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SHORT COMMUNICATION

FTIR study of Tween80/1-butyl-3-methylimidazolium hexafluorophosphate/toluene microemulsions

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Abstract With the aid of Tween80, an environmentally benign nonionic surfactant applied to medicine and food industry, the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) formed IL microemulsions with toluene. The phase diagram of the ternary system was prepared at 25 °C. It was demonstrated that there were a single-phase region and a multiple phase region in the ternary phase diagram. The single-phase region could be further divided into toluene-in-$bmimPF_6$, bicontinuous, and $bmimPF_6$-in-toluene microemulsion regions by electrical conductivity. In particular, the microstructural characteristics of the microemulsions were investigated by Fourier transform infrared spectroscopy. The results indicated that it was the hydrogen-bonded interactions between $bmimPF_6$ and Tween80 that might be the driving force for the solubilization of $bmimPF_6$ into the core of the Tween80 aggregates.

Keywords Microemulsion · Ionic liquid · Tween80 · FTIR spectroscopy

Introduction

Microemulsions have been used as a unique and versatile reaction medium for a variety of chemical reaction, such as nanoparticle preparation, organic synthesis, bioorganic synthesis, and so on [1–3]. In the traditional microemulsions, water was acted as the polar component. However, for some organic reactions, such as the Diels–Alder reaction, esterification, and polymerization, these reactants must avoid contacting with water. Therefore, in recent years, attempts have been made to prepare and study nonaqueous microemulsions [4–7]. In these investigations, water was replaced by polar nonaqueous solvents, such as ethylene glycol, formamide, and glycerol. Due to their distinct advantages over the aqueous microemulsion, these nonaqueous microemulsions have attracted much interest and have been widely applied.

Ionic liquids (ILs) offer great potential as environmentally benign solvents for synthesis or extraction [8–11]. Because ILs usually possess almost negligible vapor pressures and can be recycled easily, using ILs instead of water to prepare an IL microemulsion is a promising research field. Several papers related to IL microemulsions have been reported. Han and coworkers discovered that with the aid of TX-100, 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$) could form polar nanosized droplets dispersed in cyclohexane continuous phase, and freeze-fracturing electron microscopy indicated a droplet structure which was similar to traditional water-in-oil microemulsions [12]. Eastoe et al. explored the same system by means of small-angle neutron scattering, which indicated a regular increase in droplet volume as micelles were gradually swollen with an increase of $bmimBF_4$ content [13]. In addition, Han and his group constructed 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$)/TX-100/ethylene glycol and $bmimPF_6$/TX-100/toluene microemulsion systems; the microemulsions were characterized further by dynamic light scattering (DLS), small angle X-ray scattering, and UV–vis spectro-

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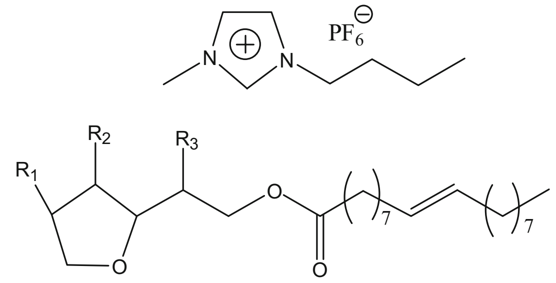
photometry, indicating the microemulsion formation with spherical droplets and the formation mechanism similar to the common microemulsions [14, 15]. Furthermore, Gao et al. demonstrated that $bmimPF_6$ could prepare microemulsions with water in the presence of nonionic surfactants TX-100 and Tween20 [16, 17]. Recently, the interaction of ionic liquid with water in the $bmimPF_6$-in-water microregions of the $bmimPF_6$/TX-100/H_2O ternary microemulsions has been studied by the dynamics of solvent and rotational relaxation of coumarin 153 and coumarin 151. The mechanism of formation of microemulsions containing $bmimBF_4$ was explored using spectroscopy techniques, and some applications of ionic liquid microemulsions to material preparation have also been attempted [18–20]. What is more, recent studies of microemulsions incorporating ILs and some recent applications of such microemulsions have been reviewed [21].

