Self-Aggregation Behavior of Fluorescent Carbazole-Tailed Imidazolium Ionic Liquids in Aqueous Solutions

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Three amphiphilic imidazolium ionic liquids (ILs), 1-[n-(N-carbazole)alkyl]-3-methylimidazolium bromide [carbazole C_n mim]Br (n = 6, 10, and 12), that incorporate a fluorescent carbazole moiety at the terminal of the hydrocarbon chain, were designed and synthesized. Their surface activity, aggregation behavior, and thermodynamics of micelle formation in aqueous solutions were systematically investigated by surface tension, electrical conductivity, and ¹H NMR spectroscopy. The incorporation of bulky carbazole groups led to the loose arrangement of [carbazole C_n mim]Br molecules at the air—water interface. Both the enhanced hydrophobicity and the $\pi - \pi$ interaction due to the incorporation of carbazole groups contributed to the lower critical micelle concentration (cmc) and higher micellar aggregation number, reflecting a strong capability of the designed carbazole-tailed imidazolium ILs for the formation of micelle. The analysis of ¹H NMR spectra revealed that the carbazole moieties may overlap with the middle methylenes of the alkyl chains. The amphiphilic carbazole-tailed imidazolium ILs demonstrated strong and stable fluorescence properties, indicating their potential application in the combined field of surface chemistry and photochemistry.

Introduction

Ionic liquids (ILs), a class of organic molten electrolytes at or near ambient temperature, are the focus of many scientific investigations due to their extraordinary physicochemical properties.^{1,2} They are environmentally benign derived from their low volatility and nonflammability. Numerous 1,3-dialkylimidazolium ILs containing various anions such as PF6-, CH₃COO⁻, CF₃COO⁻, CF₃SO₃⁻, and (CF₃SO₂)₂N⁻ have been synthesized, which are currently receiving a great deal of attention as novel media in organic synthesis, in catalysis, and in preparation of nanostructured materials.³ The physicochemical properties of the ILs can be tailored by changing the N-alkyl substituents. For example, a series of hydrophobic task-specific ILs designed to extract Hg²⁺ and Cd²⁺ from water were prepared by appending urea-, thiourea-, and thioether-substituted alkyl groups to the imidazole ring.^{4,5} A new room temperature ionic liquid incorporating an appended amine group was found to reversibly sequester CO₂.⁶ Many attempts have been made to explore functional ILs through the incorporation of additional functional substituents, which impart particular capabilities to the ILs for separation of specific metal ions, construction of ion conductive materials, etc.³

Recently, 1-alkyl-3-methylimidazolium ILs with a long-chain substituent have attracted much attention and many reports are concentrated on the micelle formation of them as amphiphiles.^{7–23} Aqueous solutions of 1-alkyl-3-methylimidazolium halides $[C_n mim]X$ (X = Cl, Br, I) with different hydrocarbon chain lengths were intensively explored using a variety of methods.^{11,14–19}

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The critical micelle concentrations (cmc's) of $[C_n mim]Br$ were found to be smaller than those of $[C_n mim]Cl$ bearing the same hydrophobic chain length owing to the weaker hydration of Br^{-.11,14} Bowers et al. proposed that the C₈mimI molecules formed regularly near-spherical micelles in aqueous solutions through the analysis of small-angle neutron scattering data.¹⁹ Wang and co-workers reported the effect of various anions (Cl⁻, Br⁻, NO₃⁻, ClO₄⁻, CH₃COO⁻, CF₃COO⁻, CF₃SO₃⁻) on the selfaggregation behavior of a series of 1-octyl-3-methylimidazolium ILs.²⁰ As a more suitable candidate in green chemistry, the selfaggregation behavior of a halogen-free IL 1-butyl-3-methylimidazolium octylsulfate [C4mim]C8SO4 was deeply examined.²¹⁻²³ Apart from the alteration of the straight-chain length, few investigations were about the incorporation of a new moiety in the hydrocarbon chain. Firestone and co-workers described the self-aggregation of thiophene-tailed imidazolium ILs in aqueous solutions.²⁴ Due to the tether of a thiophene moiety at the terminal of the hydrocarbon chain, this ionic liquid is electroactive and its oxidative polymerization yields water-soluble cationic polythiophene. Sirieix-Plénet et al. synthesized a longchain imidazolium IL containing ferrocene as a redox-active group and evaluated the amphiphilic and electrochemical properties of both reduced and oxidized forms.²⁵

Carbazole and its derivatives usually exhibit high thermal, and photochemical stability and the carbazole groups easily form relatively stable radical cations. A wide variety of substituents are easy to graft on the carbazole ring. Consequently, carbazolebased oligomers and polymers are attractive because of their unique electrochemical and optical properties.^{26,27} Because of the advantages of carbazole derivatives, three long-chain carbazole-tailed imidazolium ILs, 1-[*n*-(*N*-carbazole)alkyl]-3-methylimidazolium bromide [carbazoleC_nmim]Br (n = 6, 10, and 12), that incorporate a carbazole group at the terminal of the hydrocarbon chain, were designed and synthesized in this work.

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SCHEME 1: Synthesis of Carbazole-Tailed Imidazolium ILs



The self-aggregation and thermodynamics of micelle formation for these amphiphilic carbazole-tailed imidazolium ILs in aqueous solutions were systematically investigated. The strong and stable fluorescence properties of these amphiphilic carbazole-tailed imidazolium ILs were demonstrated due to the incorporation of functional carbazole groups.

