2^- with the TX-114 micelles very likely makes EO groups more hydrated. Differently, $\text{C}_{12}\text{mim}^+$ not only interacts with the EO groups of TX-114 by its imidazolium ring, but also interacts with the hydrophobic chain and phenyl ring by its alkyl chain. This may be the reason that the titration of $\text{C}_{12}\text{mimBr}$ to TX-114 shows no evident heat release.



Scheme 2. Illustration of the interactions between $\text{NTf}_2^-/\text{C}_{12}\text{mim}^+$ and the TX-114 micelles.

Notably, the hydrophobic interaction is related to the concentration of ILs. For the hydrophobic ILs, the hydrophobic interaction between the hydrophobic IL anions (e.g., NTf_2^-) and the TX-114 micelles can be revealed at a low concentration of the IL. In the previous reports about the interaction between micelles and hydrophilic ILs, the concentrations of the ILs are usually very high, and it was found that the effect of the ILs on surfactant solution can be regarded as the comprehensive effects of inorganic salt, cosurfactant and cosolvent, with different proportions relative to the concentration of the ILs [20]. The hydrophilic ILs, e.g., C_4mimBF_4 , at a high concentration can evidently affect the properties of the surfactant micellar solution [6,8,24]. Actually, C_4mimBF_4 in aqueous solution aggregates together with a CMC value of about 0.8 mol dm^{-3} [50], which suggests that the interaction of C_4mimBF_4 with micelles is also driven by hydrophobic interaction. At low concentration of ILs, however, the interactions of C_4mimBF_4 with micelles cannot be revealed. This also reflects that the hydrophobic IL anions (NTf_2^- and PF_6^-) interact with the micelles prior to the short alkyl substituted imidazolium cations, similarly to the interactions between CDs and ILs [32,33].

On the other hand, similar to the interaction between $\text{NTf}_2^-/\text{PF}_6^-$ and CDs [32], there possibly exists the H-bonding interaction between $\text{NTf}_2^-/\text{PF}_6^-$ and the TX-114 micelles. The H-bonding was also found in the mixed micelles of hexa(ethylene glycol) mono *n*-dodecyl ether (C_{12}E_6) and SDS [51]. Based on the calorimetric study, Golub et al. indicated that the excess enthalpy

during the formation of mixed micelles of C_{12}E_6 and SDS is attributed to both the effect of the sulfate headgroups of SDS on the hydration of the ethylene oxide (EO) groups of C_{12}E_6 in the mixed corona and the H-bonding of the sulfate headgroups with the partly dehydrated EO chain [51]. In our case, NTf_2^- and PF_6^- maybe form H-bonding with the terminal hydroxyl of the TX-114 molecules in the micelles.

In summary, both the imidazolium cations with long alkyl chain (e.g., $\text{C}_{12}\text{mim}^+$) and the hydrophobic anions (e.g., NTf_2^-) can interact with the micelles, as shown in Scheme 2. Different from $\text{C}_{12}\text{mim}^+$, NTf_2^- is located at the head group area but not penetrates into the hydrophobic core of the TX-114 micelles. Due to their hydrophobicity, the two $-\text{CF}_3$ groups are favorable to orient themselves to the inside of the TX-114 micelles. Notably, there may exist a resonance structure of NTf_2^- (form II, Scheme 2a) due to the delocalization of electrons through sulfur–nitrogen π bonding, according to the literature [52]. This study gives a further explanation of the mechanism in the improvement of the cloud point extraction of uranyl ions using TX-114 micellar solution upon the addition of NTf_2^- based ILs [4].

5. Conclusions

The hydrophobic IL anions (NTf_2^- and PF_6^-) can interact with the TX-114 micelles, leading to a variation of the key physicochemical properties of micellar solution, e.g., aggregate size, zeta potential, cloud point and micellization enthalpy. Different from the interactions of micelles with the long alkyl substituted IL cations (e.g., $\text{C}_{12}\text{mim}^+$) or the long alkyl substituted IL anions (e.g., hexanoate and hexylsulfate), NTf_2^- and PF_6^- are located at the head group area of the TX-114 micelles and interact with the EO groups of TX-114 by hydration of the EO groups and formation of H-bonding. Therefore, they insignificantly affect the CMC value and the aggregation number. Hydrophobic interaction is the main driving force for the interactions between the TX-114 micelles and the hydrophobic IL anions. Our results give a further understanding of the interactions between IL cation/anion and micelles and also give a further explanation of the mechanism in the improvement of the cloud point extraction of uranyl ions using TX-114 micellar solution upon the addition of NTf_2^- based ILs.

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