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Studies on the Micropolarities of bmimBF$_4$/TX-100/Toluene Ionic Liquid Microemulsions and Their Behaviors Characterized by UV−Visible Spectroscopy

Na Li, Yan'an Gao, Liqiang Zheng,* Jin Zhang, Li Yu, and Xinwei Li

Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, China

Ionic liquids (ILs), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$), were substituted for polar water and formed nonaqueous microemulsions with toluene by the aid of nonionic surfactant TX-100. The phase behavior of the ternary system was investigated, and microregions of bmimBF$_4$-in-toluene (IL/O), bicontinuous, and toluene-in-bmimBF$_4$ (O/IL) were identified by traditional electrical conductivity measurements. Dynamic light scattering (DLS) revealed the formation of the IL microemulsions. The micropolarities of the IL/O microemulsions were investigated by the UV−vis spectroscopy using the methyl orange (MO) and methylene blue (MB) as absorption probes. The results indicated that the polarity of the IL/O microemulsion increased only before the IL pools were formed, whereas a relatively fixed polar microenvironment was obtained in the IL pools of the microemulsions. Moreover, UV−vis spectroscopy has also shown that ionic salt compounds such as Ni(NO$_3$)$_2$, CoCl$_2$, CuCl$_2$, and biochemical reagent riboflavin could be solubilized into the IL/O microemulsion droplets, indicating that the IL/O microemulsions have potential application in the production of metallic or semiconductor nanomaterials, and in biological extractions or as solvents for enzymatic reactions. The IL/O microemulsions may have some expected effects due to the unique features of ILs and microemulsions.

Introduction

Microemulsion is an optically isotropic, transparent, and thermodynamically stable medium formed by two or more immiscible liquids which are stabilized by an adsorbed surfactant film at the liquid−liquid interface.[1] In recent years, microemulsions have been extensively applied to many fields, such as chemical reactions,[2,3] nanomaterials preparation,[4] and drug delivery systems.[5] Recently, attempts have been made to prepare and study nonaqueous microemulsions.[6−9] In this effort, water has been replaced by polar nonaqueous solvents, such as ethylene glycol, formamide, glycerol, and so on. These microemulsions have attracted much interest from both theoretical (thermodynamics, particle interactions) and practical (potential use as novel reaction media) viewpoints.[8] They have been widely applied to cosmetics, semiconductors, solar energy conversion, and microcolloids.[10] Furthermore, there should be a number of distinct advantages of the nonaqueous microemulsions over the aqueous microemulsions because they are useful media for some organic reactions such as Diels−Alder reaction, esterification, and polymerization.[11] Especially, they are more attractive for those reactants which should avoid contacting with water.

Ionic liquids (ILs) are receiving much attention as a class of neoteric solvents, because of their special physical and chemical properties, such as low volatility, wide electrochemical window, nonflammability, high thermal stability, and wide liquid range.[12−16] So far, the majority of the efforts have been focused on organic reactions, catalysis, and other processes such as electrochemistry, biochemistry, and separations.[12,17−19] Recent developments have been involved in preparation of nanomaterials and gas absorbents.[20,21]

Despite these features, solubility limitations for apolar solutes remain, which could be overcome by incorporation of hydrocarbon domains provided by normal micelles or formation of IL-in-oil (IL/O) microemulsions.[22] Using ILs instead of water to prepare an IL microemulsion has been reported. Recently, Han and his co-workers discovered that 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$) can act as polar nanosized droplets dispersed in continuous hydrocarbon solvent. Freeze-fracture electron microscopy (FFEM) indicated a droplet structure which was similar in shape to "classic" water-in-oil (W/O) microemulsions.[14] Eastoe et al. have investigated the same system by small-angle neutron scattering (SANS), which showed a regular increase in droplet volume as micelles were progressively swollen

* Corresponding author. Telephone: 86-531-88366062. Fax: 86-531-88564750. E-mail: lqzheng@sdu.edu.cn.

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with added bmimBF$_4$, behavior consistent with "classic" W/O microemulsions.[22] Furthermore, the effects of confinement of the IL bmimBF$_4$ on salvation dynamics and rotational relaxation of Coumarin 153 in TX-100/cyclohexane microemulsions have been explored using steady-state and picosecond time-resolved emission spectroscopy.[23] In addition, our recent work has shown that the interaction between the elecrtonegative oxygen atoms of oxyethylene (OE) units of TX-100 and the electropositive imidazolium ring may be the driving force for the solubilization of bmimBF$_4$ into the core of the TX-100 aggregates.[24] A small amount of added water has a great effect on the microstructure of the IL microemulsions. These water molecules are inclined to locate in the palisade layers of the microemulsion and perhaps act as a glue to stick the polar IL and the hydrophilic OE groups of TX-100, which make the microemulsion system more stable.[25]

These nonaqueous IL microemulsions are an attractive topic. They provide hydrophobic or hydrophilic nanodomains, therefore expanding potential uses of ILs in microhetergeneous systems as reaction and separation or extration media. For example, a recent report has shown that surfactant ionic liquid based microemulsions can be used to produce polymer nanoparticles, gels, and open-cell porous materials.[26] The nonaqueous IL microemulsions may expand the use of traditional microemulsions to a larger range, which is helpful to the theoretic investigation about microemulsion. Furthermore, they may have some potential applications due to the unique features of ILs and microemulsions.[14]

