Dielectric Insights into the Microcosmic Behavior of Ionic Liquid-Based Self-Assembly—Microemulsions/Micelles

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Supporting Information

ABSTRACT: Dielectric relaxation spectra of ([Bmim][BF₄]/TX-100/p-xylene) microemulsions and ([Bmim][BF₄]/TX-100) micelles were measured. A specific dielectric relaxation changing with the concentration of ionic liquids (ILs) was observed in the range of 10⁶−10⁸ Hz. When dielectric parameters were combined with the Einstein displacement equation and Bruggeman’s effective-medium approximation, the interaction between [Bmim][BF₄] and p-(1,1,3,3-tetramethylbutyl) phenoxypolyoxyethyleneglycol (TX-100) in microemulsions/micelles was presented: because of the electrostatic interaction and van der Waals force, [Bmim][BF₄] is bound around the polyethylene oxide (PEO) chains of TX-100, and once the electric field is added, ions of [Bmim][BF₄] will move along the PEO chain. The dependence of dielectric and phase parameters such as relaxation time, permittivity, and volume fraction on the mass fraction of ILs presents an evidence for our proposals about the transition of both systems with the increase of IL content. In addition, it was confirmed that percolation is a unique phenomenon in microemulsions and the percolation mechanism here belongs to static percolation. The transition process of micelles with the change of IL content is presented from the dielectric view.

1. INTRODUCTION

Since their preparation for the first time in 1914, ionic liquids (ILs) have always been the focus of attention on account of their distinctive characteristics, such as high thermal and electrochemical stability, high conductivity, nonflammability, and designability. ILs can be used to substitute traditional toxic and volatile organic solvents in many applications and consequently as alleged “green solvents,” which have extensive applications in various fields including chemical synthesis, catalysis, separation technology, biodegradation, electrochemistry, and so forth.

However, the immiscibility of many ILs and nonpolar solvents is poor, which limits the development of ILs to wider applications. The introduction of surfactants helps in the formation of self-assembled systems (such as micelles and microemulsions) in ILs, which not only overcomes that limitation but enriches the traditional ordered molecular aggregates. Therefore, this kind of system, with the advantages of both ILs and ordered microstructure, has recently become a research hotspot, and the research on their microstructure transition and characteristics can be of sustained interest for their various applications.

It is the first time that Reinsborough and Bloom reported the amphiphilic self-assembled system, the molten salt of pyridinium chloride, with a melting point of 146 °C. The first use of ILs in self-assembled systems was the formation of micelles in ethylammonium nitrate reported by Evans et al. in 1980s. With more and more new reports about amphiphilic assembled ILs, researchers have an increasing interest in the field. While in 2004, Han group, who utilized hydrophobic ILs replacing water in traditional microemulsions, prepared IL microemulsions ([Bmim][BF₄]/TX-100/cyclohexane) for the first time. In addition, they still presented three microregions of the IL microemulsions, namely, ionic liquid-in-oil (IL/O), bicontinuous (BC), and oil-in-ionic liquid (O/IL), under the help of electrical conductivity meter, dynamic light scattering, and freeze etching electron microscopy. Apart from that, they also obtained another IL microemulsion such as water/TX-100/[Bmim][PF₆] using hydrophobic IL [Bmim][PF₆] as the oil phase, and similarly, three microareas were divided by cyclic voltammetry.

Because the aggregation behavior of such systems has an important impact on their applications in synthesis, catalysis, and separation, many technologies have been used to gain insights into them, including small angle neutron scattering (SANS), ultraviolet visible spectroscopy, fluorescent probe technology, and so on. For example, for the IL micelles: with a surface tension technique and near-infrared spectrum technology, Tran and Yu obtained the critical micelle concentration of various surfactants including cetyl-...
trimethylammonium bromide, sodium dodecyl sulfate, Triton X-100, Brij-35, Brij-700, Tween-20, SB-12, and SB3-10. Gao et al. 15 first used a surface tensiometer and 1H NMR to study the aggregation behavior of nonionic surfactant p-(1,1,3,3-tetramethylibutyl) phenoxypolyoxyethyleneglycol (TX-100) in imidazolium ILs ([Bmim][PF 6] and [Bmim][BF 4]). They found that there is a strong interaction between the positively charged imidazole ring of ILs and the negatively charged ethylene oxide group of polyethylene oxide (PEO) chains on the TX-100 molecules. What is more, their results also showed that the size of micelles such as TX-100 formed in ILs ([Bmim][BF 4] and [Bmim][PF 6]) is far larger than that of spherical micelles in traditional micelles, which was attributed to the low hydrophobicity of TX-100 in ILs compared to that of aqueous systems. For IL microemulsions: through studying IL microemulsions: ([Bmim][BF 4]/TX-100/cyclohexane) by SANS, Eastoe et al. 31 found that with the increase of [Bmim][BF 4] content, the droplet volume of microemulsions increased and showed a swelling phenomenon similar with the traditional micelles. In addition, Sarkar et al. 32 found that the polarity of systems increased with the increasing content of [Bmim][BF 4] by a fluorescence probe. However, for the complex systems such as IL microemulsions and micelles, it is still an opening hotspot, and the study of their microstructures and characteristics will provide important references for their wider applications. Especially with the advent of molecular motors, understanding of the self-assembly process is increasingly significant.