TX-100 plays an important role in IL microemulsions application and theoretical study. However, it is almost a sole surfactant in the IL microemulsions. In order to expand some applications of surfactants in the IL microemulsions, it is necessary to explore the surfactants which are able to act as IL microemulsion component. Due to its toxicity, TX-100 is not an environmentally benign surfactant and not applied to drug delivery, cosmetic, and food industry. On the other hand, Tween80 has been applied to many chemical reactions and extractions as an ordinary surfactant, and it has also been applied to medicine deliver and the formulation of food-grade microemulsions as an environmentally benign surfactant [22–24]. In the present paper, with the aid of Tween80, the IL $bmimPF_6$ formed IL microemulsions with toluene. The phase diagram of Tween80/$bmimPF_6$/toluene microemulsion was constructed. Three different subregions—$bmimPF_6$-in-toluene, bicontinuous, and toluene-in-$bmimPF_6$ in the single-phase region—were differentiated by electrical conductivity. In particular, the microstructural characteristics of the microemulsions were investigated by Fourier transform infrared (FTIR) spectroscopy. The results indicated that the hydrogen-bonded interaction between $bmimPF_6$ and Tween80 might be the driving force for the solubilization of $bmimPF_6$ into the core of the Tween80 aggregates.

Experimental

Materials

Tween80 (ethoxylated sorbitan monooleate with an average degree of ethoxylation *n*=20, see structure in Scheme 1, chemical purity) was provided by Shanghai Shanpu Chemical Industry Co. Ltd (China). Toluene was produced by Tianjin Chemical Reagent Factory (China) and was of analytical grade. $bmimPF_6$ (Scheme 1) was purchased from Chemer Company (Hangzhou, China) and its purity was higher than 97%. All reagents were used without further purification.



where R_1-$(OCH_2CH_2)_xOH$, R_2-$(OCH_2CH_2)_yOH$; R_3-$(OCH_2CH_2)_zOH$; x+y+z=20

Scheme 1 Structures of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate and surfactant Tween80

Apparatus and procedures

The test microemulsions consisted of hydrophobic ionic liquid $bmimPF_6$, surfactant Tween80, and toluene. The phase diagram was determined by direct observation of the phase behavior [12, 14, 15].

In a typical experiment, $bmimPF_6$ and toluene were mixed in the glass test tube, and their masses were determined by an ISO-9001 balance with a resolution of ±0.1 mg (Beijing SARTORIUS Balance Company).The test tubes were sealed before weighting to avoid absorption of moisture from air. For each titration, the $bmimPF_6$-to-toluene weight ratio was fixed. The test tube was then placed in a constant temperature water bath at 25 °C. After thermal equilibrium had been reached, the solution was shaken. The sample was then titrated with Tween80 until the hazy and milky liquid solution became transparent and completely clear. After the clear and homogeneous microemulsions were centrifugated (30 min at 4,000×*g*), no phase separation was found. Which was an indication of the formation of the single-phase, the mass of Tween80 added was also known after adding Tween80. The composition of the solution was easily calculated from the masses of $bmimPF_6$, toluene, and Tween80, and the phase boundary was located. The phase behavior of the Tween80/$bmimPF_6$/toluene three-component microemulsions at 25 °C was shown in Fig. 1. The region marked "single phase" was transparent and the region marked "multiple phase" was turbid. By repeating the experiment for other $bmimPF_6$-to-toluene weight ratio, each titration was repeated two or three times and averaged, the phase diagram was established.