Even so, these IL microemulsions have not been intensively investigated so far, especially their potential applications have seldom been reported. It has been reported that ILs can be the preferable solvents in the synthesis and modification of nanostructured materials due to their unique properties, such as extended hydrogen bonding.[27] They have been used to make mesoporous metal oxides, polyaniline nanoparticles, and morphologically interesting nanoflakes and nanosheets and to controll the composition of Pt–Co alloys.[28–34] Moreover, ILs have been considered as a boon for the synthesis of inorganic materials.[35] Therefore, it is important to learn the potential application of ILs in the nanomaterials field as a nanosized microhetergenuous solvent.

In this paper, the phase behavior of the bmimBF$_4$/TX-100/toluene ternary microemulsion system was investigated. The environmental polarities of the bmimBF$_4$-in-toluene microemulsion was probed by UV–vis spectroscopy using methyl orange (MO) and methylene blue (MB) as absorption probes. To check the potential application of the IL microemulsions in the material and biological field, the solubilizations of metal salts such as CuCl$_2$, CoCl$_2$, Ni(NO$_3$)$_2$, and biological molecule riboflavin in the IL/O microemulsion were explored, respectively.

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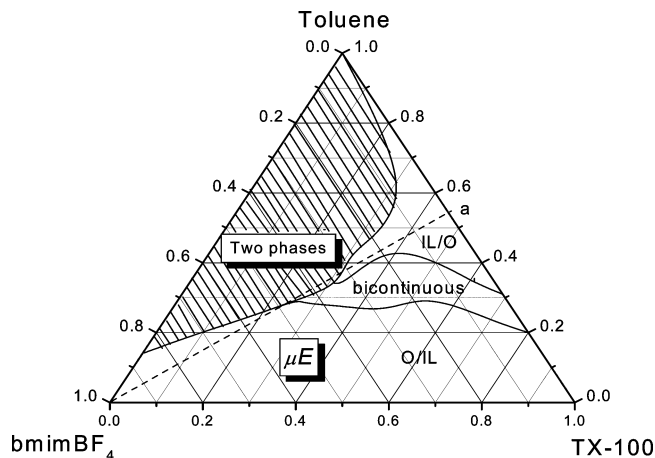
Figure 1. Phase diagram of the bmimBF$_4$/TX-100/toluene three-component system at room temperature. For line *a*, the initial TX-100 weight fraction is 0.45.

Experimental Section

Materials. TX-100 was obtained from Alfa Aesar and evaporated under vacuum at 80 °C for 4 h to remove any excess water before use. bmimBF$_4$ was prepared as reported earlier.[36] Being hygroscopic, bmimBF$_4$ can easily absorb a significant amount of water. To avoid the moisture in air, the IL was freshly made and further dehydrated before use. The dehydration process is the same as that of TX-100. Methyl orange (MO), methylene blue (MB), and toluene were provided by Beijing Chemical Reagents Co. Metal salts CuCl$_2$, CoCl$_2$, and Ni(NO$_3$)$_2$ were purchased from Shanghai Chemical Reagents Co. Biochemical reagent riboflavin was obtained from Sigma and used as received.

Apparatus and Procedures. The UV–vis spectra were performed on a computer-controlled spectrometer (UV-4100, Beijing Instrument Co.). The path length of the quartz cell used in this experiment was 1 cm. Appropriate amounts of substances were uniformly mixed in advance and then added to the quartz cell. The experiment was carried out at room temperature. The diameters of the nonaqueous IL microemulsions were determined by dynamic light scattering (DLS, Brookhaven Instrument Co., BI-200SM goniometer and BI-9000AT correlator) with an argon-ion laser operating at 488 nm. All measurements were made at the scattering angle of 90° at a temperature of 25 °C.

To introduce the probes into the micelles or microemulsions, 2.55 × 10^{-3} M MO and 3.05 × 10^{-3} M MB methanolic solutions were prepared, respectively, an appropriate amount of which was transferred into a small vial, and then the methanol was evaporated. Upon addition of reverse micellar or microemulsion solutions to the solid residue, the probes were dissolved. The molar ratio of TX-100 to MO and MB was always greater than 9.24 × 10^3 and 4.62 × 10^4. So the fluctuate of the system in the presence of the probes may be assumed negligible.[36]

Results and Discussion

Phase Behavior and Microregions of the IL Microemulsion. The phase behavior of the bmimBF$_4$/TX-100/toluene ternary system at room temperature is shown in Figure 1. A single isotropic region extending from the IL corner to the toluene corner is observed. The region marked "*μE*" is the one-phase microemulsion and "Two phases" is a two-phase region, i.e., microemulsion in equilibrium with an excess toluene or bmimBF$_4$ phase. It is evident from Figure 1 that a continuous stable single-phase microemulsion region always can be observed over the bmimBF$_4$ or toluene content range of 0–100% (wt). The single-phase microemulsion region should span the range of possible

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structure from microdroplets to bicontinuous structure. The structural transition of the microemulsion was identified by traditional conductivity measurements[14] (the results of conductivity measurements were not shown here), and three microregions, IL/O, bicontinuous, and O/IL, were also plotted in Figure 1.