Dielectric spectroscopy can provide information reflecting the microstructure, interfacial properties, and ion migration by measuring the response of the tested system to the electric field in the broadband. It has been successfully applied to the study of the traditional micelles and microemulsion systems for a long time,34−38 and in recent years, it has also been extended to the binary and ternary systems with ILs involved, especially the latter, namely, the IL microemulsion systems.39−43 Among them, Schröder et al. 44 ascribed the two relaxations to ions and water rotation, respectively, by the experimental and computational analyses of the dielectric spectroscopy. Hunger et al. 45 revealed the orientation of cations and anions of ILs by analyzing the binary system of 1-N-ethyl-3-N-methylimidazolium ethylsulfate ([emim][EtSO4]) and dichloromethane. In 2011, our group 42 first applied dielectric spectroscopy to the micelles and microemulsion systems formed by hydrophobic ILs. The interaction between them and the percolation mechanism of microemulsions were also given through dielectric analysis. After that, Chen and Nozaki 46 also reported the dielectric properties of water/TX-100/[Bmim][PF 6] microemulsions whose oil phase was replaced by hydrophobic ILs and systematically discussed the relaxation mechanism of the system. Most recently, our group47 has made a comparative research on the percolation mechanism of IL microemulsions and found that hydrophobicity of ILs has an important effect on the percolation mechanism of microemulsions.

In order to further understand the self-assembly process and physicochemical properties of the IL self-assembly systems such as IL microemulsions and micelles, this research chooses the representative systems as the research target, namely, [Bmim][BF 4]/TX-100/p-xylene (microemulsion system) and [Bmim][BF 4]/TX-100 (micelle system), which both have the involvement of hydrophilic ILs [Bmim][BF 4] and nonionic surfactant TX-100. With dielectric measurement, we managed to distinguish micelle and microemulsion systems from the dielectric perspective. Apart from that, the transition process of microemulsions and micelles with the change of IL contents, as well as the interaction between surfactants and ILs, is given, which will provide many effective references for their wider applications.

2. EXPERIMENTAL SECTION

2.1. Materials. [Bmim][BF 4] (purity >99.2%) was purchased from Shanghai Cheng Jie Chemical Co. Ltd., China, in which the residual chloride was less than 800 ppm and the water content was less than 1000 ppm. TX-100 and p-xylene were purchased from Amresco Chemical Inc. (America) and Beijing Chemical Work, respectively, which were of reagent grade. The chemical structures of them are shown in Figure 1.

Figure 2 shows the isothermal phase diagram of [Bmim][BF 4]/TX-100/p-xylene. 47 There are different colors differentiating the two phases and one phase with different microareas including IL/O, BC, and O/IL. Apart from that, the experimental paths are also shown in Figure 2; the signs denote the tested phase points of the binary micelle system [Bmim][BF 4]/TX-100 with TX-100 concentration ranging from 0 to 100 wt %. Path 1: the mass ratio of [Bmim][BF 4]/p-xylene is changed when the mass ratio of TX-100 is fixed at 50 wt %. Path 2: the mass ratio of TX-100 and [Bmim][BF 4] is increased from 0 to 100 wt %.

Figure 1. Chemical structures of [Bmim][BF 4], TX-100, and p-xylene.

Figure 2. Isothermal phase diagram of [Bmim][BF 4], TX-100, and p-xylene, and the experimental paths are represented by different signs: path 1: the mass ratio of [Bmim][BF 4]/p-xylene is changed when the mass ratio of TX-100 is fixed at 50 wt %. Path 2: the mass ratio of TX-100 and [Bmim][BF 4] is increased from 0 to 100 wt %.
wt %. The experimental path of microemulsions spans all the three microphases including IL/O, BC, and O/IL, which aims at obtaining the parameters that can illustrate the microstructure transition of the system. Experiment was carried out along the paths in Figure 2, and the total mass of each phase point was fixed at 4 g.

