Nonaqueous ionic liquid microemulsions of 1-butyl-3-methylimidazolium tetrafluoroborate, toluene and ethanol†

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The phase behavior of the ternary system consisting of the hydrophilic ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄), toluene and ethanol was investigated. Single-phase microemulsion and multiphase regions were observed in the ternary phase diagram. To the best of our knowledge, this is the first report on nonaqueous IL microemulsions prepared in the absence of traditional surfactants. The microstructures and structural transitions of the microemulsion system were investigated by cyclic voltammetry, pulse field gradient spin-echo nuclear magnetic resonance and electrical conductivity measurements. The microemulsions exhibit IL-in-toluene (IL/O), bicontinuous (BC) and toluene-in-IL (O/IL) microstructures, similarly to traditional surfactant-based microemulsions. The three kinds of microstructures were confirmed from freeze-fracture electron microscopy observations. A pearl necklace-like structure was observed in the BC microemulsion. The polarity of bmimBF₄ domains in the IL/O microemulsion was investigated by UV-visible absorption spectroscopy using methyl orange as a probe. It was found that the polarity was lower than that of the bulk bmimBF₄, and it increased with increasing bmimBF₄ content at a constant toluene–ethanol ratio.

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Introduction

Microemulsions are defined as optically isotropic, transparent, and thermodynamically stable dispersions of two or more immiscible liquids containing surfactants and possibly cosurfactants. Microemulsions have received much attention because of their applications in separation,¹ reaction engineering,² environmental engineering³ and material preparation.⁴

Surfactants are often thought necessary to stabilize microemulsions.⁵ However, in 1977 Smith *et al.*⁶ reported an oil-continuous (water-in-oil, W/O) microemulsion of hexane, 2-propanol and water. This ternary surfactant-free (or detergentless) microemulsion (SFME) contained no traditional surfactants. SFMEs have subsequently attracted much attention,^{7–11} and their phase and interfacial tension behavior have been found to be similar to those of surfactant-based microemulsions.

In most studies of traditional microemulsions, water is used as the polar component. However, recent attempts to prepare waterless microemulsions have been reported,^{12,13} where water

has been replaced by polar organic solvents including ethylene glycol,¹⁴ formamide¹⁵ and glycerol.¹⁶ Of particular interest is the replacement by room temperature ionic liquids (ILs) to provide IL microemulsions.^{17,18} ILs have useful physical and chemical properties including nonvolatility, nonflammability, thermal stability and adjustable solvation. Herein, we report a SFME of the hydrophilic IL 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄), toluene and ethanol.

Surfactant-based microemulsions can exhibit different microstructures, including oil-in-water (O/W), bicontinuous (BC) and water-in-oil (W/O) microstructures. To obtain better insight into SFMEs, their microstructures and structural transitions must be investigated. Techniques used to identify microstructures and structural transitions include cyclic voltammetry (CV),^{19–27} pulse field gradient spin-echo nuclear magnetic resonance (PGSE NMR),^{28–31} electrical conductivity (EC),^{32–35} dynamic light scattering (DLS)^{31,36} and rheology.^{37,38} Electrochemical CV is the most commonly used technique for obtaining information about the microstructures of microemulsions. It is based on the difference of the diffusion coefficients probed electrochemically in different forms of microemulsions, and ferrocene (Fc), ferricyanide or methyl viologen are often used as probes.^{22–24} PGSE NMR can be used to measure the self-diffusion coefficients of component molecules, and can provide direct information about connectivity.^{28–31} Self-diffusion coefficients of components in the continuous phase are typically much higher than those in the discrete phase. The electrical conductivity is also commonly

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used to investigate microstructures and structural changes of microemulsions, based on percolation theory.^{32,33} Gao *et al.*³⁴ used this technique to identify IL-in-oil (IL/O), BC, and oil-in-IL (O/IL) microstructures for IL microemulsions of bmimBF₄, the surfactant TX-100 and toluene.

