Journal of Colloid and Interface Science 372 (2012) 52–57

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

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# Aggregation behavior of gemini pyrrolidine-based ionic liquids 1,1′-(butane-1,4-diyl)bis(1-alkylpyrrolidinium) bromide ([$C_n$py-4-$C_n$py][$Br_2$]) in aqueous solution

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ARTICLE INFO

*Article history:*
Received 15 December 2011
Accepted 20 January 2012
Available online 28 January 2012

*Keywords:*
Gemini pyrrolidine-based ionic liquids
Aggregation behavior
Surface tension
Electrical conductivity
Steady-state fluorescence

ABSTRACT

Three gemini pyrrolidine-based ionic liquids, 1,1′-(butane-1,4-diyl)bis(1-alkylpyrrolidinium) bromide ([$C_n$py-4-$C_n$py][$Br_2$], $n = 10$, 12, 14), were synthesized. Their aggregation behavior in aqueous solution was systematically investigated by surface tension, electrical conductivity, and steady-state fluorescence. Compared with their corresponding monomers, *N*-alkyl-*N*-methylpyrrolidinium bromide ($C_n$MPB), [$C_n$py-4-$C_n$py][$Br_2$], have higher surface activity. The special structure of [$C_n$py-4-$C_n$py][$Br_2$] that has a spacer in their hydrophilic head groups results in a lower surface excess concentration ($\Gamma_{max}$) and a larger molecular cross-sectional area ($A_{min}$). Electrical conductivity studies show a lower degree of counter-ion binding to the aggregates. A smaller aggregation number ($N_{agg}$) is observed by the pyrene fluorescence quenching method. A series of thermodynamic parameters ($\Delta G^0_{agg}, \Delta H^0_{agg}, -T\Delta S^0_{agg}$) of aggregation derived from electrical conductivity indicate that the aggregation of [$C_n$py-4-$C_n$py][$Br_2$] is enthalpy-driven, while aggregation of $C_n$MPB is entropy-driven at low temperatures but enthalpy-driven at high temperatures.

## 1. Introduction

Ionic liquids (ILs) are a class of compounds composed of ions, which generally have melting points below 100 °C [1]. They have been attracting much attention as an alternative to conventional organic solvents due to their unique and advantageous properties, such as low volatility, non-flammability, high thermal stability, and ionic conductivity [2,3]. In the field of colloid and interface science, the ability of ILs to support the self-assembly of amphiphilic compounds is attractive, and hence, the aggregation behavior of surfactants in ILs has been extensively investigated [4–9]. Dialkylimidazolium salts are representative ILs and most widely used in this area. Another interest relating to ILs in colloid and interface science comes from a resemblance in chemical structure of long-chain imidazolium salts to cationic surfactants. That is, the long-chain imidazolium salts are regarded as novel surfactants, and a number of investigations have been reported on their aggregation behavior in aqueous solution [10–19]. Recently, gemini imidazolium-based ILs have been synthesized by connecting two long-chain imidazolium parts with a spacer group composed of several methylene units, and their aggregation behavior in aqueous solution was investigated [20–23]. It was revealed that the new gemini imidazolium ILs possess higher thermal stability and higher surface activity than corresponding ILs with single long chain [20–22].

Though a large amount of research has reported the aggregation behavior of surface active ILs (monomeric and gemini) in water, most have focused on the ILs with imidazolium head groups. ILs with other head groups, for example, pyrrolidinium groups, have seldom been studied. Baker and Karukstis investigated the micelle formation of monomeric long-chain pyrrolidinium salts, *N*-alkyl-*N*-methylpyrrolidinium bromide ($C_n$MPB), and detected the CMC through electrical conductivity, fluorescent measurements, and light-scattering techniques [24,25]. Our group also studied the adsorption behavior of $C_n$MPB at the air/water interface and their thermodynamic parameters of micelle formation [26]. However, the aggregation behavior of gemini pyrrolidine-based ILs has not yet been reported.

