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SHORT COMMUNICATION

Effect of polyethylene glycol (PEG-400) on the 1-butyl-3-methylimidazolium tetrafluoroborate-in-cyclohexane ionic liquid microemulsion

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Abstract The effect of a common polymer, polyethylene glycol with molecular weight of 400 (PEG-400) on the microstructure of 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$)/Triton X-100/cyclohexane ionic liquid (IL) reverse microemulsion has been investigated. The addition of PEG-400 leaded to the linear increase of the microemulsion droplet size, in accordance with the observation of dispersed phase, showing that PEG-400 was only solubilized into the polar interior of the IL microemulsions. FTIR spectroscopic analysis indicated that the addition of PEG-400 decreased the electrostatic interaction between the oxygen atoms of OE units and the positive electrical charged imidazolium cation of $bmimBF_4$. At the same time, the oxygen atoms of PEG-400 can also interact with the imidazolium cation. These results suggested that small amounts of PEG-400 entered the palisade layers of the IL microemulsion. The conductivity of the IL reverse microemulsions was decreased owing to the dilution of conducting polar cores by the addition of insulative PEG-400, indicating that PEG-400 was only solubilized into the reverse IL microemulsion interior. The conclusion was further supported by viscosity measurement.

Keywords Microemulsion · Ionic liquid · Polyethylene glycol · Dynamic light scattering · Conductivity · Viscosity · FTIR spectroscopy

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Introduction

Ionic liquids (ILs) are attracting much attention as novel solvents for chemical reactions and separations [1, 2]. They have widely been regarded as 'green solvents' owing to their potential as a recyclable alternative to the traditional organic solvents [3, 4]. ILs are nonvolatile, thermally stable, nonflammable and have extremely high ionic conductivity. Moreover, their physicochemical properties can be modulated by changing one of anion and cation [5]. These properties of ILs also make them highly desirable in many reactions of industrial importance [6]. Recently, ILs have been used to substitute for water or organic solvents to create an IL based microemulsion. The investigations of ILs based microemulsions are of great interest, and may widen the practical applications of ILs.

Han and co-workers first discovered that 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$) acts as polar nanosized droplets dispersed in a continuous hydrocarbon solvent. Freeze-fracture electron microscopy (FFEM) indicated a droplet structure which takes the same shape as "classic" water-in-oil (W/O) microemulsions [7]. Their subsequent reports have also demonstrated that IL $bmimPF_6$ could be used as polar component to be solubilized in the continuous toluene [8]. Eastoe et al. have investigated the $bmimBF_4$/TX-100/cyclohexane microemulsion system by small-angle neutron scattering (SANS) [9]. In addition, the effects of confining the IL $bmimBF_4$ on solvation dynamics and rotational relaxation of Coumarin 153 in TX-100/cyclohexane microemulsions have been explored, using steady-state and picosecond time-resolved emission spectroscopy [10]. It has been reported that 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) can substitute for organic solvents to form a novelty microemulsion with the aid of surfactant TX-100 [11]. Electrochemical cyclic voltammetry method is followed to recognize the microregions of the IL microemulsion [12, 13]. The formation mechanism of the IL microemulsions has been proposed: the interaction between the electronegative oxygen atoms of the oxyethylene (OE) units of TX-100 and the electropositive imidazolium ring may be the driving force for the solubilization of $\mathrm{bmimBF_4}$ into the core of the TX-100 aggregates [14].

These IL microemulsions not only can overcome the solubility limitations of ILs in apolar solvents but also provide hydrophobic or hydrophilic nanodomains, thereby expanding potential uses of ILs in microheterogeneous systems as reaction and separation or extraction media [9]. A recent report has shown that surfactant ionic liquid-based microemulsions can be used to produce polymer nanoparticles, gels, and open-cell porous materials [15].

Herein, we investigated the effect of the polyethylene glycol with molecular weight of 400 (PEG-400) on the $\mathrm{bmimBF_4}$-in-cyclohexane (IL/O) microemulsion. To our knowledge, there have been scarce reports about the role of added polymers in IL microemulsions. The solubilization behavior of PEG-400 in the $\mathrm{bmimBF_4}$-in-cyclohexane microemulsions has been characterized by various techniques, including dynamic light scattering (DLS), FTIR spectra, conductivity, and viscosity measurements. The current study is helpful to understand the microstructure and formation mechanism of the IL microemulsions and thus to establish a better way of using it as a new medium.

