

Supporting Information

The First Evidence for Unilamellar Vesicle Formation of Ionic Liquids in Aqueous Solutions

Huiyong Wang,[†] Lamei Zhang,[†] Jianji Wang^{*†}, Zhiyong Li[†] and Suojiang Zhang[‡]

1. The materials and methods

1-methylimidazole (99%) was from Shanghai Chem. Co.; 1-bromodecane (99%) 1-bromododecane (99%), and 1-bromotetradecane (99%) were purchased from Alfa Aeser. 6-methoxy-*N*-(3-sulfopropyl)quinolinium were from Fluka Chem. Co. and used without further purification.

Surface tensions of aqueous ILs solutions were measured with a DCA 315 tensiometer (Cahn Instruments) using a platinum plate ($20 \times 15 \times 0.127 \text{ mm}^3$) at 25.0 °C and different solution pH Values. The platinum plate was rinsed with water and ethanol, and finally flame cleaned in an alcohol burner to eliminate any contaminants before every measurement. The temperature around the sample cell was controlled by circulating water from a HAAKE DC30-K20 temperature thermostat (Thermo Electron, Germany), and the temperature was maintained to be within $\pm 0.1^\circ\text{C}$. For each sample, at least three independent sets of immersion detachment cycles were measured, which allowed the determination of an average surface tension value. The tensiometer was calibrated with double distilled water according to the method provided by the manufacturer, and the uncertainty of the surface tension measurements was estimated to be about $\pm 0.1 \text{ mJ m}^{-2}$.

The dynamic light scattering (DLS) measurements were carried out using a laser light scattering photometer (Nano-ZS90, Malvern, U. K). Light of $\lambda = 633 \text{ nm}$ from a solid-state He-Ne laser (4.0mW) was used as the incident beam. All sample solutions were filtered through a $0.22\mu\text{m}$ hydrophilic PVDF membrane filter. All measurements were made at 25.0°C and at 90° scattering angle. At least three measurements were

^{*} To whom correspondence should be addressed: E-mail: Jwang@henannu.edu.cn

taken for each solution, and the reproducibility of aggregate sizes from DLS data was found to be within $\pm 3\%$.

Negative Stain Transmission electron microscopy (TEM) was used to investigate the aggregates morphology of the ILs in aqueous solutions. A carbon Formvar-coated copper grid (200 mesh) was laid on one drop of the sample solution for 5 min. The excess liquid was removed by filter paper. After the grid partly dried, the copper grid was put onto one drop of uranyl acetate solution (1%) as the staining agent. The excess liquid was removed by filter paper. After being dried, the samples were imaged under a Philip Tecnai 20 microscope operating at 200 keV.

For cryo-TEM, a small amount (3–5 μl) of sample solution was deposited on the surface of a TEM copper grid covered by a holey carbon film. After the excess of solution was blotted away to form a thin liquid film, the grid was immediately plunged into liquid ethane cooled by liquid nitrogen (-175°C). The specimens were maintained at approximately -173°C and imaged in a transmission electron microscope (JEOL JEM1400) at an accelerating voltage of 200 kV under low dose conditions.

Steady-state fluorescence measurements were carried out with a Cary Eclipse fluorophotometer (Varian, America). Both excitation and emission band slits were fixed at 5 nm. The excitation wavelength was selected at 346 nm, while the emission wavelength was at 443 nm. The measurements were conducted at $25 \pm 1^\circ\text{C}$. All the data were acquired using the quartz cells with 1 cm path length.

2. The preparation and characterization of the ILs

The ionic liquids $[\text{C}_n\text{mim}]\text{Br}$ ($n=10, 12, 14$) were prepared and purified by using the procedure previously described in the literature.¹ Briefly, the reactions of 1-methylimidazole with excess 1-bromoalkane were performed in 1,1,1-trichloroethane under reflux at ca. 70°C for 48 h. $[\text{C}_{10}\text{mim}]\text{Br}$ were washed with 1,1,1-trichloroethane. The products $[\text{C}_{12}\text{mim}]\text{Br}$ and $[\text{C}_{14}\text{mim}]\text{Br}$ were recrystallized three times from ethyl acetate and ethyl acetate/acetonitrile (3:2 by volume), respectively, to remove any unreacted reagents. The residual solvents were

removed by heating at 70 °C under vacuum. Chemical structure of the ILs was confirmed by ¹H NMR spectroscopy (Bruker, AV-400), purity of the ILs was found to be greater than 99%.

