

# Effect of Ionic Liquids on the Aggregation Behavior of PEO-PPO-PEO Block Copolymers in Aqueous Solution

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Effect of 1-butyl-3-methyl-imidazolium bromide (BmimBr) on the aggregation behavior of PEO-PPO-PEO Pluronic P104 aqueous solution was studied by Fourier transform infrared (FTIR) spectroscopy, freeze fracture transmission electron microscopy (FF-TEM), dynamic light scattering (DLS), and NMR spectroscopy. When the BmimBr concentration was below 1.232 mol/L, the critical micelle temperature (CMT) of Pluronic P104 remained constant, while the size of micelles increased with increasing the BmimBr concentration; above this concentration, the CMT of Pluronic P104 decreased abruptly, and bigger clusters of BmimBr were formed. The selective nuclear Overhauser effect (NOE) spectrum indicates that the PO block of the P104 interacts with the butyl group of the Bmim<sup>+</sup> cation by hydrophobic interaction. It suggests that when the concentration of BmimBr is below 1.232 mol/L, there are P104 micelles in the aqueous solution with BmimBr embedding to the micellar core, while above this concentration, P104 micelles and BmimBr clusters coexist in the system.

## 1. Introduction

Room-temperature ionic liquids (RTILs) are organic salts that are liquids at ambient temperature in their pure state. They have advantageous chemical and physical properties, such as negligible vapor pressure, low toxicity, low melt points, and high chemical and thermal stability, and these unique properties offer great potential for applications in organic synthesis,<sup>1–4</sup> separations,<sup>5–8</sup> electrochemistry,<sup>9,10</sup> and material preparation.<sup>11–15</sup>

Recent studies<sup>16,17</sup> have reported the self-assembly and the aggregation behavior of common anionic, cationic, and nonionic surfactants in RTILs; the interaction between RTILs and the hydrocarbon portion of the surfactants was also found. Wang<sup>18</sup> et al. studied the phase diagrams of two ionic liquids: hydrophobic 1-butyl-3-methylimidazolium hexafluorophosphate and relatively hydrophilic 1-butyl-3-methylimidazolium tetrafluoroborate in aqueous solutions of oleyl polyoxyethylene (10) ether (Brij 97). They found that the hexagonal liquid crystalline phases formed in aqueous solutions of Brij 97 by solubilizing hydrophobic RTIL bmim-PF<sub>6</sub> and hydrophilic RTIL Bmim-BF<sub>4</sub>. Reddy's group<sup>19</sup> investigated micelle formation of sodium dodecyl sulfate (SDS) in aqueous solutions of a variety of RTILs, indicating that the critical micelle concentration of SDS is correlated with the nature of the alkyl groups in the ILs. It can be deduced from previous reports that RTILs have effects on physicochemical properties of surfactant. The investigation on the effect of RTILs on the aggregation behavior of a surfactant could be helpful in enhancing the surfactant's properties and in widening its application in related industrial area.

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymers commercially available as Poloxamers or Pluronics, are high molecular weight nonionic surfactant. They have found widespread industrial

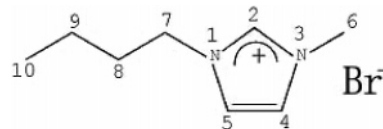


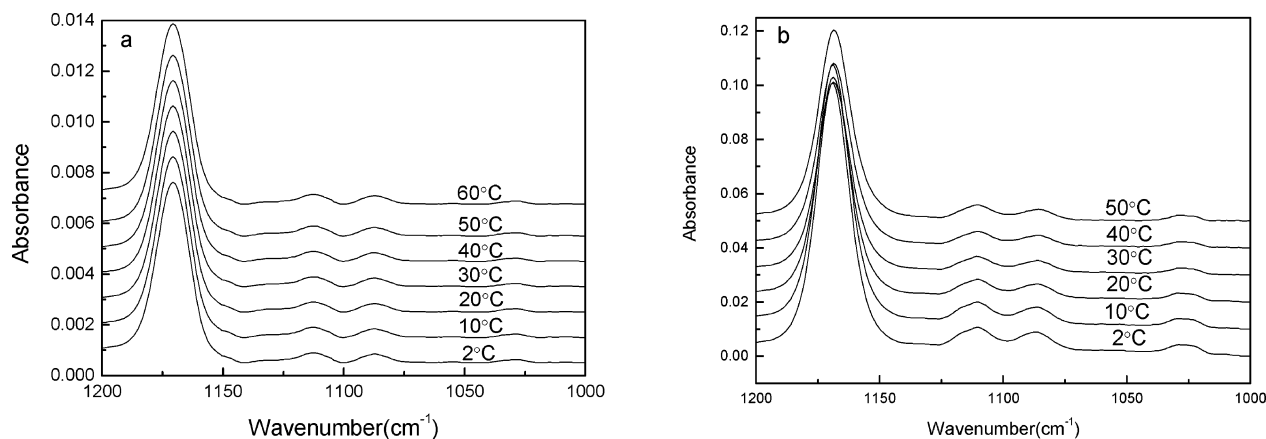
Figure 1. The structure sketch map of BmimBr.

applications in detergency, dispersion stabilization, foaming, emulsification, lubrication, separation, formulation of cosmetics and inks, drug delivery, etc. Most of the applications are related to the micelle that formed in aqueous solutions, thus micellization behavior of block copolymers has attracted much attention academically and practically. The interesting features of PEO-PPO-PEO block copolymers are their temperature-dependent self-association in aqueous solutions and their rich phase behavior. The process of self-association can be induced by increasing the block copolymer concentration to be above the critical micellization concentration and/or adjusting the temperature to exceed the critical micellization temperature.