Experimental section

Materials

PEG 400 and nonionic surfactant TX-100 were provided by Sigma-Aldrich. They were evaporated under vacuum at 80 °C for 2 h to remove excess water before use. Cyclohexane and d10-cyclohexane were purchased from Merck. $\mathrm{BmimBF_4}$ was synthesized according to the standard method by a quaternization reaction of 1-methylimidazole with 1-chlorobutane [16]. The imidazolium chloride salt was crystallized in ethyl acetate at −30 °C. The postmetathesis product was obtained by ion exchange of 1-butyl-3-methylimidazolium chloride and potassium tetrafluoroborate in distilled water and then washed with dichloromethane and dried under a high vacuum. The purity of the product was checked using ^{1}H NMR spectroscopy. $\mathrm{AgNO_3}$ solution was applied to check the remaining chloride. To avoid water, the containers with the materials were sealed tightly to avoid any further contact with air before use. The water contents of PEG 400 and $\mathrm{BmimBF_4}$ are 0.325% and 0.207%, respectively.

Apparatus and procedures

The diameters of the nonaqueous IL microemulsions were determined by dynamic light scattering (DLS, Brookhaven Instrument Co., BI-200SM goniometer and BI-9000AT correlator) with an argon-ion laser operating at 488 nm. All measurements were made at the scattering angle of 90° at a temperature of 25 °C. FTIR spectra were recorded in KBr pellets with 2-cm^{-1} resolution using a BIORAD FTS-165 spectrometer. The viscosities of samples were measured by a rheometer (HAAKE rheoStress RS75).

Sample preparation

$\mathrm{BmimBF_4}$-in-cyclohexane IL microemulsions were prepared by precise weight. The weight ratio of TX-100 and cyclohexane in the microemulsions is fixed at 11:9. The $\mathrm{bmimBF_4}$ present in the microemulsions is referred to the surfactant concentration, and expressed as the molar concentration ratio of $\mathrm{bmimBF_4}$and TX-100:

$$R = [\mathrm{bmimBF_4}]/[\mathrm{TX} - 100]$$

PEG-400 was added to the IL microemulsion and the mixtures were stirred until the dispersion became transparent. All samples used for characterizations were transparent and homogeneous.

Results and discussion

Phase behavior of the IL microemulsion

The phase behavior of $\mathrm{bmimBF_4}$/TX-100/cyclohexane ternary system at 25 °C is shown in Fig. 1. A single isotropic region extending from the IL corner to the cyclohexane corner is observed. The blank region marked "1Φ" is the one-phase microemulsion and the shadow region marked "2Φ" is a two-phase region, i.e. microemulsion in equilibrium with an excess cyclohexane or $\mathrm{bmimBF_4}$ phase. It is evident from Fig. 1 that a continuous stable single-phase microemulsion region always can be observed over the $\mathrm{bmimBF_4}$ or cyclohexane content range 0–100 wt.%. Three different microstructures: IL/O, bicontinuous, and O/IL microemulsions were recognized according to the previous reports [12, 13]. The investigated IL microemulsion system was chosen in the IL/O microemulsion region and the microemulsion composition is also marked in Fig. 1.

Dynamic light scattering

Dynamic light scattering (DLS) is a powerful technique to characterize the structural changes of microemulsions.

