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1. Introduction

Ionic liquids, which only comprise cations and anions, display several properties such as low vapor pressure, high thermal stability, high conductivity, unique solubility, and wide electrochemical windows. Thus, they are attracting significant interest as novel alternatives to water and organic solvents.^{1–4} Bulky ions and delocalized ions as well as ionic structure dissymmetry lower the melting point of these liquids. Moreover, ionic liquids can be prepared from different cation and anion combinations. Hence, their physicochemical properties, such as the melting point, density, viscosity, polarity, and hydrophobicity, can be easily controlled. The application potential of these liquids as reaction solvents,^{1,2} electrolytes,² catalysts,^{1,3} and lubricants⁴ as well as in drug delivery systems⁵ and solubilization processes⁶ is therefore being explored in a wide range of fields.

Gemini surfactants, in which two conventional monomeric surfactants are connected by a spacer, have attracted significant interest because of their excellent surface-active properties. Particularly, these surfactants display lower critical micelle

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Physicochemical and solution properties of quaternary-ammonium-salt-type amphiphilic trimeric ionic liquids[†]

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The quaternary-ammonium-salt-type amphiphilic compounds $3C_n$ tris-s-Q X (star-type; carbon number between the central amino and ammonium groups s = 2, 3) and $3C_n$ lin-3-Q X (linear-type; carbon number between the hydrophilic groups s = 3), where *n* represents the alkyl chain length (n = 8, 10, 12, 14) and X represents a counterion [hexafluorophosphate, trifluoromethanesulfonate (OTf), bis(fluorosulfonyl)amide (FSA), and bis(trifluoromethanesulfonyl)amide (NTf₂)], were synthesized. Except for $3C_{12}$ tris-3-Q OTf, these trimeric compounds presented melting points lower than 100 °C and therefore are defined as ionic liquids. Among them, $3C_n$ tris-3-Q NTf₂ (n = 8, 12, 14) and $3C_n$ lin-3-Q NTf₂ (n = 8, 10) presented melting points lower than 0 °C. The melting points of the amphiphilic trimeric ionic liquids (n = 8, 10), which were lower for the star- than for the linear-type compounds, were higher than those of the corresponding monomeric compounds but lower than those of the corresponding gemini samples. Moreover, the amphiphilic trimeric ionic liquids exhibited higher conductivities and lower viscosities than the corresponding gemini ionic liquids, while the star-type trimeric ionic liquids presented lower conductivities and higher viscosities than those of the linear-type compounds. The amphiphilic trimeric ionic liquids also readily adsorbed at the air/water interface and oriented themselves to form micelles in aqueous solution. This aggregation behavior was not observed in the monomeric and gemini ionic liquids.

> concentrations (CMCs) and a greater ability to lower the surface tension than those of the corresponding monomeric surfactants.⁷⁻¹¹ We have previously developed star- and linear-type trimeric surfactants to further improve the performance and express the functionality of gemini surfactants.¹²⁻¹⁴ The afforded products presented excellent surface-active properties, which exceeded those of the corresponding monomeric and gemini surfactants. Further, the results revealed that the melting point of the quaternary-ammonium-salt-type gemini ionic liquids could be lowered to ~ 40 °C by introducing bulky counterions and changing the dissymmetry of the alkyl chains. These surfactants also exhibited excellent adsorption properties at the air/water interface.¹⁵ We therefore predicted that the melting point could be lowered by the introduction of a bulky counterion into the star- and lineartype trimeric surfactants, thereby leading to the formation of ionic liquids. Thus, novel amphiphilic ionic liquids that exhibit both ionic liquid and surfactant properties could be developed. Notably, few reports on imidazolium-, phosphonium-, and pyridinium-type trimeric ionic liquids¹⁶⁻¹⁸ and no reports on quaternary-ammonium-salt-type amphiphilic trimeric ionic liquids are available in the literature.

> With this in mind, in this study, we synthesized the quaternaryammonium-salt-containing star- and linear-type amphiphilic trimeric compounds $3C_n$ tris-s-Q X and $3C_n$ lin-3-Q X, respectively,



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Fig. 1 Chemical structures of the quaternary-ammonium-salt-type trimeric amphiphilic compounds (a) $3C_n$ tris-s-Q X (star-type) and (b) $3C_n$ lin-3-Q NTf₂ (linear) and (c) of the counterions X.