Based on the phase diagram, a series of samples in the IL/O microemulsion region along the dilute line *a* were chosen and characterized by DLS technique. The sizes of aggregates increased from 66.2, 71.2, 83.1, 96.5 to 104.6 nm with increasing *R* values (here, we define the molar ratio of bmimBF$_4$ to TX-100 as *R*) from 1.13, 1.47, 181, 2.15 to 2.50. The result is similar to those of the typical W/O microemulsions, indicating the formation of IL/O microemulsions.[22]

Microenvironment of the IL/O Microemulsion. Both methyl orange and methylene blue are insoluble in toluene, and thus no detectable characteristic absorption is found in their toluene solutions, whereas both MO and MB are soluble in bmimBF$_4$ and also in the pure liquid surfactant TX-100. Thus, when TX-100 is added to toluene, if the concentration of TX-100 is above its critical micelle concentration (cmc), reverse micelles begin to form. Consequently, both MO and MB can be considered completely solubilized in the polar cores of reverse micelles, which consist of ethylene oxide (EO) chains of TX-100 and a few toluene molecules penetrated into the cores. If bmimBF$_4$ is added to the TX-100/toluene reverse micelles along the dilute line *a* in Figure 1, the bmimBF$_4$/TX-100/toluene ternary micreomulsion system can form. When IL is added to a certain extent, IL pools may appear and probe molecules MO or MB may move from EO groups to IL pools or still exist among EO groups. Therefore, their strong absorption bands in the UV−visible region are expected to report on the properties of the microenvironment inside the aggregates.

(a) MO as a Probe. The absorption spectra of MO in different solvents have been studied, and the absorption maximum is red-shifted with increasing polarities of the pure solvents.[37−39] The electronic transition energy of MO molecules, as reflected in the wavelength of its absorption maximum λ_{max}, is an indication of the "polarity" of the microenvironment where it is located.[37]

It has been reported that the relevant association of MO is with the EO groups of TX-100.[39] However, MO is also highly soluble in bmimBF$_4$. In order to delineate its actual preferential locations, thereby making clear the polarity of the microenvironments of the IL microemulsions, we simulated two different environments, bulk bmimBF$_4$ and EO domain, by using TX-100/bmimBF$_4$ micellar solutions as media for the probe. When the concentration of TX-100, C_{TX-100}, in bmimBF$_4$ is above its cmc (which is about 7.73×10^{-2} M), normal micelles of TX-100/bmimBF$_4$ begin to form where polar bmimBF$_4$ acts as a continuous outer phase, the hydrophobic tails of TX-100 are congregated into hydrophobic inner cores, and EO groups of TX-100 form polar outer layers. Thus, two microenvironments, pure bmimBF$_4$ and EO domain, are created in the micellar solution.

Figure 2 shows the absorption spectra of MO in bmimBF$_4$ solutions at different concentrations of TX-100. At $C_{TX-100} = 7.65 \times 10^{-3}$ M, surfactant molecules of TX-100 are dissolved in bmimBF$_4$ and no micelles form at this stage. The λ_{max} of the characteristic band in the visible range of the spectrum of MO appears at 430 nm, which is the same as that in bulk bmimBF$_4$, indicating the continuous IL phase possesses the same polarity
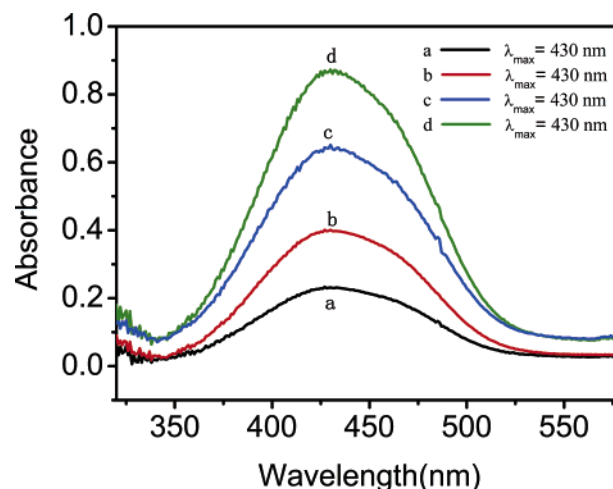
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Figure 2. Absorption spectra of MO in the TX-100/bmimBF$_4$ micellar solutions, as a function of TX-100 concentration: 5.0×10^{-3} (a), 7.84×10^{-2} (b), 0.55 (c), and 1.02 M (d). Probe concentrations from a to d: 0.6×10^{-5}, 1.0×10^{-5}, 2.0×10^{-5}, and 3.0×10^{-5}M, respectively.
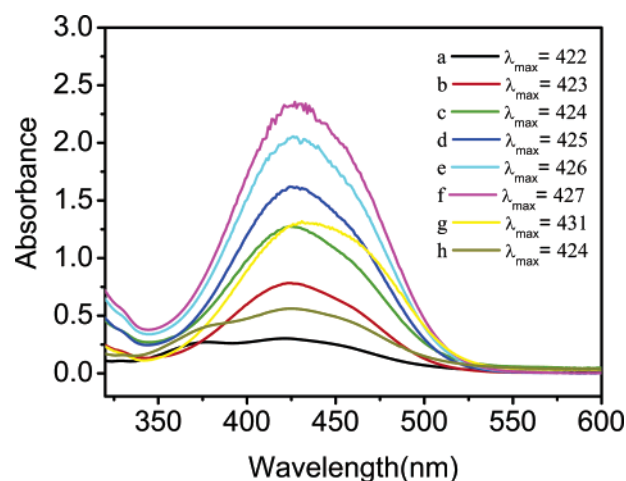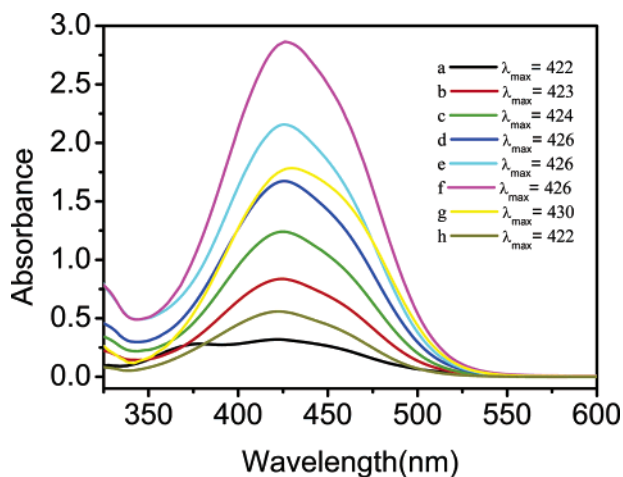

