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Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Q1 Study the effect of substituent position in aromatic counterion to self- 2 aggregation of cationic surface active ionic liquid in aqueous medium

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6 ARTICLE INFO

7 Article history:

8 Received 6 November 2014

9 Received in revised form 31 December 2014

10 Accepted 13 January 2015

11 Available online xxxx

12 Keywords:

13 Surface active ionic liquid

14 Aromatic counterions

15 Substitute effect

16 Surface adsorption

17 Micelle formation

8 ABSTRACT

Specific effects of *m*- and *p*-hydroxybenzoate anions (*m*-HB and *p*-HB) as counterion on the aggregation process of surface active ionic liquids based on 1-dodecyl-3-methylimidazolium were investigated by surface tension, conductivity and steady state fluorescence measurements. Compared to that for 1-dodecyl-3-methylimidazolium bromide (C₁₂mimBr), lower critical micelle concentration (cmc) and larger Π_{cmc} and pC_{20} values for these SAILs indicate that the introduction of aromatic counterions favors micellization and reduction of surface tension. The most incorporated salicylate anion can effectively screen electrostatic repulsion, promoting a closer arrangement of C₁₂mimSal at air–solution interface. Thus *m*- and *p*-C₁₂mimHB have smaller Γ_{max} and larger A_{min} values than C₁₂mimSal. From the results of conductivity measurements, the cmc values of these SAILs increase slightly with increasing temperature, which has similar trend with cationic SAIL, 1-alkyl-3-methylimidazolium bromide, [C_{*n*}mim]Br. The negative ΔG_m^0 values, mainly result from more negative $-T \Delta S_m^0$, reveal that the micellization process is spontaneous and entropy-driven in the whole studied temperature range. The data also show that ΔH_m^0 values of all systems are negative, which implies that the micellization process is exothermic. This work suggests that small changes, such as position of the substitute on aromatic ring of counterion, can considerably influence the micellization behavior of SAILs.

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36 1. Introduction

Ionic liquids (ILs), consisted by a large organic cation and a corresponding small anion, have attracted much attention because of its unique physicochemical properties, such as non-significant vapor pressures, non-flammability, and high ion-conductivity [1,2]. Recently, ILs have been employed widely in the fields of catalysis, preparation of novel nanostructure material, organic synthesis, electrochemistry, and liquid/liquid extraction [3–6]. More importantly, the physicochemical properties of them can be effectively and easily tuned by altering components of cation, anion, and substituent [7]. Based on this design, a large variety of ILs with different structures have been synthesized for various applications [8–11]. Among them, ILs bearing long alkyl chains have been considered as novel surfactants and are named surface active ionic liquids (SAILs). These SAILs consist of a hydrophilic headgroup and a hydrophobic tail, similar to traditional ionic surfactants [12,13]. They can form aggregates with specific structure, shape, and properties and have been widely investigated in the area of colloid and interface chemistry.

In recent years, SAILs with diverse cation, such as imidazolium, pyridinium, and piperidinium, have been widely researched [14–17].

In particular, the aggregation behavior of alkyimidazolium-based SAILs has drawn most attention. Blesica and his coworkers [18] reported that anion nature and alkyl chain length of the cation significantly influence the aggregation behavior of C_{*n*}mimX (*n* = 2–14, X = Cl, PF₆). The surface adsorption and micelle formation of three SAILs ([C₁₀mim]Br, [C₁₂mim]Br and [C₁₂mim]BF₄) with the same hydrophilic portion and different hydrophobic groups or counterions were studied by Dong et al. [19]. They also investigated the micelle formation of imidazolium SAILs with extended alkyl chains, [C₁₄mim]Br and [C₁₆mim]Br [20]. With the sustainable development of chemicals, some vital issues such as biodegradability and stability of SAILs have been widely studied [21–23]. For this reason, some even more environmentally friendly anionic SAILs have arisen, for instance, alkylsulfate anionic SAILs free of halogen. Peter et al. [24] synthesized 1-butyl-3-methylimidazolium octylsulfate ([C₄mim][C₈H₁₇SO₄]) for the first time. Latter, Biczók's group [25] explored micelle formation of [C₄mim][C₈H₁₇SO₄] in aqueous solution with conductivity as well as turbidity measurements and found that it showed excellent surface active properties when compared to the traditional surfactant, sodium octylsulfate (SOS). Our group [26] researched the aggregation behavior of 1-butyl-3-methylimidazolium dodecylsulfate ([C₄mim][C₁₂SO₄]) and N-butyl-N-methylpyrrolidinium ([C₄MP][C₁₂SO₄]), which displayed better micelle properties than sodium dodecylsulfate (SDS), 1-dodecyl-3-methylimidazolium bromide

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80 ([C₁₂mim]Br) as well as N-dodecyl-N-methylpyrrolidinium bromide
81 (C₁₂MPB).