[alkyl chain length n = 8, 10, 12, 14; *s* represents the carbon number between the central amino group and ammonium group for the star-type samples (s = 2, 3) and the carbon number between the hydrophilic groups for linear-type samples (s = 3)] with the bulky counterions (X) hexafluorophosphate (PF₆), trifluoromethanesulfonate (OTf), bis(fluorosulfonyl)amide (FSA), and bis(trifluoromethanesulfonyl)amide (NTf₂) (X = NTf₂ for 3C_ntris-2-Q X and 3C_nlin-3-Q X and PF₆, OTf, FSA, NTf₂ for 3C_ntris-3-Q X; Fig. 1). Subsequently, their ionic liquid and surface-active properties in aqueous solutions were investigated and compared to those of the corresponding monomeric and gemini compounds. Finally, we discussed the effects of the alkyl and spacer chain lengths, molecular skeleton, number of chains, and ionic liquid counterion structure on these properties.

2. Experimental

2.1. Materials

Tris(2-aminoethyl)amine hydrochloride, N,N',N'',N''-pentamethyldipropylenetriamine, *n*-octyl bromide, *n*-octyl iodide, *n*-decyl bromide, *n*-decyl iodide, *n*-dodecyl bromide, *n*-decyl iodide, and *n*-tetradecyl bromide were purchased from Tokyo Chemical Ind. Co., Ltd (Tokyo, Japan). Potassium hexafluorophosphate (KPF₆), potassium trifluoromethanesulfonate (KOTf), acetone, acetonitrile, chloroform, dimethyl sulfoxide (DMSO), ethanol, ethyl acetate, formaldehyde solution (37%), formic acid solution (98%), hexane, hydrochloric acid (1 mol dm⁻³), methanol, and sodium hydroxide were purchased from FUJIFILM Wako Pure Chemical Co., Ltd (Osaka, Japan). Tris(*N*,*N*-dimethyl-3-aminopropyl)amine was kindly supplied by Tosoh Co., Ltd (Tokyo, Japan). KNTf₂ was purchased from Kanto Chemicals Co., Inc. (Tokyo, Japan). Potassium bis(fluorosulfonyl)amide (KFSA) was kindly supplied by Nippon Shokubai Co., Ltd (Osaka, Japan). Deuterated chloroform NMR solvent was 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 M Ω cm; Darmstadt, Germany) was used in all the experiments.

2.2. Synthesis of tris(*N*-alkyl-*N*,*N*-dimethyl-2-ammonioethyl)amine tribromide ($3C_n$ tris-2-Q Br) and triiodide ($3C_n$ tris-2-Q I)¹³

Tris(2-aminoethyl)amine (10.0 g, 1.0 equiv.) in methanol was added to a stirred mixture of 37% formaldehyde (1.2 equiv.) and 98% formic acid (1.1 equiv.), and the resulting mixture was refluxed for 12 h. Next, 1 mol dm⁻³ HCl was added to the solution, which was then stirred with heating for 3 h. Subsequently, the solvent was evaporated and the residue was washed twice with methanol. Finally, the product was dried under vacuum to recover tris(*N*,*N*-dimethyl-2-aminoethyl)amine hydrochloride as a white solid.

The afforded product was added to 200 mL of methanol containing 8 g of sodium hydroxide and subsequently stirred with heating for 2–3 h. After the solvent was removed by evaporation, acetone was added to the residue and the solution was filtered to remove the inorganic salts. The solvent was then evaporated under reduced pressure to recover tris(*N*,*N*-dimethyl-2-aminoethyl)amine as a brown viscous liquid.

n-Octyl iodide, *n*-decyl iodide, *n*-dodecyl iodide, or *n*-tetradecyl bromide (6.0 equiv.) was next added slowly to stirred solutions of tris(*N*,*N*-dimethyl-2-aminoethyl)amine in ethanol. The mixtures were refluxed for at least 40 h. After the solvent in each sample was evaporated under reduced pressure, the residues were washed repeatedly, first with ethyl acetate and then with hexane. Subsequently, the products were recrystallized from ethyl acetate/ ethanol mixtures (2:1, vol/vol, for *n* = 8, 10, 12 and 1:1, vol/vol, for *n* = 14) to obtain $3C_{14}$ tris-2-Q Br and $3C_n$ tris-2-Q I (*n* = 8, 10, and 12) as white solids (Scheme S1; yields, ¹H NMR data, and elemental analysis data in the ESI†).

