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# Dilution Method Study on the Interfacial Composition, Thermodynamic Properties, and Structural Parameters of the [bmim][$BF_4$] + Brij-35 + 1-Butanol + Toluene Microemulsion

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*Supporting Information*

**ABSTRACT:** The dilution method was used to research the interfacial composition, thermodynamic parameters, and structural parameters of [bmim][$BF_4$] + Brij-35 + 1-butanol + toluene ionic liquid/oil (IL/O) microemulsion. The effects of the mole ratio of [bmim][$BF_4$] to Brij-35 ($R$) and the addition of water on the above parameters were investigated. Studies of the interfacial composition revealed that cosurfactants at the interface ($n_a^i$) increased with the increase of $R$ and decreased with the increase of additional water. This indicated that more cosurfactants were required to form a IL/O microemulsion than that of the traditional water/oil (W/O) microemulsion. The $\Delta G_t^\circ$ values of transfer process of cosurfactants from the continuous oil phase to the interfacial region were all negative, which suggested that the IL/O microemulsion formed spontaneously. The absolute values of $\Delta G_t^\circ$ increased with the increase of $R$ and additional water. The results showed that the IL/O microemulsion with additional water formed more spontaneously and more stably. The $\Delta S_t^\circ$ values were mostly positive, which implied that the formation processes of the IL/O microemulsions were entropy-driven. The greater number of cosurfactants at the interfacial layer contributed to form smaller ionic liquid droplets. Thus, smaller ionic liquid droplets were obtained with the increase in $R$, while larger droplets were obtained with the addition of water.

## 1. INTRODUCTION

Ionic liquids (ILs) are organic salts which are liquids at ambient conditions.[1] They are attracting wide interest in many fields of chemistry, because of their unusual properties including nonvolatility, nonflammability, excellent thermal stability, higher ionic conductivity, and wide electrochemical windows. ILs are widely applied in electrochemistry, analytical chemistry, organic synthesis, separation, synthetic nanochemistry, and other fields.[1−31] So they are thought as a recyclable alternative to the traditional organic solvents. ILs can be regarded as environmentally friendly, that is, "green" chemicals, making them highly desirable in many important processes of industry.[27−31]

Recently, extensive efforts have been dedicated to theoretical studies on a variety of microemulsion systems containing ILs, including IL—organic solvent,[32−43] IL—water,[46,47] IL—carbon dioxide,[44] and IL—IL[45] systems. The nonaqueous IL microemulsions provide hydrophobic or hydrophilic nanodomains by surfactant assemblies which may expand the potential application of traditional microemulsions to a larger range due to their unique features. Furthermore, with the discovery of novel IL microemulsions, their formation mechanism and microstructure have been explored by various techniques.[32−52] Among the research, the ternary phase IL microemulsions have been intensively investigated; however, the interfacial composition, thermodynamic properties, and structural parameters of IL microemulsions and the changes with surfactant concentration and temperature are unknown. To the best of our knowledge, pseudoternary phase IL microemulsions have seldom been reported. Therefore, a fundamental understanding of the interfacial composition, thermodynamic properties, and structural parameters of IL microemulsions is required and important.

The conventional pseudoternary phase W/O microemulsion is composed by surfactant, cosurfactant, water, and oil. Because of their amphiphilic nature, surfactants get adsorbed at the oil/water interface to render stability to the dispersion by preventing coalescence. The cosurfactants (usually short chain alcohols) play an important role by blending with surfactants and partition between the coexisting aqueous and oleic phases to control the bending elasticity of the interfacial layer offering stability to the dispersion. In the elucidation of the nature of the oil/water interface, detailed knowledge of (a) the interfacial composition (relative population of surfactant and cosurfactant in the interfacial region), (b) the distribution of the cosurfactant between the interfacial region and the bulk oil phase, (c) thermodynamics of transfer of cosurfactant from the oleic phase to the interface, and (d) the structural parameters, namely, radii of the droplet ($R_e$) and the water pool ($R_w$) and effective thickness of the interfacial layer ($l$), are essential.

In view of the above, a simple but ingenious method of dilution has been used by a number of workers to research common W/O microemulsions.[53−63] In the method of dilution, a stable W/O microemulsion at a fixed amount of water and surfactant is prepared using a threshold volume of cosurfactant. Then the system is destabilized by adding oil, and the addition of