3. The *P* parameters calculated from surface tension of aqueous ILs solutions

P parameter is defined by the following equation:

$$P=V/AL \quad (1)$$

where *V* is the volume of surfactant tail, *L* is the tail length, and *A* is surface area of the hydrophilic head unit at the hydrophobic-hydrophilic interface. The values of parameters *V* and *L* in eq. (1) at 25 °C can be obtained by the following equations, respectively:²

$$V = (27.4 + 26.9n_c) \times 10^{-3} \text{ nm}^3 \quad (2)$$

$$L = (0.15 + 0.1265n_c) \text{ nm} \quad (3)$$

In these equations, *n_c* is the carbon number of the alkyl chain in the imidazolium cation. The values of parameter *A* can be estimated from the Gibbs adsorption isotherm:

$$A = 1/(\Gamma_m N_A) \quad (4)$$

$$\Gamma_m = -(1/RT) \times (\partial\gamma/\partial \ln C)_T \quad (5)$$

where Γ_m is the maximum excess surface concentration, N_A is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), *R* is the gas constant (8.314 J/(mol K)), *T* is the absolute temperature, *C* is the surfactant concentration in bulk solution and γ is the surface tension of the solutions. The calculated Γ_m , *A* and *P* values at 25 °C are listed in Table S1.

Table S1 The values of the maximum excess surface concentration (Γ_{max}), *A* and molecular packing parameter *P* at 25 °C.

IL	Inflection point	Γ_{max} ($10^6 \text{ mol} \cdot \text{m}^{-2}$)	<i>A</i> (nm ²)	<i>P</i>
[C ₁₀ mim]Br	First	1.72	0.965	0.217
	Second	2.46	0.674	0.311
	Third	4.11	0.404	0.518
[C ₁₂ mim]Br	First	1.91	0.869	0.241
	Second	3.26	0.510	0.411
	Third	4.66	0.347	0.589
[C ₁₄ mim]Br	First	1.96	0.847	0.248
	Second	3.82	0.506	0.484
	Third	4.72	0.352	0.598

4. Size distribution for the aggregates of [C₁₂mim]Br with the IL concentration in aqueous solutions

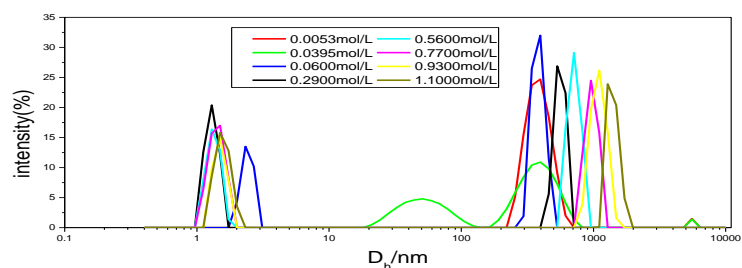


Figure S1. The size distribution for the aggregates of [C₁₂mim]Br in aqueous solutions with the IL concentrations observed by DLS.

In this figure, the peaks with diameter of 1 to 2 nm are pseudomorph to the theory of dynamic light scattering.³ The broad signal at about 50 nm observed at the concentration of 0.0395 mol/L may be resulted from the different sizes of the micelles presented in this solution.

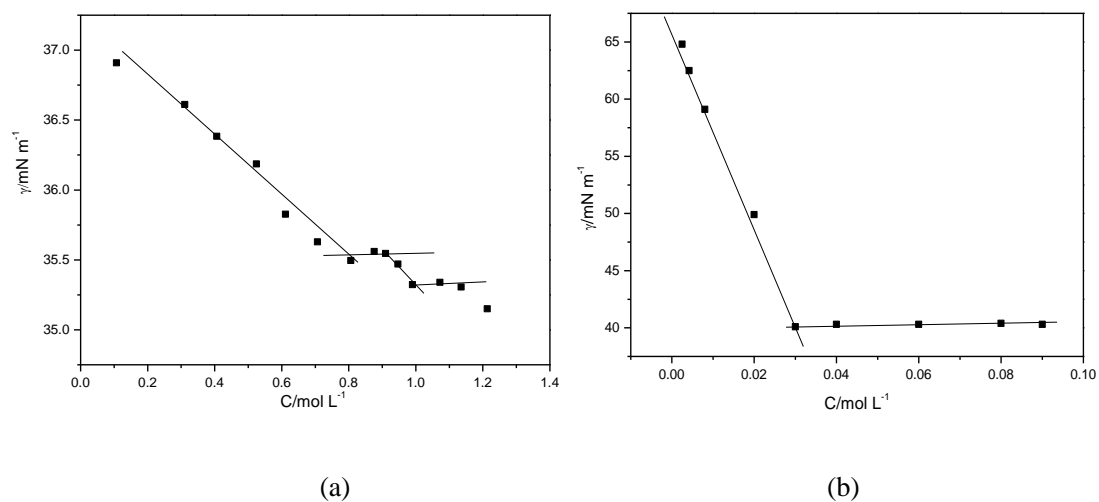


Figure S3. Plots of the surface tension of [C₁₀mim]Br in water as a function of the IL concentration at 25 °C: (a) high concentration; (b), low concentration.