The current study explores SFMEs of bmimBF₄, ethanol and toluene, and investigates the resulting SFME microstructures and structural transitions. Nonaqueous IL SFMEs of this ternary system can exhibit bmimBF₄-in-toluene, BC and toluene-in-bmimBF₄ microstructures. The polarity of bmimBF₄ domains in the IL/O microemulsion is examined by ultraviolet-visible (UV-vis) absorption spectroscopy using methyl orange (MO) as a probe. To the best of our knowledge, this is the first report on IL-based SFMEs. Such SFMEs may have special applications in material preparation, separation and reaction engineering because of their waterless and surfactant-free nature.

Experimental

Materials

All chemicals used were of standard laboratory reagent grade. Toluene and ethanol were purchased from Yantai Chemical Reagents Co., and MO was from Beijing Chemical Reagent Co. IL bmimBF₄ was obtained from Fluka Chemie, and was dried under vacuum at 50 °C until constant weight before use. Ultrapure water with a resistivity of 18.25 MΩ CM was obtained using an AFZ-1000-U purification system, and was used throughout this study.

Phase diagram construction

The phase diagram of the bmimBF₄-ethanol-toluene ternary system was constructed by titration with ethanol as follows. A mixture with desired volume ratio of toluene to bmimBF₄, $R_{T/IL}$, was prepared in a dry test tube. An appropriate volume of ethanol was added under magnetic stirring at 25.0 ± 0.2 °C. The phase boundary was determined by observing the transition from turbidity to transparency or *vice versa*. Repeating this experiment for other $R_{T/IL}$ values allowed the phase diagram to be established. The entire procedure was repeated three times, and an average value was used. The component content was expressed as the volume fraction in the ternary phase diagram.

CV measurements

CV was performed using a CHI model 660D electrochemical work station (Shanghai Chenhua Instrument Factory, P. R. China) with a three-electrode cell, which consisted of a glass carbon working electrode (electrode area 0.07 cm²), AgCl/Ag reference electrode and Pt wire counter electrode. The spacing between adjacent electrodes was 2.0 cm. Before each measurement, the working electrode was polished using 0.05 mm aluminum oxide slurries and then thoroughly washed with ultrapure water. The electrode was then sonicated in ultrapure water for ~5 min and used immediately. The potential was scanned from -0.2 to +0.8 V with a sweep rate range of 20–100 mV s⁻¹. Experiments were carried out at 25.0 ± 0.2 °C under a nitrogen atmosphere to exclude oxygen. Fc was selected as the

electroactive probe with a fixed initial concentration of 0.65 g L⁻¹, and the concentration of the probe changed with the addition of toluene. The Fc concentration had little effect on diffusion coefficients, since the shape and size of microemulsions were not affected by the presence of the electroactive probe over a large concentration range.^{21,23}

The apparent diffusion coefficient of the electroactive probe, D_p (m² s⁻¹), in the microemulsions was obtained from the Randles-Sevcik equation¹⁹

$$i_p = 0.447 F^{3/2} R^{-1/2} T^{-1/2} A n^{3/2} D_p^{1/2} c \nu^{1/2}, \quad (1)$$

where i_p is the peak current for a redox-active reversible system, F is the Faraday constant, R is the gas constant, T is the absolute temperature, A is the area of the working electrode, n is the number of electrons involved in oxidation or reduction, c is the concentration of the electroactive probe, and ν is the sweep rate.