82 The main purpose of this study is to investigate the influence of
83 salicylate isomers as counterions on the self-aggregation behavior of
84 SAILs by surface tension, steady-state fluorescence and conductivity
85 measurements over a temperature range from 25 to 55 °C. The ob-
86 tained micellization parameters and thermodynamic parameters
87 for *m*-C₁₂mimHB and *p*-C₁₂mimHB (chemical structures are shown
88 in Scheme 1) are compared to those estimated for C₁₂mimSal. Our
89 experimental results suggest that the position of the substituent on
90 aromatic ring of counterion can considerably influence the micelliza-
91 tion process. Understanding the role of counterion played in the self-
92 aggregation behavior of SAILs is significant to promote its potential
93 application in the areas of nano-structured material fabrication,
94 drug delivery, etc.

95 2. Experimental section

96 2.1. Materials

97 1-Methylimidazole (99%) was purchased from Acros Organics and
98 distilled prior to use. 1-Bromododecane (98%), *m*-Hydroxybenzoic
99 (99%) and *p*-Hydroxybenzoic (99%) were all obtained from J&K Scientific
100 Co., Ltd. and used as received. Dichloromethane, ethyl acetate and
101 ethyl alcohol were all purchased from Tianjin Fuyu Chemical Reagent
102 Company of China. Triply distilled water was used to prepare aqueous
103 solutions.

104 2.2. Synthesis of SAILs

105 C₁₂mimBr was prepared according to the procedures reported previ-
106 ously [27]. C₁₂mimHB was synthesized by the neutralization method.
107 An aqueous solution of C₁₂mimBr was allowed to pass through a column
108 which was filled with anion exchange resin to obtain C₁₂mimOH. Then,
109 the C₁₂mimOH aqueous solution was neutralized with equal molar
110 hydroxybenzoic. C₁₂mimHB was obtained after removing water and
111 dried under vacuum for 48 h at 55 °C.

112 Both the purity of *m*-C₁₂mimHB and *p*-C₁₂mimHB were ascertained
113 by the ¹H NMR spectrum with a Bruker Avance 300 spectrometer. For
114 *m*-C₁₂mimHB, ¹H NMR (CDCl₃, δ/ppm): 0.87 (t, 3H, H₈), 1.04–1.32 (d,
115 18H, H₇), 1.54 (t, 2H, H₆), 3.82 (s, 3H, H₂), 3.88 (t, 2H, H₅), 6.76 (d, 1H,
116 arom. H₁₂), 7.01 (t, 1H, arom. H₁₁), 7.14 (m, 2H, H₃ and H₄), 7.26 (s,
117 1H, arom. H₉), 7.37 (d, 1H, arom. H₁₀), and 9.43 (s, 1H, H₁). For *p*-
118 C₁₂mimHB, ¹H NMR (CDCl₃, δ/ppm): 0.86 (t, 3H, H₈), 1.20–1.24 (d,
119 18H, H₇), 1.68 (t, 2H, H₆), 3.72 (s, 3H, H₂), 4.00 (t, 2H, H₅), 6.73 (d, 2H,
120 arom. H₉ and arom. H₁₂'), 7.19 (m, 2H, H₃ and H₄), 7.75 (m, 2H, arom.
121 H₁₀' and arom. H₁₁'), and 9.42 (s, 1H, H₁).

122 The melting points of *m*-C₁₂mimHB and *p*-C₁₂mimHB are 61.7 °C and
123 42.1 °C, respectively, determined on a Perkin Elmer Diamond differen-
124 tial scanning calorimeter. Thus, the imidazolium-based surfactants

prepared in this work belong to ILs (with melting point below 100 °C),
and can be named SAILs.