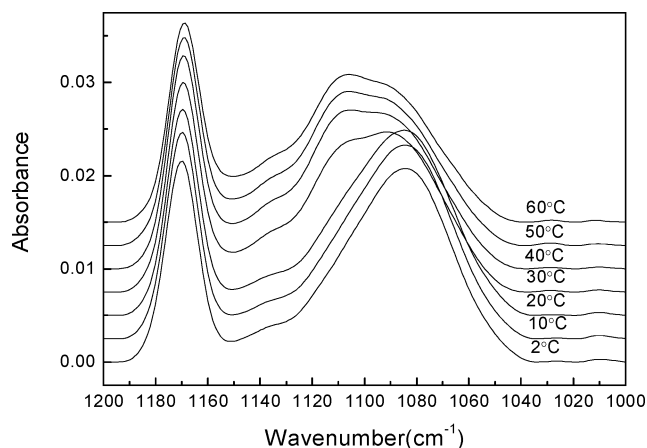
The addition of salts was found to have a strong effect on the cloud point and the critical micellization temperature of the PEO-PPO-PEO block copolymers; it was discussed in terms of "salting in" and "salting out" effect and followed the Hofmeister series.<sup>20</sup> The effect of various organic substances on the phase behavior of the PEO-PPO-PEO block copolymers was also investigated. The experimental investigations revealed that methanol, ethanol, and formamide prevent the onset of micellization for Poloxamer F87 in water, while butanol and hydrazine favor micelle formation.<sup>21</sup> The effect of medium-chain aliphatic alcohols enhance micellization for Pluronic 85 in water; the effect increases with the alcohol chain length in the C4–C6 series.<sup>22</sup>

RTILs have the inorganic anion and organic cation, and they might modify the micellization of the PEO-PPO-PEO block copolymers, as the polarities and the structure of the RTILs are easily changed. They may enrich the phase diagram of the PEO-

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**Figure 2.** Infrared spectra of (a) 0.308 mol/L BmimBr aqueous solution and (b) 3.08 mol/L BmimBr aqueous solution.



**Figure 3.** Infrared spectra of 5% P104 in BmimBr aqueous solutions (0.616 mol/L) in the range of 1200–1000  $\text{cm}^{-1}$  at different temperatures.

PPO-PEO block copolymers greatly, and thus improve the application of the block copolymers. However as far as our knowledge, there is no report to study the effect of ionic liquids on the phase behavior of PEO-PPO-PEO block copolymers.

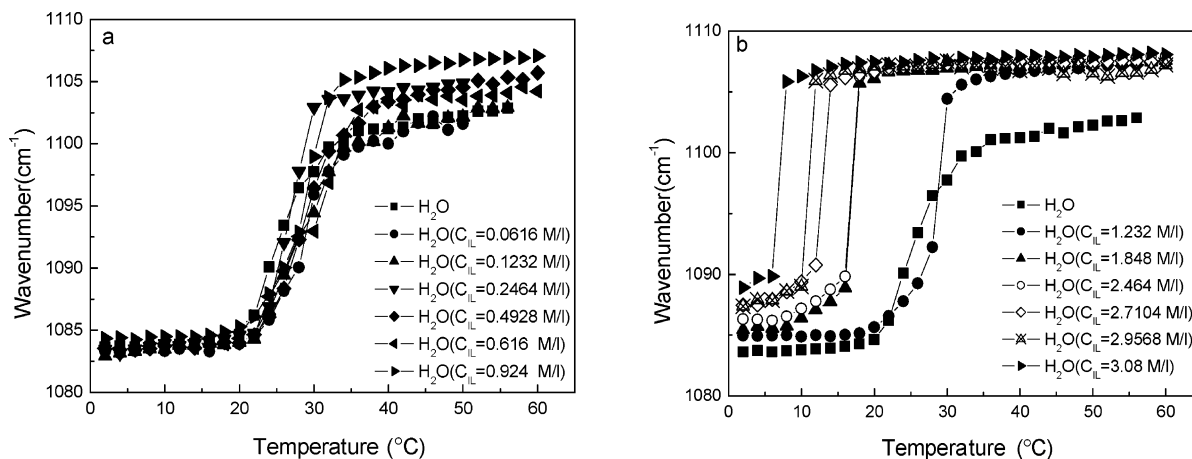
In this paper, the Fourier transform infrared spectroscopy (FTIR), freeze-fracture transmission electron microscopy (FF-TEM), dynamic light scattering (DLS), and NMR spectroscopy were used to study the effect of 1-butyl-3-methylimidazolium bromide on the aggregation behavior of Pluronic P104. The aim of this study was to find the interaction mechanism between ionic liquid and PEO-PPO-PEO block copolymer, so that we

could use ionic liquid to control the properties of the polymer micelle in various application fields.

