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Characterization and solution properties of adamantane-containing quaternary-ammonium-salt-type amphiphilic ionic liquids



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ABSTRACT

Quaternary-ammonium-salt-type amphiphilic compounds ($[C_nAdA][X]$, where *n* represents the alkyl chain length (n = 1, 2, 4, 6, 8, or 10), X represents a counterion such as $[BF_4]^-$, $[PF_6]^-$, trifluoromethanesulfonate ($[OTf]^-$), bis(fluorosulfonyl)amide ($[FSA]^-$), or bis(trifluoromethanesulfonyl)amide ($[NTf_2]^-$), and Ad and A of AdA represent the adamantane structure and quaternary ammonium group, respectively) were synthesized. The melting points of the prepared compounds were determined by differential scanning calorimetry, and the derivatives with melting points lower than 100 °C were classified as ionic liquids for subsequent analyses. The amphiphilic ionic liquids, $[C_nAdA][NTf_2]$ (n = 6 and 8), exhibited the lowest melting points (30.6 and 38.7 °C, respectively). Further, the $[C_nAdA][NTf_2]$ series of amphiphilic ionic liquids exhibited significantly lower conductivities and higher viscosities than the corresponding ionic liquids without the adamantane moiety, $[C_n][NTf_2]$. The viscosities of $[C_nAdA][NTf_2]$ (n = 6 and 8) decreased significantly with increasing temperature, and showed a larger temperature dependence than that of the viscosities of the $[C_n][X]$ series. The amphiphilic ionic liquids, $[C_8AdA][X]$ readily adsorbed at the air/water interface and oriented themselves but did not show the critical micelle concentration in the concentration range over which they could be dissolved in water. The amphiphilic ionic liquids and compounds tended to form ion pairs or premicelles, such as dimers or trimers, in aqueous solutions. (2019) Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids are salts that have melting points lower than 100 °C. These were first reported by Wilkes et al. in 1992 [1]. Ionic liquids are stable in both air and water, and generally exist in liquid state at room temperature. Recently, they have been the subject of extensive research efforts [2], because of their advantageous properties such as nonvolatility, nonflammability, and environmental friendliness, and they are attracting interest as novel solvents that are different from water and conventional organic solvents [2-7]. Ionic liquids can be prepared with different combination of cations and anions. Hence, their physicochemical properties, such as their melting point, density, viscosity, polarity, and hydrophobicity can be controlled readily. They are therefore being extensively explored for use as reaction solvents [2,3], electrolytes [2,4], catalysts [2,4,5], lubricants [8], and drug delivery systems [9]. Ionic liquids with different structures and functions, such as external-stimuli-responsive ionic liquids [10], magnetic ionic liquids [11], and cellulose-dissolving ionic liquids [12] have been reported,

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and the development of other novel ionic liquids with better performance and greater functionality is expected in the future.

Adamantane (tricyclo[3,3,1,1]decane, $C_{10}H_{16}$) has a saturated hydrocarbon cyclic tetrahedral structure with its 10 carbons bonded as in diamond. Adamantane has many useful chemical and physical properties owing to its peculiar structure. Some examples of the expected properties are its transparency, rigidity, high hydrophobicity, lubricity, and heat resistance due to the high CH density and weak interstitial interaction. Adamantane and its derivatives are widely used in the research and development of various pharmaceutical products, display materials, and photoresists. Recently, we molecularly designed and synthesized monomeric and bola-type cationic surfactants possessing an adamantane moiety, and revealed an increase in the hydrophobicity and decrease in the critical micelle concentration (CMC) of the molecules upon introducing the adamantane unit, as well as the solubilization of naphthalene and fatty acids [13,14].

It is known that amphiphilic ionic liquids containing an alkyl chain show surface activities and form aggregates in an aqueous solution, similar to surfactants [15]. However, these amphiphilic ionic liquids are mostly based on imidazole [16,17] and amine-salt-containing protictype compounds [18], and there have been very few reports on quaternary-ammonium-salt-type amphiphilic ionic liquids [19,20]. Chujo et al. synthesized adamantane-containing imidazolium-based amphiphilic ionic liquids and reported the lowest melting point (21

 $[\]label{eq:abbreviations:DMSO, dimethyl sulfoxide; OTf, trifluoromethanesulfonate; FSA, bis (fluorosulfonyl) amide; NTf_2, bis(trifluoromethanesulfonyl) amide.$

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°C) for an ionic liquid with an alkyl chain length of 12 [21]. Further, introduction of the bulky adamantane unit into the structure of ionic liquids instead of the imidazolium unit is expected to further lower the melting point of the ionic liquid. There have been no reports on the preparation of adamantane derivatives of quaternary-ammonium-salttype amphiphilic compounds or the evaluation of their properties as ionic liquids and their surface activity in aqueous solutions.