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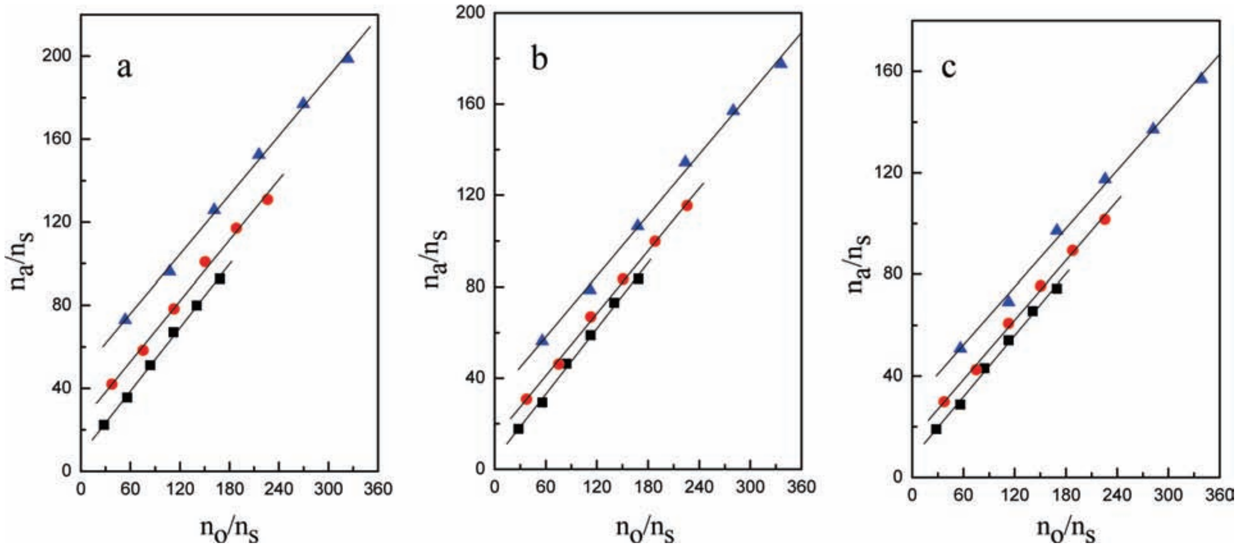

**Figure 1.** Plot of $n_a/n_s$ vs $n_o/n_s$ for [bmim][BF$_4$] + Brij-35 + 1-butanol + toluene IL/O microemulsion systems with different $R$ at 298 K (a), 308 K (b), and 318 K (c). ■, $R$ = 1.34; ●, $R$ = 1.77; ▲, $R$ = 2.66.

oil abstracts the cosurfactants from the interface to oil phase, which cause the interface unstable. Afterward the system is restabilized by the addition of a minimum amount of cosurfactants, which replenish the deficiency and restabilize the system. The procedure is repeated for a number of times, and the distribution parameters and the relation with thermodynamic parameters and structural parameters can be calculated and analyzed from the dilution method.

In this paper, we communicated results of the dilution method on the IL/O microemulsions using polyoxyethylene (23) lauryl ether (Brij-35) as surfactant, hydrophilic IL 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]) as the disperse phase, 1-butanol as cosurfactant, and toluene as the oil phase at different temperatures, (298, 308, and 318) K. The values of the composition of cosurfactant and surfactant at the interfacial region and the distribution of cosurfactant between the interfacial region and the continuous oil phase were calculated. The standard Gibbs free energy, enthalpy, and entropy of the transfer of cosurfactant from the oil phase to the interfacial region were also estimated. The structural parameters of the IL/O microemulsions were calculated by analyzing the experimental data. Furthermore, the effect of the [IL]/[Brij-35] mole ratio (R) and the addition of water on the above parameters was investigated. This study aims to improve the basic understanding of the formation and microstructure of IL/O microemulsions.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]) was obtained from Centre for Green Chemistry and Catalysis, LICP, CAS, Lanzhou, China. Polyoxyethylene (23) lauryl ether (Brij-35) was obtained from Serva Feinbiochemica GmbH & Co., Heidelberg, Germany. Toluene (≥ 99.5 %) was purchased from Rionlon (Tianjin) BoHua Medical Chemistry Co. Ltd., China. 1-Butanol (≥ 99.5 %) was purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. All of these chemicals were used without further purification. Distilled water was used in the experiments.

**2.2. Dilution Experiments.** In the dilution experiments, 1.0 g ($8.3 \cdot 10^{-4}$ mol) of surfactant Brij-35 was taken in a stoppered dry test tube, and 5 mL of toluene and 0.5 g of [bmim][BF$_4$] were added to it. The sample was then placed in a thermostat water bath (temperature control accuracy ± 0.1 K), stirred constantly using a magnetic stirrer, and kept well covered to prevent loss by evaporation. The 1-butanol was added slowly to the initially turbid mixture until the solution became just clear at the temperature of the experiment, allowing sufficient time for equilibration. The volume of 1-butanol at that point was noted. At this stage, 5 mL of toluene was added to the system to destabilize it. The cloudy solution was then made just clear by addition of the 1-butanol, and the quantity of 1-butanol added was also recorded. This procedure was repeated five times, noting the volume of the oil and the 1-butanol necessary at each step for obtaining a clear and stable IL/O microemulsion. The entire procedure was followed at three temperatures: (298, 308, and 318) K. This process was repeatedly followed in the dilution experiment.[53−63] To investigate the effect of the [IL]/[Brij-35] mole ratio, the mass of Brij-35 varied from 1.0 g ($8.3 \cdot 10^{-4}$ mol), 1.5 g ($12.5 \cdot 10^{-4}$ mol), to 2.0 g ($16.7 \cdot 10^{-4}$ mol) at 0.5 g of [bmim][BF$_4$] fixed. To investigate the effect of the additional water, the mass ratio of IL to additional water ($m_{IL}/m_{H_2O}$) changed from 1, 2, 3, to 4 with the whole mass weight of IL with additional water fixed at 0.5 g and Brij-35 fixed at 1.0 g. Each set of experiments was repeated two or three times, and the average of the values obtained was used for data processing and analysis.