2.3. Synthesis of tris(*N*-alkyl-*N*,*N*-dimethyl-3-ammoniopropyl)amine tribromide (3C_ntris-3-Q Br)

n-Octyl bromide, *n*-decyl bromide, *n*-dodecyl bromide, or *n*-tetradecyl bromide (6.0 equiv.) was added slowly to stirred solutions of tris(*N*,*N*-dimethyl-3-aminopropyl)amine (1.0 equiv.) in acetonitrile. The mixtures were refluxed for at least 40 h. Subsequently, the solvent was evaporated under reduced pressure and the collected residues were washed repeatedly, first with ethyl acetate and then with acetone. The products were recrystallized from ethyl acetate/ethanol mixtures (4:1, vol/vol) to form $3C_n$ tris-3-Q Br (*n* = 8, 10, 12, 14) as a white solid (Scheme S1; yields, ¹H NMR data, and elemental analysis data in the ESI[†]).

2.4. Synthesis of methylalkylbis[3-(dimethylalkylammonio)propyl]ammonium tribromide (3C_nlin-3-Q Br)

n-Octyl bromide, *n*-decyl bromide, *n*-dodecyl bromide, or *n*-tetradecyl bromide (6.0 equiv.) was added slowly to stirred solutions of N,N,N',N'',N''-pentamethyldipropylenetriamine (1.0 equiv.) in acetonitrile. The mixtures were refluxed for 45 h. After the solvent in each sample was evaporated under reduced pressure, the residues were washed repeatedly, first with hexane and then with ethyl acetate. The products were recrystallized from a mixture of ethyl acetate and methanol (6:1, vol/vol) to form $3C_n$ lin-3-Q Br (n = 8, 10, 12, 14) as a yellow-white solid (Scheme S1; yields, ¹H NMR data, and elemental analysis data in the ESI†).

2.5. Anion-exchange of the halide ions with the counter anions PF_6 , OTf, FSA, and NTf_2

Exactly 1.0 equiv. $3C_{12}$ tris-3-Q Br aqueous solution was added to 3.6 equiv. KPF₆, KOTf, and KFSA aqueous solutions, while aqueous solutions (1.0 equiv.) of $3C_n$ tris-2-Q I (n = 8, 10, 12), $3C_{14}$ tris-2-Q Br, $3C_n$ tris-3-Q Br (n = 8, 10, 12, 14), and $3C_n$ lin-3-Q Br were added to KNTf₂ aqueous solution. The mixtures were stirred with heating for 10 h. The purification procedures for the derivative with each counterion are as follows.

2.5.1 $3C_{12}$ tris-3-Q PF₆. After the solution was filtered, the residue was washed fivefold with water and then dried. Next, acetone was added to the dried residue and the resultant mixture was filtered to remove the inorganic salt. The solvent in the filtrate was then removed by evaporation. Next, chloroform was added to the residue and the resultant mixture was filtered to remove the inorganic salt. This was followed by evaporation to remove the solvent in the filtrate.

2.5.2 $3C_{12}$ tris-3-Q OTf. After the solvent in the solution was evaporated under reduced pressure, acetone was added to the residue to remove the inorganic salt and the filtrate was evaporated. Chloroform was then added to the residue and the mixture was filtered to remove the inorganic salt. This was followed by evaporation to remove the solvent in the filtrate.

2.5.3 $3C_{12}$ tris-3-Q FSA, $3C_n$ tris-2-Q NTf₂, $3C_n$ tris-3-Q NTf₂, and $3C_n$ lin-3-Q NTf₂. After the upper phase was removed by decantation, the residues were washed fivefold with water and subsequently dried. Acetone was then added to each residue and the resultant mixtures were filtered to remove the inorganic salt. Next, the solvent in each filtrate was removed by evaporation and chloroform was added to each residue. Each resultant mixture was filtered to remove the inorganic salt and the solvent in each filtrate was removed by evaporation. Further, ethyl acetate was added to the residues produced from $3C_n$ tris-2-Q I (n = 8, 10, 12) and $3C_{14}$ tris-2-Q Br and subsequently filtered to remove the inorganic salt. The solvent in each filtrate was removed by evaporation.

All the residues were then dried under reduced pressure to afford tris(*N*-alkyl-*N*,*N*-dimethyl-2-ammonioethyl)amine, tris(*N*-alkyl-*N*,*N*-dimethyl-3-ammoniopropyl)amine, and methylalkylbis[3-(dimethylalkylammonio)propyl]ammonium [PF₆, OTf, FSA, and NTf₂] as a white solid ($3C_{12}$ tris-3-Q PF₆), a yellow-white solid ($3C_{12}$ tris-3-Q OTf), a yellow viscous material ($3C_{12}$ tris-3-Q FSA), clear and orange viscous materials ($3C_n$ tris-2-Q NTf₂), yellow viscous materials and solids ($3C_n$ tris-3-Q NTf₂), and clear and yellow viscous liquids ($3C_n$ lin-3-Q NTf₂) (Scheme S1, yields, ¹H NMR data, and elemental analysis data in the ESI†).