In this study, quaternary-ammonium-salt-type amphiphilic compounds with an adamantane moiety were designed and synthesized. The amphiphiles have the structure of $[C_nAdA][X]$, where *n* represents the alkyl chain length; n = 1, 2, 4, 6, 8, 10, or 12, (here, for n = 1, commercially available trimethyladamantylammonium bromide was used), X represents the counterion ($[BF_4]^-$, $[PF_6]^-$, $[OTf]^-$, $[FSA]^-$, or $[NTf_2]^-$), and Ad and A of AdA represent an adamantane moiety and a quaternary ammonium group, respectively (see Fig. 1a). We investigated their properties as ionic liquids as well as their surface activity in aqueous solutions in comparison with those of the corresponding parent compounds without the adamantane moiety ($[C_n][X]$, n = 2, 4, 6, 8, 10; see Fig. 1b). Further, we discuss the effects of the adamantane structure, alkyl chain length, and structure of the counterion of the derivatives on the properties of $[C_nAdA][X]$.

2. Experimental

2.1. Materials

1-Aminoadamantane hydrochloride, ethyl bromide, n-butyl bromide, n-hexyl bromide, n-octyl bromide, n-decyl bromide, and ndodecyl bromide were purchased from Tokyo Chemical Ind. Co., Ltd. (Tokyo, Japan). Silver tetrafluoroborate (Ag[BF₄]), potassium hexafluorophosphate (K[PF₆]), potassium trifluoromethanesulfonate (K[OTf]), acetone, acetonitrile, chloroform, dimethyl sulfoxide (DMSO), ethanol, ethyl acetate, formaldehyde solution (37%), formic acid solution (98%), hexane, 1 mol dm⁻³ hydrochloric acid, methanol, 2-propanol, and sodium hydroxide were obtained from FUJIFILM Wako Pure Chemical Co., Ltd. (Osaka, Japan). Potassium bis (trifluoromethanesulfonyl)amide (K[NTf₂]) was purchased from Kanto Chemicals Co., Inc. (Tokyo, Japan). Potassium bis(fluorosulfonyl)amide (K[FSA]) was kindly supplied by Nippon Shokubai Co., Ltd. (Osaka, Japan). Trimethyladamantylammonium bromide was supplied by Idemitsu Kosan Co. Ltd. (Tokyo, Japan). Deuterated chloroform and deuterated dimethyl sulfoxide used as NMR solvents were purchased from Cambridge Isotope Laboratories Inc. (Andover, USA). All chemicals were used as received without further purification. Water from a Merck KGaA Direct–Q UV system (resistivity = $18.2 \text{ M}\Omega$ cm, Darmstadt, Germany) was used in all the experiments.

2.2. Synthesis of N, N-dimethyl-N-alkyladamantylammonium bromide ([C_nAdA][Br]) [13]

1-Aminoadamantane hydrochloride was added to 200 mL of methanol containing 8 g of sodium hydroxide, and the solution was stirred with heating for 2 h. Then, the solvent was removed by rotary evaporation and the residue was washed at least thrice with water to recover 1aminoadamantane as a white solid.

A solution of 1-aminoadamantane (1.0 equiv.) in methanol was added to a stirred mixture of 37% formaldehyde (4.0 equiv.) and 98% formic acid (3.0 equiv.), and the resulting mixture was refluxed for 12 h. After that, the solvent was removed by evaporation, water was added to the residue, and the pH of the solution was adjusted to 1–2 with 1 mol dm⁻³ HCl. Then, the solvent was evaporated, the residue was washed repeatedly, first with hexane and then with ethyl acetate, and the product was dried under vacuum to recover *N*, *N*-dimethylaminoadamantane hydrochloride as a white solid (Scheme S1). The structure was confirmed by ¹H NMR spectroscopy (see Supplementary material).

The obtained product was added to 200 mL of methanol containing 8 g of sodium hydroxide, and stirred with heating for 2 h. After the solvent was removed by evaporation, ethyl acetate was added to the residue, and the solution was heated and filtered to remove inorganic salts. The solvent was evaporated under reduced pressure to recover *N*, *N*-dimethylaminoadamantane as a yellow liquid.