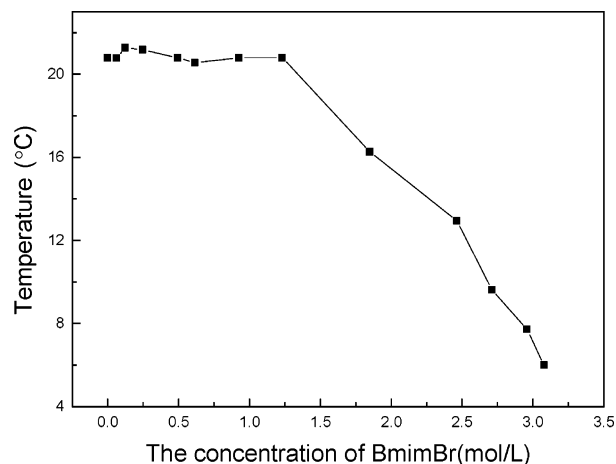
## 2. Experimental Section

**2.1. Materials.** PEO-PPO-PEO block copolymer Pluronic P104 was obtained from BASF Corp. and used without further purification. The polymer has a molecular weight of 5900 and a PEO content of 40%. On the basis of molecular weight and chemical composition, it can be represented by the formula  $\text{EO}_{27}\text{PO}_{61}\text{EO}_{27}$ . The ionic liquid, 1-butyl-3-methylimidazolium bromide, was synthesized according to a method previously described.<sup>23</sup> BmimBr structure is shown in Figure 1. A 10% (w/v) Pluronic P104 aqueous solution was prepared by dissolving an appropriate amount of the polymer in distilled water with gentle agitation and was stored in a refrigerator. A Pluronic P104/ionic liquid/water system was prepared by mixing 0.5 mL 10% P104 aqueous solutions and  $x$  mL ( $x < 0.5$ ) ionic liquids and adding distilled water to make a total volume of 1 mL.

**2.2. FTIR Spectroscopy.** FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with a resolution of  $2 \text{ cm}^{-1}$  using a DTGS (deuteriotriglycine sulfate) detector. The temperature of the sample was measured by a thermocouple inserted into a stainless steel block containing the sample cell. This system comprises a Graseby-Specac temperature cell (P/N 21525), and the temperature measurement is accurate to  $0.1^\circ\text{C}$ . FTIR spectra were recorded by scanning 64 times. The equilibration time for each measurement was 1 min. The polymer–ionic liquid–water mixtures were sandwiched between two  $\text{BaF}_2$  windows of an IR cell, and a spacer was also



**Figure 4.** Temperature dependence of frequency of C–O stretching band in infrared spectra of 5% Pluronic P104 aqueous solution with different concentrations of BmimBr.



**Figure 5.** The change of the CMT of P104 with the addition of BmimBr.

nipped to prevent evaporation during measurement. The samples were first cooled to 0 °C by liquid nitrogen and then heated stepwise with a 2 °C interval. The OPUS spectroscopic software was used for data handling.

**2.3. FF-TEM.** The specimens were plunged into ethane cooled by liquid nitrogen. The cryo-fixed samples were fractured at 153 K and  $10^{-4}$  Pa in a Balzer BAF 400D freeze-etching

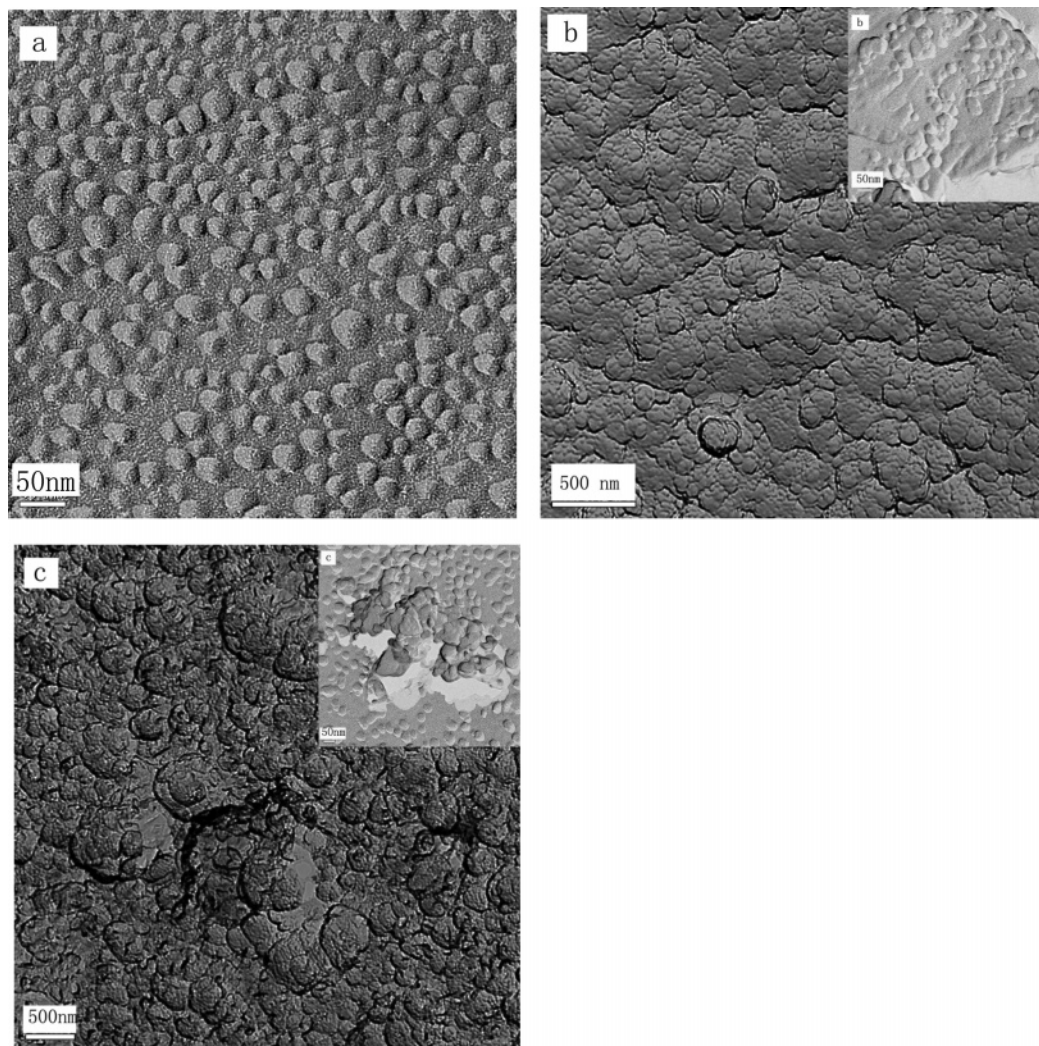
apparatus and shadowed by platinum/carbon at an angle of 45°. The replicas were cleaned to remove sample residuals and examined with a Philips Tecnai 20 and Jeal JEM-100cx electron microscope.