2.6. Characterization

The melting points of the quaternary-ammonium-salt-type amphiphilic trimeric 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 a heating rate of $0.2 \,^{\circ}\text{C} \, \min^{-1}$ under a nitrogen atmosphere and the acquired data were corrected and analyzed using Shimadzu TA-60WS (Kyoto, Japan) software. 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 50 and 60 $^{\circ}$ C using a Brookfield DV-2T system (Middleborough, MA, USA). The solubilities were determined by mixing 0.01–50 mL of water or organic solvent with 0.01–0.1 g of ionic liquid or compound.

The electrical conductivities of the neat amphiphilic ionic liquids and their aqueous solutions were measured using a TOA CM-30R system (Tokyo, Japan). The Krafft temperature $(T_{\rm K})$ and CMC values of the ionic liquids in aqueous solution were then determined from the afforded data. To determine the Krafft temperature of the amphiphilic trimeric ionic liquids, their clear aqueous solutions (0.0010 wt%) were prepared by dissolving them in hot water and incubating the obtained solution in a refrigerator at \sim 5 °C for at least 24 h. The surface tensions of the neat ionic liquids and their aqueous solutions were measured using a Teclis Tracker tensiometer (Lyon, France) using 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: $\Gamma = -(1/iRT)(d\gamma/d\ln C)$ and $A = 1/(N\Gamma)$, where γ is the surface tension, C is the ionic liquid concentration, R is the gas constant (8.31 J K^{-1} mol⁻¹), T is the absolute temperature, and N is Avogadro's constant. The value of i, which is the number of ionic species assumed to be completely dissociated in aqueous solution, was taken to be 4 for the amphiphilic trimeric ionic liquids investigated in this study. The fluorescence of pyrene 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 \times 10⁻⁶ mol dm⁻³. The measurements of the solution properties were performed at 25.0 \pm 0.5 $^{\circ}$ C.

Results and discussion

3.1. Melting points of the amphiphilic derivatives

Fig. 2 illustrates the relationship between the melting point and alkyl chain length *n* for the star- and linear-type amphiphilic trimeric compounds with NTf₂⁻ counterions ($3C_n$ tris-2-Q NTf₂, $3C_n$ tris-3-Q NTf₂, and $3C_n$ lin-3-Q NTf₂). These trimeric compounds displayed melting points of less than 100 °C and could therefore be defined as ionic liquids. The melting points of the trimeric ionic liquids differed according to their molecular skeleton. Thus, for the star-type $3C_n$ tris-2-Q NTf₂ and $3C_n$ tris-3-Q NTf₂ (except for $3C_8$ tris-2-Q NTf₂), the melting point slightly decreased with increasing alkyl chain length. On the other hand,



Fig. 2 Relationship between the melting points and alkyl chain lengths *n* for the quaternary-ammonium-salt-type trimeric ionic liquids: $3C_n$ tris-2-Q NTf₂ (\bullet), $3C_n$ tris-3-Q NTf₂ (\blacksquare), and $3C_n$ lin-3-Q NTf₂ (\blacktriangle).

the melting points of the linear-type $3C_n$ lin-3-Q NTf₂ were less than 0 °C for n = 8, 10 and significantly increased as the alkyl chain length was increased from 8 to 14. This suggested that the linear-type trimeric ionic liquids were more affected by van der Waals forces than the star-type ionic liquids, especially when the alkyl chain length was increased. The melting point of the star-type 3C_ntris-s-Q NTf₂ significantly decreased to less than 0 °C for all the alkyl chain lengths when the spacer chain length was increased from 2 to 3. This was more marked for the melting temperatures in the range of 40–50 °C for n = 10, 12, 14. The decrease in the melting temperature was attributed to the increased flexibility of the cation and the decrease in the van der Waals forces with increasing distance between the alkyl chains as the spacer chain was enlarged. The melting points of the linear-type $3C_n$ lin-3-Q NTf₂ with n = 8, 10 were lower than those of the corresponding star-type 3C_ntris-3-Q NTf₂, while those of $3C_n$ lin-3-Q NTf₂ with n = 12, 14 were higher. Further, based on the counterion, the melting point of the star-type $3C_{12}$ tris-3-Q X was lowered in the order: $OTf^- > PF_6^- > FSA^- >$ NTf_2^{-} . Notably, the melting points of the ionic liquids comprising FSA^- and NTf_2^- ions were lower than room temperature (Table S1, ESI[†]).