## 3. RESULTS AND DISCUSSION

### 3.1. Interfacial Composition of the IL/O Microemulsion.

*3.1.1. Effect of the [IL]/[Brij-35] Mole Ratio (R).* The basic conceptions related to the dilution method and also the estimation of the structural parameters of the respective IL/O microemulsion systems, which is similar to the previous description of a W/O microemulsion,[53−63] are represented in Supporting Information.

Figure 1 shows the dilution plots of $n_a/n_s$ (total number of moles of 1-butanol in system/total number of moles of surfactant in system) versus $n_o/n_s$ (total number of moles of toluene in system/total number of moles of surfactant in system) with a varying molar ratio of IL to surfactant ($R$) at a fixed amount, 0.5 g, of [bmim][BF$_4$]. Three representative plots at different temperatures are illustrated in Figure 1. The plots are strikingly linear. The intercepts of the straight lines corresponding to the values of $n_a^i/n_s$ (number of moles of 1-butanol at droplet interface/total number of moles of surfactant in system) are listed in Table 1, which indicated that a part of 1-butanol had populated the droplet interface to form a mixed film together with the surfactant. The slopes of the straight lines $n_a^o/n_o$ (number of moles of 1-butanol in bulk oil phase/total number of moles of toluene in system) corresponding to the values of 1-butanol in oil phase required for the formation of a stable IL/O microemulsion are also listed in Table 1. It was obvious that both $n_a^o/n_o$ and $n_a^i/n_s$ depended on $R$ and temperature.

From Table 1, it was clearly evident that when $R$ increased (the increase in IL content), more $n_a^i$ were required for the formation of stable IL/O microemulsion systems at constant temperature. With increasing IL content, in turn, the interfacial areas were extended, and the requirement of cosurfactants at the interface to stabilize the droplets was gradually increased. On the contrary, with $R$ increasing, the values of $n_a^o/n_o$ decreased, which meant less $n_a^o$ were required for the formation of stable IL/O microemulsion systems. With the increase in IL content at a constant oil content, thereby $n_o$ relatively decreased. To maintain a constant value of $k$ (which equaled $n_a^o/n_o$) at a given temperature, $n_a^o$ had to be decreased; that is, less molecules of 1-butanol got solubilized in the oil.

On the other hand, no systematic trend on the interface $n_a^i$ with the variation of temperature was noticed from Table 1. The values of $n_a^i$ gradually decreased from (298 to 308) K and then increased at 318 K for microemulsion systems with $R$ = 1.34 and 1.77. But for microemulsions with $R$ = 2.66, the values of $n_a^i$ gradually decreased from (298 to 318) K. On the whole, the $n_a^i$ decrease with temperature increasing. With temperature increasing, the polyoxyethylene (PEO) chains of Brij-35 folded due to the strength of hydrogen bond between C$_2$—H of the imidazolium cation and ethoxy/hydroxyl of PEO became weak,[64] and in consequence PEO chains tended to pack at the interface and occupied a larger interface area of the droplet. Therefore, the unoccupied intersurface area at the interface was reduced, and $n_a^i$ was gradually lowered. The values of $n_a^o/n_o$ decreased with the temperature increase, which indicated that the mass of 1-butanol dissolved in toluene decreased as temperature increased.

*3.1.2. Effect of $m_{IL}/m_{H_2O}$.* Figure 2 shows the dilution plots of $n_a/n_s$ versus $n_o/n_s$ with varying the mass ratio of IL/addition of water ($m_{IL}/m_{H_2O}$) and the total mass weight of IL with additional water fixed at 0.5 g and Brij-35 fixed at 1.0 g. The values of $n_a^o/n_o$ and $n_a^i/n_s$ were calculated from the slopes and intercepts of the straight lines, respectively, which are listed in Table 2. It was evident that both $n_a^o/n_o$ and $n_a^i/n_s$ varied with $m_{IL}/m_{H_2O}$.