**2.4. NMR Spectroscopy.** The NMR spectrum were recorded at ambient temperature on a Bruker Advance 600 spectrometer at a Larmor frequency of 600.13 MHz for proton, equipped with a microprocessor-controlled gradient unit and an inverse-detection multinuclear BBI probe with an actively shielded z-gradient coil. Assignments of the various resonance signals were based on previous studies.<sup>24</sup> The selective nuclear Overhauser effect spectroscopy (NOESY) spectra were acquired by the method reported by Scott et al.<sup>25</sup> Chemical shifts ( $\delta$ ) are relative to external standard DSS ( $\delta = 0.000$  ppm in  $^1\text{H}$  NMR spectra for all concentrations and temperatures).

**2.5. Dynamic Light Scattering (DLS).** The mean diameter and polydispersity of Pluronic P104 aggregates were determined by the dynamic light scattering (DLS) method using a Brookhaven 90Plus nanoparticle size analyzer (Brookhaven Instruments Corp.) with a 15 mW solid-state laser at room temperature. All analyses were run in triplicate, and the results were reported as the average values.

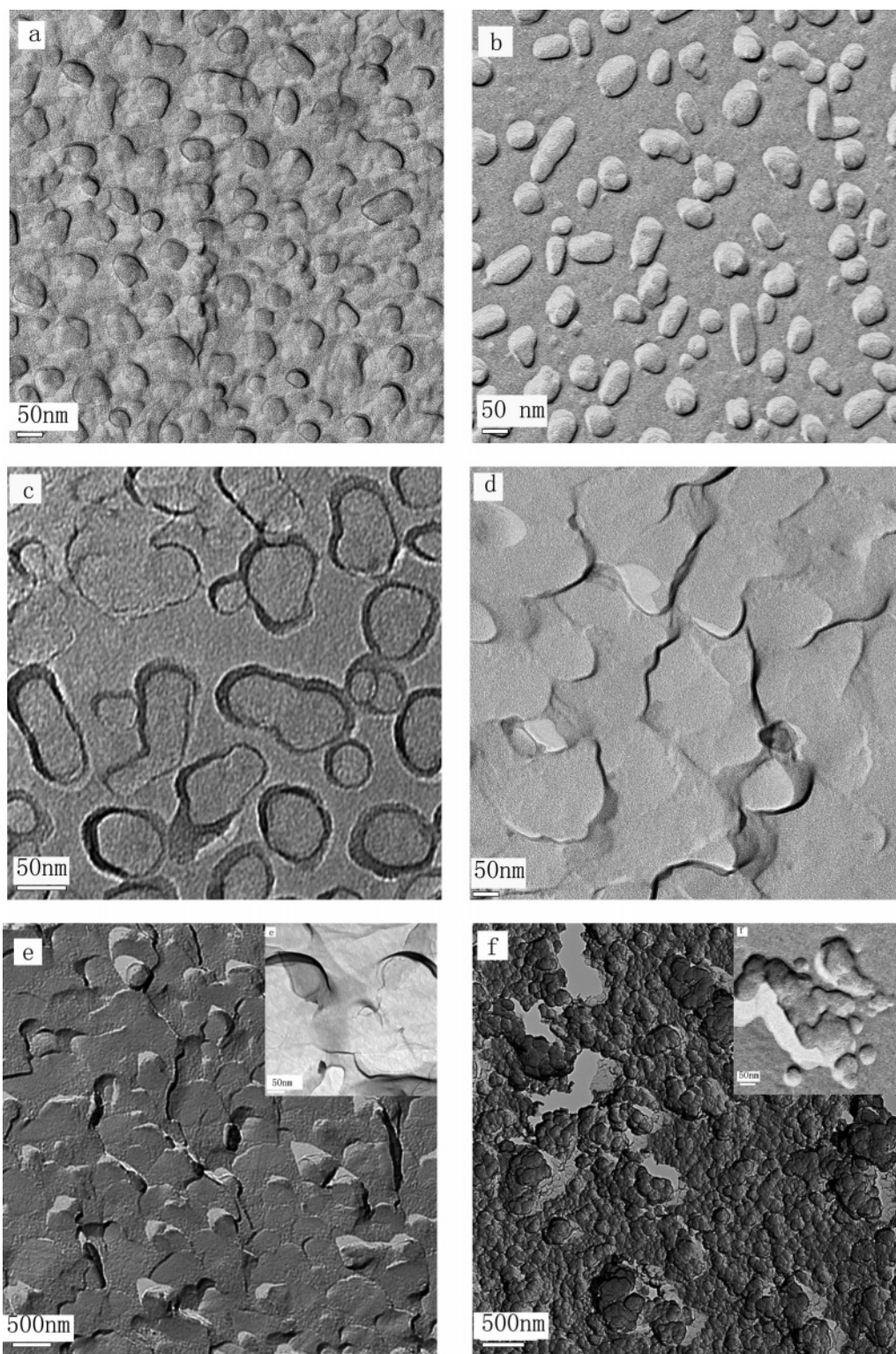
### 3. Results and Discussion

**3.1. Effect of BmimBr on Aggregation of Pluronic P104 by FTIR Spectroscopy.** Figure 2 shows the infrared spectra in



**Figure 6.** Freeze-fracture electron micrograph of (a) the 5 wt % Pluronic P104 aqueous solution, (b) 0.308 mol/L BmimBr aqueous solution, and (c) 3.08 mol/L BmimBr aqueous solution.





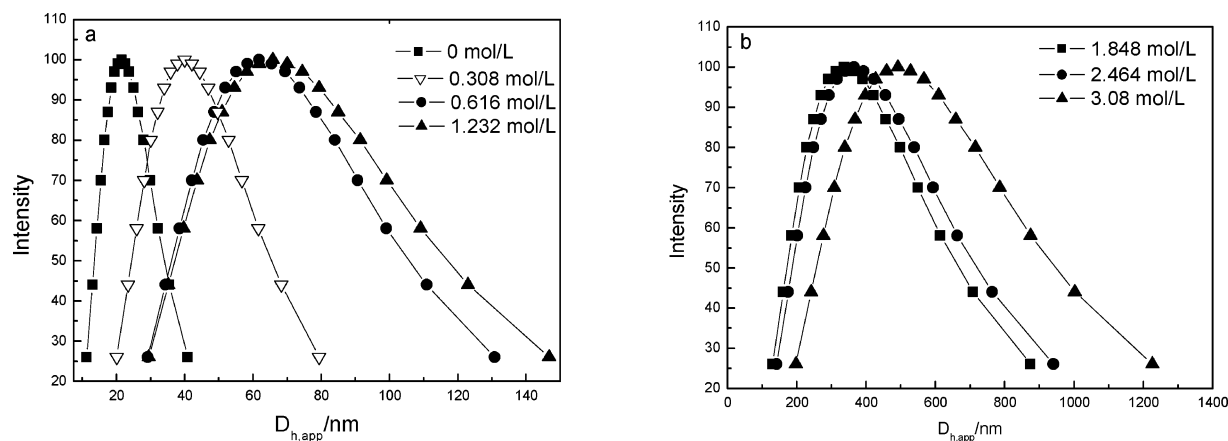