Experimental Section

Materials. Carbazole, 1,6-dibromohexane, 1,10-dibromodecane, 1,12-dibromododecane, and 1-methylimidazole were purchased from Acros Organics. Potassium carbonate, dimethylformamide (DMF), dichloromethane, anhydrous magnesium sulfate, ethyl acetate, diethyl ether, acetonitrile, and petroleum ether are analytical grade reagents and were obtained from Tianjin Kermel Chemicals Co., Ltd. D_2O and CDCl₃ were purchased from Sigma-Aldrich. All chemicals were used without further purification. Triply distilled water was used throughout the whole experiments.

Synthesis of Carbazole-Tailed Imidazolium ILs. ILs [carbazoleC_nmim]Br (n = 6, 10, 12) were synthesized according to Scheme 1, and the products were characterized by ¹H NMR, mass spectrometry (MS), and differential scanning calorimetry (DSC).

N-(6-Bromohexyl)carbazole (1).²⁸ A mixture of carbazole (10.0 g, 0.06 mol), 1,6-dibromohexane (14.6 g, 0.06 mol), and K₂CO₃ (24.9 g, 0.18 mol) in DMF (20 mL) was stirred at room temperature overnight. Then, the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over anhydrous MgSO₄. After evaporation of the solvent, the resulting residue was purified by chromatography with petroleum ether as an eluent. This afforded the pure N-(6-bromohexyl)carbazole (1) as a colorless crystal (yield, 35%). ¹H NMR (CDCl₃, δ /ppm relative to TMS): 1.36-1.51 (m, 4H, alkyl protons), 1.77-1.93 (m, 4H, alkyl protons), 3.36 (t, 2H, -CH₂Br), 4.31 (t, 2H, -NCH₂-), 7.23 (t, 2H, aromatic protons), 7.40 (d, 2H, aromatic protons), 7.46 (t, 2H, aromatic protons), 8.10 (d, 2H, aromatic protons). N-(10-Bromodecyl)carbazole (2) and N-(12-bromododecyl)carbazole (3) were synthesized using the same procedure as described for compound 1.

N-(10-Bromodecyl)carbazole (2). Yield: 34%. ¹H NMR (CDCl₃, δ /ppm relative to TMS): 1.24-1.39 (m, 12H, alkyl protons), 1.78-1.91 (m, 4H, alkyl protons), 3.39 (t, 2H, $-CH_2Br$), 4.30 (t, 2H, $-NCH_2-$), 7.23 (t, 2H, aromatic protons), 7.40 (d, 2H, aromatic protons), 7.47 (t, 2H, aromatic protons), 8.11 (d, 2H, aromatic protons).

N-(12-Bromododecyl)carbazole (3). Yield: 30%. ¹H NMR (CDCl₃, δ/ppm relative to TMS): 1.24–1.42 (m, 16H, alkyl protons), 1.81–1.91 (m, 4H, alkyl protons), 3.40 (t, 2H, –CH₂Br), 4.30 (t, 2H, –NCH₂–), 7.23 (t, 2H, aromatic

protons), 7.41 (d, 2H, aromatic protons), 7.47 (t, 2H, aromatic protons), 8.11 (d, 2H, aromatic protons).

1-[6-(N-Carbazole)hexyl]-3-methylimidazolium Bromide (4). ²⁹ A mixture of compound 1 (10.0 g, 0.03 mol) and 1-methylimidazole (14.8 g, 0.18 mol) in acetonitrile (200 mL) was refluxed at 75-80 °C for 48 h under nitrogen purge. After evaporation of the solvent, the crude product was washed three times with warm ethyl acetate and then three times with diethyl ether to provide 1-[6-(N-carbazole)hexyl]-3-methylimidazolium bromide (4) as a brownish solid (yield, 92%; mp, 59 °C). ¹H NMR (CDCl₃, δ /ppm relative to TMS): 1.26–1.37 (m, 4H, alkyl protons), 1.75-1.86 (m, 4H, alkyl protons), 3.99 (s, 3H, -NCH₃), 4.16 (t, 2H, -NCH₂-, adjacent to the carbazole ring), 4.30 (t, 2H, -NCH₂-, adjacent to the imidazole ring), 7.22 (t, 2H, carbazole protons), 7.27 (d, 2H, carbazole protons), 7.39 (d, 2H, carbazole protons), 7.46 (t, 2H, carbazole protons), 8.07-8.09 (d, 2H, imidazole protons), 10.32 (s, 1H, imidazole protons). MS (m/z): calcd, 412; found, 332 (M-Br). 1-[10-(N-Carbazole)decyl]-3-methylimidazolium bromide (5) and 1-[12-(N-carbazole)dodecyl]-3-methylimidazolium bromide (6) were synthesized using the same procedure as that for compound 4.

1-[10-(N-Carbazole)decyl]-3-methylimidazolium Bromide (5). Yield: 92%; mp, 47 °C. ¹H NMR (CDCl₃, δ /ppm relative to TMS): 1.22–1.30 (m, 12H, alkyl protons), 1.84–1.88 (m, 4H, alkyl protons), 4.09 (s, 3H, –NCH₃), 4.28 (t, 2H, –NCH₂–, adjacent to the carbazole ring), 4.31 (t, 2H, –NCH₂–, adjacent to the imidazole ring), 7.22 (t, 2H, carbazole protons), 7.26 (d, 2H, carbazole protons), 7.41 (d, 2H, carbazole protons), 7.45 (t, 2H, carbazole protons), 8.09–8.11 (d, 2H, imidazole protons), 10.81 (s, 1H, imidazole protons). MS (*m*/*z*): calcd, 468; found, 388 (M–Br).