From Table 2, it can be easily seen that more $n_a^i$ were required for the formation of stable IL/O microemulsion systems at a constant temperature with $m_{IL}/m_{H_2O}$ increasing (IL mass content increasing). In turn, with the increase of additional water in the disperse phase, the requirement of cosurfactants at the interface gradually decreased. With a similar variation trend for

**Table 1. Interfacial Compositions and Bulk Compositions $n_a^o/n_o$, $n_a^i/n_s$, $n_s$, and $n_a^i$ of the [bmim][BF$_4$] + Brij-35 + 1-Butanol + Toluene IL/O Microemulsion with Different $R$ at Different Temperatures**[a]

| $R$ | $T$/K | $n_a^o/n_o$ | $n_a^i/n_s$ | $10^3$ $n_s$/mol | $10^3$ $n_a^i$/mol |
|---|---|---|---|---|---|
| 1.34 | 298 | 0.509 | 8.06 | 1.68 | 13.5 |
| | 308 | 0.479 | 4.23 | 1.68 | 7.11 |
| | 318 | 0.403 | 7.61 | 1.67 | 12.7 |
| 1.77 | 298 | 0.487 | 23.6 | 1.25 | 29.5 |
| | 308 | 0.456 | 13.6 | 1.25 | 17.0 |
| | 318 | 0.391 | 15.1 | 1.25 | 18.9 |
| 2.66 | 298 | 0.476 | 47.3 | 0.87 | 41.2 |
| | 308 | 0.444 | 31.3 | 0.84 | 26.3 |
| | 318 | 0.382 | 29.3 | 0.84 | 24.6 |

[a] Note: $n_a^{IL}$ (number of moles of 1-butanol in IL) values of (4.10, 2.93, and 1.67) mmol for 1-butanol per 0.5 g [bmim][BF$_4$] at (298, 308, and 318) K, respectively, were taken in the calculation.[65] The uncertainty limits of $n_a^o/n_o$, $n_a^i/n_s$, and $n_a^i$ are ± 2 %.

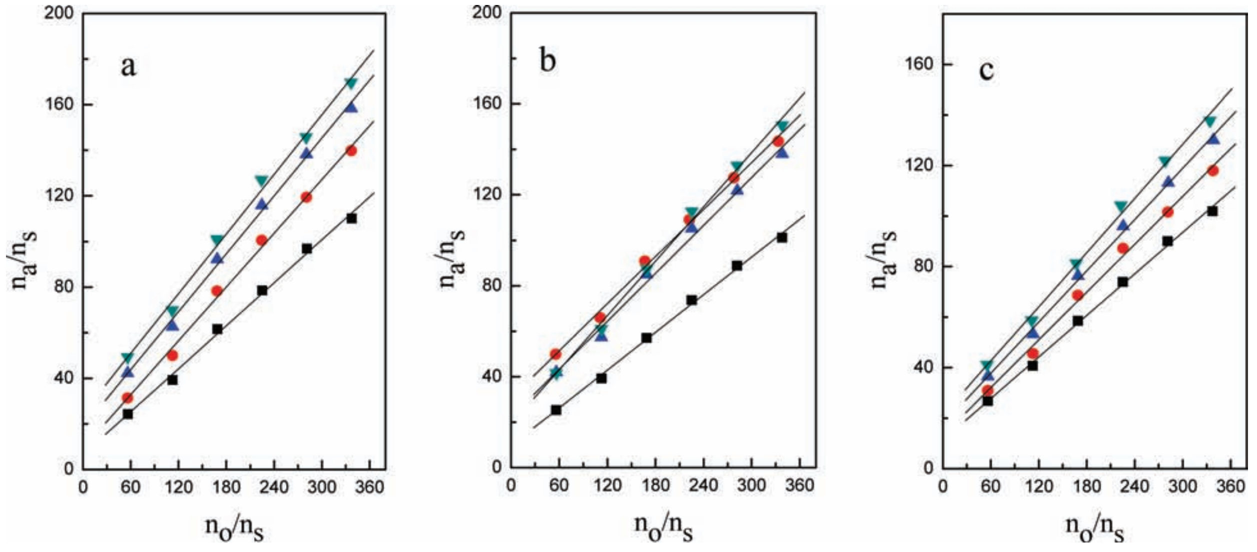

**Figure 2.** Plot of $n_a/n_s$ vs $n_o/n_s$ for [bmim][BF$_4$] + Brij-35 + 1-butanol + toluene IL/O microemulsion systems with different $m_{IL}/m_{H_2O}$ at 298 K (a), 308 K (b), and 318 K (c). ■, $m_{IL}/m_{H_2O}$ = 1; ●, $m_{IL}/m_{H_2O}$ = 2; ▲, $m_{IL}/m_{H_2O}$ = 3; ▼, $m_{IL}/m_{H_2O}$ = 4.