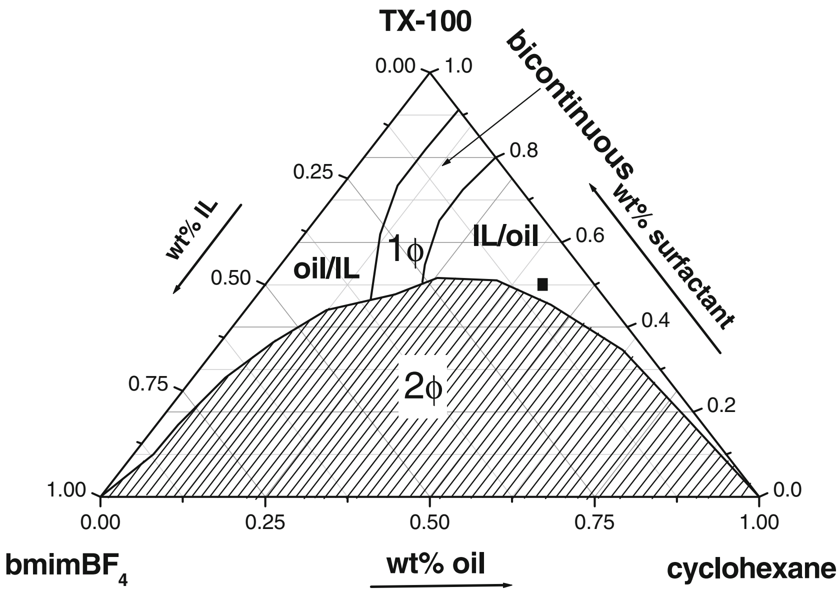

Fig. 1 Phase diagram of the mixture $bmimBF_4$/Triton X-100/cyclohexane at 25 °C, the studied microemulsion composition is marked with a *filled square*; 49.9 wt.% Triton X-100, 40.8 wt.% cyclohexane, and 9.3 wt.% $bmimBF_4$, i.e. [$bmimBF_4$]/[Triton X-100] molar ration, R=0.53

Therefore, it can provide some useful information about the effect of additive on the structure of microemulsions [17–19]. Han et al. have studied the solubilization behavior of $bmimBF_4$ in the $bmimBF_4$-in-cyclohexane IL microemulsion [7]. It has shown that the diameter of the IL microemulsion droplet increased with increasing $bmimBF_4$ content. The swelling behavior of the microemulsion droplet, in terms of the dependence of ellipsoid volume V on [$bmimBF_4$]/[TX-100] mole ratio R, is consistent with the volume of dispersed nanodomains being directly proportional to the amount of added IL, which is common to many droplet microemulsions [20]. Figure 2 shows the size and size distribution of the $bmimBF_4$-in-cyclohexane microemulsion with R=0.53, at the different amount of added PEG-400. It is obvious that the diameter of the IL microemulsion droplet increased with the added PEG-400. Figure 3 shows that the diameter of the IL microemulsion droplet is directly proportional to the amount of added PEG-400. The swelling behavior is similar with that of solubilized $bmimBF_4$ in the $bmimBF_4$-in-cyclohexane microemulsion [7]. By considering that PEG-400 has a very limited solubility in cyclohexane, it is thus deduced that the added PEG-400 may be only solubilized into the polar interior of the $bmimBF_4$-in-cyclohexane microemulsion. Therefore, PEG-400 seems to act as a dispersed phase to be solubilized into the cores of the IL microemulsion. Nevertheless, the role of PEG-400 is actually much different from that of $bmimBF_4$. It has been reported that TX-100 does not form dried reverse micelles in toluene or benzene [21, 22], whereas the addition of $bmimBF_4$ would eventually lead to the formation of large-sized microemulsion aggregations. The electrostatic attraction between the electropositive imidazolium cation of $bmimBF_4$ ($bmim^+$) and electronegative oxygen atoms of ethylene (OE) units of TX-100 is considered to be the driving force of solubilizing $bmimBF_4$ into the TX-100 aggregates [14]. Besides, hydrogen bond interaction between C2-H of $bmim^+$ and ethoxy or terminal hydroxyl of TX-100; between BF_4^- and H^- of the terminal hydroxyl may be contribute to the formation of IL microemulsion. The possible contribution of dipole-induced dipole type of interaction between TX-100 phenyl π-cloud and $bmim^+$ can not also be excluded. It is, thus obvious, that the addition of $bmimBF_4$ induced the formation of these IL microemulsions. The induced formed IL microemulsion is

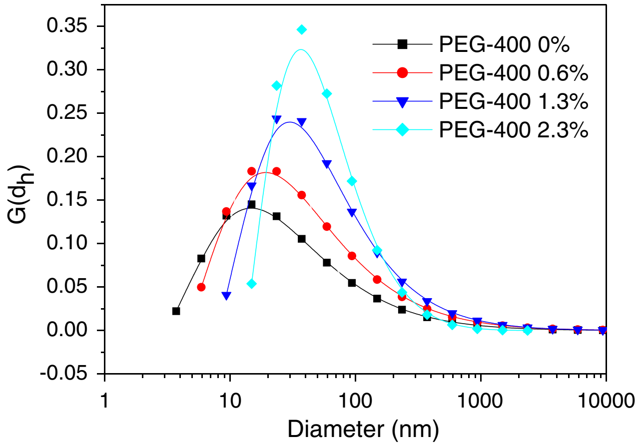

Fig. 2 Variation of the size and size distribution of the $bmimBF_4$-in-cyclohexane IL microemulsion with the added PEG-400