1-[12-(*N*-Carbazole)dodecyl]-3-methylimidazolium Bromide (6). Yield: 92%; mp, 40 °C. ¹H NMR (CDCl₃, δ /ppm relative to TMS): 1.21–1.37 (m, 16H, alkyl protons), 1.82–1.90 (m, 4H, alkyl protons), 4.10 (s, 3H, –NCH₃), 4.27 (t, 2H, –NCH₂–, adjacent to the carbazole ring), 4.30 (t, 2H, –NCH₂–, adjacent to the imidazole ring), 7.21 (t, 2H, carbazole protons), 7.29 (d, 2H, carbazole protons), 7.40 (d, 2H, carbazole protons), 7.47 (t, 2H, carbazole protons), 8.09–8.11 (d, 2H, imidazole protons), 10.54 (s, 1H, imidazole protons). MS (*m*/ z): calcd, 496; found, 416 (M–Br).

Methods. Surface tension measurements were carried out by a surface tensiometer (model JYW-200B, Chengde Dahua Instrument Co., Ltd., accuracy ± 0.01 mN/m). The surface tension was determined with a single-measurement method. All measurements were repeated at least twice. A low-frequency conductivity analyzer (model DDS-307, Shanghai Precision & Scientific Instrument Co., Ltd., accuracy $\pm 1\%$) was used to measure the electrical conductivity of the aqueous solutions. ¹H NMR spectra were recorded on a Bruker Avance 400



Figure 1. Surface tension as a function of concentration for $[carbazoleC_6mim]Br (\blacksquare)$, $[carbazoleC_{10}mim]Br (●)$, and $[carbazoleC_{12}mim]Br (▲)$ in aqueous solutions at 25 °C.

spectrometer equipped with a pulse field gradient module (*Z* axis) using a 5 mm BBO probe. ¹H NMR spectra were run at 400.13 MHz, and the chemical shifts were referred to 4,4-dimethyl 4-silapenfane sodium sulfonate (DSS) as the external standard. The standard 2D NOESY pulse sequence was used in the 2D NOESY experiments with a mixing time of 800 ms. All of the samples were dissolved in D₂O. The fluorescence excitation and emission spectra were carried out using a PerkinElmer LS-55 spectrofluorometer (PE Company, U.K.) equipped with a thermostatted cell holder at 25 \pm 0.1 °C. The slit widths were fixed at 15 and 10 nm for the excitation and the emission, respectively.

Results and Discussion

Surface Properties and Micellization Parameters. Surface tension measurements were carried out to evaluate the surface activity of three carbazole-tailed imidazolium ILs in aqueous solutions. Figure 1 depicts the surface tension (γ) versus concentration (C) plots for [carbazoleC_nmim]Br (n = 6, 10, 12) aqueous solutions at 25 °C. The surface tension of [carbazoleC-"mim]Br aqueous solutions progressively decreases with the increase in concentration and then reaches a plateau region, indicating that the micelles are formed and the concentration of the break point corresponds to the critical micelle concentration (cmc). Rebelo and co-workers reported that the surface tension of $[C_n mim]Cl$ aqueous solutions decreased even for n < 8, but these compounds did not show a plateau at higher concentrations because the hydrophobicity is not stong enough to form micelles.⁸ Although the alkyl chain is rather short for [carbazoleC₆mim]Br, the incorporation of a carbazole moiety increases its hydrophobicity, which leads to the appearance of micelles. The values of the cmc and the surface tension at the cmc (γ_{cmc}) for three carbazole-tailed imidazolium ILs are listed in Table 1, together with those reported for $[C_n mim]Br (n = 6,$ 8, 10, 12, 14, and 16). It can be seen that $[carbazoleC_nmim]Br$ has a much bigger $\gamma_{\rm cmc}$ value than [C_nmim]Br, suggesting the low surface concentration at the cmc, or in other words the loose packing of [carbazoleC_nmim]Br molecules at the air-water interface. This result would be attributed to the steric hindrance bulky carbazole moieties. Compared with of [carbazoleC₆mim]Br, the smaller values of γ_{cmc} for $[carbazoleC_{10}mim]Br$ and $[carbazoleC_{12}mim]Br$ are ascribed to the increased hydrophobicity resulting from the extension of the hydrocarbon chain. The nearly same values of $\gamma_{\rm cmc}$ for [carbazoleC₁₀mim]Br and [carbazoleC₁₂mim]Br are reasonable, since they are only slightly different in the hydrocarbon chain length.30

The values of cmc decrease in the order [carbazoleC₆mim]Br > [carbazole C_{10} mim]Br > [carbazole C_{12} mim]Br, in accordance with the increased hydrophobicity owing to the extension of the hydrocarbon chain. When compared with [C_nmim]Br, [carbazoleC_nmim]Br has a much lower cmc even if the latter has a relatively short alkyl chain, e.g., [carbazoleC₆mim]Br < [carbazoleC₁₀mim]Br < $[C_{12}mim]Br$, $[C_{14}mim]Br$, [carbazoleC₁₂mim]Br < [C₁₆mim]Br. The higher γ_{cmc} means that the saturation of surface adsorption is attained at low bulk surfactant concentration, which results in the micelle formation at low concentration. This must be one of the reasons for the remarkably low cmc of [carbazoleC_nmim]Br. Moreover, the existence of $\pi - \pi$ interaction among adjacent carbazole moieties facilitates the formation of micelles, as $\pi - \pi$ interaction is much stronger than the normal hydrophobic interaction among the alkyl chains,31 and thus, the cmc becomes smaller. As previously reported,¹¹ the cmc for $[C_n mim]Br$ is smaller than those for traditional cationic surfactants (e.g., alkyltrimethylammonium bromides) having the same hydrocarbon chain length, due to the point charge on the alkyltrimethylammonium cation as compared to the delocalized positive charge on the imidazolium ring and the ubiquitous hydrogen bonds among the imidazolium cations.^{32,33} Herein, these carbazole-tailed imidazolium ILs that incorporate a carbazole moiety at the terminal of the hydrocarbon chain have a stronger capability for the formation of micelles.