The electrical conductivity was performed using a conductivity meter produced by Shanghai REX Instrument Factory (Model DDS-11A). The cell constant of the electrode was calibrated with KCl solution of different concentrations

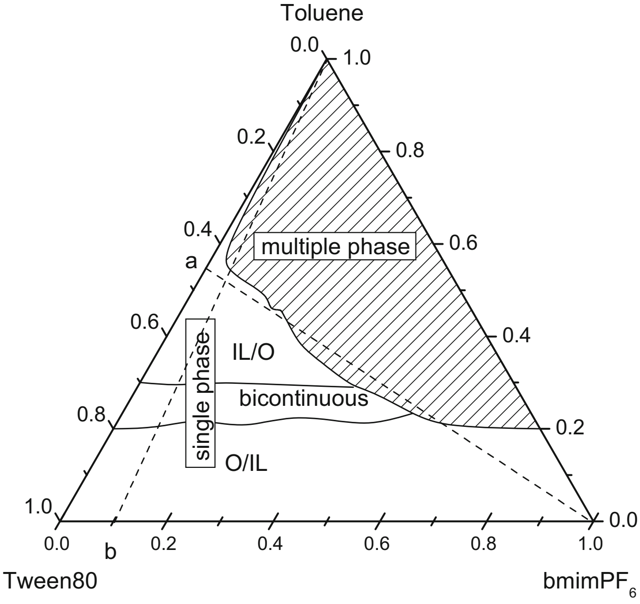


Fig. 1 Phase diagram of the bmimPF$_6$/Tween80/toluene three-component system at 25 °C. For line *a*, the initial Tween80 weight fraction is 0.45

and was 0.96 cm^{-1}. In the experiments, bmimPF$_6$ and Tween80 were mixed in a glass test tube by fixing weight ratios of bmimPF$_6$/Tween80. A certain amount of toluene was added. After the solution was shaken, the sample and the electrode were sealed in a glass cell, which was placed in a constant temperature water bath at 25 °C (DF-101S Magnetism Msier), and when thermal equilibrium was reached, the electrical conductivity was recorded and the sample was repeatedly titrated with toluene until the transparent liquid solution became turbid.

DLS was used for the determination of the nonaqueous IL microemulsion size distributions employing a Malvern Nano ZS instrument with a He–Ne laser. The viscosity of the continuous phase for each mixture was first measured by NDJ-1 Rotating Viscosimeter (Shanghai, China). All measurements were made at the scattering angle of 90° at 25 °C.

FTIR spectra were recorded with a BioRADFTS-165 spectrometer using a spectral range of 500–4,000 cm^{-1} and an effective resolution of 2 cm^{-1}. A cell of CaF$_2$ windows and variable path length was used. The path length was fixed at 0.05 mm and was determined with the interference fringes method [25].

Results and discussion

Phase diagram studies

The phase behavior of the Tween80/bmimPF$_6$/toluene microemulsion at 25 °C is shown in Fig. 1. A single-phase microemulsion region is more concentrated on the higher Tween80 region of the phase diagram and expands from Tween80 apex to the middle portion of the triangle. The region separates from the multiphase domain and is attached to the zero toluene line of the phase. If toluene is added to the mixture of bmimPF$_6$ and Tween80, there should be some kind of gradually structural transition in the microemulsion, and the transition should span the range of possible structures from microdroplets to bicontinuous structures. Therefore, the structural transition of the single-phase microemulsion region can be investigated.

Conductivity measurements and microregions of the bmimPF$_6$ microemulsions

Because the conductivity method was feasible for identifying microstructures of IL microemulsions [12, 15, 26], in this work, we determined the subregion of the single-phase region by this method. Dilution series of the microemulsions were prepared by fixing weight ratios of bmimPF6/Tween80, but varying toluene content.

Gao et al. [26] demonstrated that, for IL microemulsion, with increasing oil content, the electrical conductivity changed according to four successive stages: The initial increase of conductivity could indicate the formation of O/IL microemulsions. The next nonlinear decrease revealed that medium underwent a structural transition and became bicontinuous. The third section of curve, linear decrease of conductivity could be interpreted as the consequence of the formation of IL/O microregion; the final nonlinear decrease of conductivity corresponded to the existence of a percolation phenomenon. Furthermore, they drew a conclusion that the microregions obtained by conductivity measurements were in agreement with those obtained by electrochemical cyclic voltammetry experiments.