**Figure 7.** FF-TEM micrographs of Pluronic P104 and BmimBr in aqueous solution with the concentration of Pluronic P104 fixed at 5 wt % and the concentration of BmimBr at (a) 0.308 mol/L, (b) 0.616 mol/L, (c) 1.232 mol/L, (d) 1.848 mol/L, (e) 2.464 mol/L, and (f) 3.08 mol/L, respectively.

the range of  $1200\text{--}1000\text{ cm}^{-1}$  of the BmimBr aqueous solution of different concentrations at different temperatures. It is present in Figure 2 that there is a strong peak around  $1170\text{ cm}^{-1}$ . It is assigned to the in-plane CH deformation of the ring.<sup>26–28</sup> The shape and the position of the peak remain essentially constant in aqueous solutions of different IL concentrations with the increase of the temperature.

Figure 3 shows the FTIR spectra of 5% Pluronic P104 in BmimBr (0.616 mol/L) aqueous solution in the range of  $1200\text{--}$

$1000\text{ cm}^{-1}$ . The broad band around  $1080$  is assigned to the C–O–C stretching band of Pluronic P104.<sup>29,30</sup> It can be seen that the polymer band is distinct from the BmimBr band. The shape and the position of the peak associated with BmimBr does not change with the increase of its concentration or the temperature, while the C–O–C stretching band of Pluronic P104 shows distinct change as the temperature increases.