Applying the Gibbs adsorption isotherm to the surface tension plots, the maximum surface excess concentration (Γ_{max}) and the area occupied by a single amphiphile molecule at the air—water interface (A_{min}) were estimated.³⁴ Γ_{max} and γ_{cmc} both reflect the arrangement situation of amphiphile molecules at the air—water interface. [carbazoleC_nmim]Br has a significantly smaller Γ_{max} value than [C_nmim]Br, which is consistent with the larger γ_{cmc} as discussed above due to the loose molecular arrangement at the air—water interface. Correspondingly, the bigger A_{min} of [carbazoleC_nmim]Br was obtained, which is in accordance with the smaller Γ_{max} .

Electrical conductivity measurements were employed to study the micellar self-aggregation behavior of three carbazole-tailed imidazolium ILs in aqueous solutions. Figure 2 presents the specific conductivity (κ) as a function of concentration (C) for [carbazoleC_nmim]Br aqueous solutions at 25 °C. Each plot fits into two straight lines with different slopes. The break originates from the micellization of amphiphiles. The slope of the linear region above the cmc is smaller than that below the cmc, indicating an effective loss of ionic charges owing to the binding of counterions on the micellar surface.³⁵ The values of cmc estimated from the break point are given in Table 1, which are in good accordance with those obtained from surface tension measurements. The logarithmic plot of cmc (in mol/L) against the alkyl chain length of [carbazoleC_nmim]Br follows the Stauff-Klevens rule (Figure S1 in the Supporting Information). The linear trend appeared with a slope of -0.23 (correlation coefficient = 0.999); the absolute value of the slope is meaningfully smaller than that reported for $[C_n mim]Br (-0.28)^{12}$ and for most conventional ionic surfactants (around -0.3).³⁰ The slope is a measure of the free energy associated with the transfer of a methylene unit from a bulk solution to the micellar interior. The different slope between [carbazoleC_nmim]Br and $[C_n mim]$ Br reveals that the incorporation of a carbazole moiety alters the effect of an additional methylene group on the cmc. It is suggested that the hydrophobic effect of alkyl hydrocarbon chains is somewhat weakened by the presence of bulky carbazole groups, although the cmc is lowered due to the $\pi - \pi$

TABLE 1: Surface Properties and Micellization Parameters of [carbazoleC_nmim]Br (n = 6, 10, 12) and [C_nmim]Br (n = 6, 8, 10, 12, 14, and 16) in Aqueous Solutions at 25 °C

		cmc (mM)					
	a	b	d	$\gamma_{\rm cmc}~({\rm mN/m})$	$\Gamma_{\rm max}~(\mu {\rm mol}/{\rm m}^2)$	A_{\min} (Å ²)	
[carbazoleC6mim]Br	5.07	6.07	4.65	60.1	0.786	211	
[carbazoleC ₁₀ mim]Br	0.712	0.785	0.533	56.2	0.869	191	
[carbazoleC ₁₂ mim]Br	0.188	0.260		56.3	0.861	193	
$[C_6 mim]Br^d$	600	400	797				
$[C_8 mim]Br^d$	150	150	141				
$[C_{10}mim]Br^e$	29.3	32.9	31	39.7	1.72	96.7	
$[C_{12}mim]Br^e$	10.9	8.5	11	39.4	1.91	86.8	
[C ₁₄ mim]Br ^f	2.8	2.6		39.2	1.96	84.7	
[C ₁₆ mim]Br ^f	0.55	0.65		39.1	2.03	81.6	

^{*a*} Determined from surface tension measurements. ^{*b*} Determined from electrical conductivity measurements. ^{*c*} The average values determined from ¹H NMR spectra. ^{*d*} Reported in refs 15 and 17. ^{*e*} Reported in refs 11 and 17. ^{*f*} Reported in refs 12 and 14.



Figure 2. Specific conductivity as a function of concentration for $[carbazoleC_6mim]Br$ (\blacksquare), $[carbazoleC_{10}mim]Br$ (\spadesuit), and $[carbazoleC_{12}mim]Br$ (\blacktriangle) in aqueous solutions at 25 °C. The cmc values are denoted by vertical marks.

interaction as well as the hydrophobic interaction among carbazole groups.

¹H NMR Spectra. ¹H NMR analyses were focused on [carbazoleC₆mim]Br and [carbazoleC₁₀mim]Br, since the proton signals in the ¹H NMR spectra of [carbazoleC₁₂mim]Br were illegible due to its low cmc. Figures 3 and 4 show the proton assignments and ¹H NMR spectra for [carbazoleC₆mim]Br and [carbazoleC₁₀mim]Br, respectively, at concentrations below and above the cmc in D_2O . Before the formation of micelles, no significant change in chemical shifts is observed, since the [carbazoleC_nmim]Br molecules are only dissolved in D_2O as monomers. However, upon micellization, some small multiplets unite into broad ones especially for the [carbazoleC₁₀mim]Br system (Figure 4), indicating the formation of thermodynamically stable self-assemblies.⁹ The chemical shifts (δ_{obs}) of protons [carbazoleC6mim]Br discernible for and [carbazoleC10mim]Br at different concentrations in D2O are given in Tables S1 and S2 in the Supporting Information, respectively.