Ethyl bromide, *n*-butyl bromide, *n*-hexyl bromide, *n*-octyl bromide, *n*-decyl bromide, or *n*-dodecyl bromide (2.0 equiv.) was added slowly to a stirred solution of *N*, *N*-dimethylaminoadamantane (1.0 equiv.) in acetonitrile. The mixture was refluxed for 30 h. After the solvent was evaporated under reduced pressure, the residue was washed repeatedly, first with hexane and then with ethyl acetate, and the product was recrystallized from 2-propanol to obtain *N*, *N*-dimethyl-*N*alkyladamantylammonium bromide [C_nAdA][Br] (n = 2, 4, 6, 8, 10, or12) as a white solid (Scheme S1) (see Supplementary material for yields, ¹H NMR data, and elemental analysis).

2.3. Ion-exchange of Br^- in $[C_nAdA][Br]$ with $[BF_4]^-$, $[PF_6]^-$, $[OTf]^-$, $[FSA]^-$, and $K[NTf_2]^-$

The aqueous solution of trimethyladamantylammonium bromide or N, N-dimethyl-N-alkyladamantylammonium bromide (1.0 equiv.) was added to an aqueous solution of Ag[BF₄], K[PF₆], K[OTf], K[FSA], or K [NTf₂] (1.1 equiv.), and the mixture was stirred with heating for 10 h. The purification procedure for the derivative with each counterion is described below.

 $[C_nAdA][BF_4]$: After the precipitated gray solid was removed by filtration, the solvent in the filtrate was evaporated under reduced



Fig. 1. Chemical structures of (a) adamantane-containing quaternary-ammonium-salt-type amphiphilic compounds, $[C_nAdA][X]$ (n = 1-12), (b) amphiphilic compounds without the adamantane moiety, $[C_n][X]$ (n = 2-10), and (c) counterions, X.

pressure. The residue was dissolved in acetone for n = 1 and in chloroform for n = 2, 4, 6, 8, 10, and 12. The insoluble inorganic salt was removed by filtration and the solvent in the filtrate was evaporated. The residue was washed repeatedly with ethyl acetate and the product was recrystallized from a mixture of ethyl acetate and methanol (3:1, vol/vol) to obtain the target compound.

 $[C_nAdA][PF_6]$: After the solution was filtered, the residue was washed five times with water and then dried. Hot acetone was added to the dried residue, and then it was filtered to remove the inorganic salt. The solvent in the filtrate was removed by evaporation, and the residue was recrystallized from acetone.

 $[C_nAdA][OTf]$: After the solvent in the solution was evaporated under reduced pressure, chloroform was added to the residue. The inorganic salt was removed by filtration, and the filtrate was evaporated.

 $[C_nAdA][FSA]$ and $[C_nAdA][NTf_2]$: Once the white solid precipitated, the solution was filtered to recover the solid. On the other hand, in the case where the solution separated into two phases, the upper phase was removed by decantation to recover the bottom liquid phase. The residue was washed five times with water and then dried. Chloroform was added to the dried residue, and it was then filtered to remove the inorganic salt, and the solvent in the filtrate was removed by evaporation.

These residues were dried under reduced pressure to obtain *N*, *N*-dimethyl-*N*-alkyladamantylammonium [BF₄, PF₆, OTf, FSA, or NTf₂] as a white solid or a clear yellow viscous material (Scheme S1) (see Supplementary material for yields, ¹H NMR data, and elemental analysis).

2.4. Characterization

The melting points of the adamantane-containing amphiphilic compounds were determined by differential scanning calorimetry (DSC; Shimadzu DSC-50 system, Kyoto, Japan). For the measurements, 2 mg of the compound was placed in a hermetically sealed aluminum pan; an empty aluminum pan was used as the reference. The measurements were performed at the heating rate of 0.2 $^{\circ}$ C min⁻¹ in a nitrogen atmosphere, and the obtained data was corrected and analyzed using the software, Shimadzu TA-60WS (Kyoto, Japan). The water contents of the amphiphilic ionic liquids were determined using a coulometric titration system (Hiranuma AQV-200, Karl Fischer, Tokyo, Japan). The viscosities were measured at 35, 45, 55, and 65 °C using a Brookfield DV-2T system (Middleborough, MA, USA).