In the present work, the gemini ILs with pyrrolidinium head groups, 1,1′-(butane-1,4-diyl)bis(1-alkylpyrrolidinium) bromide ([$C_n$py-4-$C_n$py][$Br_2$], $n = 10$, 12, 14), were synthesized, and their aggregation behavior was investigated. A series of useful parameters were obtained and were compared with their corresponding monomer $C_n$MPB. The data obtained in the present study will be useful in understanding the role of the special structure in affecting the aggregation behavior of ILs and in the design of new-type ILs. Moreover, the gemini pyrrolidine-based ILs may have potential application in the fields related to colloid and interface science,

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doi:10.1016/j.jcis.2012.01.040

such as skin care [27], textile industry [28], and construction of porous materials [29].

## 2. Materials and methods

### 2.1. Materials

The chemical structure of gemini pyrrolidine-based ILs with a four-methylene spacer group is shown in Fig. 1. Their detailed synthesis process is presented in the Supporting Information. Pyrrolidine, 1-bromodecane, 1-bromododecane, 1-bromotetradecane, and 1,4-dibromobutane were purchased from Aladdin Chemical Reagent Co., Ltd. Acetone, isopropanol, potassium iodide, and potassium carbonate are all analytical grade reagents and were purchased from Tianjin Kemiou Reagent Co. Pyrene was purchased from Fluka. Benzophenone was obtained from Beijing Yucai fine chemical plant. All chemicals were used without further purification. Triply distilled water was used to prepare all the solutions.

The melting temperatures determined by PerkinElmer DSC8500 are 54.5 °C, 75.3 °C, and 95.5 °C for $[C_{10}py\text{-}4\text{-}C_{10}py][Br_2]$, $[C_{12}py\text{-}4\text{-}C_{12}py][Br_2]$, and $[C_{14}py\text{-}4\text{-}C_{14}py][Br_2]$, respectively. By definition, the organic salts whose melting temperature is lower than 100 °C are called ionic liquids, so we can also call these compounds “gemini ionic liquids”.

### 2.2. Methods

#### 2.2.1. Surface tension

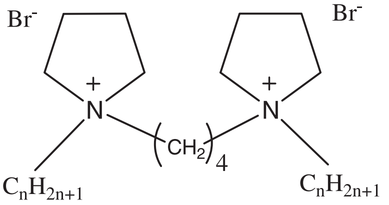
Surface tensions of the solutions were measured by a surface tensiometer (Model JYW-200B, Chengde Dahua Instrument Co.), equipped with a platinum ring. Each datum is an average of five individual points, with an accuracy of $\pm 0.2\ mN\ m^{-1}$. The samples were equilibrated in the measuring vessel for 15 min to minimize the drift due to adsorption kinetics. The temperature was controlled by a water circulation jacket connected to a thermostat.

#### 2.2.2. Electrical conductivity

A low-frequency conductivity analyzer (Model DDS-307, Shanghai Precision & Scientific Instrument Co., Ltd., accuracy of ±1%) was used to measure the electrical conductivities of the solutions.

#### 2.2.3. Fluorescence measurement

Fluorescence measurements were carried out using a PerkinElmer LS-55 spectrofluorometer (PE Company, UK) equipped with a thermostat cell holder at 25 °C. The excitation wavelength was 335 nm. Emission spectra were detected from 350 to 450 nm with the slit widths fixed at 2.5 and 10 nm for emission and excitation. The concentration of pyrene was fixed at $1.0 \times 10^{-6}$ M in all the measurements.



$[C_npy\text{-}4\text{-}C_npy][Br_2]$ ($n$ = 10, 12, 14)

**Fig. 1.** Chemical structure of gemini pyrrolidine-based ILs.

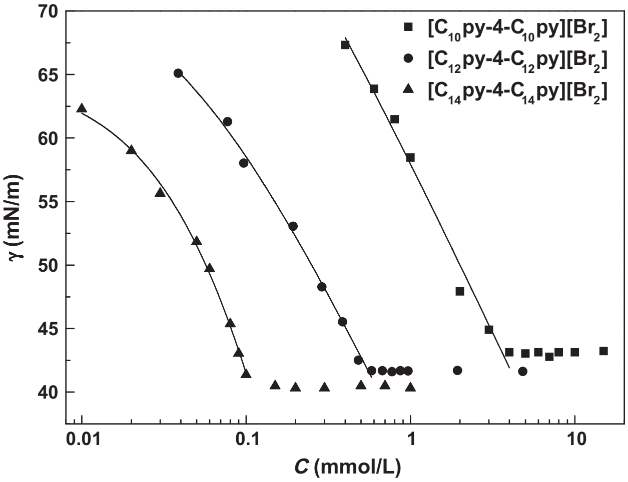


**Fig. 2.** Surface tension versus concentration plots for the three gemini pyrrolidine-based ILs in aqueous solution at 25 °C. The polynomial lines fitted to the pre-CAC data were used to calculate surface excesses.