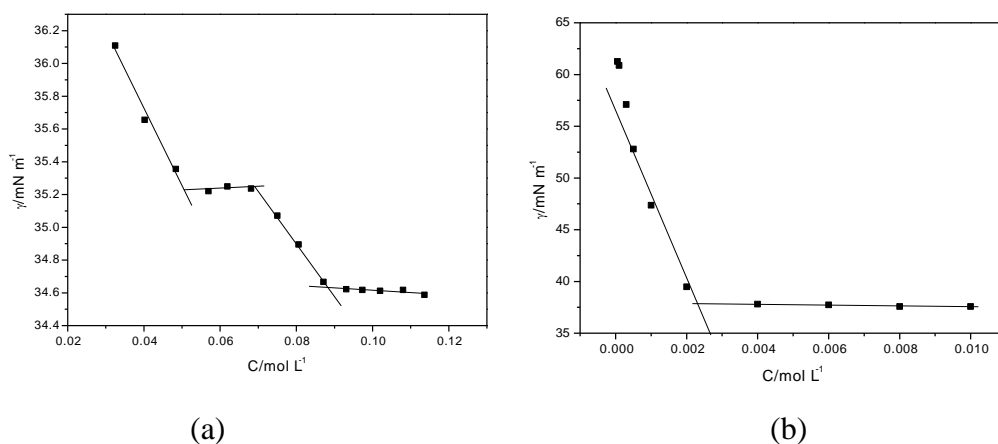


Figure S4. Plots of the surface tension of $[C_{14}mim]Br$ in water as a function of the IL concentration at 25 °C: (a), high concentration; (b), low concentration.

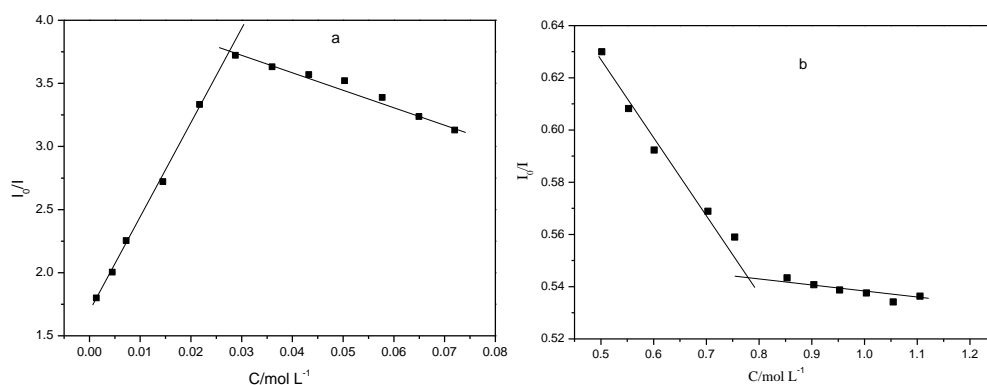


Figure S5. Stern-Volmer plots of SPQ fluorescence quenching by bromide ions at 298.15K: a, low concentration of $[C_{10}mim]Br$; b, high concentration of $[C_{10}mim]Br$.

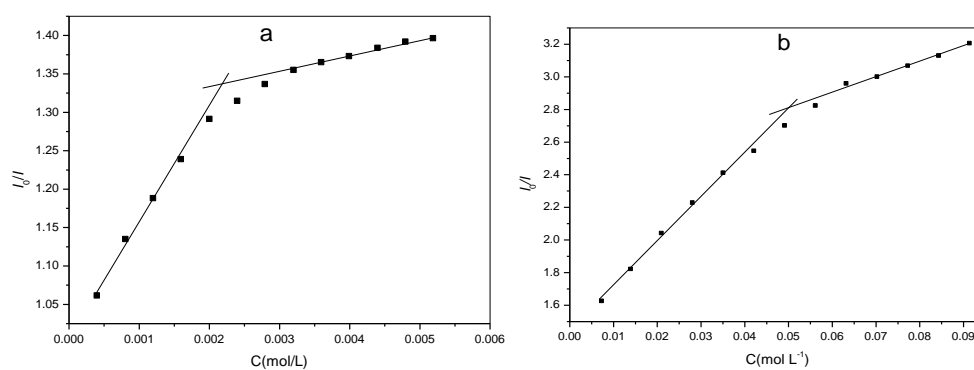


Figure S6. Stern-Volmer plots of SPQ fluorescence quenching by bromide ions at 298.15K: a, low concentration of $[C_{14}mim]Br$; b, high concentration of $[C_{14}mim]Br$.

[C₁₄mim]Br.

Reference

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