The electrical conductivities of the neat amphiphilic ionic liquids and their aqueous solutions were measured using a TOA CM-30R system (Tokyo, Japan). From the data, the Krafft temperatures and CMC values of the ionic liquids in aqueous solutions were determined. The surface tensions of neat ionic liquids and their aqueous solutions were measured with a Teclis Tracker tensiometer (Lyon, France) by the pendant drop technique. The surface excess concentration (Γ /mol m⁻²) and occupied area per molecule (A) of the amphiphilic ionic liquids at the air/water interface were calculated using the Gibbs adsorption isotherm equations: $\Gamma = -(1/iRT)(d\gamma/iRT)$ d ln*C*) and $A = 1/(N\Gamma)$ [22], where γ is the surface tension, *C* is the concentration of the ionic liquid, R is the gas constant (8.31 J K⁻¹ mol⁻¹), *T* is the absolute temperature, and *N* is the Avogadro's constant. The value of *i*, which is the number of ionic species assumed to be completely dissociated in the aqueous solution, was taken to be 2 for the adamantane-containing amphiphilic ionic liquids investigated in this study. The fluorescence of pyrene [23,24] in the amphiphilic ionic liquid solutions was measured using a JASCO FP-6300 system (Tokyo, Japan). The concentration of pyrene in the ionic liquid solutions was 1×10^{-6} mol dm⁻³. The aqueous solutions of the adamantane-containing amphiphilic ionic liquids and compounds were prepared using ultra-pure water from a Direct-Q UV system, and the measurements were performed at 25.0 \pm 0.5 °C.

3. Results and discussion

3.1. Melting points of the amphiphilic derivatives

Fig. 2 shows the relationship between the melting point (see Table S1) and alkyl chain length *n* for the amphiphilic compounds, $[C_nAdA][X]$ (X = $[BF_4]^-$, $[PF_6]^-$, $[OTf]^-$, $[FSA]^-$, and $[NTf_2]^-$). The melting points of adamantane-containing amphiphilic compounds decrease in the following order based on the type of counterion: $[Br]^- > [PF_6]^- > [BF_4]^- > [OTf]^- > [FSA]^- > [NTf_2]^-$ except for $[C_8AdA][BF_4]$ and $[C_8AdA]$ [OTf]. The series of $[C_nAdA][FSA]$ compounds (with the exception of *n* = 2 and 12) and $[C_nAdA][NTf_2]$ compounds (with the exception of *n* = 2) that contain bulky counterions have melting points lower than 100 °C. That is, they can be classified as ionic liquids. In general, ionic liquids are salts consisting of cations and anions with weak electrostatic interactions [1].

Ionic liquids have low melting points than inorganic salts because they contain organic ions with a bulky structure [25]. In particular, [C₆AdA][NTf₂] and [C₈AdA][NTf₂] are almost in the liquid state at room temperature (their melting points are 30.6 and 38.7 °C, respectively). The melting points of adamantane-containing amphiphilic ionic liquids $([C_nAdA][X])$ are higher than those of the corresponding derivatives without adamantane $([C_n][X])$ (see Fig. S1), indicating that there is no decrease in the melting point with the introduction of the bulky adamantane moiety into the structure, which is due to the rigidity and symmetry of adamantane [26]. The melting point of amphiphilic derivatives [C_nAdA][FSA] and [C_nAdA][NTf₂] first tended to decrease with an increase in the alkyl chain length from 2 to 4 or 6, respectively, and increased slightly with a further increase in the alkyl chain length. We speculate that the melting point decreased because of the breakage of the symmetry of the cation by adamantane and decreased interaction between the cation and anion in the case of derivatives with a shorter alkyl chain. Further, as the alkyl chain length increased, the melting point increased owing to van der Waals forces between the alkyl chains. On the other hand, the melting points of amphiphilic derivatives without the adamantane moiety, $[C_n][FSA]$ and $[C_n][NTf_2]$ are the lowest at the alkyl chain length of 8 (7 °C for $[C_8][FSA]$ and <0 °C for $[C_8][NTf_2]$). This result indicates that the effect of the van der Waals forces in adamantane-containing ionic liquids manifests at a shorter alkyl chain length than for the ones without adamantane. The melting point of [C₁][NTf₂] containing tetramethylammonium group is 133 °C [27] while that of [C₁AdA][NTf₂], in which one of the methyl groups is replaced with adamantane, is 96 °C. The melting point of [C₁][NTf₂] is high because of the symmetry of the tetramethylammonium cation.



Fig. 2. Relationship between the melting point and alkyl chain length *n* for $[C_nAdA][X]$: $X = Br^{-}(\bullet)$; $[BF_4]^{-}(\bullet)$; $[PF_6]^{-}(\bullet)$; $[OTf]^{-}(\bullet)$; $[FSA]^{-}(\bullet)$; $[NTf_2]^{-}(\bullet)$.