The melting points of the star-type amphiphilic trimeric ionic liquids (n = 8, 10) were higher than those of the corresponding monomeric ionic liquids ($C_8 \text{ NTf}_2$ and $C_{10} \text{ NTf}_2$; lower than -20 °C)¹⁵ but lower than those of the amphiphilic gemini ionic liquids (C_8 -2- $C_8 \text{ NTf}_2$, 76.2 °C and C_{10} -2- $C_{10} \text{ NTf}_2$, 85.8 °C).¹⁵ Based on the molecular skeleton, the melting points were in the order: gemini > trimeric > monomeric. This trend was attributed to the structures of the three types of compounds: the trimeric ionic liquids have stronger van der Waals forces than the monomeric ionic liquids, owing to the presence of the three alkyl chains connected by spacers. However, these spacers are more flexible than those of the corresponding gemini ionic liquids.

3.2. Characterization of the amphiphilic trimeric ionic liquids

The melting points of the amphiphilic star-type trimeric compounds $3C_{12}$ tris-3-Q X (X = PF₆⁻ and FSA⁻) were also less than 0 °C and thus they were also defined as ionic liquids. Further, because the water contents of these amphiphilic trimeric ionic liquids were less than 400 ppm, the properties of these ionic liquids could be easily investigated.

Table 1 lists the conductivity (κ), zero-shear viscosity (η_0) and density (d) of the amphiphilic trimeric ionic liquids (n = 8, 10, 12)comprising NTf₂⁻ counterions along with those of the corresponding monomeric ionic liquids ($C_n NTf_2$, n = 8, 10, 12). These trimeric ionic liquid parameters were measured at 50 °C because of their significantly high viscosity. Moreover, because the melting point of 3C10 tris-2-Q NTf2 was greater than 50 °C, its parameters were measured at 60 °C. The conductivities of the star-type 3C_ntris-s-Q NTf₂ were higher than those of the lineartype $3C_n$ lin-3-Q NTf₂, thereby demonstrating the difference in their molecular skeletons. This occurred because the star-type ionic liquids comprising tris(2-aminoethyl)amine skeletons have a flexible structure comprising three alkyl chains that extend radially from the central amino group. Thus, the distances between the ammonium cations are longer than those of the linear-type ionic liquids with diethylenetriamine skeletons. The viscosities were higher for the linear- than the star-type ionic liquids. This was attributed to the strong interaction and tight entanglement between the alkyl chains of the former compounds because of the short distance between them. The increase in spacer chain length from 2 to 3 led to an increase in the conductivity and a decrease in the viscosity. As discussed in Section 3.1, this occurred because of the decrease in the van der Waals forces and flexibility of the molecular structure with increasing spacer chain length. The star- and linear-type trimeric ionic liquids presented lower conductivities (1/123- to 1/26-fold) and higher viscosities (10- to 100-fold) compared to those of the corresponding monomeric ionic liquids. They also displayed lower conductivities and higher viscosities than those of the gemini ionic liquids C_8 -2- C_6 NTf₂ (21.7 mS m⁻¹ at 65 °C,

Table 1 Melting point (T_m), conductivity (κ), viscosity (η_0), and density (*d*) values of the amphiphilic trimeric ionic liquids at 50 °C

Ionic liquid	$T_{\rm m}/^{\circ}{\rm C}$	$\kappa/{ m mS}~{ m m}^{-1}$	η_0 /Pa s	$d/g \text{ cm}^{-3}$	
3C ₈ tris-2-Q NTf ₂	4.4	1.91	8.93	1.33	
3C ₁₀ tris-2-Q NTf ₂	50.1	1.18^{a}	13.9^{a}	1.28^{a}	
3C ₁₂ tris-2-Q NTf ₂	48.6	1.01	11.8	1.24	
3C ₈ tris-3-Q NTf ₂	-0.7	1.75	5.17	1.33	
3C ₁₀ tris-3-Q NTf ₂	0.6	1.53	5.49	1.29	
$3C_{12}$ tris-3-Q NTf ₂	-3.8	1.30	6.73	1.24	
3C _s lin-3-Q NTf ₂	-19.9	0.624	15.7	1.33	
3C ₁₀ lin-3-O NTf ₂	-5.2	0.560	16.5	1.28	
$3C_{12}$ lin-3-Q NTf ₂	46.6	0.493	17.7	1.24	
C ₈ NTf ₂	$< -20^{15}$	86.8	0.0466	1.31^{b}	
$C_{10}NTf_2$	$< -20^{15}$	73.4	0.0746	1.22^{b}	
$C_{12}NTf_2$	29.2	60.8	0.0943	1.22	

^a 60 °C. ^b 25 °C.