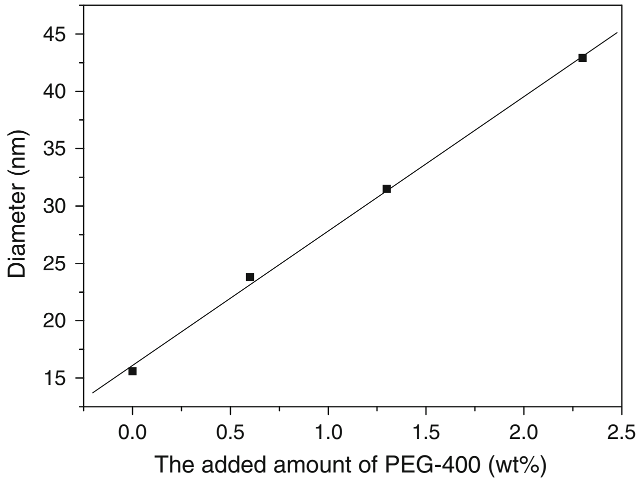

Fig. 3 The diameters of the bmimBF$_4$-in-cyclohexane IL microemulsion as a function of the added PEG-400

relative with the special structure and properties of both bmimBF$_4$ and TX-100. Our current experiment also revealed that the IL microemulsion would be destroyed when small amounts of PEG-400 were added to the bmimBF$_4$-in-cyclohexane microemulsion that is close to the boundary of two-phase region. The result suggests that PEG-400 destroyed the microemulsion stability, which is different from the role of water in the bmimBF$_4$-in-benzene microemulsion [23, 24]. In that case, the added water molecules bridged a hydrogen-binding network of water-cation; water-anion of bmimBF$_4$; water-OE units of TX-100 and water–water interaction. Such hydrogen-binding network is stronger than the electrostatic attraction of electropositive bmim$^+$ and electronegative oxygen atoms of OE units of TX-100 and, thus, enhanced the stability of the IL microemulsion [24].

In addition, we can see that the size distribution of the bmimBF$_4$-in-cyclohexane microemulsion did not change remarkably with the addition of PEG-400, which means that the droplet structure of the IL microemulsion was not changed. The effect of polymers on the traditional microemulsions has been widely reported. For some amphiphilic block polymers, the addition of the polymers can lead to the appearance of large-sized microemulsion clusters. These polymer molecules embed into the interior of the reverse microemulsion droplet with the hydrophilic parts of the polymer and connected some microemulsion droplets [24]. For the currently studied PEG-400, it has been mentioned above that it is highly immiscible with cyclohexane, but miscible with bmimBF$_4$ and TX-100. Therefore, it is not possible to bridge the microemulsion droplets into microemulsion clusters like amphiphilic block polymers. High single distribution of the IL microemulsion droplets further indicates that PEG-400 molecules are only solubilized into the polar interior of the IL microemulsion.

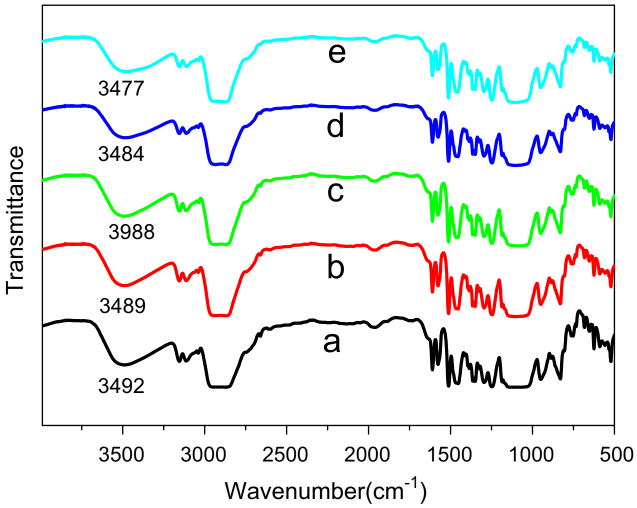

Fig. 4 FTIR spectroscopy of the bmimBF$_4$-in-cyclohexane IL microemulsion as a function of the added PEG-400 content. **a** 0%, **b** 0.3%, **c** 0.6%, **d** 1.3%, **e** 2.3% of the IL microemulsion