The wavenumber shift of the C–O–C stretching band of the Pluronic P104 with the increase of the temperature in various



**Figure 8.** Average hydrodynamic diameter and scattering intensity of Pluronic P104 and BmimBr in aqueous solution with the concentration of Pluronic P104 fixed at 5 wt %, and the concentration of BmimBr is between (a) 0~1.232 mol/L and (b) 1.848~3.08 mol/L.

ionic liquid concentrations is shown in Figure 4. The CMT (critical micellization temperature) values were obtained from the first inflection of the wavenumber versus the temperature sigmoidal curve. The change of the CMT of P104 with the addition of BmimBr is shown in Figure 5. It can be seen that the addition of a small amount of BmimBr to the Pluronic P104 aqueous solution has little effect on the CMT, but when the concentration of the BmimBr in the aqueous solution reaches to the 1.232 mol/L, the CMT of the Pluronic P104 aqueous solution decreases greatly. The values of the CMT decrease from 20 to 16 °C abruptly when the concentration of BmimBr is 1.848 mol/L.

Many researchers<sup>31–33</sup> have studied the effect mechanism of inorganic salt on the CMT of the PEO-PPO-PEO block copolymers. The inorganic salts decrease the CMT of the block copolymers continuously, which is related to the hydrated ions of the salts. But for the ionic liquids, as shown in Figure 4, they decrease the CMT of the PEO-PPO-PEO block copolymers discontinuously. It suggests that the organic part of the RTILs plays an important role in the interaction between RTILs and block copolymer.

**3.2. Effect of BmimBr on Aggregation of Pluronic P104 by FF-TEM and DLS Methods.** FF-TEM can yield direct imaging of the size, aggregates, and shape of the liquid sample. The FF-TEM micrographs of Pluronic P104 aqueous solution and BmimBr aqueous solutions are shown in Figure 6. Several features can be readily observed: (a) 5% Pluronic P104 forms micelles in aqueous solution and their diameter is about 20 nm. (b) 5% BmimBr forms loose clusters in water. (c) 50% BmimBr forms condensed clusters in water.

The FF-TEM micrographs of Pluronic P104 and BmimBr in aqueous solution with fixed polymer concentration (5 wt %) and different BmimBr concentrations are shown in Figure 7. It can be seen from the Figure 7 that a small amount of BmimBr has few effects on Pluronic P104 micelles. The size of Pluronic P104 micelles increases when increasing the BmimBr concentration. When the concentration of the BmimBr is above 1.232 mol/L, BmimBr clusters appear except for the polymer micelles, the diameter of the aggregates becomes bigger abruptly, and the granularity becomes less.

The size and distribution of the aggregates in the mixed system were further examined by DLS. Figure 8 shows the scattering intensity for the average hydrodynamic diameter ( $D_h$ ), measured at room temperature, of 5% Pluronic P104 in aqueous solution or different concentrations of BmimBr aqueous solutions. Pluronic P104 forms micelles in aqueous solution and in BmimBr aqueous solutions when the concentration of BmimBr

**TABLE 1: Mean Diameter of Pluronic P104 and BmimBr in Aqueous Solution with the Concentration of Pluronic P104 Fixed at 5 wt %, and the Concentration of BmimBr Is Different**

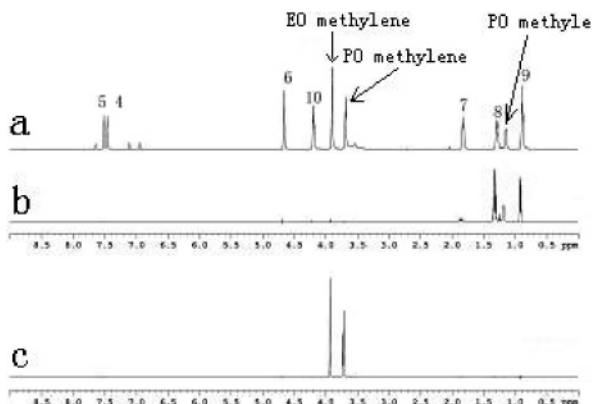
BmimBr concentration	effective diameter (nm)	polydispersity
0 mol/L	21.5	0.165
0.308 mol/L	40	0.191
0.616 mol/L	61.8	0.231
1.232 mol/L	65.8	0.268
1.848 mol/L	337.8	0.397
2.464 mol/L	366.1	0.390
3.08 mol/L	492.4	0.360

is below 1.232 mol/L, but the diameter of the micelle increases with the addition of BmimBr. While above this concentration it forms big aggregates. The polydispersity of micelles or aggregates, evaluated through the ratio  $\mu_2/\Gamma^2$  by cumulants analysis, where  $\mu_2$  is the second moment in the cumulants expansion of the correlation function and  $\Gamma$  is the decay rate, is shown in Table 1. It has been found that the mean diameter of micelles increased from 21 to 65 nm and the polydispersity of micelles increased from 0.165 to 0.268 when the concentration of BmimBr increased from 0 to 1.232 mol/L, while above this concentration, the mean diameter increased abruptly to 337.8 nm and polydispersity increased to 0.397.