2.10 Pa s at 50 °C).¹⁵ This was attributed to their larger number of alkyl chains and thus, the stronger van der Waals forces between them. The densities of the trimeric ionic liquids were in the range of 1.24–1.34 g cm⁻³. Generally, ionic liquids present high densities (>1.0 g cm⁻³) because they solely consist of ions.^{19,20} Notably, the densities of both the amphiphilic trimeric and monomeric ionic liquids were higher than those of conventional ionic liquids and decreased with increasing alkyl chain length. On the other hand, no difference in the densities of the star- and linear-type ionic liquids was observed.

3.3. Solubility in various organic solvents

Table 2 lists the solubilities of the amphiphilic trimeric ionic liquids $[3C_{12}$ tris-2-Q NTf₂, $3C_{12}$ tris-3-Q X (X = PF₆, FSA, NTf₂), and 3C12lin-3-Q NTf2] and compounds (3C12tris-3-Q OTf) in water and the organic solvents DMSO, methanol, acetone, ethyl acetate, chloroform, benzene, and hexane. The amphiphilic trimeric ionic liquids displayed very low solubility in water but were highly soluble (>45 wt%) in organic solvents such as DMSO, methanol, and acetone. The solubilities of the trimeric ionic liquids comprising FSA⁻ and NTf₂⁻ counterions in ethyl acetate were significantly higher than those of the ionic liquids comprising PF_6^- and OTf^- ions. The gemini ionic liquids were insoluble in chloroform and benzene.¹⁵ On the other hand, the trimeric ionic liquids were soluble in these two solvents, thereby indicating that these compounds display excellent solubilities in a wide range of organic solvents of different polarities (DMSO, methanol, acetone, ethyl acetate, chloroform, and benzene); this was attributed to the increased number of alkyl chains. Particularly, compared to that of the linear-type 3C12 lin-3-Q NTf2, the solubility of the star-type 3C12 tris-2-Q NTf2 was higher in chloroform and slightly higher in benzene. Notably, all the samples were insoluble in hexane. These results revealed that the solubilities of the amphiphilic trimeric ionic liquids and compounds in various organic solvents were affected by the molecular skeleton, counterion, and number of alkyl chains.

3.4. Solution properties of the amphiphilic trimeric ionic liquids

The solution properties of the amphiphilic trimeric ionic liquids $3C_{12}$ tris-2-Q NTf₂, $3C_{12}$ tris-3-Q NTf₂, and $3C_{12}$ lin-3-Q NTf₂, including their Krafft temperature, conductivity, surface tension, and pyrene fluorescence, were next investigated. Because the solutions were clear with no visible precipitates, the $T_{\rm K}$ values



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Fig. 3 Variations in the (a) conductivity, (b) surface tension, and (c) pyrene fluorescence intensity ratio (l_1/l_3) with different concentrations of the trimeric ionic liquids $3C_{12}$ tris-2-Q NTf₂ (\bullet), $3C_{12}$ tris-3-Q NTf₂ (\blacksquare), and $3C_{12}$ lin-3-Q NTf₂ (\blacktriangle) at 25 °C.

of the ionic liquids were estimated to be less than 5 $^{\circ}$ C. Therefore, their solution properties were evaluated at 25 $^{\circ}$ C.

Fig. 3 presents the plots of the conductivity, surface tension, and pyrene fluorescence intensity ratio (I_1/I_3) as functions of the concentration for the amphiphilic trimeric ionic liquids $3C_{12}$ tris-2-Q NTf₂, $3C_{12}$ tris-3-Q NTf₂, and $3C_{12}$ lin-3-Q NTf₂. The data revealed that an increase in the concentration increased the conductivity and decreased the surface tension of the trimeric ionic liquids, while both plots displayed a clear break point, which was considered as the CMC. Further, the pyrene intensity ratio decreased from 1.8 to ~1.5 with increasing concentration. These results indicated that amphiphilic trimeric ionic liquids adsorbed at the air/water interface and formed micelles in aqueous solutions.