Further, the melting point of $[C_1AdA][NTf_2]$ is lower than that of $[C_1]$ [NTf₂] because the distance between the cation and anion is increased, and thus the interaction between them weakens, and they could not be packed densely owing to the bulkiness of adamantane. Considering that the melting point of adamantane is 269 °C [26,28], it is interesting to note that the melting point of adamantane could be decreased to a value close to room temperature with the introduction of an alkyl chain into the structure of adamantane; that is, by constructing a quaternary-ammonium-salt-type amphiphilic structure.

3.2. Characterization of adamantane-containing amphiphilic ionic liquids

The water contents of the adamantane-containing amphiphilic ionic liquids [C_nAdA][X] (n = 1, 4, 6, 8, and 10) and [C_nAdA][NTf₂] (n = 1, 4, 6, 8, 10, and 12) were determined to be <100 ppm. Therefore, it was deemed that investigating the properties of these ionic liquids would not be problematic. Table 1 shows the conductivity (κ), zero-shear viscosity (η_0) , density (ρ) , and surface tension (γ) of amphiphilic ionic liquids [C₆AdA][NTf₂] and [C₈AdA][NTf₂] along with those of the corresponding amphiphilic ionic liquids without adamantane [C₆] [NTf₂] and [C₈][NTf₂]. The adamantane-containing amphiphilic ionic liquids showed much lower conductivity and higher viscosity compared to those of the amphiphilic derivatives without adamantane. The viscosity increases because of the decreased mobility of the cationic portion of the molecule with the rigid adamantane moiety; the conductivity decreases as a result of the decreased ionic mobility. The conductivities of both the ionic liquids, [C₈AdA][NTf₂] with adamantane and [C₈] [NTf₂] without adamantane, increased with an increase in the temperature between 45 and 65 °C at a similar rate (see Fig. S2). The viscosity of $[C_nAdA][NTf_2]$ and $[C_n][NTf_2]$ (n = 6 and 8) decreased with an increase in the temperature. Further, the rate of decrease in the viscosity with temperature for $[C_nAdA][NTf_2]$ is much larger than that for $[C_n][NTf_2]$ (see Fig. S3). A large difference in the viscosity of amphiphilic ionic liquids with and without adamantane is observed at 35 and 45 °C, whereas their viscosities become almost same at 65 °C. Thus, the amphiphilic ionic liquids with adamantane show a larger temperature-dependence of viscosity compared to that of the amphiphilic ionic liquids without adamantane. At the same alkyl chain length, the density of the adamantane-containing amphiphilic ionic liquid, [CnAdA][NTf2] is almost the same as that of the corresponding derivative, $[C_n][NTf_2]$ without adamantane; that is, no difference in density is observed after the introduction of adamantane into the structure. Further, the surface tensions of $[C_nAdA][NTf_2]$ are higher than those of the corresponding $[C_n]$ [NTf₂] derivatives.

Thus, the introduction of adamantane into the structure of quaternary-ammonium-salt-type ionic liquids led to remarkable differences in the surface tension and variation of the conductivity and viscosity with temperature.

3.3. Solubility in various organic solvents

The solubilities of adamantane-containing amphiphilic compounds $[C_8AdA][X]$ (X = [FSA]⁻ and [NTf₂]⁻), which are ionic liquids, and $[C_8AdA][X]$ (X = [BF₄]⁻, [OTf]⁻, and [NTf₂]⁻), which are not ionic liquids, in various organic solvents such as DMSO, methanol, acetone,