**Table 2. Interfacial Compositions and Bulk Compositions $n_a^o/n_o$, $n_a^i/n_s$, $n_s$, and $n_a^i$ of the [bmim][BF$_4$] + Brij-35 + 1-Butanol + Toluene IL/O Microemulsion with Different $m_{IL}/m_{H_2O}$ at Different Temperatures**[a]

| $m_{IL}/m_{H_2O}$ | $T$/K | $n_a^o/n_o$ | $n_a^i/n_s$ | $10^4\ n_s$/mol | $10^3\ n_a^i$/mol |
|---|---|---|---|---|---|
| 1 | 298 | 0.314 | 6.53 | 8.38 | 5.47 |
| | 308 | 0.277 | 9.67 | 8.37 | 8.09 |
| | 318 | 0.274 | 11.4 | 8.38 | 9.55 |
| 2 | 298 | 0.393 | 9.28 | 8.40 | 7.80 |
| | 308 | 0.345 | 30.6 | 8.49 | 26.0 |
| | 318 | 0.315 | 13.2 | 8.37 | 11.0 |
| 3 | 298 | 0.423 | 18.4 | 8.40 | 15.4 |
| | 308 | 0.352 | 22.2 | 8.36 | 18.6 |
| | 318 | 0.338 | 17.5 | 8.36 | 14.6 |
| 4 | 298 | 0.436 | 24.9 | 8.40 | 20.9 |
| | 308 | 0.399 | 19.0 | 8.37 | 15.9 |
| | 318 | 0.357 | 21.3 | 8.47 | 18.0 |

[a] Note: $n_a^{IL}$ values of (4.10, 2.93, and 1.67) mmol for 1-butanol per 0.5 g [bmim][BF$_4$] at (298, 308, and 318 )K, respectively,[65] and $n_a^w$ (number of moles of 1-butanol in water) values of (0.499, 0.459, and 0.438) mmol for 1-butanol per 0.5 g $H_2O$ at (298, 308, and 318) K, respectively, were taken in the calculation. The uncertainty limits of $n_a^o/n_o$, $n_a^i/n_s$, and $n_a^i$ are ± 2 %.

**Table 3. Thermodynamic Parameters for Transfer of 1-Butanol from the Oil Phase to the Interfacial Region $\Delta G_t^o$, $\Delta S_t^o$, and $\Delta H_t^o$ of the [bmim][BF$_4$] + Brij-35 + 1-Butanol + Toluene IL/O Microemulsion with Different $R$ at Different Temperatures**[a]

| | $T$ | $\Delta G_t^o$ | $\Delta S_t^o$ | $\Delta H_t^o$ |
|---|---|---|---|---|
| $R$ | K | kJ·mol$^{-1}$ | J·K$^{-1}$·mol$^{-1}$ | kJ·mol$^{-1}$ |
| 1.33 | 298 | −2.40 | −40.2 | −14.4 |
| | 308 | −2.34 | 28.4 | 6.40 |
| | 318 | −2.97 | 97.2 | 27.9 |
| 1.77 | 298 | −2.66 | −0.45 | −2.80 |
| | 308 | −2.79 | 26.2 | 5.28 |
| | 318 | −3.19 | 53.0 | 13.7 |
| 2.66 | 298 | −2.75 | 12.0 | 0.82 |
| | 308 | −2.95 | 28.0 | 5.67 |
| | 318 | −3.31 | 44.0 | 10.7 |

[a] Note: The uncertainty limits of $\Delta G_t^o$, $\Delta H_t^o$, and $\Delta S_t^o$ are ± 3 %, ± 5 %, and ± 8 %, respectively.

$n_a^o/n_o$, the values of $n_a^o/n_o$ increased with $m_{IL}/m_{H_2O}$ increasing, which meant more cosurfactants solubilized in the oil. So, much more cosurfactants were required for the formation of stable IL/O microemulsions than that of W/O microemulsions.

The values of $n_a^o/n_o$ also decreased with temperature increasing as description above. However, the values of $n_a^i$ did not decrease with the temperature increase on the whole. When the additional water content increased to $m_{IL}/m_{H_2O} = 1$, $n_a^i$ increased with the temperature increase. When more water was presented in disperse phase, we should not only consider the change of hydrogen bond between imidazolium cation and PEO but also the changes of hydrogen bond between $H_2O$ and PEO, imidazolium cations and $H_2O$, and the $BF^{4-}$ anion and $H_2O$.[36]

### 3.2. Thermodynamics of Transfer of Cosurfactants to the Interface.

*3.2.1. Effect of the [IL]/[Brij-35] Mole Ratio (R).* The standard Gibbs free energy change ($\Delta G_t^o$), the standard enthalpy change ($\Delta H_t^o$), and the standard entropy change ($\Delta S_t^o$) for the transfer of 1-butanol from the continuous oil phase (toluene) to the interfacial region of three microemulsion systems with varying $R$ at three different temperatures were calculated according to eqs 8 to 10 in Supporting Information, and the data are presented in Table 3. All of the values of $\Delta G_t^o$ were negative and suggested that IL/O microemulsions formed spontaneously. The same result was also obtained for aqueous microemulsions.[53−63]

It was evident from Table 3 that the absolute values of $\Delta G_t^o$ increased with $R$ increasing at constant temperature. With $R$ increasing, the relative retention of cosurfactants in oil decreased (as reflected from the values of $n_a^o/n_o$), and the cosurfactants in interfacial region ($n_a^i$) increased as listed in Table 1. In other words, the cosurfactants tended to transfer to the interface and favored to associate with the surfactants at the interface with the increase in $R$. The higher absolute values of $\Delta G_t^o$ indicated a comparable stronger interaction between surfactant and cosurfactant at the interface, which corroborated well with the degree of spontaneity of the transfer process.