PGSE NMR measurements

Self-diffusion coefficients for each component in the microemulsions were determined at 25 ± 0.2 °C using a Bruker Avance 600 spectrometer equipped with cryoprobe TCI 5 mm indirect detection, a pulse field gradient (PFG) probe, and a 10 A highland gradient amplifier. This combination provided a z -gradient strength, g , of up to 0.535 T m⁻¹. Experiments were performed by varying g and holding all other timing parameters constant.²⁹

The relationship between the echo attenuation and self-diffusion coefficient, D_s (m² s⁻¹), is given by^{29,31}

$$A = A_0 \exp[-g^2 \gamma^2 D_s \delta^2 (\Delta - \delta/3)], \quad (2)$$

where A is the measured signal intensity, A_0 is the signal intensity for zero g , γ is the gyromagnetic ratio for the ¹H nucleus, δ is the gradient pulse length, and Δ is the time between the two gradients in the pulse sequence. Typically, a Δ of 20 ms, δ of 2500–5000 μs, and g ranging from 1.070×10^{-2} (2% strength) to 50.825×10^{-2} (95% strength) T m⁻¹ over 16 steps were used. The PGSE NMR data were acquired with the ledbp2s pulse program from Bruker Topspin software.

The self-diffusion coefficients for toluene, ethanol and bmimBF₄ were measured from the peaks of -CH₃ (2.09 ppm), -CH₃ (1.06 ppm) and N-CH₃ (3.66 ppm) moieties, respectively. In addition, the self-diffusion coefficients of the neat solvents (D_s^0) toluene, bmimBF₄ and ethanol were measured from CD₃C₆H₅, a binary mixture of D₂O-bmimBF₄ (14 : 25, v/v), and a binary mixture of D₂O-ethanol (8 : 25, v/v), respectively.

All reported values were obtained from the average of three independent measurements.

Electrical conductivity measurements

A low-frequency (50 Hz) conductivity meter (DDS-12DW, Shanghai Lida Precision Instrument Co., Ltd., P. R. China) with an accuracy of $\pm 1\%$ was used to measure the conductivity of microemulsions at 25.0 ± 0.2 °C.

FFEM observations

Freeze-fracture electron microscopy (FFEM) observations were performed to study the microemulsion microstructures. Fracturing and replication were carried out in a high-vacuum freeze-etching system (EM BAF060, Leica, Germany). The fracture surface was replicated by shadowing with Pt-C. The metal replicas were viewed using a transmission electron microscope (JEM-1400, JEOL, Japan).

UV-vis absorption measurements

UV-vis absorption spectra were recorded using a computer controlled UV-vis spectrometer (TU-1901, Beijing Purkinje General Instrument Co. Ltd., P. R. China), with a 1 cm path-length quartz cell. Appropriate amounts of components were uniformly mixed in advance and then added to the cell. Experiments were carried out at 25 ± 0.2 °C.

Results and discussion

Phase behavior of the bmimBF₄-ethanol-toluene system

The ternary phase diagram of the bmimBF₄-ethanol-toluene system at 25.0 ± 0.2 °C is shown in Fig. 1. A single isotropic region above the bmimBF₄ or toluene volume content range of 0–100% was observed. The blank region marked “single phase” is the microemulsion region in which the system is transparent. The shadowed region marked “multiphase” is the microemulsion region in equilibrium with an excess bmimBF₄ or toluene phase, in which the system is turbid under stirring. The single-phase microemulsion region occupies about 75% of the total phase diagram. The effect of temperature on the phase behavior of the ternary system was examined, and no change in phase diagram was observed over the temperature range of 25–45 °C (Fig. S1†). This indicates that the temperature has no obvious influence on phase behavior, perhaps because of the absence of traditional surfactants in this system.

Fig. 1 Phase diagram of the bmimBF₄-ethanol-toluene ternary system at 25 ± 0.2 °C. I, II and III represent toluene-in-bmimBF₄ (O/IL), BC and bmimBF₄-in-toluene (IL/O) regions, respectively. Samples a, b, and c were chosen for FFEM observations.

For traditional oil/water/surfactant microemulsions, W/O microemulsions can be formed at low water content and the oil resides in the continuous phase. Assuming no phase separation and that the system remains isotropic, increasing the water content progressively should lead to a gradual structural transition. This transition should span the range of possible structures from microdroplets to BC structures. A similar structural transition was observed in IL microemulsions containing traditional surfactants.^{17,18} Similarly, for the current nonaqueous IL SFME, the single-phase channel is well suited for studying microstructures and structural transitions.