Figure 3. Absorption spectra of MO in the bmimBF$_4$/TX-100/toluene microemulsions (before dehydration) along line *a*, as a function of bmimBF$_4$ content with $R = 0$ (a), 0.70 (b), 1.17 (c), 1.58 (d), 2.11 (e), and 2.71 (f) and with pure IL (g) and pure TX-100 (h). Probe concentrations from a to h: 1.0×10^{-5}, 2.0×10^{-5}, 3.0×10^{-5}, 4.0×10^{-5}, 5.0×10^{-5}, 5.5×10^{-5}, 3.0×10^{-5}, and 1.5×10^{-5} M, respectively.

as that of bulk bmimBF$_4$. When C_{TX-100} is above its cmc in bmimBF$_4$, TX-100/bmimBF$_4$ normal micelles appear; however, the λ_{max} remains constant, suggesting that the presence of micelles has no effect on λ_{max}. If MO molecules prefer to locate in the EO domain, the λ_{max} will not change followed by ambient environment[37] and will present a relatively small value which is similar to that of the polar cores of TX-100/toluene reverse micelles ($\lambda_{max} = 422$ nm, shown in Figure 3). Therefore, it can be speculated that MO is soluble in the bulk bmimBF$_4$, instead of being solubilized in the polar outer layer of the TX-100/bmimBF$_4$ micelles. Thus, one can deduce that, in the bmimBF$_4$/TX-100/toluene IL microemulsion solution, if IL pools appear, the MO molecules will move gradually from the EO domain into the bmimBF$_4$ pools.

The effect of successive addition of bmimBF$_4$ on the microenvironment in the reverse micelles of TX-l00/toluene is demonstrated by the MO spectra in Figure 3. (Here TX-100 is used as received without dehydration.) With an increase of the *R* value from 0 to 2.71 along the dilute line *a*, λ_{max} of MO is

Figure 4. Absorption spectra of MO in the bmimBF$_4$/TX-100/toluene microemulsions (after dehydration) along line *a*, as a function of bmimBF$_4$ content with $R = 0$ (a), 0.70 (b), 1.17 (c), 1.58 (d), 2.11 (e), and 2.71 (f) and with pure IL (g) and pure TX-100 (h). Probe concentrations from a to h: 1.0×10^{-5}, 2.0×10^{-5}, 3.0×10^{-5}, 4.0×10^{-5}, 5.0×10^{-5}, 5.5×10^{-5}, 4.0×10^{-5}, and 1.5×10^{-5} M, respectively.