2.2. Dielectric Measurements. The 4294A precision impedance analyzer from Agilent Technologies (Made in Japan) was used to carry out the dielectric measurements from 40 Hz to 110 MHz. The dielectric measurement cell with concentrically cylindrical platinum electrodes was connected to the impedance analyzer by a 1607E Spring Clip fixture (Agilent Technologies, Made in Japan). The capacitance \( C_\text{s} \) and conductance \( G_\text{s} \) can be directly obtained by the measurement. The capacitance and conductance of specimens \( C_i \) and \( G_i \) can be calculated by correcting the original data \( C_\text{s} \) and \( G_\text{s} \). Then, the permittivity \( \varepsilon \) and conductivity \( \kappa \) can be calculated by the equations \( \varepsilon = C_i / C_s \) and \( \kappa = G_i \varepsilon_0 / C_s \) \([C_i \text{ is the cell constant and } \varepsilon_0 \text{ is the permittivity of vacuum } (\varepsilon_0 = 8.8541 \times 10^{-12} \text{ F·m}^{-1})]\).

3. RESULTS AND DISCUSSION

3.1. Different Dielectric Behaviors of Micelles/Microemulsions. Figure 3a,b shows the dielectric spectroscopy of binary micelles and ternary microemulsions. It can be seen that there is an obvious relaxation in the range of \( 10^6 \)-\( 10^8 \) Hz for both systems. The frequency and intensity of relaxation change with the increase of IL contents, which indicates that there may be some change for the internal structure of aggregates caused by the change of the composition in the system. Using the Cole–Cole model equation (eq 1) containing a relaxation term \( (i = 1) \) to fit the data obtained, the best fitting results are represented as the solid line in Figure 3.

$$
\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon_h + \sum_i \frac{\varepsilon_l - \varepsilon_h}{1 + (j\omega\tau_i)^\beta}
$$

where \( i \) denotes the number of relaxation and \( \varepsilon^* \) is the complex permittivity. \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of permittivity; the latter is also called dielectric loss and can be expressed as \( \varepsilon'' = (\kappa - \kappa_l)/\omega\varepsilon_0 \), where \( \kappa_l \) is the low-frequency limit of conductivity, \( \varepsilon_l \) and \( \varepsilon_h \) are the low- and high-frequency limit of permittivity, \( \omega_0 \) is the characteristic frequency of relaxation, \( \tau = (2\pi\omega_0)^{-1} \) is the relaxation time, and \( \beta(0 < \beta \leq 1) \) is a parameter related to the distribution of relaxation time, \( j = \sqrt{-1} \).

Figure 4a,b is obtained by plotting the dielectric increment (\( \Delta\varepsilon \)) and relaxation time (\( \tau \)) against the IL content for both systems. It can be seen that the dielectric parameters of the micelles (red lines and circles) are larger than those of the microemulsions (blue lines and squares) at the measured concentration range of ILs. In addition, with the change of IL content, the dielectric parameters of both systems all show inflection points, but the trend and inflection points are completely different, which indicates that the addition of \( p \)-xylene has an important influence on the system. It shows that the dielectric parameters can be used to distinguish micelles and microemulsions and be used as an indicator of the microstructural transition which will be discussed in the next section.

3.2. Phase Transition of Micelles/Microemulsions. In order to present the specific microstructure transition process happened in both tested systems, the Hanai equation based on the Bruggeman’s effective-medium approximation has been used to the dielectric parameters we obtained. It is a classic theoretical equation that can be used to calculate and discuss the phase parameters [including the permittivity and conductivity of the spherical droplet interior (\( \varepsilon_i, \kappa_i \) and...
than 0.1, the Table S2 (the permittivity of [Bmim][BF4] is tested systems can be calculated, and the results are listed in microemulsion system: for micelles, when there are three regions whether it is in micelles or change with the increase of TX-100 and ILs. It is obvious [Bmim][BF4]/TX-100 or [Bmim][BF4]/TX-100/0.2, \( \phi \) becomes close to 1. At this moment, there are just a few surfactants and they are in twos or threes dispersed in IL bulk, so the volume of ILs can be approximated as the volume of micelles, namely, the volume of bulk. When the content of the surfactants reaches a certain value (0.2), the micelles are formed in the system. However, the micelles are a little looser because of the relatively less surfactants. With the increase of surfactants, micelles gradually become denser, and accordingly, they decrease little by little. When the content of surfactants is over 0.76, the increase of surfactant content is dominant, and the micelle volume can be regarded as the volume of surfactants contained in the system. It is worth mentioning that the concentration partition here is nearly consistent with that of the dependence of \( \Delta \epsilon \) and \( \tau \) on ILs (Figure 4), which both give the evidence for the changes of microstructure in the system.