The values of $\Delta H_t^o$ were mostly positive except for $R = 1.33$ and $R = 1.77$ at 298 K, which showed that the transfer of 1-butanol from oil to the interface was endothermic and the transfer process absorbed heat. The values of $\Delta S_t^o$ were all positive except for $R = 1.33$ and $R = 1.77$ at 298 K. It indicated that the IL/O microemulsion forming systems ended up in disordered states. As a result, IL/O microemulsion systems were mostly endothermic with appreciable positive entropy change; the formation of the [bmim][BF$_4$] + Brij-35 + 1-butanol + toluene microemulsion process was entropy-driven.

*3.2.2. Effect of $m_{IL}/m_{H_2O}$.* The absolute values of $\Delta G_t^o$ increased with $m_{IL}/m_{H_2O}$ decreasing at constant temperature. In other words, with the addition of water in the disperse phase, the formation of microemulsion became more and more spontaneous. This result coincided with the study of Gao et al. Their research showed that the addition of a small amount of water to the reverse IL microemulsion of [bmim][BF$_4$]/TX-100/benzene contributed to the stability of microemulsion. Fourier transform IR showed that the added water molecules were located in the palisade layers and mainly behaved as bound water and trapped water. $^1$H NMR and $^{19}$F NMR spectra suggested that the added water molecules built the hydrogen binding network of imidazolium cations and $H_2O$ and the $BF^{4-}$ anion and $H_2O$ and at the same time the electronegative oxygen atoms of the oxyethylene units of TX-100 and $H_2O$ in the palisade layers, which made the palisade layers more firm and thus increased the stability of the microemulsion.[36]

Compared the effect of $R$ and $m_{IL}/m_{H_2O}$ on the values of $\Delta G_t^o$ and $n_a^i$, it can be seen that increasing $R$ favors the transfer of cosurfactant to interface (Table 3) and $n_a^i$ increase (Table 1), while the addition of water favors the transfer of cosurfactant to interface (Table 4) but $n_a^i$ decrease (Table 2). The reason for this opposite trend is that, with $R$ increasing, the moles of surfactant Brij-35 decrease. To form stable IL/O microemulsions, more 1-butanol molecules are required together with Brij-35 to form the interface layer. But, with the addition of water, the PEO groups will hydrogen bond with $H_2O$, and the interface layer will become firm. So the requirement of 1-butanol at the interface is reduced.

The values of $\Delta H_t^o$ were mostly positive except for $m_{IL}/m_{H_2O} = 1$, 2, and 3 at 318 K, which showed that the transfer of 1-butanol from oil to the interface was endothermic and the

**Table 4. Thermodynamic Parameters for the Transfer of 1-Butanol from the Oil Phase to the Interfacial Region, $\Delta G_t^o$, $\Delta S_t^o$, and $\Delta H_t^o$, of the [bmim][BF$_4$] + Brij-35 + 1-Butanol + Toluene IL/O Microemulsion with Different $m_{IL}/m_{H_2O}$ at Different Temperatures**[a]

| | | $\Delta G_t^o$ | $\Delta S_t^o$ | $\Delta H_t^o$ |
|---|---|---|---|---|
| $m_{IL}/m_{H_2O}$ | T/K | $kJ \cdot mol^{-1}$ | $J \cdot K^{-1} \cdot mol^{-1}$ | $kJ \cdot mol^{-1}$ |
| 1 | 298 | −3.19 | 61.6 | 15.2 |
| | 308 | −3.66 | 32.4 | 6.32 |
| | 318 | −3.84 | 3.35 | −2.84 |
| 2 | 298 | −2.88 | 68.6 | 17.6 |
| | 308 | −3.40 | 35.0 | 7.38 |
| | 318 | −3.58 | 1.40 | −3.14 |
| 3 | 298 | −2.87 | 61.4 | 15.4 |
| | 308 | −3.34 | 30.8 | 6.15 |
| | 318 | −3.49 | 0.35 | −3.38 |
| 4 | 298 | −2.86 | 17.6 | 2.39 |
| | 308 | −3.08 | 27.6 | 5.42 |
| | 318 | −3.41 | 37.6 | 8.55 |

[a] Note: The uncertainty limits of $\Delta G_t^o$, $\Delta H_t^o$, and $\Delta S_t^o$ are ± 3 %, ± 5 %, and ± 8 %, respectively.