red-shifted and smaller than that in pure IL. The intensity of the MO absorption band increases due to the increasing of its concentration. The absorption maximum of MO, at $R = 0$, 0.70, 1.17, 1.58, 2.11, and 2.71 and in the bulk bmimBF$_4$, are 422, 423, 424, 425, 426, 427, and 431 nm, respectively. The results are similar to those of the bmimBF$_4$/TX-100/cyclohexane system investigated by Han and his co-workers.[14] However, we discovered that water had a great effect on the UV−vis absorption spectra of the nonaqueous IL microemulsion. When TX-100 was strictly dehydrated and the bmimBF$_4$ used was made freshly, the absorption spectra are greatly different from those before dehydration. The obtained results are shown in Figure 4. When R is in the range of 0.70−1.17, the absorption maximum λ_{max} of MO is red-shifted from 422 to 424 nm. Unexpectedly, with further addition of bmimBF$_4$, when $R = 1.58$, 2.11, and 2.71, the absorption maximum λ_{max} remains constant at $\lambda_{max} = 426$ nm. Normally, the polarity of the microenvironment of the droplet of the microemulsion successively increases with the addition of water molecules, reflected by a successive increase in λ_{max}. Therefore, the current UV−vis spectra results are somewhat unusual. The possible reason may be explained as follows: When bmimBF$_4$ is added to the TX-100/toluene reverse micellar solutions, bmimBF$_4$ molecules are bound to the EO groups of TX-100 in the polar cores. Here, MO molecules are still solubilized in the EO domain. As the IL content increases, the polarity of the polar core is increased, so λ_{max} is red-shifted from 422 to 424 nm. After the bound bmimBF$_4$ reaches equilibrium, subsequently added IL molecules accumulate to form IL pools in the core of the microemulsion. At this stage, the polar core consists of polar outer shell (EO groups) and IL pools. Thus, the MO molecules begin to move from the polar outer shell into the IL pools. Because the polarity of the IL pools is greater than that of the polar outer shell, the λ_{max} of MO presents a larger value, namely, 426 nm.

For traditional aqueous microemulsion, bound water molecules interact strongly with the polar groups of surfactants through counterions that are in the vicinity of the interface.[40] This part of bound water has a restricted mobility and a lack of normal hydrogen-bonded structure and thus contributes to a low polarity.
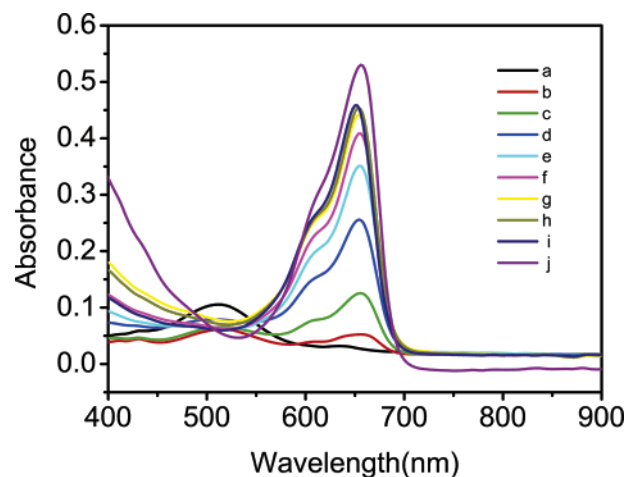

Figure 5. Absorption spectra of MB in the bmimBF$_4$/TX-100/toluene microemulsions along line *a*, as a function of bmimBF$_4$ content with $R = 0$ (a), 0.06 (b), 0.19 (c), 0.48 (d), 0.86 (e), 1.30 (f), 1.58 (g), 2.11 (h), and 2.71 (i) and with pure IL (j). Probe concentration: 1.0×10^{-5} M.

The polarity of the microemulsion is eventually dominated by the competitive contribution from two types of waters, bound water and free water that possess a hydrogen-bonding characteristic similar to the bulk phase. Generally, the polarity of the solubilized water in microemulsions was much lower than that of the bulk water and would change over a large range with the addition of water molecules. However, for the current IL microemulsion, when IL pools form, the λ_{max} of MO is constant with increasing IL content, indicating that the polarity of IL pools is unchanged. One of the reasons is that the polarity difference between the EO domain ($\lambda_{max} = 422$ nm) and bmimBF$_4$ ($\lambda_{max} = 430$ nm) is very small; the addition of bmimBF$_4$ would change the polarity of the IL microemulsion in a relatively small range. The other reason is that bmimBF$_4$ molecules are bound to the EO groups of TX-100 through weak electrostatic interaction between positive electrical charged imidazolium rings and electronegative oxygen atoms of EO groups.[41] The electrostatic interaction is relatively weaker than that of hydrogen bonds. So, the properties of bmimBF$_4$ would not change as greatly as those observed for the solubilized water in microemulsions. In this case, the polarity of IL pools in the IL microemulsion would remain constant even though the volume of the pool is successively increased.

(b) MB as a Probe. The absorption spectrum of MB does not show regular polarity dependence. However, the complexation between TX-100 and MB in the reverse micellar media is found to be very sensitive to its interaction with its local environment, suggesting that MB may be an effective absorption probe for the investigation of nonionic reverse micelles.[38]

Figure 5 shows the effect of successive addition of bmimBF$_4$ on the absorption spectra of MB in the TX-100/toluene reverse micelles. The λ_{max} of MB in the TX-100/toluene reverse micelles is 512 nm (Figure 5a), remarkably different from that of MB in pure bmimBF$_4$ (Figure 5j). The formation of a 1:1 complex between MB and TX-100, which leads to a remarkable blue shift of the MB absorption band, has been evidenced in the reverse micelles of TX-100 in mixed solvents of cyclohexane and hexanol.[42] Therefore, the absorption band at 512 nm may be ascribed to the complex formation between MB and TX-100 in the reverse micelles. As the bmimBF$_4$ content is increased to R

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= 0.06, the λ_{max} remains constant. At the same time, a new absorption band with an absorption maximum at 654 nm which resembles the characteristic absorption of MB in pure bmimBF$_4$ appears. Further addition of bmimBF$_4$ to the IL microemulsion leads to a gradual decrease in the intensity of the band at the lower wavelength region and a simultaneous increase in the intensity of the band at the higher wavelength region. This phenomenon indicates that there exist two distinguishable states of MB, namely, free MB and bound MB that is present in the complex between MB and TX-100.