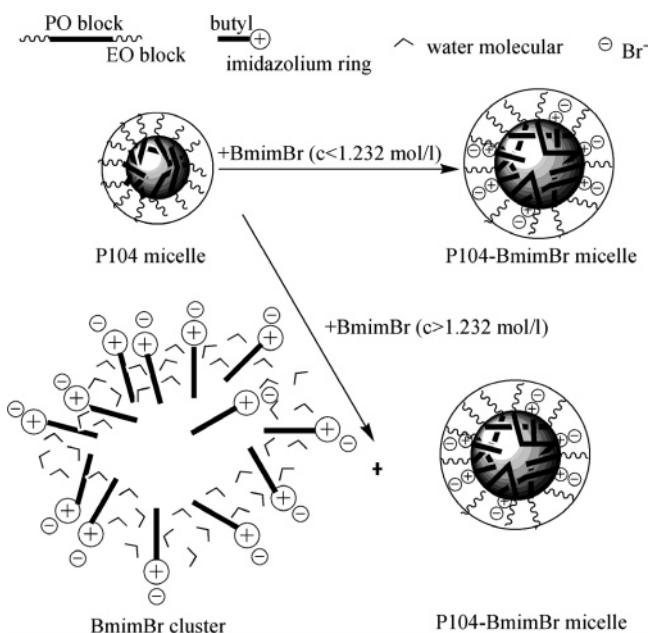
**3.3. Effect of BmimBr on Aggregation of Pluronic P104 by NMR.** The selective NOE NMR experiment was carried out to study the interaction between the Pluronic P104 and BmimBr in aqueous solution. The nuclear Overhauser effect (NOE) which is caused by cross-relaxation, is particularly useful for the study of weak interactions. The result is shown in Figure 9. Spectrum a is the normal  $^1\text{H}$  NMR spectrum of the mixtures of Pluronic P104 and BmimBr aqueous solution. Spectrum b was recorded when the selective pulse was on the PO methyl and that gives rise to strong NOE effects at H8 and H9 of the imidazolium cation. It suggests that there is interaction between the PO block and the butyl group of the imidazolium cation. Spectrum c was recorded when the selective pulse was on the EO methylene. Except for EO methylene peak, there's only PO methylene peak appearing in spectrum c. It is shown that there is no interaction between the EO block and ionic liquid. Pluronic P104 interacts with the BmimBr by the hydrophobic interaction between the PO block and the butyl group of the imidazolium group.

A schematic map to describe the effect of ionic liquid BmimBr on aggregation of Pluronic P104 is presented in Figure 10. In 5% Pluronic P104 aqueous solution at room temperature, Pluronic P104 forms micelles in water. When BmimBr is added





**Figure 9.** The normal  $^1\text{H}$  NMR spectrum and the selective NOE spectra of Pluronic P104 and BmimBr in aqueous solution. (The concentration of Pluronic P104 is 5% (wt/v), and the concentration of BmimBr is 1.848 mol/L.)



**Figure 10.** Schematic map of the different types of complexes formed when BmimBr was added to 5% Pluronic P104 aqueous solution.

to the P104 aqueous solution, the organic cations of the BmimBr are embedded in the micelle core through the hydrophobic interaction between the PO blocks and the butyl group of the Bmim<sup>+</sup>. With the increase of BmimBr concentration, more and more Bmim<sup>+</sup> are embedded in the aggregates, so that the Pluronic P104 micelles become bigger and bigger. As is reported<sup>34</sup> that RTILs are not likely to dissociate in its aqueous solution (except at infinite dilution), it can be deduced that the Bmim<sup>+</sup> is embedded into the Pluronic P104 micelle with Br<sup>-</sup> connected to it, so the addition of the ionic liquids has little effect on the bulk water, and thus the CMT of Pluronic P104 is almost not changed.

When the concentration of BmimBr reaches to 1.232 mol/L, the BmimBr molecules are saturated in the P104 micelle, and the residue BmimBr form clusters just as they do in their aqueous solutions.<sup>34</sup> The aggregates in the P104/BmimBr/water include the P104-BmimBr micelle and the BmimBr clusters, as shown in Figure 7 panels d–f. In such situations, the water molecules are easier to bind to the BmimBr clusters than to the P104 micelles, so the CMT of the P104 aqueous solutions decreased distinctly. As more BmimBr is added, more water

molecules are bonded to the Bmim<sup>+</sup> clusters, which leads to the decrease of the CMT of Pluronic P104.

#### 4. Conclusion

The effect of BmimBr on the aggregation behavior of Pluronic P104 in aqueous solution was studied by FTIR spectroscopy, FF-TEM, DLS, and NMR spectroscopy. It can be deduced from the FTIR spectra that the CMT of Pluronic P104 almost remains constant when the concentration of BmimBr is below 1.232 mol/L, while it decreases abruptly when the BmimBr concentration is above 1.232 mol/L.

The DLS results and FF-TEM micrographs showed that the size of the aggregate increased as the BmimBr concentration approaches toward 1.232 mol/L, and above this concentration, big BmimBr clusters formed in the solution.

The selective NOE spectrum indicates that the PO block of the Pluronic P104 interacts with the butyl group of the Bmim<sup>+</sup> cation by hydrophobic interaction. It can be deduced that BmimBr molecules are embedded to the P104 micelle by the hydrophobic interaction when little BmimBr is added to the P104 aqueous solution, and a BmimBr-P104 micelle is formed when the concentration of BmimBr is below 1.232 mol/L. As the bulk water in the solution is not effected the addition of the BmimBr, the CMT of P104 is almost not changed. While above this concentration, the residue BmimBr molecules form clusters which compete with the P104 micelle for water, so the CMT of P104 decreases greatly.