ethyl acetate, chloroform, benzene, and hexane were determined by mixing 0.01–10 mL of water or an organic solvent with 0.01–0.1 g of the ionic liquid. The adamantane-containing amphiphilic ionic liquids and compounds [C₈AdA][X] have lower solubilities in water than the corresponding ionic liquids and compounds [C₈][X] without adamantane (see Table S2), because of the hydrophobicity of adamantane. The solubility of [C₈AdA][X] in water increases in the following order based on the counterion: $[NTf_2]^- < [FSA]^- < [PF_6]^- <$ $[OTf]^{-} < [BF_4]^{-}$ (Table S3). Further, the solubility of $[C_nAdA][NTf_2]$ decreases with an increase in the alkyl chain length (see Table S4). The adamantane-containing amphiphilic ionic liquids with [FSA]⁻ and [NTf₂]⁻ counterions also have excellent solubility in a wide range of organic solvents with different polarities (DMSO, methanol, acetone, and ethyl acetate), especially in ethyl acetate (see Table S3). The solubilities of ionic liquids without adamantane, $[C_n][NTf_2]$ in chloroform was determined to be below 0.8 wt% for $n \le 6$, whereas those of [C_nAdA] [NTf₂] with adamantane were found be above 45 wt% at all alkyl chain lengths. The solubilities of adamantane-containing amphiphilic ionic liquids [C_nAdA][NTf₂] in benzene increased significantly with an increase in the alkyl chain length from 8 to 10 (see Table S4), and were higher compared to those of $[C_n][NTf_2]$ at the same alkyl chain length. Further, both types of ionic liquids, with and without adamantane, were found to be insoluble in non-polar hexane. Thus, the introduction of adamantane into guaternary-ammonium-salt-type ionic liquids improved their solubilities in various organic solvents. The solubility of adamantane is 10.9 wt% in benzene and 10.8 wt% in hexane [29], whereas the solubility of C_nAdA X is 0.5–31 wt% in benzene and it is almost insoluble in hexane (solubility, <0.01 wt%) (see Table S3). Thus, the solubility of the compounds in non-polar organic solvents decreased with the introduction of quaternary ammonium unit into the adamantane structure.

3.4. Solution properties of adamantane-containing amphiphilic ionic liquids

The solution properties of the adamantane-containing amphiphilic ionic liquids $[C_nAdA][X]$ ($n = 1, 4, 6, and 8, X = [FSA]^- and [NTf_2]^-$) and the amphiphilic compounds $[C_nAdA][X]$ (n = 1 and 8, $X = [BF_4]^-$, $[PF_6]^-$, and $[OTf]^-$) that are not ionic liquids, including their Krafft temperature, conductivity, surface tension, and pyrene fluorescence in their solutions were determined.

3.4.1. Krafft temperature (T_K)

Clear aqueous solutions of the adamantane-containing amphiphilic ionic liquids and compounds (0.050–0.020 wt%) were prepared by dissolving them in hot water and incubating the obtained solution in a refrigerator at ~5 °C for at least 24 h. As the solutions were clear with no visible precipitates, the $T_{\rm K}$ value for the ionic liquids and compounds was estimated to be <5 °C. The amphiphilic ionic liquids, [C₁AdA][FSA] (0.20 wt%), [C₆AdA][FSA] (0.050 wt%), [C₈AdA][FSA] (0.010 wt%), and [C₁AdA][NTf₂] (0.20 wt%) precipitated in the solution. Therefore, the temperature of the cooled solution was gradually increased under constant stirring, and the conductance (κ) was measured over the temperature range of 0.5 to 5.0 °C. Initially, the conductivity increased rapidly with increasing temperature because of the gradual dissolution of the

Table 1

Melting point (T_m), conductivity (κ), viscosity (η_0), density (ρ), and surface tension (γ) values of amphiphilic ionic liquids [C_n AdA][NTf₂] and [C_n [[NTf₂].

Ionic liquid	T _m ∕°C	$\frac{\kappa}{mS} m^{-1}$			η ₀ /mPa s				$ ho$ /g cm $^{-3}$	γ /mN m ⁻¹	
		35 °C	45 °C	55 °C	65 °C	35 °C	45 °C	55 °C	66 °C	45 °C	45 °C
$[C_6AdA][NTf_2]$ $[C_8AdA][NTf_2]$ $[C_6][NTf_2]$ $[C_8][NTf_2]$	30.6 38.7 28.8 <0	5.34 112	12.1 71.1	24.2 89.1	33.1 100	865 82.9	503 461 53.8 68.7	276 257 39.0 46.7	186 155 27.8 32.7	1.33 1.27 1.33 1.27	34.2 33.7 30.7 30.6

amphiphilic ionic liquid (see Fig. S4). Subsequently, it increased gradually owing to the increase in the ionic mobility. $T_{\rm K}$ was taken as the temperature at which the conductivity versus temperature plot exhibited an inflection point. The adamantane-containing amphiphilic ionic liquids with the formula $[C_1AdA][X]$ (X = $[FSA]^-$ and $[NTf_2]^-$) do not possess an alkyl chain, however, their T_K values at 0.20 wt% (25.5 and 26.5 °C, respectively) are higher than those of the $C_n X$ (n = 4 and 6) derivatives without adamantane ($T_{\rm K}$ < 5 °C). As mentioned above, the solubility of the derivatives in water was significantly lowered upon the introduction of the hydrophobic adamantane moiety. Further, the $T_{\rm K}$ values of amphiphilic ionic liquids $[C_1AdA][X]$ (X = $[FSA]^-$ and $[NTf_2]^-$) are higher than those of $[C_1AdA][X]$ (X = $[BF_4]^-$, $[PF_6]^-$, and $[OTf]^{-}$) ($T_K < 5$ °C). The T_K values of the amphiphilic ionic liquids and compounds, $[C_8AdA][X]$ (X = $[BF_4]^-$ (0.20 wt%), $[PF_6]^-$ (0.010 wt%), [OTf]⁻ (0.10 wt%), [FSA]⁻ (0.0050 wt%), and [NTf₂]⁻ (0.0050 wt%)) are <5 °C. Therefore, their other solution properties were evaluated at 25 °C.