When R reaches 0.48, the intensity of the band at the higher wavelength region is stronger and the band at the lower wavelength region disappears. At bmimBF$_4$ content lower than $R = 0.48$, bmimBF$_4$ molecules bind directly to the EO groups and MB molecules are present mainly as bound MB molecules. When R reaches 0.48, a sudden color change of the IL microemulsion solution appears from pink to blue, indicating that the state of MB completely transits from bond MB to free MB. At $R > 1.58$, the intensity of the absorption band at the higher wavelength region does not change with further addition of IL, indicating that IL pools begin to form.

A possible reason about the effects of the IL content on the MB absorption spectra in TX-100 reverse micelles may be explained as follows: in the TX-100/toluene reverse micelles, the strong interaction between MB and TX-100 leads to the formation of a 1:1 complex MB−TX-100. When IL is added to the reverse micelles, bmimBF$_4$ molecules are bound to the EO groups of TX-100 in the polar cores. The complex MB−TX-100 begins to decrease, which can lead to the decreased absorbance at the lower wavelength region. Additional bmimBF$_4$ to the TX-100/toluene micelles can be expressed by the following equilibrium:

$$\text{MB−TX-100} + n\text{IL} = \text{MB−}x\text{IL} + \text{TX-100−}(n-x)\text{IL} \tag{1}$$
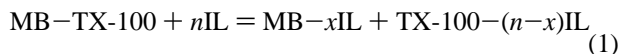
At the same time, more and more bmimBF$_4$ molecules begin to dissolve MB, resulting in a successive increase in intensity of the absorption at the higher wavelength region, the characteristic band of free MB. When the IL content R reaches 0.48, MB is mainly present as its free form in the IL, not being bound by TX-100. So the band at the lower wavelength region disappears. At this stage, bmimBF$_4$ molecules are still in the polar outer shell of the microemulsion. As the IL content increases, the polarities of the microenvironment increase, so the intensity of the absorption band at the higher wavelength region increases accordingly. When R reaches 1.58, the IL pools form; with further addition of IL, the pools become larger but the polarities of the pools are constant, so the intensity and λ_{max} of the band are nearly unchanged. The result is the same as that when using MO as a probe.

Solubilizations of Metal Salts and Biochemical Species. The use of traditional W/O reverse microemulsions as microreactors is well-established. Several different processes have been investigated, including enzymatic reactions[43−46] and synthesis of metallic or semiconductor nanomaterials.[47−52] Currently, one of the interests in this work is to investigate the possibility of solubilization of ionic metal compounds and biochemical reagent in the IL microemulsion.
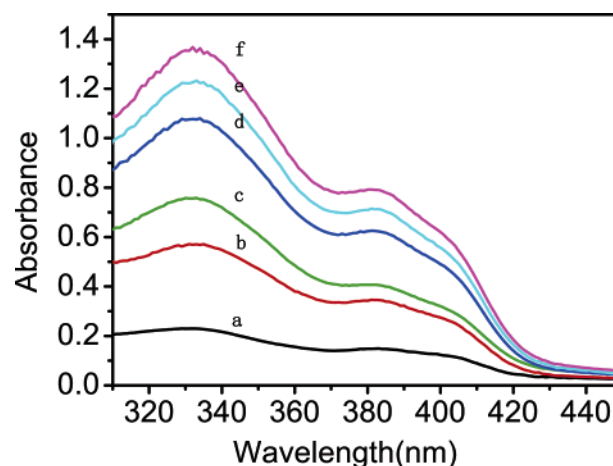

Figure 6. Absorption spectra of riboflavin in IL/O microemulsions as a function of bmimBF$_4$ content with $R = 0.30$ (a), 0.90 (b), 1.20 (c), 1.58 (d), 1.84 (e), and 2.11 (f).
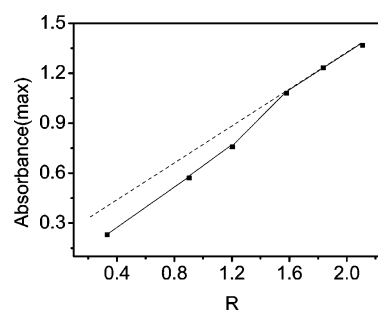

Figure 7. Maximum absorbance intensities of riboflavin in the IL microemulsions with different R values. (The components of the samples are the same as those in Figure 6.)

(a) Solubilization of Biochemical Reagent. In biochemistry, a number of intractable questions focus on the separation of biological molecules. The use of microemulsion droplets to extract biological molecules and support biological reactions has been investigated.[50−52] Riboflavin, a yellow-orange compound, was chosen as a molecular spectroscopic probe, which does not dissolve in toluene, pure TX-100, and TX-100/toluene reverse micelles. However, if IL/O microemulsions form, the system takes on a yellow-orange transparent phase, indicating that the microemulsion droplets can solubilize riboflavin.