FTIR spectroscopic analysis

To further delineate the actual locations of PEG-400 molecules in the bmimBF$_4$-in-cyclohexane microemulsion, it is necessary to study the states and state change of every composition in the IL microemulsion by FTIR technique. Figure 4 shows the variation of FTIR spectroscopy of the bmimBF$_4$-in-cyclohexane microemulsion with the added PEG-400 to the system. Evidently, the characteristic absorbance of bmimBF$_4$ and TX-100 was not changed remarkably with increasing PEG-400 content except the band of terminal OH-stretching vibration of TX-100. It is obvious that the OH-stretching vibration of TX-100 appeared at 3,492 cm^{-1} in the absence of PEG-400, whereas gradually shifted to a low-frequency region,

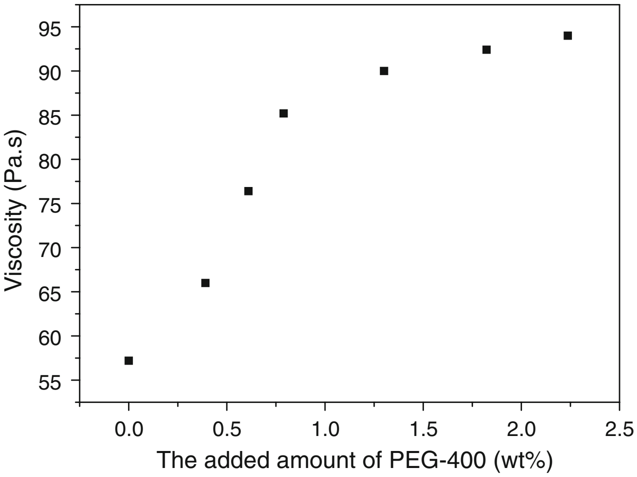

Fig. 5 Apparent viscosities of bmimBF$_4$-in-cyclohexane microemulsion with R=0.53 containing different amount of PEG-400 at 25 °C

3,477 cm^{-1} with successively increasing the amount of added PEG-400. It is known that the terminal hydroxyl of TX-100 hydrogen bonded with the oxygen atoms of OE units or terminal hydroxyl groups of other TX-100 molecules. After adding bmimBF$_4$, the positive electrical charged imidazolium cation of bmimBF$_4$ can electrostatically attract the electronegative oxygen atoms of OE units. As a consequence, the hydrogen bond interaction was weakened, which resulted in the OH-stretch band appearing in a high-frequency region of IR spectrum [25]. However, the electrostatic attraction would weaken when PEG-400 was added to the IL microemulsion. The reason is that the oxygen atoms of PEG-400 can also electrostatically attract the electropositive imidazolium cation of bmimBF$_4$. Such a comparison will lead to the decrease of electrostatic interaction between the oxygen atoms of OE units and positive electrical charged imidazolium cation. As a result, OH-stretch band will move to a low-frequency region of IR spectrum. Besides, the addition of PEG-400 can increase the hydrogen bonding between the oxygen atoms and terminal hydroxyl of PEG-400, which also attributes to the low-frequency shift.

From the result of FTIR spectra, we can see that the addition of PEG-400 leads to the decrease of electrostatic interaction between the oxygen atoms of OE units and positive electrical charged imidazolium cation. The electrostatic interaction has been considered as the driving force of solubilizing bmimBF$_4$ into the TX-100 aggregates. Accordingly, the addition of PEG-400 would cause the bmimBF$_4$-in-cyclohexane microemulsion unstable, which is also in good agreement with our experimental observation. By consideration that the addition of PEG-400 weakened the electrostatic attraction between the oxygen atoms of OE units and positive electrical charged imidazolium cation and at the same time the oxygen atoms of PEG-400 interacted with the imidazolium cation of bmimBF$_4$, we can judge that small amounts of bmimBF$_4$ molecules entered the palisade layers of the IL microemulsions.

Viscosity

Figure 5 shows the apparent viscosities of bmimBF$_4$-in-cyclohexane microemulsion with R=0.53 containing different amount of PEG-400 at 25 °C. The viscosity of the microemulsions increased when PEG-400 was added. However, the magnitude of increase is relatively smaller compared with the previous report, where an amphiphilic graft copolymer dramatically increased the viscosity of microemulsion by 2,000 times; the addition of graft polymer leads to the formation of large polymer-droplet aggregations [17]. The hydrophilic side chains of graft polymer inset the interface film of surfactant at the oil/water interface and thus polymer molecules link the microemulsion droplets. In the current study, especially considering that PEG-400 is highly immiscible with cyclohexane, we further argue that the added PEG-400 is only solubilized into the bmimBF$_4$ polar cores. The increase of viscosity is only due to the increase of microemulsion droplet size. The solubilization of another polymer, polyvinylpyrrolidone (PVP) in the microstructure of bmimBF$_4$/TX-100/cyclohexane microemulsions has been very recently investigated and a similar result was also obtained [26].

