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Aggregation Behavior of Surfactants in Ionic Liquids

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Introduction

Micellar aggregations of surfactants in ionic liquids (ILs) have been intensively studied recently [1-3]. For example, Li et al. [1] reported the aggregate formation of fluorinated cationic surfactants in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($BMImTf_2N$) and analyzed this aggregate formation thermodynamically. However, few reports have described the existence of a micellar aggregate in ILs. In this study we have systematically investigated the micelle behavior of a series of nonionic surfactants in various ILs based on the 1-alkyl-3-methylimidazolium cation by means of SAXS measurements.

Experiment

Samples were prepared by mixing stock solutions of 1-alkyl-3-methylimidazolium tetrafluoroborate ($C_n$minBF$_4$, n = 2, 4, 8) and nonionic surfactant (Brij 30, Brij 52, Brij 56, Brij 58, Brij 35, Brij 700) at fixed weight ratio. For example, in the case of C_4minBF$_4$/Brij 35 binary system, 1.2 g of Brij 35 was added to 1 mL of C_4minBF$_4$. After each addition of surfactant, the sample was mixed thoroughly and allowed to equilibrate for 60 min. The SAXS measurements were performed at 35°C at BL-6A. The scattering data was detected by a PILATUS 300K.

Results and Discussion

Fig. 1 shows the SAXS profiles of the C_4minBF$_4$ and C_8minBF$_4$ binary system consisted of various nonionic surfactants. A broad scattering peak from micellar aggregates is observed, and the shift in peak position (q_{max}) to lower q angle is found with the increase of EO units of surfactant in the case of C_4minBF$_4$/Brij systems. As shown in Table 1, the repeat distance, d, can be obtained from the scattering peak, q_{max}, according to the relation $d=2\pi/q_{max}$. On the other hand, in the case of C_8minBF$_4$/Brij systems, the repeat distance d does not monotonically increase with the increase of EO units, implying that the length of alkyl chains of ILs and EO units of the surfactant strongly reflects the repeat distance. 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 detailed analysis is in progress.

Table 1. Repeat distance calculated from the scattering peak.

Sample	C_2minBF$_4$		C_4minBF$_4$		C_8minBF$_4$	
	q_{max}	d / nm	q_{max}	d / nm	q_{max}	d / nm
Brij30	-	-	-	-	2.13	2.9
Brij52	-	-	-	-	1.71	3.7
Brij56	-	-	1.048	6.0	1.67	3.7
Brij58	0.939	6.7	1.092	5.8	1.64	3.8
Brij35	0.866	7.3	1.160	5.4	2.21	2.8
Brij700	0.562	11.2	0.743	8.5	2.81	2.2

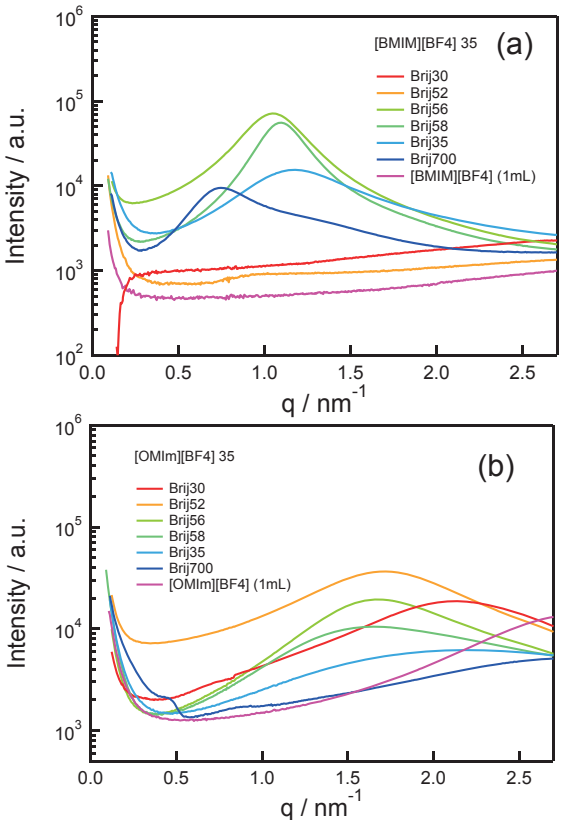

Fig. 1. SAXS profiles of the binary system for (a) C_4minBF$_4$/Brij and (b) C_8minBF$_4$/Brij.

References

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