Saturated riboflavin IL solution is used to adjust the molar ratio of bmimBF$_4$ to surfactant, R, along the dilute line a. Thus, there could be a series of IL microemulsions with different R values. The UV−vis spectra for riboflavin with different R values are shown in Figure 6. There are two absorbance peaks at 331 ± 2 and 384 ± 2 nm. The maximum absorbance of riboflavin increases with the addition of saturated IL solution; however, the plot of maximum absorbance peak values versus riboflavin concentrations is not linear (Figure 7). The maximum absorbances are distinctly low (relative to the dashed line) for the IL microemulsion with low IL content such as $R = 0.3, 0.9$, and 1.2. The reason is that the behavior of solubilized IL in these microemulsion systems is markedly different from that of bulk

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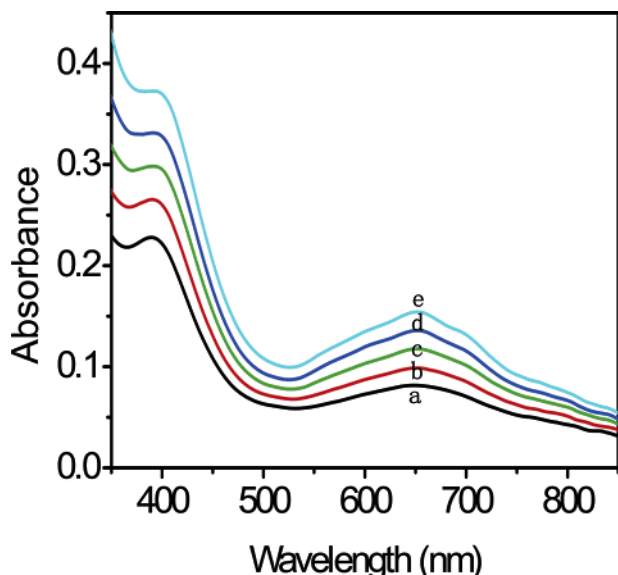
Figure 8. Absorption spectra of $Ni(NO_3)_2$ in the IL/O microemulsions as a function of $bmimBF_4$ content with $R = 0.90$ (a), 1.12 (b), 1.34 (c), 1.58 (d), and 1.84 (e).
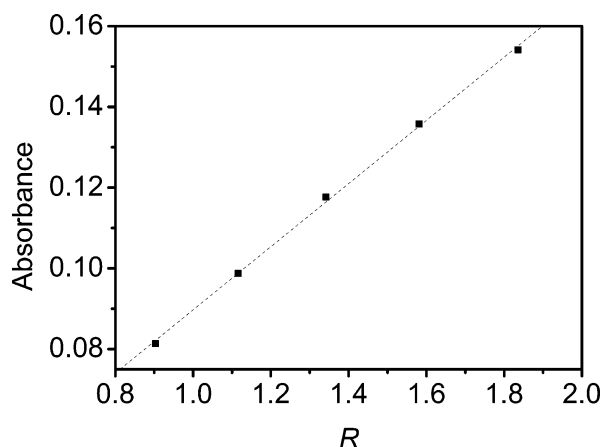

Figure 9. Maximum absorbance intensity of $Ni(NO_3)_2$ in the ionic liquid microemulsions with different R values. (The components of the samples are the same as those in Figure 8.)

IL, and the bulk IL content is too small to solubilize riboflavin in microemulsion with a small R value. It is expected that in these samples a portion of the riboflavin was still in the solid-state dispersed in these microemulsion droplets.[53] Even so, this class of novel IL microemulsions has the potential to solubilize biological molecules.

(b) Solubilization of Metal Salts. $Ni(NO_3)_2$ is chosen as a molecular spectroscopic probe mainly due to the fact that $Ni(NO_3)_2$ does not dissolve in toluene and pure TX-100 but will dissolve in the TX-100/toluene reverse micelles and microemulsions. Similarly, saturated IL solution of $Ni(NO_3)_2$ was used to prepare the IL microemulsion in this work. Figure 8 shows the UV–vis spectra for $Ni(NO_3)_2$ in the IL microemulsions with different R values. The λ_{max} appears at about 652 nm, indicating that $Ni(NO_3)_2$ is solubilized in the IL microemulsion. The absorbance intensity increases with increasing R values, because of the gradually increased concentration of $Ni(NO_3)_2$ in the microemulsion system. Figure 9 shows the maximum absorbance of $Ni(NO_3)_2$ at different R values. As can be seen the maximum absorbance increases linearly with R values, which is in agreement

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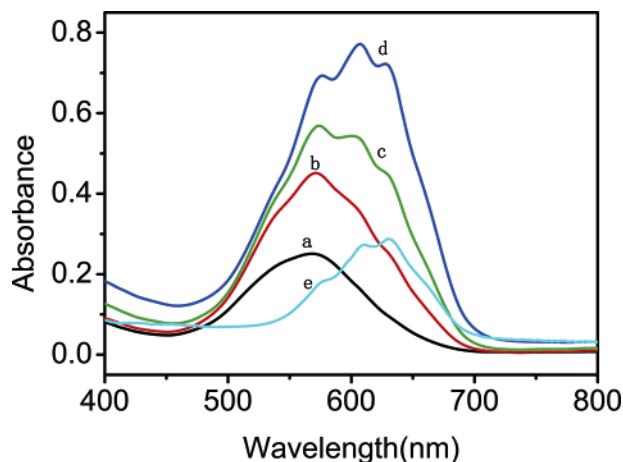