2.3. Surface tension measurements

Surface tension measurements were measured on the Krüss-K12
tensiometer (Krüss Company, Germany, accuracy ± 0.01 mN·m⁻¹)
using the plate method at 25 °C. All measurements were performed
for at least three times until the values were reproducible.

2.4. Steady-state fluorescence measurements

The fluorescence measurements were carried out on Tianjin
Gangdong fluorimeter F-280 (China) at 25 °C. Pyrene was used as a fluo-
rescent probe which concentration was kept constant at 1 × 10⁻⁶
mol·L⁻¹. The fluorescence emission spectra wavelength ranged from
350 to 500 nm with the excitation wavelength at 335 nm. Slit widths
for emission and excitation were fixed at 2.5 and 10 nm, respectively
[28]. I₁/I₃ was used to stand for the intensity ratio of the first
(373 nm) and the third (383 nm) vibronic peaks of pyrene.

2.5. Conductivity measurement

Conductivity was performed on a low-frequency conductivity ana-
lyzer (Model DDSJ-308A, Shanghai Precision & Science Instrument Co.,
Ltd. of China). The temperature was controlled by a HAAKE DC30-K20
thermostatic bath (Karlsruhe, Germany) within ± 0.1 °C. Each conduc-
tivity was recorded when its accuracy was better than 1% within 2 min.

3. Results and discussion

3.1. Surface properties and micellization parameters

Surface tension determination was carried out in order to evaluate
the surface activities of C₁₂mimHB in aqueous solutions. Fig. 2 exhibits
the surface tension (γ) as a function of concentration (C) for *m*-
C₁₂mimHB and *p*-C₁₂mimHB at 25 °C. For both SAILs, the surface tension
values decrease gradually with the increasing concentration up to a
plateau region, above which a nearly constant value can be obtained.
It is note worthy that the absence of a minimum around the breakpoint
indicates the high purities of the products prepared. The breakpoint of
the curves corresponds to the cmc and the obtained values are summa-
rized in Table 1, along with the corresponding data for C₁₂mimSal re-
ported by our group [29]. (See Fig. 1.)

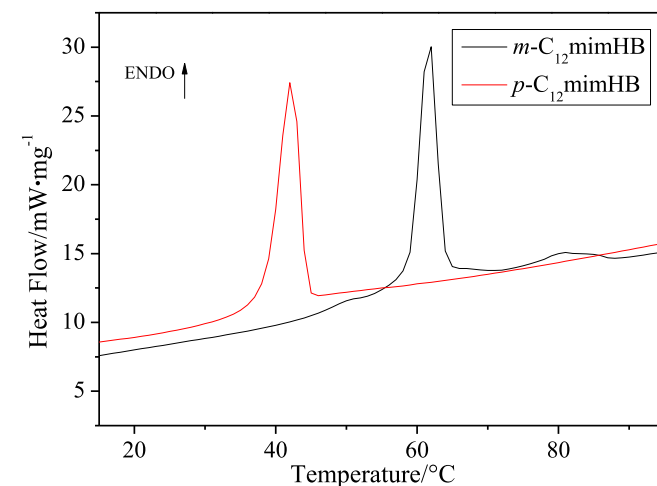
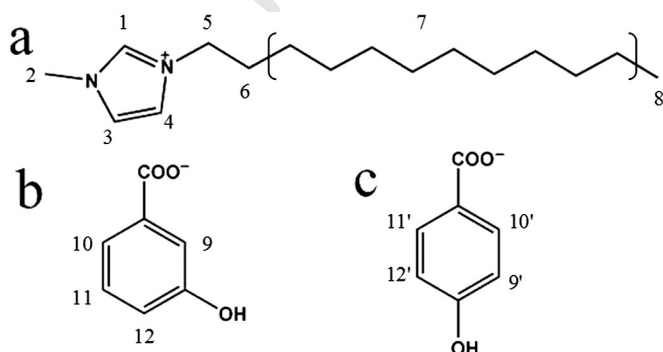


Fig. 1. Example DSC thermograms of as-synthesized ionic liquids measured at a heating rate of 10 °C·min⁻¹.



Scheme 1. Chemical structures of C₁₂mim⁺ (a), *m*-HB⁻ (b) and *p*-HB⁻ (c).

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