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Aggregation Behavior of Surfactants in Ionic Liquids

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Introduction

Room-temperature ionic liquids (RTILs) are a new class of organic solvents that are stable over a large range of temperatures and have negligible vapor pressures. Surfactant organization in RTILs has opened new research directions towards micellar catalysis into ILs, salvation enhancement for apolar entities and lyotropic properties. Recently, microemulsions have been obtained in IL-oil mixtures and only premicellar aggregation has been detected in pure ILs [1-3]. However, no clear demonstration of the existence of a micellar phase in ILs has been reported yet. In this study we have investigated the behavior of a series of nonionic surfactants in various ILs based on the 1-alkyl-3-methylimidazolium cation with various counter anions by means of SAXS measurements.

Experimental

Samples were prepared by mixing stock solutions of 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$) (or 1-butyl-3-methylimidazolium hexafluorophosphate ($BMImPF_6$)) and nonionic solid surfactant, Brij 35 or Brij700, at various weight ratios. For example, in the case of $EMImBF_4$/Brij 35 binary system, 0.6 g (or 1.2 g) of Brij 35 was added to 1 mL of $EMImBF_4$. After each addition of surfactant, the sample was mixed thoroughly and allowed to equilibrate for 60 min. The SAXS measurements were performed at 40°C at BL-6A or 15A. The scattering data was detected by a CCD camera with an X-ray image intensifier or PILATUS 100K.

Results and Discussion

Fig. 1 shows the SAXS profiles of the $EMImBF_4$/Brij 35 and $BMImPF_6$/Brij 35 binary system with various weight ratios. The SAXS profiles presented in Fig. 1(a) indicate a lamellar structure in $EMImBF_4$/Brij 35, and the repeat distance of the lamellar structure, d, can be obtained as 18.0 nm from the scattering factor corresponding to 1st scattering peak, q_1, according to the relation $d=2\pi/q_1$. In the case of $EMImBF_4$/Brij 700, the repeat distance of d is ca. 23.0 nm, implying that the length of alkyl chains and EO units of the surfactant strongly reflects the repeat distance. On the other hand, only the broad scattering peak (centered around 1.2-1.3 nm^{-1}) from micellar aggregates can be detected in $BMImPF_6$/Brij 35, as shown in Fig. 1(b). This might suggest that the interaction between alkyl chain of ILs and EO units of surfactant in the palisade layer correlates with the phase behavior of surfactant aggregations in ILs. The anion effect (BF_4^-, PF_6^-) on the phase behavior is also examined for better understanding of the interactions inside the ILs/surfactant binary systems.

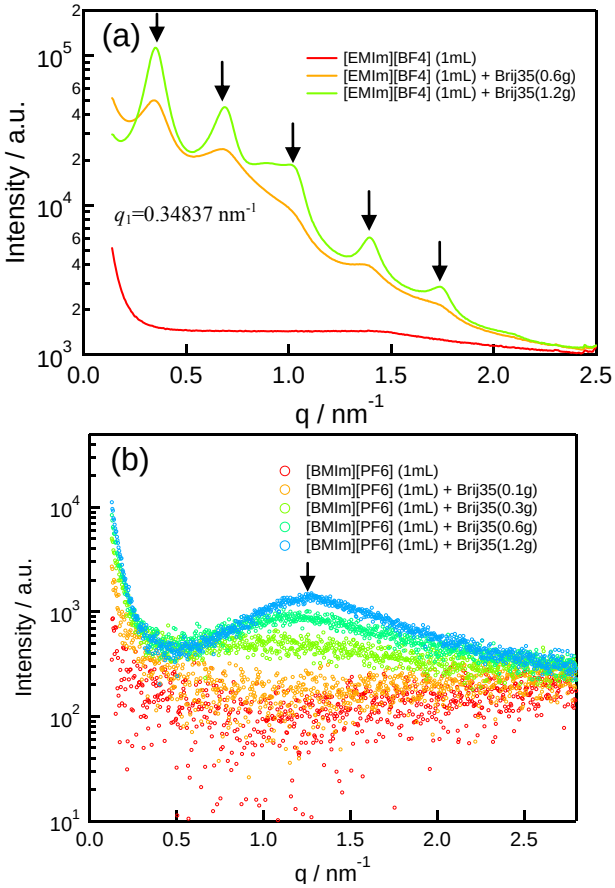

Fig. 1. SAXS profiles of the binary system with various weight ratios for (a) $EMImBF_4$/Brij 35 and (b) $BMImPF_6$/Brij 35.

References

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