Figure 3. Proton assignments and ¹H NMR spectra of [carbazoleC₆mim]Br at concentrations below (3 and 4 mM) and above (8 and 10 mM) the cmc in D_2O at 25 °C. The dashed lines denote the undeuterated protons of DSS.



Figure 4. Proton assignments and ¹H NMR spectra of [carbazoleC₁₀mim]Br at concentrations below (0.2 and 0.3 mM) and above (0.8 and 1.0 mM) the cmc in D_2O at 25 °C. The dashed lines denote the undeuterated protons of DSS.

The protons included in the present carbazole-tailed imidazolium ILs would be classified into three groups, imidazole protons ($H_{4,5}$ and H_6 ; no signal for H_2 is observed due to the deuteration), protons in the alkyl chain (H_{7-11}), and carbazole



Figure 5. Schematic illustration of the proposed structures of micelles formed by [carbazole C_n mim]Br (n = 10 as an example). Circles denote the hydrophilic heads. Wavy lines denote the alkyl chains. Cylinders denote the terminal carbazole moieties.

protons (H_{12}) . As can be seen in Figures 3 and 4, the chemical shifts of the entire protons move upfield upon micellization. The ring current effect originating from the carbazole groups would be responsible for the upfield shift of protons in the alkyl chains, similar to the case for nitrophenoxy-tailed quaternary ammonium surfactants.³⁶ That is, the protons in the alkyl chains located above and below the plane of nearby carbazole rings will resonate at a higher applied field due to the ring current effect. In addition, this ring current effect has quite rigorous geometrical restriction; only the protons localized in the field of the ring are substantially shifted.^{36,37} The 2D NOESY spectra of 10.0 mM [carbazoleC₆mim]Br in D₂O were provided in Figure S2 of the Supporting Information. The protons in the hydrophobic chains interact with the carbazole protons (H_{12}) , and the NOE intensities of the cross peaks of H_{12}/H_9 are strong. Therefore, the terminal carbazole groups preferentially locate at the interior of micelles and overlap with the middle few methylenes in the alkyl chains.³⁶ The insertion of carbazole moieties into the micelles creates the upfield shift of the carbazole protons (H_{12}) , since the less polar media reduce the deshielding effect on the aromatic protons.³⁸ On the basis of the above discussions, a possible packing structure of [carba $zoleC_nmim$]Br molecules in a micelle is depicted in Figure 5. This staggered arrangement favors the compact stacking of hydrophobic parts of [carbazoleC_nmim]Br in the micellar interior and decreases the unfavorable contact with water.

Protons of the methyl group directly attached to the imidazole ring (H₆) display an upfield shift upon micellization but with a lower magnitude compared to the protons in the alkyl chain, which was also observed for the 1-butyl-3-methylimidazolium tetrafluoroborate [C₄mim]BF₄ system.⁹ The magnetic environment of the methyl protons would not be changed so significantly upon micellization because the methyl group attached to the imidazole ring is located at the micellar surface and contacts with D₂O. Thus, the rather insensitive feature of δ for methyl protons upon micellization looks reasonable. In contrast, the upfield shift of imidazole protons (H_{4,5}) is quite remarkable. This large upfield shift associated with the micellization may be interpreted as follows. The extremely low field for the resonance of H_{4,5} would be attributed to the hydrogen-bond



Figure 6. Variation of $\Delta \delta (\delta_{obs} - \delta_{mon})$ for the H_{4,5} signals versus the reciprocal concentration of [carbazoleC₆mim]Br (left) and [carbazoleC₁₀mim]Br (right) in D₂O at 25 °C.

interaction of the imidazole protons with D₂O oxygen.^{39–42} When the micelles are formed, the binding of counterions on the micellar surface takes place as demonstrated by electrical conductivity data, and some D₂O molecules around H_{4,5} are replaced by Br⁻. The hydrogen-bond interaction would occur between H_{4,5} and Br⁻, but it must be much weaker compared with the hydrogen bonding with D₂O oxygen. Thus, the downfield shift of H_{4,5} caused by the hydrogen-bond interaction in the monomeric state is significantly reduced upon micellization, and consequently, the remarkable upfield shift is observed for H_{4,5} protons.

The cmc of amphiphiles can be obtained on the basis of the concentration dependence of ¹H NMR chemical shifts.³⁶ When the exchange rate of an amphiphile molecule between the bulk solution and the micelle is fast on the NMR time scale, the observed chemical shift (δ_{obs}) can be expressed as a weighted average of the chemical shifts of the monomer (δ_{mon}) and the micelles (δ_{mic})

$$\delta_{\rm obs} = \delta_{\rm mon} \left(\frac{C_{\rm mon}}{C_{\rm T}} \right) + \delta_{\rm mic} \left(\frac{C_{\rm mic}}{C_{\rm T}} \right) \tag{1}$$

where C_{mon} , C_{min} , and C_{T} are the concentrations of amphiphiles existing as monomers, in micelles, and the total concentration, respectively. On the assumption that the monomer concentration remains constant above the cmc,

$$\delta_{\rm obs} = \delta_{\rm mic} - \left(\frac{\rm cmc}{C_{\rm T}}\right) (\delta_{\rm mic} - \delta_{\rm mon}) \tag{2}$$