Diffusion behavior of the Fc probe in the nonaqueous IL microemulsions

According to eqn (1), i_p will linearly increase with $v^{1/2}$ for a given electrode and a constant electroactive probe concentration. The D_p of the electroactive probe can be calculated from a linear regression of the slope of i_p versus $v^{1/2}$, using the known surface area of the electrode. For microemulsions involving an electrochemical probe completely solubilized in the microemulsion droplets, D_p in eqn (1) corresponds to the microemulsion droplet diffusion coefficient, since the probe diffuses with the microemulsion droplets.²⁵ To verify the diffusion-controlled nature of the process, CV experiments using Fc as an electrochemical probe were carried out at various scan rates in the microemulsion environments. This is because only the diffusion controlled electrochemical charge transfer is suited to study the microstructure of microemulsions with CV.¹⁹

Typical plots of anodic peak current i_p versus $v^{1/2}$ for two microemulsions, in which the volume ratio of ethanol to bmimBF₄, $R_{E/IL}$, is one and the volume fractions of toluene, f_T , are 30 and 45%, are shown in Fig. 2. They are straight lines passing through the origin, and similar results were obtained for all other systems prepared in this study. This indicates that electron transport of the electrode reaction in the microemulsions is diffusion controlled.^{20,27} Thus, Fc is a suitable electrochemical probe for studying the microstructures and structural transitions of the nonaqueous IL SFMEs.

Fig. 2 Scan rate dependence of anodic peak current in the IL microemulsions with $R_{E/IL} = 1$, for f_T of (a) 30 and (b) 45%.

Changes in D_p in the microemulsions were examined along various toluene dilution lines for $R_{E/IL}$ values of 7, 3, 1.67, 1, 0.6, 0.33 and 0.143. As examples, Fig. 3 shows the change in D_p as a function of f_T for $R_{E/IL} = 3$, 1.67 and 1. D_p increases monotonically with the increasing toluene content over the entire single-phase microemulsion region. However, as is marked in Fig. 3, all three curves can be divided to three successive stages: initial gradual increase, subsequent relatively dramatic change, and final gradual increase again. These results indicate that the change of toluene content can induce the structural transition of the microemulsion system.³⁴

Fig. 3 Diffusion coefficient (D_p) of Fc as a function of f_T at (a) $R_{E/IL} = 3$, (b) $R_{E/IL} = 1.67$ and (c) $R_{E/IL} = 1$.

F_c is expected to preferentially probe the oil environment because of its limited solubility in bmimBF₄. At low f_T (e.g. <18% for $R_{E/IL} = 3$), the relatively low D_p value indicates a microemulsion of O/IL type, where bmimBF₄ is the continuous phase. This is because D_p should correspond to the diffusion coefficient of toluene-in-bmimBF₄ microemulsion droplets in this particular case. Guéring and Lindman³⁰ suggested that molecules confined in a closed domain would give rise to a low self-diffusion coefficient. The diffusion coefficient increases with the increasing droplet size, but as long as the diffusion of the probe is confined in microemulsion droplets, this increase is slow. Therefore, the gradual change of D_p at low f_T shows that the microstructure of the microemulsion is unchanged.

At high f_T (e.g. >38% for $R_{E/IL} = 3$), the relatively high D_p value indicates a microemulsion of IL/O type, where toluene is the continuous phase. In this case, the diffusion coefficient of the probe corresponds to the continuous toluene medium. Guéring and Lindman³⁰ suggested that molecules occurring in the continuous medium would be characterized by rapid diffusion. Thus, D_p in a continuous toluene structure exhibits a higher value than that in a droplet structure. Similarly, the gradual increase in D_p at high f_T shows that the microstructure of the microemulsion is unchanged.