As a typical example, Fig. 2 shows the variation of electrical conductivity as a function of toluene weight content. The composition of the samples changed in a single-phase microemulsion region along the dilution line b (marked in Fig. 1). The initial increase of electrical conductivity (AB) indicates the formation of an O/IL microemulsion, showing that toluene droplets are dispersed in bmimPF$_6$ continuous phase. This phenomenon might be interpreted as follows: Adding a cosolvent (benzene, toluene) to ionic liquid increases the conductivity of the ionic liquid. This is due to the fact that the cosolvent can decrease accumulation of ion pairs or ions, increase the numbers of charge carriers, and improve ionic mobility of the ionic liquid [27]. Similarly, with an adding of a small amount of toluene to mixtures of bmimPF$_6$ and Tween80, there are microdroplets of toluene covered by a Tween80 film which is dispersed in a continuous bmimPF$_6$ medium. The concentration of microdroplets increase and the volume

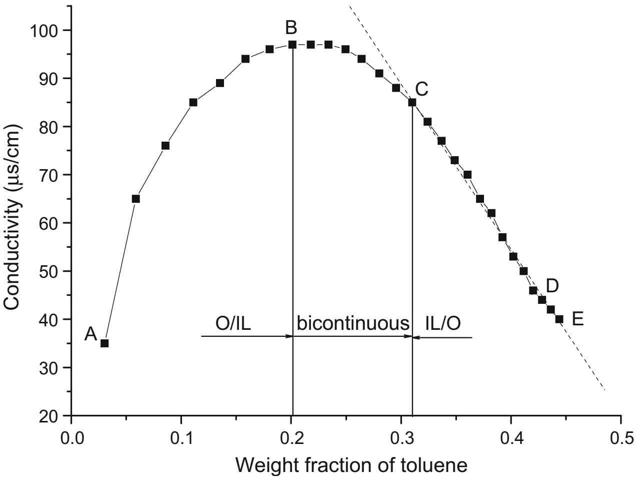


Fig. 2 Electrical conductivity of the microemulsions as a function of toluene content, bmimPF$_6$/Tween80=1:9 (Fig. 1, line b)

of microdroplets gets bigger with the addition of toluene, the microdroplets play the above mentioned role, the dissociation of ion pairs is enhanced in the presence of the microdroplets, the amount of charge carriers is increased, and the ionic mobility is improved, so the conductivity of the investigated system increases. The next nonlinear decrease (BC) reveals that the medium undergoes a structural change and becomes bicontinuous, such as a network of bmimPF$_6$ tubes in a toluene matrix, or a network of toluene tubes in a bmimPF$_6$ matrix, with toluene and bmimPF$_6$ regions stretching over large distances. This is due to increasing growth and interconnection of the toluene in bmimPF$_6$ domains. The CD section of the curve indicates a linear decrease in conductivity. This is as a result of the formation of IL/O microemulsion resulting from the partial fusion of clustered inverse droplets, indicating the bmimPF$_6$ droplets dispersed in toluene continuous phase. The DE section of the curve is the existence of a percolation phenomenon, suggesting inverse droplet aggregation appeared. The curve in Fig. 2 illustrates the occurrence of three types of subregion: O/IL, bicontinuous, and IL/O microemulsions.

Similarly, the experiments for other samples with different initial weight ratios of bmimPF$_6$/Tween80 were repeated. On the basis of conductivity data, the three types of subregions in the single-phase microemulsion were determined. The three subregions marked “O/IL, bicontinuous, and IL/O” in the single-phase are shown in Fig. 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 94.8, 105.8, 122.0, to 124.1 nm with increasing *R* (bmimPF$_6$-to-Tween80 molar ratio) values from 0.99, 1.09, 1.19 to 1.21. The results demonstrated bmimPF$_6$ can exist as nanosized polar domains dispersed in toluene with the aid of Tween80.

FTIR characterization

As FTIR spectra provide some useful information on the conformation of the molecules and formation mechanism of the microemulsions, FTIR spectroscopy is frequently used to obtain information about the microstructure of microemulsions. The IL microemulsions have been prepared, but the state and conformation of ILs in the IL microemulsions have been reported scarcely. So our study aims at acquiring a picture of the molecular interactions in the different microstructure in the bmimPF$_6$-in-toluene reverse microemulsions of bmimPF$_6$/Tween80/toluene system by FTIR spectroscopy.