**Table 5. Structural Parameters $R_{IL}$, $R_e$, $l$, $N_d$, $\tilde{N}_s$, and $\tilde{N}_a$ of the [bmim][BF$_4$] + Brij-35 + 1-Butanol + Toluene IL/O Microemulsion with Different $R$ at Different Temperatures**

| R | T/K | $R_{IL}$/nm | $R_e$/nm | $l$/nm | $N_d$ | $\tilde{N}_s$ | $\tilde{N}_a$ |
|---|---|---|---|---|---|---|---|
| 1.34 | 298 | 3.72 | 4.37 | 0.65 | $1.06 \cdot 10^{19}$ | 95 | 767 |
| | 308 | 6.20 | 6.96 | 0.76 | $2.21 \cdot 10^{18}$ | 458 | 1937 |
| | 318 | 3.90 | 4.56 | 0.66 | $9.11 \cdot 10^{18}$ | 110 | 839 |
| 1.77 | 298 | 1.65 | 2.17 | 0.52 | $1.08 \cdot 10^{20}$ | 7 | 164 |
| | 308 | 2.57 | 3.16 | 0.59 | $2.66 \cdot 10^{19}$ | 28 | 385 |
| | 318 | 2.36 | 2.94 | 0.58 | $3.47 \cdot 10^{19}$ | 22 | 328 |
| 2.66 | 298 | 1.06 | 1.52 | 0.46 | $3.59 \cdot 10^{20}$ | 1 | 69 |
| | 308 | 1.46 | 1.96 | 0.50 | $1.22 \cdot 10^{20}$ | 4 | 130 |
| | 318 | 1.53 | 2.04 | 0.51 | $1.04 \cdot 10^{20}$ | 5 | 142 |

**Table 6. Structural Parameters $R_{IL}$, $R_e$, $l$, $N_d$, $\tilde{N}_s$, and $\tilde{N}_a$ of the [bmim][BF$_4$] + Brij-35 + 1-Butanol + Toluene IL/O Microemulsion with Different $m_{IL}/m_{H_2O}$ at Different Temperatures**

| $m_{IL}/m_{H_2O}$ | T/K | $R_{IL}$/nm | $R_e$/nm | $l$/nm | $N_d$ | $\tilde{N}_s$ | $\tilde{N}_a$ |
|---|---|---|---|---|---|---|---|
| 1 | 298 | 5.41 | 6.13 | 0.72 | $2.08 \cdot 10^{18}$ | 242 | 1583 |
| | 308 | 3.91 | 4.72 | 0.81 | $5.63 \cdot 10^{18}$ | 89 | 865 |
| | 318 | 3.45 | 4.08 | 0.63 | $8.40 \cdot 10^{18}$ | 60 | 684 |
| 2 | 298 | 4.00 | 4.65 | 0.65 | $5.20 \cdot 10^{18}$ | 97 | 903 |
| | 308 | 1.51 | 2.02 | 0.51 | $1.13 \cdot 10^{20}$ | 4 | 138 |
| | 318 | 2.99 | 3.60 | 0.61 | $1.28 \cdot 10^{19}$ | 39 | 517 |
| 3 | 298 | 2.25 | 2.81 | 0.56 | $3.09 \cdot 10^{19}$ | 16 | 300 |
| | 308 | 1.95 | 2.49 | 0.54 | $4.90 \cdot 10^{19}$ | 10 | 228 |
| | 318 | 2.34 | 2.91 | 0.57 | $2.71 \cdot 10^{19}$ | 18 | 324 |
| 4 | 298 | 1.76 | 2.29 | 0.53 | $6.74 \cdot 10^{19}$ | 8 | 187 |
| | 308 | 2.19 | 2.75 | 0.56 | $3.35 \cdot 10^{19}$ | 15 | 286 |
| | 318 | 2.00 | 2.55 | 0.55 | $4.54 \cdot 10^{19}$ | 11 | 239 |

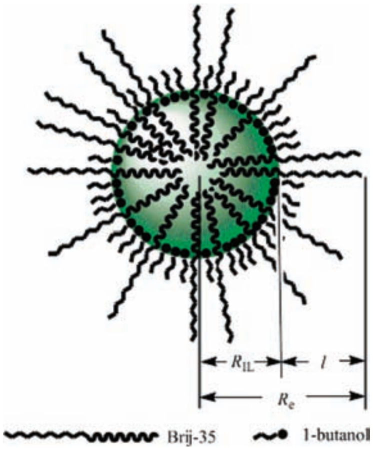

**Figure 3.** Structure of the [bmim][BF$_4$] + Brij-35 + 1-butanol + toluene IL/O microemulsion: $R_{IL}$, effective radius of the IL droplet; $R_e$, effective radius of droplet including the interface; $l$, effective thickness of the interfacial layer.

transfer process absorbed heat. The values of $\Delta S_t^o$ were all positive. It indicated that the formation of the IL/O microemulsion with additional water also ended up in disordered state, and the formation process was entropy-driven.