For the microemulsions (Figure 5b), the volume fraction \( (\phi) \) of dispersed droplets grows with the increase of the ILs overall. According to the increasing amplitude, the dependence of \( \phi \) on the ILs could be divided into three regions by two inflection points \( (w_{\text{IL}} = 0.1 \) and 0.2). What is more, these inflection points are identical to those in the phase diagram (Figure 2). This is a corroboration for the credibility of such a dielectric analysis method, and it also confirms the important role of the component content on the microstructure of the system. From Figure 5b, it can be seen that when \( w_{\text{IL}} \) is less than 0.1, the \( \phi \) rapidly increases with \( w_{\text{IL}} \). It is reasonable that with the addition of ILs, they are gradually accumulated in the drops of IL/O, which swells the IL droplets and then increases the volume of microaggregates. When \( w_{\text{IL}} \) is in the range of 0.1–0.2, the volume of microphase changes slowly. This segment is BC, that is, IL continuous phase and oil continuous phase are formed (see the inset in Figure 5b). Therefore, \( \phi \) is not sensitive to the change of \( w_{\text{IL}} \). When \( w_{\text{IL}} \) reaches more than 0.2, it can be seen that \( \phi \) experiences a sudden jump and is then stably maintained at about 0.7 (Figure 5b). Changing from BC to O/IL requires the reorientation and reassociation of surfactants, which causes \( \phi \) to increase. After the recombination of surfactants, the O/IL formed. Then, the added IL was dispersed in the bulk phase, which has no obvious effect on \( \phi \).

3.3. Interaction of Surfactants and ILs. Because of the presence of anions and cations which are involved in the formation of microphase interface, it will be much helpful for understanding the microstructure of such systems if we can explicate the interaction between ILs and surfactants. For this reason, we try to make clear the interaction mechanism by using the Einstein displacement equation to calculate the interaction between the ions in the system. According to the Einstein displacement equation, the time \( \tau \) that a relaxation process needs can be expressed as follows:

\[
\tau = \langle \bar{x} \rangle^2 / 2D_
\]

where \( D \) is the diffusion coefficient and can be calculated from eq 5 and \( \bar{x} \) is the distance of ion movement.

\[
D = (RT/F^2)(\lambda/\nu)
\]

where \( R \), \( F \), and \( \nu \) are gas constant, Faraday constant, and the ionic charge, respectively, \( \lambda \) is the molar conductivity of the independent ionic motion law (eq 6)

\[
\Lambda_m^0 = \nu \lambda_+ + \nu \lambda_-
\]

where \( \Lambda_m^0 \) is the limit molar conductivity of [bmm][BF4], \( \Lambda_m \) (bmm)[BF4], 298 K) = 9.37 S m⁻¹ M⁻¹, and \( \lambda_+ \) for [bmm][BF4], 298 K) = 5.17 S m⁻¹ M⁻¹.

Putting the values of each parameter in eq 5, the infinite dilution diffusion coefficient of [BF4]⁻ can be calculated: \( D^\infty([\text{BF}_4]^-, 298 \text{ K}) = 1.12 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \). Therefore, replacing the values of \( \tau \) and \( D \) in eq 4, the distance of ion movement \( \bar{x} \) can be obtained (see Table 1).