The FTIR spectra in the bmimPF$_6$-in-toluene microemulsion along *a* as a function of bmimPF$_6$ content at a fixed bmimPF$_6$-to-Tween80 molar ratio (*R*) are shown Fig. 3. Obviously, in the FTIR spectra of bmimPF$_6$-in-toluene microemulsion, the characteristic vibration wave number of bmimPF$_6$ are almost shielded by the bands of Tween80; only the bands at 3,172 and 3,126 cm^{-1} (pure bmimPF$_6$), which are attributed to the C–H ring stretching vibration of the imidazolium, are clearly visible, and shift to low-frequency regions, vibrating 3,159 and 3,113 cm^{-1} (*R*=1.75), respectively. A few changes are obviously found for these two bands, indicating that they may reflect some state of bmimPF$_6$ in the IL microemulsions. Moreover, Fig. 3 also reveals that as *R*=0, the O–H stretching of the terminal hydroxyl group of Tween80 is at 3,455 cm^{-1}, which indicates that there is intermolecular

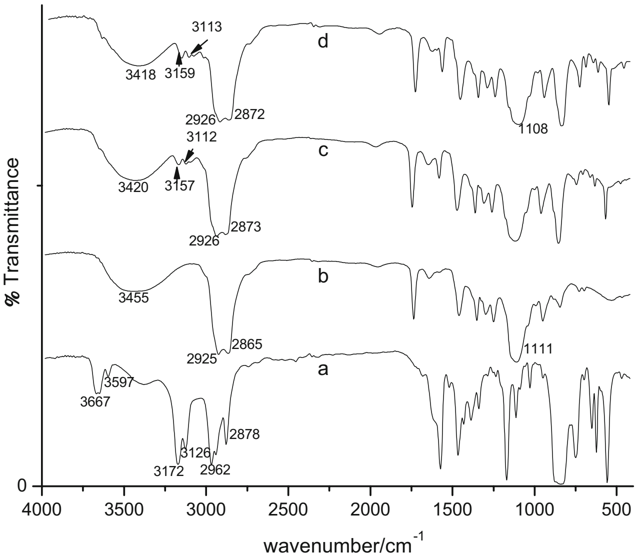
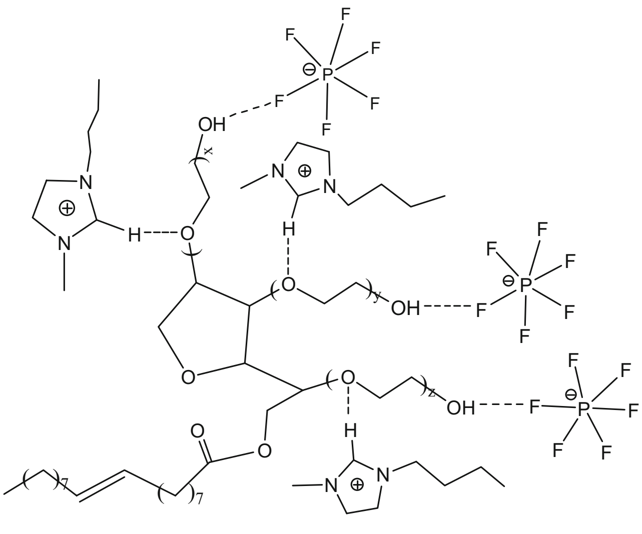


Fig. 3 FTIR spectra of *a* bmimPF$_6$, *b*–*d* the bmimPF$_6$-in-toluenemicroemulsions along *a* with *R*=0 (*b*), 1.25 (*c*), and 1.75 (*d*)