3.4.2. Conductivity, surface tension, and pyrene fluorescence

Figs. 3 and 4 show the plots of the conductivity, and surface tension and pyrene fluorescence intensity ratio, I_1/I_3 , as functions of the concentration, respectively, for the adamantane-containing amphiphilic ionic liquids $[C_8AdA][X]$ (X = $[FSA]^-$ and $[NTf_2]^-$) and compounds $[C_8AdA]$ [X] (X = $[BF_4]^-$, $[PF_6]^-$, and $[OTf]^-$) with melting points above 100 °C that are not ionic liquids. The conductivity of [C₈AdA][X] increases with increasing concentration, and the conductivity vs. concentration curve shows an inflection point. On the other hand, the surface tension decreases (without remaining constant) with increasing concentration, while the pyrene I_1/I_3 ratio remains constant (without any decrease) with increasing concentration, and no inflection point is observed in the plots. The broken lines in Fig. 4 show the concentration corresponding to the inflection point in the conductivity vs. concentration plot (C_{LP}) for each solution. These results indicate that $[C_8AdA][X]$ derivatives do not form micelles in aqueous solutions, although they adsorb at the air/water interface in the concentration range over which they could be dissolved in water. It has been previously reported that amphiphilic compounds with short alkyl chains (n = 8) exhibit two inflection points in their conductivity plots [30-32]. The inflection point at the higher concentration corresponds to the CMC, as confirmed by the results of the surface tension and fluorescence measurements. Further, the inflection points at concentrations lower than the CMC are attributable to the formation of an ion pair between the ammonium cation and its counterion or premicelles such as dimers or trimers. The amphiphilic



Fig. 3. Variation in conductivity with the concentration of amphiphilic ionic liquids and compounds $[C_8AdA][X]$ at 25 °C: $X = [BF_4]^-(\bullet)$; $[PF_6]^-(\bullet)$; $[OTf]^-(\bullet)$; $[FSA]^-(\bullet)$; $[NTf_2]^-(\bullet)$.



Fig. 4. Variation in surface tension and pyrene fluorescence intensity ratio I_1/I_3 with the concentration of amphiphilic ionic liquids and compounds $[C_8AdA][X]$ at 25 °C: X = X = $[BF_4]^-(\bullet)$; $[PF_6]^-(\bullet)$; $[OTf]^-(\bullet)$; $[FSA]^-(\bullet)$; $[NTf_2]^-(\bullet)$; the broken lines shows C_{LP} obtained from the electrical conductivity measurement.

ionic liquids and compounds [C₈AdA][X] did not exhibit a second inflection point in their conductivity plots because of their poor solubility in water owing to the hydrophobic adamantane in their structure and the hydrophobic counterion.