## 3. Results and discussion

### 3.1. Surface active properties of gemini pyrrolidine-based ILs

The surface tension versus $[C_npy\text{-}4\text{-}C_npy][Br_2]$ concentration plots in aqueous solution is shown in Fig. 2. The surface tension gradually decreases with increasing $[C_npy\text{-}4\text{-}C_npy][Br_2]$ concentration and then reaches a plateau region, indicating that the aggregates are formed and the concentration of the break point corresponds to the critical aggregate concentration (CAC). The surface tension at the CAC is defined as $\gamma_{CAC}$. Furthermore, the absence of a minimum around the break point confirms the high purities of these gemini pyrrolidine-based ILs. The values of the CAC and $\gamma_{CAC}$ for the three gemini ILs are listed in Table 1. It is seen that the values of CAC decrease with increasing chain length of $[C_npy\text{-}4\text{-}C_npy][Br_2]$, in accordance with the increased hydrophobicity owing to the extension of the hydrocarbon chain. When compared with $C_nMPB$, the CAC values of $[C_npy\text{-}4\text{-}C_npy][Br_2]$ are about one order of magnitude lower than those of $C_nMPB$ (the CMC values are 55.5, 13.6, and 3.3 mmol/L for $C_{10}MPB$, $C_{12}MPB$, and $C_{14}MPB$, respectively [24]). Also, the $\gamma_{CAC}$ values of $[C_npy\text{-}4\text{-}C_npy][Br_2]$ are somewhat lower than those of $C_nMPB$ (42.4 mN/m for $C_{12}MPB$ and 42.7 mN/m for $C_{14}MPB$ [26]). These results demonstrate that the surface activity of $[C_npy\text{-}4\text{-}C_npy][Br_2]$ is superior to that of $C_nMPB$. In comparison with gemini imidazolium-based ILs $[C_nim\text{-}4\text{-}C_nim][Br_2]$, the CAC values of $[C_npy\text{-}4\text{-}C_npy][Br_2]$ are almost the same with $[C_{14}im\text{-}4\text{-}C_{14}im][Br_2]$ and somewhat lower than those of $[C_nim\text{-}4\text{-}C_nim][Br_2]$ ($n$ = 10, 12) (the CMC values are 0.10, 0.72, and 4.50 mmol/L for $[C_{10}im\text{-}4\text{-}C_{10}im][Br_2]$, $[C_{12}im\text{-}4\text{-}C_{12}im][Br_2]$, and $[C_{14}im\text{-}4\text{-}C_{14}im][Br_2]$, respectively [22]). However, the $\gamma_{CAC}$ values of $[C_npy\text{-}4\text{-}C_npy][Br_2]$ are higher than those of $[C_nim\text{-}4\text{-}C_nim][Br_2]$ (35.2 mN/m for $[C_{10}im\text{-}4\text{-}C_{10}im][Br_2]$, 35.7 mN/m for $[C_{12}im\text{-}4\text{-}C_{12}im][Br_2]$, and 37.2 mN/m for $[C_{14}im\text{-}4\text{-}C_{14}im][Br_2]$ [22]). This indicates that the effectiveness of the surface tension reduction of $[C_npy\text{-}4\text{-}C_npy][Br_2]$ is lower than that of $[C_nim\text{-}4\text{-}C_nim][Br_2]$. The adsorption efficiency, $pC_{20}$, is defined as [30]

$$pC_{20} = -\log C_{20} \tag{1}$$

where $C$ is the molar concentration of surfactant and $C_{20}$ represents the concentration required to reduce the surface tension of pure solvent by $20\ mN\ m^{-1}$. The larger the $pC_{20}$ value, the higher the adsorption efficiency of the surfactant is. It can be seen that the values of $pC_{20}$ increase with increasing the hydrophobic chain length