At intermediate f_T (e.g. 18 < f_T < 38% for $R_{E/IL}$), the relatively dramatic change of D_p indicates that the microstructure of the microemulsion is different from the droplet structures of the microemulsions. According to the principle of distinguishing subregions in microemulsions using the apparent diffusion coefficient,^{23,27,34} this result suggests that a BC microstructure, in which bmimBF₄ and immiscible toluene are both local continuous phases, is formed.

It is needed to note that no dramatic changes in D_p are observed for microemulsions along the toluene dilution lines with $R_{E/IL} = 0.33$ and 0.143 (Fig. S2†), indicating that no microstructure transition occurs in this region. Thus, microemulsions in this region are of an O/IL type.

Based on above CV results, three types of microemulsion microstructures are recognized: toluene-in-bmimBF₄ (O/IL), bicontinuous (BC) and bmimBF₄-in-toluene (IL/O). The subregions identified are also marked in Fig. 1.

Self-diffusion coefficients of components in the nonaqueous IL/O microemulsions

PGSE-NMR was used to determine the self-diffusion coefficient for each component in the microemulsions. Unfortunately, the signal strength of toluene in the O/IL and BC microemulsion types was too weak to evaluate the diffusion coefficient of toluene. Thus, only results of the IL/O microemulsions are described.

According to eqn (2), $\ln(A/A_0)$ will increase linearly with g^2 for a given gradient pulse length δ and constant time Δ . Fig. 4 shows the variation of $\ln(A/A_0)$ with g^2 for bmimBF₄ in both the microemulsion ($R_{E/IL} = 3, f_T = 0.34$) and D₂O–bmimBF₄ (14 : 25, v/v) mixture. The two straight lines pass through the origin, and similar results were obtained for all other systems investigated in the IL/O subregion. This indicates that the PGSE-NMR

Fig. 4 Plots of $\ln(A/A_0)$ versus g^2 for (a) D_2O –bmimBF₄ (14 : 25, v/v) and (b) bmimBF₄–ethanol–toluene microemulsion with $f_T = 0.34$.

technique is suitable for measuring the self-diffusion coefficient for each component in both nonaqueous IL/O SFMEs and neat solvents.

Fig. 5 shows the changes in self-diffusion coefficients of bmimBF₄, ethanol and toluene as a function of f_T , along the toluene dilution line with $R_{E/IL} = 3$ in the IL/O subregion. The self-diffusion coefficients of toluene, ethanol and bmimBF₄ decrease successively, and D_s of toluene is much higher than that of bmimBF₄. This result corresponds to an oil-continuous microstructure with discrete IL domains.^{28–31} The intermediate D_s value for ethanol arises from amphiphilic ethanol simultaneously dissolving in both the bmimBF₄ and toluene phases.

Considering the inherent mobility of each component, the relative self-diffusion coefficient (D_s/D_s^0), defined as the ratio between solvent self-diffusion in the microemulsion and that in the neat solvent, has been suggested for exploring the microstructures of microemulsion systems.^{28,29} The D_s^0 of neat toluene is measured to be $3.16 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, and is in good agreement with that ($2.66 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) reported by Pickup and Blum.³⁹ D_s^0 of bmimBF₄ in the D_2O –bmimBF₄ (14 : 25, v/v) mixture is measured to be $2.55 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. For microemulsions at $f_T = 0.50, 0.56$ and 0.58 along the dilution line with $R_{E/IL} = 3$, D_s/D_s^0 values for bmimBF₄ are calculated to be 1.77, 2.18 and 2.31, respectively, whereas those for toluene are 0.45, 0.53 and 0.53,

Fig. 5 Self-diffusion coefficients of bmimBF₄, ethanol and toluene as a function of f_T in the microemulsion with $R_{E/IL} = 3$.

respectively. The D_s/D_s^0 values of bmimBF₄ are much higher than those of toluene, and similar results have been reported in the literature.²⁹ The opposite order trend between D_s and D_s/D_s^0 values for bmimBF₄ and toluene arises from the effect of the system viscosity on the component self-diffusion.^{29,31}