Table 3 lists the values of the CMC, degree of micelle ionization α , surface tension at the CMC (γ_{CMC}), surface excess concentration (Γ), occupied area per molecule (A), and standard free energies of adsorption (ΔG_{ads}°) and micellization (ΔG_{mic}°) of the amphiphilic trimeric ionic liquids along with those of the

Compound	Water	DMSO	Methanol	Acetone	Ethyl acetate	Chloroform	Benzene	Hexane
3C ₁₂ tris-2-Q NTf ₂	$_{2}$ tris-2-Q NTf ₂ 0.003 >46 >54 >56 >53		>40	11	a			
3C ₁₂ tris-3-Q PF ₆	0.006	>46	>56	>56	0.03	1.4	0.1	a
3C12tris-3-Q OTf	0.007	>46	>56	>56	5	38	21	a
3C ₁₂ tris-3-Q FSA	0.006	>46	>56	>55	>52	20	8.6	a
3C ₁₂ tris-3-Q NTf ₂	0.006	$>\!45$	>58	>50	>50	19	10	a
3C ₁₂ lin-3-Q NTf ₂	0.007	>50	>46	>53	>50	25	7	a

^a Insoluble.

Table 3 Values of the Krafft temperature ($T_{\rm K}$) at 0.0010 wt%, critical micelle concentration (CMC), surface tension at the CMC ($\gamma_{\rm CMC}$), surface excess concentration (Γ), occupied area per molecule (A), and standard free energies of adsorption (ΔG_{ads}°) and micellization (ΔG_{mic}°) for the amphiphilic trimeric ionic liquids $3C_{12}$ tris-s-Q NTf₂ and $3C_{12}$ lin-3-Q NTf₂ obtained from the surface tension plots at 25 °C

Ionic liquid	$T_{\rm K}/^{\circ}{ m C}$	CMC/mmol dm ⁻³	Α	$\gamma_{\rm CMC}/{ m mN}~{ m m}^{-1}$	$\Gamma \times 10^6/mol m^{-2}$	A/nm ²	$\Delta G_{ m ads}^{\circ}/{ m kJ}~{ m mol}^{-1}$	$\Delta G_{ m mic}^{\circ}/ m kJ~mol^{-1}$
3C ₁₂ tris-2-Q NTf ₂ 3C ₁₂ tris-3-Q NTf ₂ 3C ₁₂ lin-3-Q NTf ₂	<5 <5 <5	0.00602 0.0103 0.00608	0.012 0.21 0.18	41.4 48.3 42.1	1.18 0.990 0.428	1.41 1.68 3.88	$-79.4 \\ -67.9 \\ -116$	$-53.4 \\ -44.0 \\ -46.7$
3C ₁₂ tris-2-Q Br 3C ₁₂ lin-3-Q Br	$<5^a$ $<5^a$	0.139^{13} 0.14^{23}	0.224^{13} 0.19^{23}	32.3 ¹³	0.820^{13} 1.75^{23}	2.03^{13} 1.47^{23}	-85.0^{13}	-36.3^{13} -37.4^{23}
^a 0.20 wt%.								

trimeric surfactant comprising the counterion Br⁻. The ΔG°_{ads} and ΔG°_{mic} values of the amphiphilic trimeric ionic liquids were calculated from the equations:^{21,22}

$$\Delta G_{\rm mic}^{\circ} = RT \left(\frac{1}{3} + \beta\right) \ln \left(\frac{\rm CMC}{55.3}\right) - \left(\frac{RT}{3}\right) \ln 3 \tag{1}$$

$$\Delta G_{\rm ads}^{\circ} = \Delta G_{\rm mic}^{\circ} - \frac{\pi_{\rm CMC}}{\Gamma}$$
(2)

where $\pi_{\rm CMC}$ is the surface pressure at the CMC ($\pi_{\rm CMC} = \gamma_0 - \gamma_{\rm CMC}$; γ_0 and $\gamma_{\rm CMC}$ are the surface tensions of water and the ionic liquid solution at the CMC, respectively) and β is the binding degree of the counterion with the micelle ($\beta = 1 - \alpha$; α is obtained from the conductivity plot). The CMCs of the trimeric ionic liquids comprising the counterion NTf₂⁻ were much lower than those of the trimeric surfactants containing the counterion Br⁻. This suggested that the amphiphilic trimeric ionic liquids display excellent micelle-forming ability in aqueous solutions. The CMC of the linear-type $3C_{12}$ lin-3-Q NTf₂ was lower than that of the star-type $3C_{12}$ tris-3-Q NTf₂, indicating the high micelle-forming ability of the former. The decrease in spacer chain length for the star-type ionic liquids led to a slight decrease in the CMC. These results were supported by the absolute values of ΔG_{mic}° .