The adsorption and orientation of amphiphilic compounds at the air/ water interface are related to their excess surface concentration, Γ , and the occupied area per molecule, A, which can be calculated from the slope of the linear curve for the dependence of the surface tension with the concentration for concentrations lower than the CMC and the Gibbs adsorption isotherm equations. Table 2 shows the concentration for ion-pair or premicelle formation ($C_{LP.}$) (CMC for [C_8AdA][Br]), the degree of dissociation (α), Γ , A, and pC_{20} values determined from the conductivity and surface tension plots. The $C_{1,P}$ values increase in the following order based on the counterion: $[BF_4]^- > [OTf]^- > [PF_6]^- >$ $[FSA]^- > [NTf_2]^-$, indicating that the amphiphilic ionic liquids with $[FSA]^-$ and $[NTf_2]^-$ counterions form ion pairs or premicelles at low concentrations. Further, the C_{LP} values decreased with an increase in the hydrophobicity of the counterion. The A values of the amphiphilic ionic liquids and compounds [C₈AdA][X] increased in the following order based on the counterion: $[BF_4]^- < [PF_6]^- < [OTf]^- < [FSA]^- <$ $[NTf_2]^-$ (see Fig. S5). This order indicates that the larger the radius of the counterion is, the larger the occupied area is. In particular, the occupied area of amphiphilic ionic liquids with [FSA]⁻ and [NTf₂]⁻ counterions was found to be large, which indicates that they adsorb widely at the air/water interface and orient by themselves. The pC_{20} of the amphiphilic ionic liquids and compounds [C₈AdA][X] increased in the following order based on the counterion: $[Br]^- < [BF_4]^- < [PF_6]^- < [OTf]^- <$ $[FSA]^- < [NTf_2]^-$. The amphiphilic ionic liquids with $[FSA]^-$ and [NTf₂]⁻ counterions adsorbed efficiently at the air/water interface despite being bulky. Thus, it can be concluded that the adsorption behaviors of [C₈AdA][X] at the air/water interface are significantly affected by the structure of the counterion; the amphiphilic ionic liquids adsorb widely at the interface but orient themselves efficiently.

4. Conclusions

In this study, we designed and synthesized adamantane-containing quaternary-ammonium-salt-type amphiphiles using five different counterions ($[BF_4]^-$, $[PF_6]^-$, $[OTf]^-$, $[FSA]^-$, or $[NTf_2]^-$), and investigated their physicochemical properties as ionic liquids as well as their properties in aqueous solutions. The melting points of the amphiphilic ionic liquids increased with the incorporation of the adamantane moiety into their structure. The adamantane-containing amphiphilic ionic liquids have higher viscosities and lower conductivities than the

Compound	T _m ∕°C	<i>Τ</i> _K /°C	$C_{\text{L.P.}}$ /mmol dm ⁻³	CMC /mmol dm ⁻³	α	$\frac{\Gamma \times 10^6}{/mol \; m^{-2}}$	A /nm ²	pC ₂₀
[C ₈ AdA][BF ₄]	139.2	<5 (0.20 wt%)	3.01	-	0.80	1.83	0.906	2.37
[C ₈ AdA][PF ₆]	162.3	<5 (0.050 wt%)	0.108	-	0.83	1.45	1.15	3.10
[C ₈ AdA][OTf]	151.3	<5 (0.10 wt%)	1.67	-	0.63	1.32	1.25	2.75
[C ₈ AdA][FSA]	76.3	<5 (0.0050 wt%)	0.107	-	0.76	1.12	1.62	3.38
[C ₈ AdA][NTf ₂]	38.7	<5 (0.0050 wt%)	0.0941	-	0.84	0.889	1.87	3.61
[C ₈ AdA][Br]	211.0	<5 (0.20 wt%)	-	27.1	0.30	1.76	0.943	1.78

Melting point (T_m), Krafft temperature (T_K), concentration for ion-pair formation ($C_{LP.}$), CMC, α , surface excess concentration (Γ), occupied area per molecule (A), and adsorption efficiency (pC_{20}) values of amphiphilic ionic liquids and compounds [C_8AdA][X] at 25 °C.

 C_{LP} , concentration at which ion pairs or premicelles are formed.

corresponding ionic liquids without the adamantane moiety, because of the structural rigidity of adamantane. The adamantane-containing amphiphilic ionic liquids with [FSA]⁻ and [NTf₂]⁻ counterions have excellent solubilities in organic solvents, such as DMSO, methanol, acetone, ethyl acetate, chloroform, and benzene, with different polarities. The amphiphilic ionic liquids with [FSA]⁻ and [NTf₂]⁻ counterions showed a large occupied area per molecule at the air/water interface. This resulted in their wide interfacial adsorption, while they oriented themselves efficiently. Thus, in this study, we elucidated the effects of the adamantane structure, alkyl chain length, and counterion structure on the physicochemical and aqueous-solution properties of adamantanecontaining quaternary-ammonium-salt-type ionic liquids. Although adamantane is a highly crystalline and rigid molecule, it is worth noting that the melting points of adamantane-containing quaternaryammonium-salt-type amphiphilic ionic liquids are relatively low at ~30 °C, and they exhibit unique characteristics, for e.g., their viscosity depends on the temperature and they adsorb at the air/water interface. In the future, we expect that it would be possible to synthesize novel high-performance functional amphiphilic ionic liquids through molecular design for various industrial applications, for example, as lubricants, drug delivery agents, new media for organic reactions, and electrolytes for electrochemical devices.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.molliq.2019.111586.

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