**3.3. Structural Parameters of IL/O Microemulsions.** Different structural parameters $R_{IL}$, $R_e$, $l$ (i.e., $R_e - R_{IL}$), $N_d$ (total number of droplets), $\tilde{N}_s$ (average aggregation number of surfactant per droplet), and $\tilde{N}_a$ (average aggregation number of 1-butanol per droplet) with each droplet for the IL/O microemulsion systems with varied $R$ and $m_{IL}/m_{H_2O}$ at different temperatures, have been computed by using different equations which were provided in the Supporting Information. The results are presented in the Tables 5 and 6 and Figure 3.

The values of $R_{IL}$ were lower than those of $R_e$ in all of the cases. It was interesting to find that the $R_{IL}$ and $R_e$ decreased with $R$ increasing from Table 5, which was the opposite to the variety of traditional W/O microemulsions.[58,59] The values of $l$ also decreased with $R$ increasing. The interfacial layer was composed by Brij-35 and 1-butanol. Obviously, the increase in the amount of 1-butanol at the interfacial layer will reduce $l$ since the carbon chain length of 1-butanol is much shorter than that of Brij-35. The variation of $l$ was the opposite to the variation of $n_a^i$ listed in Table 1. A larger droplet size led to the total number of the droplets ($N_d$) decrease at a constant IL content, as shown in Table 5.

From Table 6, it can be see that the $R_{IL}$ and $R_e$ increased as the amount of addition of water increased. This result indicated that the addition of water expanded the droplet core. The total number of the droplets ($N_d$) decreased with additional water increasing. Comparing Tables 2 and 6, as the same variation described above, the greater number of 1-butanol molecules at the interfacial layer ($n_a^i$) with constant $m_{IL}/m_{H_2O}$, the thinner interfacial layers ($l$) were formed. The values of $\tilde{N}_s$ and $\tilde{N}_a$ increased as droplet size increased in all cases studied.

## 4. CONCLUSIONS

In the present study we first used the dilution method to investigate the interfacial composition, thermodynamic parameters, and structural parameters of the [bmim][BF$_4$] + Brij-35 + 1-butanol + toluene IL/O microemulsion. The dilution method for understanding the pseudoternary phase microemulsion has been found to be reasonable. The IL-based microemulsions have shown different advantages over the traditional ones in the preparation of nanostructures. For example, nanocrystals, polymer nanoparticles, gels, and open-cell porous materials can be produced by using IL-based microemulsions as a template. Especially the water containing IL microemulsion can be used as an ideal medium to prepare porous or hollow nanomaterials. Therefore, it is important to have knowledge of the effect of IL-based microemulsions on nanoparticle formation and the related formation mechanism. The fundamental knowledge of the interfacial composition, thermodynamic properties, and structural parameters of IL microemulsions is necessary and helpful to understand the final morphology, microstructure, and the formation mechanism. In view of the above, the effects of preparation, such as the [IL]/[Brij-35] mole ratio ($R$) and the mass ratio of IL to additional water ($m_{IL}/m_{H_2O}$), on the interfacial composition, thermodynamic parameters, and structural parameters of IL/O microemulsion were studied. All of the parameters varied according to different trends with $R$ and $m_{IL}/m_{H_2O}$. The following conclusions can be drawn from the study:

1. With the increase in $R$ (IL content increasing), more cosurfactants at the interface ($n_a^i$) were required for the formation of stable IL/O microemulsions. With the decrease in $m_{IL}/m_{H_2O}$ (water mass content increasing), the requirement of cosurfactants at the interface was gradually decreased.
2. The $\Delta G_t^\circ$ values of transfer of 1-butanol from the continuous oil phase to the interfacial region were all negative, which suggested that the IL/O microemulsions as well as aqueous microemulsions formed spontaneously. The absolute values of $\Delta G_t^\circ$ increased with the increase of $R$. The absolute values of $\Delta G_t^\circ$ increased with the increase of additional water. The results showed that the IL/O microemulsions with additional water formed more spontaneously just like the present of water enhanced the stability of IL/O microemulsion reported by Gao et al.[36]
3. The enthalpy changes of the process were mostly endothermic. The $\Delta S_t^\circ$ values were mostly positive which implied that the formation processes of [bmim][BF$_4$] + Brij-35 + 1-butanol + toluene IL/O microemulsions were entropy-driven processes.
4. With $R$ increasing, smaller IL droplets were obtained. The addition of water expanded the droplet core of the IL/O microemulsion. The increase of the number of cosurfactants at the interfacial layer was conducive to forming a small droplet IL/O microemulsion and thin interfacial layer ($l$).

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Basics of the dilution method and structural parameters of the microemulsion. This material is available free of charge via the Internet at http://pubs.acs.org.

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