The relationship between the diffusion coefficient (D) of a component molecule and the viscosity (η) of the continuous medium is given by the well-known Stokes–Einstein equation:

$$D = k_B T / 6\pi r \eta, \quad (3)$$

where k_B is the Boltzmann constant and r is the hydrodynamic radius of the diffusion molecule. D is inversely proportional to η . The viscosities of the microemulsions and neat solvents were measured using a capillary viscometer at 25 °C. The viscosities of neat toluene and the D_2O –bmimBF₄ (14 : 25, v/v) mixture are 0.54 and 3.34 mPa s, respectively, and those of the microemulsions with $R_{E/IL} = 3$ at $f_T = 0.50, 0.56$ and 0.58 are 1.15, 1.05 and 1.02 mPa s, respectively. Ratios between the viscosities of neat toluene and the three microemulsions are in the range of 0.47–0.53, and are close to the D_s/D_s^0 values (0.45–0.53) for the component toluene. However, the ratios between the viscosities of the D_2O –bmimBF₄ (14 : 25, v/v) mixture and the three microemulsions are in the range of 2.90–3.27, which are higher than the D_s/D_s^0 values (1.77–2.31) for the component bmimBF₄. This suggests that toluene and bmimBF₄ exist as the continuous and discrete phases, respectively, in the three microemulsions.³¹

From the above discussion, it follows that the relative self-diffusion coefficient (D_s/D_s^0) cannot visually reveal the microstructures of the microemulsions in which the viscosity of one component is much higher than the other. Based on the Stokes–Einstein equation, $D\eta$ is only a function of temperature for a given component, and thus reflects the intrinsic diffusion nature of components at a given temperature. Therefore, we suggest a relative diffusion parameter (α_D) for examining the microstructure of a microemulsion:

$$\alpha_D = D_s \eta / D_s^0 \eta^0, \quad (4)$$

where η and η^0 are the viscosities of the microemulsion and neat component, respectively. In a microemulsion, the component with higher α_D should form the continuous phase; conversely, that with lower α_D should form the dispersed (or discrete) phase.

Fig. 6 shows α_D values for toluene and bmimBF₄ in microemulsions with $R_{E/IL} = 3$, at $f_T = 0.50, 0.56$, and 0.58 . All α_D values (0.96–1.03) of toluene are close to unity, whereas those (0.61–0.71) of bmimBF₄ are less than unity. Higher α_D values of toluene in the microemulsions studied suggest that toluene is the continuous phase whereas bmimBF₄ is the discrete phase, *i.e.*, a bmimBF₄-in-toluene microstructure, which is consistent with the CV results.

Electrical conductivity behavior of the nonaqueous IL microemulsions

Toluene is insulative and bmimBF₄ is conductive in bmimBF₄–ethanol–toluene microemulsions. This system is in accordance

Fig. 6 Relative diffusion parameter (α_D) of bmimBF₄ and toluene as a function of f_T in the microemulsion with $R_{E/IL} = 3$.

with percolation theory, and the electrical conductivity may be used to identify the subregions of the microemulsion.³⁴ Typical curves of electrical conductivity (κ) versus f_T along the toluene dilution lines with $R_{E/IL} = 1.67$ and 1 are shown in Fig. 7. Similar results were obtained for other $R_{E/IL}$ values (Fig. S3†). κ exhibits an initial slight increase followed by an obvious nonlinear decrease and finally a linear decrease, with

Fig. 7 Electric conductivity of the microemulsions as a function of f_T at $R_{E/IL} = 1.67$ (a) and 1 (b).

increasing f_T . According to Clause *et al.*³² and ref. 17 and 35, the initial slight increase arises from the successive increase of conductive O/IL microemulsion droplets, indicating the formation of the O/IL microemulsion. The following nonlinear decrease indicates that the medium undergoes a structural transition and becomes BC, because of the progressive growth and interconnection of O/IL microdomains. The final linear decrease of κ could be interpreted as a consequence of forming IL/O microdomains from the partial fusion of clustered inverse microdroplets. Fig. 7 evidently shows the illustration of the presence of three different types of microstructures, *i.e.*, O/IL, BC and IL/O microemulsions. The boundary points between these three microdomains are the same as those observed by the CV measurements (Fig. 3). Similar results have been reported in the literature¹⁸ for the surfactant-based IL microemulsions.