The γ_{CMC} value of the star-type trimeric ionic liquid $3C_{12}$ tris-2-Q NTf₂ was 8 mN m^{-1} higher than that of the trimeric surfactant 3C12tris-2-Q Br. This indicated that owing to steric hindrance, the introduction of a bulky structure into the counterion reduced the adsorption efficiency at the air/water interface. The γ_{CMC} values of the trimeric ionic liquids with spacer chain lengths of 3 were lower for the linear-type 3C₁₂lin-3-Q NTf₂ than for the star-type 3C₁₂tris-3-Q NTf₂. This indicated that the linear-type ionic liquids were highly oriented at the air/water interface. The three alkyl chains, which exist in the linear conformation of dipropylenetriamine, facilitated the interaction. On the other hand, in the star-type ionic liquids, the alkyl chains exist in a ring around tris(2-aminopropyl)amine. As a result, the linear-type 3C12lin-3-Q NTf2 efficiently lowered the surface tension of the water. Further, the decrease in the spacer chain length for the star-type ionic liquids led to a decrease in the surface tension, as was observed for the linear-type ionic liquid. This was attributed to increased interaction as a result of the close proximity of the alkyl chains. In our previous study,¹⁵ the quaternary-ammonium-salt-type gemini and monomeric ionic liquids did not display surface-active properties such as CMC

and surface tension because of their poor water solubility. On the other hand, the amphiphilic trimeric ionic liquids with three dodecyl chains and bulky NTf2⁻ counterions exhibited good water solubility and excellent properties such as micelle forming ability and interfacial adsorption. This was not observed with the gemini ionic liquids. The A values of the linear-type trimeric compounds were larger in the presence of the counterions NTf_2^{-} than Br⁻, while the reverse trend was observed for the star-type trimeric compounds. These trends can be explained by the positions of the bulky counterions. Thus, in the linear-type ionic liquids, the bulky counterions are mainly present at the interface because the three ammonium cations are linearly and rigidly connected by the propylene spacers. On the other hand, in the star-type ionic liquid, the bulky counterions can exist in the molecular skeleton because of their flexible structure. The A value of the linear-type 3C12lin-3-Q NTf2 was also larger than that of the star-type 3C12tris-3-Q NTf2. The results also revealed that the linear-type trimeric ionic liquid adsorbed widely at the air/water interface, while it oriented itself efficiently in aqueous solutions.

Conclusions

In this study, we designed and synthesized quaternaryammonium-salt star- and linear-type trimeric amphiphiles. We then investigated their physicochemical properties as ionic liquids as well as their properties in aqueous solutions to develop novel amphiphilic ionic liquids comprising both surfactant and ionic liquid properties. Thus, their melting points were lower than those of the corresponding gemini ionic liquids, despite the presence of three long alkyl chains. Moreover, the star-type $3C_n$ tris-3-Q NTf₂ (n = 8, 10, 12, 14) and linear-type $3C_n$ lin-3-Q NTf_2 (*n* = 8, 10) exhibited melting points that were lower than room temperature. The amphiphilic linear-type trimeric ionic liquids presented lower conductivities and higher viscosities than their star-type counterparts, indicating that the alkyl chains of the linear-type trimeric ionic liquids were tightly entangled. The amphiphilic trimeric ionic liquids were soluble in the lowpolarity solvents chloroform and benzene. They also displayed excellent solubilities in a wider range of organic solvents of different polarities than did the gemini ionic liquids. Interestingly, although the quaternary-ammonium-salt-type gemini and monomeric ionic liquids did not exhibit surface-active properties such as CMC, the trimeric ionic liquids adsorbed at the air/water interface and formed micelles in aqueous solutions. The lineartype trimeric ionic liquids efficiently lowered the surface tension of water and displayed a higher micelle-forming ability than their star-type counterparts in aqueous solutions.

In this study, we elucidated the effects of the alkyl chain length, number of alkyl chains, spacer chain length, molecular skeleton, and counterion structure on the physicochemical and solution properties of quaternary-ammonium-salt-type amphiphilic trimeric ionic liquids. Many problems, such as lowering of the melting points and improvement of their solubility in water, still need to be addressed for the development of feasible amphiphilic ionic liquids comprising both ionic liquid and surfactant properties. However, the melting points of the startype trimeric ionic liquid 3C12tris-3-Q NTf2 and linear-type ionic liquids C_n lin-3-Q NTf₂ (n = 8, 10) could notably be lowered to less than 0 °C and these products also exhibited surface-activity in aqueous solutions. Thus, we predict the future development of high-performance functional amphiphilic ionic liquids and their use in various industrial applications such as new media for organic reactions, solubilizates, and lubricants as well in separation and extraction processes.

Conflicts of interest

There are no conflicts to declare.

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