 δ_{mon} and δ_{mic} can be estimated by extrapolation of the plots of δ_{obs} versus C_{T} and δ_{obs} versus $1/C_{\text{T}}$, respectively. An example of δ_{obs} versus $1/C_{\text{T}}$ plots for the H_{4,5} proton of [carbazoleC₆mim]Br and [carbazoleC₁₀mim]Br is shown in Figure 6. The plot furnishes two straight lines with the intersection corresponding to the cmc. Together with δ_{mon} and δ_{mic} , the cmc values obtained from the different protons of [carbazoleC₆mim]Br and [carbazoleC₁₀mim]Br are collected in Table 2, which are slightly lower than those in H₂O because D₂O is a more structured liquid.⁴³

The aggregation number (N) can also be estimated by ¹H NMR chemical shifts.^{36,44} According to the mass action model, the aggregation equilibrium of amphiphiles can be quantified

$$K = \frac{[S_N]}{[S]^N} \tag{3}$$

where S and S_N are the monomer and the aggregated form of

TABLE 2: Micellization Parameters of $[carbazoleC_6mim]Br$ and $[carbazoleC_{10}mim]Br$ Estimated by the Analysis of the Chemical Shifts

		$\delta_{ m mon}$ (ppm)	$\delta_{ m mic}$ (ppm)	cmc (mM)	Na	$N^{\prime a}$
[carbazoleC6mim]Br	H _{4.5}	8.285	7.454	4.80	35	1.2
	H_7	4.487	3.629	4.52	38	1.4
	H_{11}	4.010	3.204	4.59	34	1.3
	H_6	3.757	3.608	4.29	39	1.5
[carbazoleC10mim]Br	$H_{4,5}$	8.227	7.659	0.529	46	1.9
	H_7	4.442	3.669	0.549	44	1.9
	H_{11}	4.065	3.643	0.533	48	1.8
	H_6	3.798	3.731	0.521	47	1.9

 ${}^{a}N'$ and N expressed as the aggregation number at concentrations below and above the cmc.



Figure 7. Plots of $\log[C_{T}(|\delta_{obs} - \delta_{mon}|)]$ versus $\log[C_{T}(|\delta_{mic} - \delta_{obs}|)]$ for [carbazoleC₆mim]Br (solid symbols) and [carbazoleC₁₀mim]Br (open symbols) at 25 °C.

amphiphiles and K is the equilibrium constant. Then, the relation between K and the chemical shift can be given as

$$\log[C_{\rm T}(|\delta_{\rm obs} - \delta_{\rm mon}|)] = N \log[C_{\rm T}(|\delta_{\rm mic} - \delta_{\rm obs}|)] + \log NK + (1 - N) \log(|\delta_{\rm mic} - \delta_{\rm mon}|) \quad (4)$$

Therefore, the slope of a $\log[C_{\rm T}(|\delta_{\rm obs} - \delta_{\rm mon}|)]$ versus $\log[C_{\rm T}(|\delta_{\rm mic} - \delta_{\rm obs}|)]$ plot yields the aggregation number. The chemical shift data of [carbazoleC₆mim]Br and [carbazoleC₁₀mim]Br plotted according to eq 4 are shown in Figure 7. Two straight lines are observed, and the intersection appears at the cmc. Table 2 outlines the values of N' and N expressed as the aggregation number at concentrations below and above the cmc, respectively. Below the cmc, [carbazoleC_nmim]Br exists as single monomers. When the concentration is above the cmc, N corresponds to the micelles formed by [carbazoleC_nmim]Br.

Temperature Dependence of Micellization Parameters. Electrical conductivity measurements at different temperatures (20, 25, 30, 35, and 40 °C) were carried out to evaluate the thermodynamics of micelle formation for these carbazole-tailed imidazolium ILs. An example of the results for [carbazoleC₁₀mim]Br is shown in Figure 8 (the relevant information of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br is listed in Figure S3 of the Supporting Information). The values of cmc for [carbazoleC_nmim]Br (n = 6, 10, 12) at different



Figure 8. Specific conductivity as a function of concentration for [carbazoleC₁₀mim]Br in aqueous solutions at different temperatures.

temperatures are collected in Table 3. With the increase in temperature, the cmc for [carbazoleC_nmim]Br displays the same trend as reported for [C_nmim]Br and conventional ionic surfactants.¹² The effect of temperature on cmc is usually discussed in terms of two contrary factors.⁴⁵ The increase in temperature causes the decrease in the hydration degree of the hydrophilic headgroups, which is favorable to the micelle formation. In contrast, an increased temperature may cause the disruption of the water structures surrounding the hydrophobic chains, which weakens the hydrophobic effect and is unfavorable to the micelle formation. From the data in Table 3, the second factor is predominant in the investigated temperature range.

Shanks and Franses developed the mixed electrolyte model of micellar solution, which has been frequently applied to estimate the micellization parameters such as the degree of counterion binding (β) and the aggregation number (N).⁴⁶ Applying this model, the combinations of N and β for the present systems were determined so as to provide a best fit curve to the experimental molar conductance (Λ). The detailed procedure for the analysis is given in the Supporting Information. The values of β and N estimated by this procedure are summarized in Table 3. A comparison between calculated and experimental molar conductance is shown in Figure 9 for [carbazoleC₁₀mim]Br as an example (the relevant information of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br is demonstrated in Figure S4 of the Supporting Information). It is clearly seen that the agreement between the calculated and experimental Λ is satisfactory. Furthermore, the values of N estimated by the mixed electrolyte model are in accordance with those determined by ¹H NMR data. With the increase of the hydrocarbon chain length, the values of N increase, which is a reasonable trend.