FFEM observations

FFEM is another useful tool for characterizing the size and shape of aggregates in microemulsions. To examine the three different microstructures, FFEM observations were performed for samples with bmimBF₄-ethanol-toluene volume ratios ($R_{IL/E/T}$) of 25 : 9 : 6, 12 : 19 : 19 and 4 : 19 : 27 (marked by *a*, *b* and *c*, respectively, in Fig. 1), representing the O/IL, BC and IL/O subregions, respectively. Fig. 8 shows the FFEM images of these samples. Spherical droplets are clearly observed for sample *a* in the O/IL microregion and sample *c* in the IL/O microregion. The mean diameters of the O/IL and IL/O microemulsion droplets are ~ 70 and 100 nm, respectively. Interestingly, a pearl necklace-like structure was observed for sample *b* in the BC microregion, corresponding to both IL and oil being continuous phases in this structure.⁴⁰ These images verify the presence of three different subregions in the microemulsion system: O/IL, BC and IL/O microregions.

Polarity of bmimBF₄ domains in the nonaqueous IL/O microemulsion

UV-vis absorption spectroscopy is often used to characterize the microenvironment of microemulsion droplets, and MO is often used as the solvatochromic probe.⁴¹ The UV-vis absorption maximum, $\lambda_{\max}$, of MO is sensitive to the local microenvironment. As the polarity of the droplet domains increases, $\lambda_{\max}$ of MO shifts to longer wavelengths (red shift).^{17,18,27} Fig. 9 shows UV-vis absorption spectra at different volume fractions of bmimBF₄, f_{IL} , in the IL/O microemulsions containing 0.096 mmol L⁻¹ MO with $R_{E/T} = 9 : 11$. With an increase of f_{IL} from 0.07 to 0.30, $\lambda_{\max}$ of MO increases from 425 to 429 nm. This red shift indicates that the polarity of bmimBF₄ domains increases with increasing f_{IL} . The $\lambda_{\max}$ values of MO in pure bmimBF₄ and ethanol were measured to be 434 and 416 nm, respectively. Thus, the polarity of the microenvironment of solubilized MO is intermediate between those of bulk bmimBF₄ and ethanol. The polarity of bmimBF₄ domains in the bmimBF₄-in-toluene microemulsions is lower than that of the bulk bmimBF₄. Similar results have been observed in many surfactant-based aqueous microemulsions⁴² and nonaqueous IL microemulsions.^{35,43}

Fig. 8 FFEM images of samples with $R_{IL/E/T}$ of (a) 25 : 19 : 6 in the O/IL microregion, (b) 12 : 19 : 19 in the BC microregion and (c) 4 : 19 : 27 in the IL/O microregion.

Fig. 9 Absorbance of MO in the IL/O microemulsion with $R_{E/T} = 9 : 11$ as a function of f_{IL} . The MO concentration is $0.096 \text{ mmol L}^{-1}$.

Conclusion

The nonaqueous IL microemulsions of bmimBF₄, ethanol and toluene were prepared in the absence of traditional surfactants. Such microemulsions could exhibit three different microstructures, *i.e.*, IL/O, BC and O/IL. A pearl necklace-like morphology for the BC microemulsion was observed from FFEM images. The polarity of bmimBF₄ domains in the IL/O microemulsion was lower than that of the bulk bmimBF₄, and increased with the increasing bmimBF₄ content. To the best of our knowledge, this is the first report on nonaqueous IL SFMEs.

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