From Table 1, it can be seen that except that several values are exceptionally large up to dozens of nanometers when the content of ILs is very little (\( \leq 0.15 \)), others are all approximately at around 2–3 nm. According to the literature, the length value of PEO chains is \( \langle \bar{x} \rangle = 20 \text{ Â}, \text{namely, 2.0 nm. Accordingly, there is a reason to believe that the relaxation is caused by the fluctuations of the IL anions along the PEO chain} \).
chains in the barrier layer of TX-100 (see the broken circle in Figure 6): in both systems, because the van der Waals force from PEO chains will bind the cations [Bmim]⁺ to distribute around the PEO chains so that the diffusibility of [Bmim]⁺ becomes smaller. In addition, the anions [BF₄]⁻ are bound near the PEO chains by the electrostatic interaction from cations [Bmim]⁺, but the interaction is relatively weak, so [BF₄]⁻ still can be “free” to move and have diffusion coefficient D. Once the electric field is added, the anions will fluctuate with the electric field in order to balance the distribution along the PEO chain. For the abnormal values of micelles (when \( \gamma_{IL} < 0.15 \)), it may be reasonable: when there is only a small amount of ILs and the remaining is a large number of surfactants, it means the intermolecular distance is a little narrow so that the ions are mutually shared by different PEO chains of TX-100. As a result, ions move among several different chains, which makes the ions to reach up to the length sum of several PEO chains. It can also be confirmed from the values of permittivity (see Table S1 in the Supporting Information). From Table S1, it can be seen that the values of permittivity when \( \gamma_{IL} \leq 0.15 \) are nearly two times larger than those of permittivity when \( \gamma_{IL} > 0.15 \), which indicates that the system has a larger polarity when \( \gamma_{IL} \leq 0.15 \). Also, the

ordered arrangement of several adjacent PEO chains will cause a large polarity, which provides an evidence for the rationality of the proposed mechanism above.

On the basis of the model that the micellar particles with volume fraction \( \Phi \) and conductivity \( \kappa \), disperse in the medium with the conductivity \( \kappa_p \), eq 7 (Hanai derived from the Bruggeman’s effective-medium approximation) was used to calculate the number of ILs bound nearby the PEO chains:

\[
\frac{1}{\kappa} = 1 - \Phi
\]

(7)

Because the TX-100 is dissolved in hydrophilic [Bmim]-[BF₄] ILs, the micelles they formed meet the conditions of \( \kappa \geq \kappa_p \), \( \kappa_s \geq \kappa_p \), so eq 7 can be simplified to

\[
\frac{1}{\kappa} = 1 - \gamma \Phi
\]

(8)

Because [Bmim][BF₄] is a hydrophilic IL, the hydrophilic PEO chains of TX-100 will be directed to the external of micelles, as shown in Figure 6. It is known from the previous discussion that the strong van der Waals interaction between PEO chains and [Bmim]⁺ makes PEO chains associate with a certain amount of [Bmim]⁺, which changes the effective volume fraction of TX-100 from \( \Phi \) to \( \gamma \Phi \), where \( \gamma \) is the volume ratio of micelles bound with cations and bare micelles, so eq 8 can be changed to

\[
\frac{1}{\kappa} = 1 - \gamma \Phi
\]

(9)

The experimental values of the dc conductivity (\( \kappa \)) of the system are put into (\( \kappa/\kappa_p \))³/³ and then (\( \kappa/\kappa_p \))³/³ is plotted against \( \Phi \) as shown in Figure 7. From Figure 7, it can be clearly seen that when \( \Phi \leq 48\% \), (\( \kappa/\kappa_p \))³/³ showed a linear relationship with \( \Phi \), indicating that TX-100 in ILs exists in the form of spherical micelles at this moment. \( \gamma = 1.43 \) can be obtained from the slope of the linear relationship in Figure 7.

As mentioned above, \( \gamma \) is the volume ratio of micelles bound with cations and bare micelles; then, the values of \( \gamma - 1 \) are the volume ratio of cations [Bmim]⁺ and TX-100 and can be calculated by eq 10

\[
\gamma - 1 = \frac{V_c M_c}{V_{TX} c_{TX} M_{TX}}
\]

(10)

![Figure 6. Interaction model of TX-100 and [Bmim][BF₄]. “⊕” represents the [Bmim]⁺ and “⊕” represents the [BF₄]⁻ in dotted circle.](image)
where \( V, c, \) and \( M \) are volume, molar concentration, and relative molecular mass, respectively. \( \gamma, \nu_c, \) and \( M_c \) individually denote \( \gamma, \) cations in bulk, and cations bound with TX-100. Therefore, the number of cations bound with each TX-100 can be calculated by eq 11

\[
\gamma = \frac{c_{ac}}{c_{TX}} = (\gamma - 1) \frac{\nu_{TX} M_{TX}}{\nu_c M_c}
\]

Putting \( M_{TX} = 646.85, \) \( \nu_{TX} = 0.9756 \text{ nm}^3, \) \( \nu_c = 0.218 \text{ nm}^3, \) \( M_c = 139.21, \) and \( \gamma = 1.43 \) into eq 11, \( n_{ac} = 9.0 \) can be calculated, which indicates that each TX-100 is bound with nine \([\text{Bmim}]^+\).