The aggregation numbers of $[C_n mim]$ Br micelles have been determined through different methods, e.g., 18 for [C₆mim]Br (¹H NMR measurements¹⁷), 25 for $[C_8 mim]Br$ (¹H NMR measurements¹⁷), 35 for $[C_{10}mim]Br$ (fluorescence quenching¹⁶), 43 and 44 for $[C_{12}mim]Br$ (conductivity measurements¹² and fluorescence quenching,¹⁸ respectively), 61 and 59 for [C₁₄mim]Br (conductivity measurements¹² and fluorescence quenching,18 respectively), and 76 and 66 for [C16mim]Br (conductivity measurements¹² and fluorescence quenching,¹⁸ respectively). Though the values of N generally depend on the determination method, those for [carbazoleC_nmim]Br and [C_nmim]Br seem to be comparable in regard to the available data. The relatively higher N of [carbazoleC_nmim]Br is ascribable to the enhanced hydrophobicity derived from the incorporation of carbazole groups and the $\pi - \pi$ interaction among adjacent carbazole groups which favor the micelle formation.

TABLE 3: Critical Micelle Concentration (cmc), Degree of Counterion Binding (β), Aggregation Number (N), and Thermodynamic Parameters of Micelle Formation for [carbazoleC_nmim]Br (n = 6, 10, 12) in Aqueous Solutions at Various Temperatures

	<i>t</i> (°C)	cmc (mM)	β	Ν	$\Delta G_{\rm m}^{\circ}$ (kJ/mol)	$\Delta H_{\rm m}^{\rm o}$ (kJ/mol)	$-T\Delta S_{\rm m}^{\circ}$ (kJ/mol)
[carbazoleC6mim]Br	20	5.68	0.70	37	-37.2	-28.1	-9.11
	25	6.07	0.70	34	-37.4	-33.7	-3.72
	30	6.85	0.68	33	-37.5	-39.0	1.48
	35	7.71	0.69	37	-37.1	-44.1	6.98
	40	8.73	0.69	36	-37.2	-49.1	11.9
[carbazoleC10mim]Br	20	0.748	0.70	40	-44.1	-38.5	-5.61
	25	0.785	0.71	42	-44.1	-42.8	-1.25
	30	0.864	0.71	47	-44.1	-46.6	2.57
	35	0.962	0.71	48	-44.1	-50.8	6.68
	40	1.06	0.68	44	-43.8	-54.7	10.9
[carbazoleC ₁₂ mim]Br	20	0.223	0.70	57	-47.2	-9.22	-38.0
	25	0.260	0.72	60	-47.7	-26.9	-20.8
	30	0.307	0.72	58	-47.9	-44.0	-3.89
	35	0.372	0.70	58	-47.9	-60.5	12.6
	40	0.460	0.70	57	-47.5	-76.6	29.1

Thermodynamics of Micelle Formation. The phase separation model and mass action model are commonly used to evaluate the standard free energy of micelle formation ($\Delta G_{\rm m}^{\circ}$). The latter takes into account the fraction of counterions restricted at the micellar surface and is more suitable as a model for ionic surfactants. For 1:1 type ionic surfactants, $\Delta G_{\rm m}^{\circ}$ is estimated according to the relation⁴⁷

$$\Delta G_{\rm m}^{\rm o} = (1 + \beta) RT \ln x_{\rm cmc} \tag{5}$$

where *R* is the ideal gas constant, *T* is the absolute temperature, and x_{cmc} is the cmc in mole fraction units. Then, the standard enthalpy of micelle formation (ΔH_m^o) is determined by the Gibbs-Helmholtz equation. The standard entropy of micelle formation (ΔS_m^o) is calculated by the Gibbs equation. On the basis of the cmc and β in Table 3, the values of ΔG_m^o , ΔH_m^o , and $-T\Delta S_m^o$ for [carbazoleC_nmim]Br were obtained.

All of the values of $\Delta G_{\rm m}^{\circ}$ are negative being characteristic of spontaneous micelle formation, and $\Delta G_{\rm m}^{\circ}$ becomes more negative with the elongation of the hydrocarbon chain. For [carbazoleC₆mim]Br and [carbazoleC₁₀mim]Br, the contribution of the $\Delta H_{\rm m}^{\circ}$ term to negative $\Delta G_{\rm m}^{\circ}$ is much bigger than that of the $-T\Delta S_{\rm m}^{\circ}$ term throughout the measured temperature range. This is different from the case of alkyl hydrocarbon surfactants, in which the $-T\Delta S_{\rm m}^{\circ}$ term is a dominant factor to produce negative $\Delta G_{\rm m}^{\circ}$ in the low temperature region; $\Delta H_{\rm m}^{\circ}$ becomes even positive at low temperature.³⁰ The large negative $\Delta H_{\rm m}^{\circ}$ value observed for the present carbazole-tailed imidazolium ILs must

be attributed to the attractive $\pi - \pi$ interaction among adjacent carbazole moieties acting in the micellar aggregates. The similar effect of $\pi - \pi$ interaction on the micelle formation has been reported for phenyl-tailed and nitrophenoxy-tailed surfactants.^{31,36,48} When the alkyl chain is elongated, the hydrophobic effect would become strong and the contribution of the entropy term would remarkable. Actually, for become the case of [carbazoleC₁₂mim]Br, $-T\Delta S_{\rm m}^{\circ}$ governs $\Delta G_{\rm m}^{\circ}$ at low temperature, and with the increase in temperature, a crossing temperature appears for the role of the enthalpy term and the entropy term playing in determination of $\Delta G_{\rm m}^{\circ}$. This phenomemon is usually observed for alkyl hydrocarbon surfactants.³⁰ Therefore, the micelle formation process for [carbazoleC,mim]Br with short alkyl chains (n = 6, 10) is enthalpy-driven throughout the whole temperature range investigated, whereas for [carbazole-C₁₂mim]Br, it is entropy-driven at low temperatures followed by reversal to enthalpy-driven at high temperatures.