Figure 10. UV–vis absorption spectra of $CoCl_2$ in the IL microemulsions with $R = 0.70$ (a), 1.17 (b), 1.58 (c), and 2.11 (d) and with pure IL (e). $CoCl_2$ concentration: 1 (a), 2 (b), 3 (c), 4 (d), and 1 mM (e).

with the Lambert–Beer plot.[54] However, the result is different from that of riboflavin. In that case, excess riboflavin is separated out from the saturated IL solution due to the lack of bulk properties of IL when the R value is relatively small, whereas, if $Ni(NO_3)_2$ is separated out from the IL saturated solution, the separated $Ni(NO_3)_2$ will be solubilized into the polar outer shell of the IL microemulsion. Thus, the maximum absorbance of $Ni(NO_3)_2$ would not change obviously due to the resolubilization of $Ni(NO_3)_2$. So the maximum absorbance is still linear with R value. The UV–vis spectroscopy confirms that metal salt $Ni(NO_3)_2$ could be solubilized in the IL microemulsions.

$CoCl_2$ is also used to investigate the solubilization of metal salts in the IL microemulsion. $CoCl_2$ is chosen as a probe to take advantage of the obvious color and absorption characteristics of the Co^{2+}. Furthermore, the Co element has attracted much attention in the preparation and processing of materials, especially nanoscale semiconductors and metal materials. Therefore, it is necessary to check the solubilization of this metal salt in the IL microemulsion and thus explore the feasibility of using the IL microemulsion as template to prepare nanoscale semiconductor or metal materials.

Figure 10 shows the UV–vis absorption spectra of $CoCl_2$ in the IL microemulsion with different R values. At low $bmimBF_4$ content ($R = 0.70$, 1.17), there is only one absorbance peak appearing at 573 ± 2 nm. However, when $R > 1.58$, three absorbance peaks appear at 573, 608, and 630 nm, respectively, which are the same as that in pure $bmimBF_4$ (Figure 10e). It is suggested that when a small amount of $bmimBF_4$ is added to the TX-100/toluene reverse micelle, $bmimBF_4$ molecules are bound to the EO groups of TX-100 in the polar core; the properties of the bound $bmimBF_4$ molecules are different from that in the bulk IL. So the absorption spectra of $CoCl_2$ are different from that in pure IL. However, after the IL pools form, the properties of the free $bmimBF_4$ molecules in the IL pools are similar to that in the bulk IL. So, the absorption spectra show the same absorption band. The formation of IL pools at $R > 1.58$ is further confirmed here.

In addition, the solubilization of $CuCl_2$ in the IL microemulsion is also investigated by UV–vis spectroscopy. $CuCl_2$ does not dissolve in toluene but dissolves in the TX-100/toluene reverse micelles and microemulsions. The absorption spectra of $CuCl_2$ in the IL microemulsion are shown in Figure 11. The λ_{max} of the

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The solubilizations of both biochemical reagent and metal salts indicate that the IL/O microemulsions have potential application in the production of metallic or semiconductor nanomaterials, also in biological extractions or as solvents for enzymatic reactions.

Conclusion

In summary, microemulsions consisting of bmimBF$_4$, surfactant TX-100, and toluene were prepared, and the phase behavior of the ternary system was investigated. The UV$-$vis absorbance spectra of MO and MB were used to investigate the micropolarities of bmimBF$_4$-in-toluene (IL/O) microemulsions. The results indicated that, with the addition of the bmimBF$_4$ into the TX-100/toluene reverse micelles, the polarity of the IL/O microemulsions increased, but when the IL pools began to form, the polarity of the IL pools was constant. We have also demonstrated that biological molecule riboflavin and metal salts such as Ni(NO$_3$)$_2$, CoCl$_2$, and CuCl$_2$ can be solubilized in the IL/O microemulsion droplets. These results are essential to the use of IL/O microemulsions as solvent systems in the preparation and processing of semiconductors, nanomaterials, enzyme-catalyzed reactions, and extraction applications.

Figure 11. Maximum absorbance intensities of CuCl$_2$ in the IL microemulsions with $R = 0$ (a), 0.70 (b), 1.17 (c), 1.58 (d), and 2.11 (e). CuCl$_2$ concentration: 6 (a), 2 (b), 4 (c), 6 (d), and 8 mM (e).

characteristic band is red-shifted with the increase of R values. The result accords with that reported by Meziani and Sun.[54] In their report, Cu(NO$_3$)$_2$ was solubilized in PFPE-NH$_4$ stabilized water-in-CO$_2$ microemulsion and presented a lower absorption wavelength (blue shift) than that in its aqueous solution. Due to the weak salvation of Cu^{2+}, the spectrum was significantly blue-shifted,[53] whereas, according to McCleskey and his co-workers, effects contributing to the blue shift may include interaction of Cu^{2+} with hydrophilic headgroups of the surfactant molecules and a decrease in the polarity of water in the micellar core.[55]

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