Compared with traditional micelles (TX-100/water), it is due to the volume effect of ILs that the number of cations bound on each TX-100 in IL micelles is less than that in water solution (20−30),\(^51,52\) which can also be confirmed by the other methods reported.\(^47\)

### 3.4. Percolation in Microemulsions.

The percolation phenomenon indicates the transformation process of microstructure of microemulsions and usually is an important physicochemical characteristic of microemulsions. As the red dots shown in Figure 8a, conductivity has a significant jump in the range of 0.075−0.2—the BC of \([\text{Bmim}][\text{BF}_4]/\text{TX-100}/p\)-xylene, which is more obvious in Figure 8b. Compared with that of \([\text{Bmim}][\text{BF}_4]/\text{TX-100} \) micelles (black dots) in Figure 8a, there is a reason to believe that percolation is a unique phenomenon for microemulsions.

From Figure 8, the so-called percolation phenomenon can be seen, namely, a rapid increase in BC. At present, there are two theories about the explanation of percolation. One is the static percolation theory:\(^53\) percolation is raised by the two channels of oil and water formed in BC, which accelerates the migration of ions. The other is the dynamic percolation theory:\(^54,55\) near the percolation threshold, a continuous rearrangement of percolation clusters is formed because of the interaction between the droplets, and ions constantly collide, move, and exchange through the percolation clusters, resulting in the occurrence of percolation. No matter which kind of theory, it is predicted that the conductivity data of the hydrophilic phase ([Bmim][BF\(_4\)] in this work) will follow the scaling relation when the concentration is below or above the percolation concentration threshold

\[
\kappa_1 \propto |C_p - C|^{s'} \\
\kappa_1 \propto |C_p - C|^{\mu}
\]

where the values of \( s \) are predicted to be 0.7\(^53\) and 1.2\(^51,52\) for static and dynamic percolation, respectively, whereas the values of \( \mu \) are 1.9\(^55,56\) for both theories.

Figure 9 shows the dependence of \( \kappa \) on \( |w_{ILp} - w_{IL}| \), in which the hollow and solid data represent the data below and above the percolation threshold, respectively. The shadow part (\( w_{IL} = 7.5\text{−}14.0\%)\) shows that the scaling relation meets \( s = 0.63 \) from the slope, which is close to the predicted value 0.7 of the static percolation theory. To a certain extent, it indicates that it is the static percolation process that occurs in microemulsions, that is, ions are transferred through the formed continuous phase like a pipeline (as the inset in Figure 9). Other data in Figure 9 (nonshaded region) cannot be described by dynamic or static percolation theory. It may be mainly due to the fact that ILs, which act as hydrophilic phases in IL microemulsions, possess high conductivity, which makes it not fully satisfied with the hypothesis of percolation theory when the content of ILs is too high. From the above conclusion, the high...
conductivity of [Bmim][BF₄] makes the microemulsion percolation process not easy to detect compared with that in water. However, the dependence of the dc conductivity on the concentration of ILs near the percolation threshold is consistent with that of the static percolation theory predicted, which gives an evidence for the existence of the percolation process and BC microregion.

4. CONCLUSIONS

The microstructure transition of micelles and microemulsions with ILs involved was investigated by dielectric spectroscopy, and the relaxation mechanism is ascribed to the directional movement of anions of the ILs along the PEO chains of TX-100. On the basis of the Bruggeman’s effective-medium approximation, it is calculated that each TX-100 is bound with nine [Bmim]+ cations, which is far less than the number (20–30) of water bound on each TX-100, indicating that the volume effect of ILs has an important effect on their microstructure. In addition, the dependence of the dielectric parameters on the IL content shows the different experience of the formation of the micelles and microemulsions, which provides a credible reference for their applications in different occasions and proves that dielectric spectroscopy can be used as a powerful "indicator" to distinguish micelles and microemulsions. According to the concentration dependence of conductivity combined with percolation theory, the percolation process of microemulsions in this work tends to be static percolation when \( n_{IL} \) is in the range of 7.5–14.0%. In addition, the existence of BC microphase is confirmed from the dielectric perspective, which will be helpful for the effective application (especially drug delivery, catalysis, and synthesis) of this kind of systems.

ASSOCIATED CONTENT

Supporting Information

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Dielectric parameters obtained by fitting and the phase parameters (PDF)

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Notes

The authors declare no competing financial interest.

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