Fluorescence Properties. The fluorescence properties of $[carbazoleC_nmim]Br$ (n = 6, 10, 12) in aqueous solutions were detected at various concentrations. As a typical example, the excitation and emission spectra for aqueous solutions of $[carbazoleC_{10}mim]Br$ at a concentration of 0.1 mmol/L are illustrated in Figure 10 (the excitation and emission spectra of $[carbazoleC_6mim]Br$ and $[carbazoleC_{12}mim]Br$ are demonstrated in Figures S5 and S6 of the Supporting Information). Both excitation and emission spectra show significant and strong fluorescence behaviors. The excitation spectrum exhibits several peaks at 255, 286, and 342 nm. When excited at different



Figure 9. Molar conductance versus the square root of the concentration for [carbazoleC₁₀mim]Br. Circles are experimental values. Solid lines are calculated curves obtained by the procedure described in the Supporting Information.



Figure 10. Excitation (a) and emission (b–e) spectra of [carbazoleC₁₀mim]Br in aqueous solutions at a concentration of 0.1 mmol/L. λ_{em} (nm) = 370 (a); λ_{ex} (nm) = 255 (b), 286 (c), 310 (d), 342 (e).

excitation wavelengths, only the emission intensity varies and the emission peak keeps constant at 370 nm. Samanta and coworkers reported that common imidazolium ILs, 1-ethyl-3methylimidazolium tetrafluoroborate [C₂mim]BF₄, 1-butyl-3methylimidazolium hexafluorophosphate [C₄mim]PF₆, and [C₄mim]Cl are weakly fluorescent and their emission peaks are very strongly dependent on the excitation wavelength.^{49,50} The strong and stable fluorescence properties of the currently investigated carbazole-tailed imidazolium ILs are due to the incorporation of the fluorescence properties moiety. Importantly, the designed amphiphilic carbazole-tailed imidazolium ILs with strong and stable fluorescence properties may be applied in the combined field of surface chemistry and photochemistry.

Conclusion

The micelle formation of fluorescent carbazole-tailed imidazolium ILs [carbazoleC_nmim]Br (n = 6, 10, 12) in aqueous solutions was explored by surface tension, electrical conductivity, and ¹H NMR. The incorporation of a carbazole moiety further improves the capability of imidazolium ILs for the formation of micelle; that is, [carbazoleC_nmim]Br has a much lower cmc than $[C_n mim]$ Br even if the former has a relatively short alkyl chain. The terminal carbazole groups preferentially intercalated with several methylene groups in the alkyl chains, and thus, the staggered arrangement in micelles was formed. By fitting ¹H NMR data with the mass action model and by fitting electrical conductivity data with the mixed electrolyte model, the aggregation numbers were successfully estimated and in excellent accordance. The micelle formation process for [carbazoleC_nmim]Br with short alkyl chains (n = 6, 10) is enthalpy-driven throughout the whole temperature range (20, 25, 30, 35, and 40 °C). This behavior would be attributed to attractive $\pi - \pi$ interaction among carbazole groups occurring in the micellar interior. As for [carbazoleC₁₂mim]Br, it is entropy-driven at low temperatures but enthalpy-driven at high temperatures. These carbazole-tailed imidazolium ILs present strong fluorescence properties, and their emission peaks are independent of the excitation wavelength. Carbazole-based compounds are fascinating as charge-transporting and photoconductive materials. The stable fluorescence properties of these carbazole-tailed imidazolium ILs together with the outstanding properties of ILs would extend their applications in electrochemical and optical fields.

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Supporting Information Available: Figure S1 showing the logarithmic plot of cmc against the number of carbon atoms in the alkyl chain of carbazole-tailed imidazolium ILs; Tables S1 and S2 showing the ¹H NMR chemical shifts of [carbazoleC₆mim]Br and [carbazoleC₁₀mim]Br at different concentrations; Figure S2 showing 2D NOESY spectra of 10.0 mM [carbazoleC₆mim]Br in D₂O; Figure S3 showing the specific conductivity as a function of concentration for [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br in aqueous solutions at different temperatures; Figure S4 showing the molar conductance versus the square root of the concentration for [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br; Figures S5 and S6 showing the excitation and emission spectra of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br in aqueous solutions at 0.5 showing the excitation and emission spectra of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br; Figures S5 and S6 showing the excitation and emission spectra of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br in aqueous solutions at 0.5 showing the excitation and emission spectra of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br in aqueous solutions at 0.5 showing the excitation and emission spectra of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br in aqueous solutions at 0.5 showing the excitation and emission spectra of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br in aqueous solutions at 0.5 showing the excitation and emission spectra of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br in aqueous solutions at 0.5 showing the excitation and emission spectra of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br in aqueous solutions at 0.5 showing the excitation and emission spectra of [carbazoleC₆mim]Br and [carbazoleC₁₂mim]Br in aqueous solutions at 0.5 showing the excitation and emission spectra of [carbazoleC₆mim]Br in aqueous solutions at 0.5 showing the excitation and emission spectra of [carbazoleC₆mim]Br in aqueous solutions at 0.5 showing the excitation at 0.5 showing the excitation

tions; and a detailed analysis of the conductivity data. This material is available free of charge via the Internet at http:// pubs.acs.org.

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