Conclusion

The current results presented in this study show that the polyethylene glycol (PEG-400) has effects on the bmimBF$_4$-in-cyclohexane IL microemulsions. With increasing of PEG-400 content, the IL microemulsions showed a regular swelling behavior with the dispersed phase. The results indicated that PEG-400 was solubilized into the polar interior of the bmimBF$_4$-in-cyclohexane IL microemulsions. As a result, the stability of the IL microemulsion was decreased. Moreover, it can be deduced that the oxygen atoms of PEG-400 interacted with the imidazolium cation of bmimBF$_4$, showing that small amounts of bmimBF$_4$ molecules entered the palisade layers of the IL microemulsions.

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References

1. Mehnert CP, Cook RA, Dispenziere NC, Afeworki M (2002) J Am Chem Soc, 124:12932
2. Gao YA, Li ZH, Du JM, Han BX, Li GZ, Hou WG, Shen D, Zheng LQ, Zhang GY (2005) Chem Eur J 11:5875
3. Seth D, Chakraborty A, Setua P, Sarkar N (2006) Langmuir 22:7768
4. He Y, Li Z, Simone P, Lodge TP (2006) J Am Chem Soc 128:2745
5. Patrascu C, Gauffre F, Nallet F, Bordes R, Oberdisse J, de Lauth-Viguerie N, Mingotaud C (2006) Chem Phys Chem 7:99
6. Wang Z, Liu F, Gao Y, Zhuang W, Xu L, Han B, Li G, Zhang G (2005) Langmuir 21:4931
7. Gao HX, Li JC, Han BX, Chen WN, Zhang JL, Zhang R, Yan DD (2004) Phys Chem Chem Phys 2914.
8. Li JC, Zhang JL, Gao HX, Han BX, Gao L (2005) Colloid Polym Sci 283:1371
9. Eastoe J, Gold S, Rogers SE, Paul A, Welton T, Heenan RK, Grillo I (2005) J Am Chem Soc 127:7302
10. Chakrabarty D, Seth D, Chakraborty A, Sarkar N (2005) J Phys Chem B 109:5753

11. Gao YA, Han SB, Han BX, Li GZ, Shen D, Li ZH, Du JM, Hou WG, Zhang GY (2005) Langmuir 21:5681
12. Gao YA, Li N, Zheng LQ, Zhao XY, Zhang SH, Han BX, Hou WG, Li GZ (2006) Green Chem 8:43
13. Gao YA, Wang SQ, Zheng LQ, Han SB, Zhang X, Lu DM, Yu L, Ji YQ, Zhang GYJ (2006) Colloid Interface Sci 301:612
14. Gao YA, Zhang J, Xu HY, Zhao XY, Zheng LQ, Li XW, Yu L (2006) Chem Phys Chem 7:1554
15. Yan F, Texter J (2006) Chem Commun 2696.
16. Dupont J, Consorti CS, Suarez PAZ, Souza RF (1999) Organic Syntheses 79:236
17. Laia CAT, Brown W, Almgren M, Costa SMB (2000) Langmuir 16:465
18. Michel E, Filali M, Aznar R, Porte G, Appell J (2000) Langmuir 16:8702
19. Gonzalez-Blanco C, Velazquez MM, Ortega F (1997) Langmuir 13:6095
20. Nave S, Eastoe J, Heenan RK, Steytler D, Grillo I (2000) Langmuir 16:8741
21. Almgren M, van Stam J, Swarup S, Lofroth JE (1986) Langmuir 2:432
22. Zhu DM, Schelly ZA (1992) Langmuir 8:48
23. Gao YA, Li N, Zheng LQ, Bai XT, Yu L, Zhao XY, Zhang J, Zhao MW, Li Z (2007) J Phys Chem B 111:2506
24. Holmberg A, Piculell L, Nyden M (2002) J Phys Chem B 106:2533
25. Zhou N, Li Q, Wu J, Chen J, Weng S, Xu G (2001) Langmuir 17:4505
26. Gao YA, Voigt A, Hilfert L, Sundmacher K (2008) Colloid Surface A 329:146