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#### References and Notes

- (1) Welton, T. *Chem. Rev.* **1999**, 99, 2071–2083.
- (2) Avery, T. D.; Jenkins, N. F.; Kimber, M. C.; Lupton, D. W.; Taylor, D. K. *Chem. Commun.* **2002**, 28–29.
- (3) Huddleston, J. G.; Willauer, H. D.; Swatoski, P. P.; Visser, A. E.; Rogers, R. D. *Chem. Commun.* **1998**, 1765–1766.
- (4) Smietana, M.; Mioskowski, C. *Org. Lett.* **2001**, 3, 1037–1039.
- (5) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, 39, 3772–3789.
- (6) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, 124, 14247–14254.
- (7) Chun, S.; Dzyuba, S. V.; Bartsch, R. A. *Anal. Chem.* **2001**, 73, 3737–3741.
- (8) Blanchard, L. A.; Brennecke, J. F. *Ind. Eng. Chem. Res.* **2001**, 40, 287–292.
- (9) Sun, I. W.; Hussey, C. L. *Inorg. Chem.* **1989**, 28, 2731–2737.
- (10) Masahiro, Y. F.; Douglas, R. M.; Patrick, C. K.; Maria, F. *Electrochem. Commun.* **2006**, 8, 445–449.
- (11) Kim, K.; Demberelnyamba, D.; Lee, H. *Langmuir* **2004**, 20, 556–560.
- (12) Zhou, Y.; Antonietti, M. *J. Am. Chem. Soc.* **2003**, 125, 14960–14961.
- (13) Taubert, A. *Angew. Chem., Int. Ed.* **2004**, 43, 5380–5382.
- (14) Brezesinski, T.; Erpen, C.; Iimura, K.; Smarsly, B. *Chem. Mater.* **2005**, 17, 1683–1690.
- (15) Scheeren, C. W.; Machado, G.; Dupont, J.; Fichtner, P. F. P.; Teixeira, S. R. *Inorg. Chem.* **2003**, 42, 4738–4742.
- (16) Anderson, J. L.; Pino, V.; Hagberg, E. C.; Sheares, V. V.; Armstrong, D. W. *Chem. Commun.* **2003**, 2444–2445.
- (17) Fletcher, K. A.; Pandey, S. *Langmuir* **2004**, 20, 33–36.
- (18) Wang, Z.; Liu, F.; Gao, Y.; Zhuang, W.; Xu, L.; Han, B.; Li, G.; Zhang, G. *Langmuir* **2005**, 21, 4931–4937.
- (19) Beyaz, A.; Oh, W. S.; Reddy, V. P. *Colloids Surf., B* **2004**, 35, 119–124.
- (20) Bahadur, P.; Pandya, K.; Almgren, M.; Li, P.; Stilbs, P. *Colloid Polym. Sci.* **1993**, 271, 657–667.

- (21) Armstrong, J.; Chowdhry, B.; Mitchell, J.; Beezer, A.; Leharne, S. *J. Phys. Chem.* **1996**, *100*, 1738–1745.
- (22) Caragheorgheopol, A.; Caldararu, H.; Dragutan, I.; Joela, H.; Brown, W. *Langmuir* **1997**, *13*, 6912–6921.
- (23) Huddleson, G. J.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. *Chem. Commun.* **1998**, 1765–1766.
- (24) Dupont, J.; Suarez, P. A. Z.; Souza, R. F. D.; Burrow, R. A.; Kingtzing, J. P. *Chem.—Eur. J.* **2000**, *6*, 2377–2381.
- (25) Scott, K.; Stonehouse, J.; Keeler, J.; Hwang, T. L.; Shaka, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4199–4200.
- (26) Saha, S.; Hayashi, S.; Kobayashi, A.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 740–741.
- (27) Shi, F.; Deng, Y. *Spectrochim. Acta, Part A* **2005**, *62*, 239–244.
- (28) Berg, R. W.; Deetlefs, M.; Seddon, K. R.; Shim, I.; Thompson, J. M. *J. Phys. Chem. B* **2005**, *109*, 19018–19025.
- (29) Guo, C.; Liu, H. Z.; Chen, J. Y. *Colloid. Polym. Sci.* **1999**, 277, 376–381.
- (30) Su, Y.; Liu, H. Z.; Wang, J.; Chen, J. Y. *Langmuir* **2002**, *18*, 865–871.
- (31) Alexandridis, P.; Holzwarth, J. F. *Langmuir* **1997**, *13*, 6074–6082.
- (32) Jain, N. J.; Aswal, V. K.; Goyal, P. S.; Bahadur, P. *Colloids Surf. A* **2000**, *173*, 8–94.
- (33) Aswal, V. K.; Goyal, P. S.; Kohlbrecher, J.; Bahadur, P. *Chem. Phys. Lett.* **2001**, *349*, 458.
- (34) Miki, K.; Westh, P.; Nishikawa, K.; Koga, Y. *J. Phys. Chem. B* **2005**, *109*, 9014–9019.