hydrogen binding among the Tween80 molecules; with the adding of R (up to R=1.75), it gradually shifts to 3,418 cm^{-1}, the band of the spectra widens, and the intensity of vibration strengthens. The two results may be interpreted as follow: First, in Tween80/toluene reverse micelles, the terminal hydroxyl groups of Tween80 are hydrogen bonded with the oxygen atoms of the oxyethylene (OE) units or terminal hydroxyl groups of other Tween80 molecules. However, after adding bmimPF$_6$ to the above solution, because C2–H of bmim$^+$ is more active than other hydrogen atoms of bmim$^+$ [28], C2–H of bmim$^+$ is hydrogen bonded to –O– of OE unit in Tween80 [29]. So, the C–H ring stretching vibration of the imidazolium ring shifts to a low-frequency region, up to R=1.75, the bands vibrate at 3,159 and 3,113 cm^{-1}, and due to the fact that the band at 1,111 cm^{-1} as R=0, which is attributable to C–O–C stretching vibration of OE unit in Tween80, shifts to a low-frequency region, vibrating at 1,108 cm^{-1} (up to R=1.75), the result offers a proof for the above conclusion. Secondly, there is hydrogen-bonding interaction between PF$_6^-$ and H– of the Tween80 hydroxyl terminal, which is stronger than that between –O– of the OE unit and H– of the Tween80 hydroxyl terminal or hydroxyl terminal and hydrogen atom of hydroxyl terminal in Tween80. Thus, this factor enhances the hydrogen-bonding interaction which results in the O–H stretching band appearing in the low-frequency region of the IR spectrum (Scheme 2 shows suggested possible interactions between bmim$^+$/PF$_6^-$ and Tween80). The two interactions might be the driving force for solubilizing bmimPF$_6$ into the core of the Tween80 aggregates. In addition, as shown in Fig. 3, the C–H stretching vibration of the OE units in Tween80 appears at 2,865 cm^{-1}. However, on an increase of bmimPF$_6$ content, up to R= 1.75, the electronegativity of the adjacent oxygen atoms increases; thus, the band gradually moves to a high-frequency region, vibrating at 2,872 cm^{-1}. On the basis of above spectra data, one could draw the conclusion that there are hydrogen-bonding interactions between bmimPF$_6$ and Tween80 and the interactions drive bmimPF$_6$ into the core of Tween80 aggregates.



Scheme 2 The proposed interactions between bmim$^+$/PF$_6^-$ and Tween80 are shown

It is important to mention that Behera et al. [30] investigated the changes in the properties of aqueous solutions of TX-100 upon addition of 2.1 wt.% of bmimPF$_6$. Based on the conductivity data and behavior of a variety of molecular absorbance, the partitioning of bmimPF$_6$ into TX-100 micellar phase was inferred and the presence of H-bonding interaction between bmimPF$_6$ and TX-100 was proposed. Our data of FTIR spectra in the bmimPF$_6$-in-toluene microemulsion of bmimPF$_6$/Tween80/toluene system and analysis, on the other hand, took into account that the possibility of hydrogen-binding interaction between bmimPF$_6$ and Tween80 is the driving force for solubilizing bmimPF$_6$ into the core of the Tween80 aggregates. This may turn out to be useful about understanding ionic liquid microemulsion and many applications involving media acted as ionic liquid microemulsion.

Conclusions

In summary, microemulsions consisting of bmimPF$_6$, surfactant Tween80, and toluene were prepared. The phase behavior of the ternary system was investigated. The bmimPF$_6$-in-toluene (IL/O), bicontinuous, and toluene-in-bmimPF$_6$ (O/IL) microregions of the nonaqueous IL microemulsions were identified by traditional electrical conductivity measurements on the basis of percolation theory. In the Tween80/toluene system, FTIR spectra showed that, after adding bmimPF$_6$ to Tween80/toluene system, the O–H stretching of the terminal hydroxyl group of Tween80 shifted to a low-frequency region and so did the C–H stretching of the imidazolium ring; the vibration wave number, ascribed to C–O–C of OE unit in Tween80, moved also to a low-frequency region; and the results indicated that there were hydrogen-bonding interactions between PF$_6^-$ and H– of the Tween80 hydroxyl terminal, between C2–H of bmim$^+$ and –O– of OE unit in Tween80. The interactions might be the driving force for solubilizing bmimPF$_6$ into the core of the Tween80 aggregates. This study might have some potential application in different fields, such as organic or bioorganic synthesis, inorganic materials, and medicine or food industry, and help to understand ionic liquid microemulsions.

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