

# Synthesis and Solution Properties of Adamantane-Containing Quaternary Ammonium Salt-type Cationic Surfactants: Hydrocarbon-based, Fluorocarbon-based and Bola-type

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**Abstract:** Quaternary ammonium salt-type cationic surfactants with an adamantyl group (hydrocarbon-type;  $C_n$ AdAB, fluorocarbon-type;  $C_m^F C_3$ AdAB, bola-type; Ad-*s*-Ad, where *n*, *m* and *s* represent hydrocarbon chain lengths of 8–16, fluorocarbon chain lengths of 4–8, and spacer chain length of 10–12) were synthesized via quaternization of *N,N*-dimethylaminoadamantane and *n*-alkyl bromide or 1, *n*-dibromoalkane. Conductivity and surface tension were measured to characterize the solution properties of the synthesized adamantyl group-containing cationic surfactants. In addition, the effects of hydrocarbon and fluorocarbon chain lengths and spacer chain length between headgroups on the measured properties were evaluated by comparison with those of conventional cationic surfactants. The critical micelle concentration (CMC) of  $C_n$ AdAB and Ad-*s*-Ad was 2/5 of that for the corresponding conventional surfactants  $C_n$ TAB and bola-type surfactants with similar number of carbons in the alkyl or alkylene chain; this was because of the increased hydrophobicity due to the adamantyl group. A linear relationship between the logarithm of CMC and the hydrocarbon chain length for  $C_n$ AdAB was observed, as well as for  $C_n$ TAB. The slope of the linear correlation for both surfactants was almost the same, indicating that the adamantyl group does not affect the CMC with variations in the hydrocarbon chain length. Similar to conventional surfactants  $C_n$ TAB, the hydrocarbon-type  $C_n$ AdAB is highly efficient in reducing the surface tension of water, despite the large occupied area per molecule resulting from the relatively bulky structure of the adamantane skeleton. On the other hand, the bola-type Ad-*s*-Ad resulted in increased surface tension compared to  $C_n$ AdAB, indicating that the curved chain between adamantyl groups leads to poor adsorption and orientation at the air–water interface.

**Key words:** adamantane, adamantyl group, cationic surfactant, fluorocarbon chain, bola type

## 1 INTRODUCTION

Adamantane (tricyclo[3,3,1,1]decane,  $C_{10}H_{16}$ ), which consists of 10 carbons bonded in the same structure as diamond, is a saturated hydrocarbon cyclic tetrahedral structure<sup>1–4</sup>. The peculiar structure of adamantane is known to provide many useful chemical and physical properties. Examples of its expected properties are its bulkiness, rigidity, high hydrophobicity, heat resistance, oil-solubility, lubricity, and sublimability<sup>5–7</sup>. Various molecular designs and selective organic synthesis methods utilizing the properties of adamantane have been developed. Ada-

mantite (brand name) is an adamantane derivative product developed by Idemitsu Kosan Co., Ltd which possesses the above properties, and has been marketed and used in various fields. Because adamantane is an existing chemical substance that does not lead to acute toxicity, sub-acute oral toxicity or sub-acute dermal toxicity, it is widely used in the research and development of various pharmaceutical products by taking advantage of its hydrophobic or lipophilic properties based on its high CH density. Amantadine, which is one adamantane derivatives (1-aminoadamantane), is effective in inhibiting the proliferation of the influ-

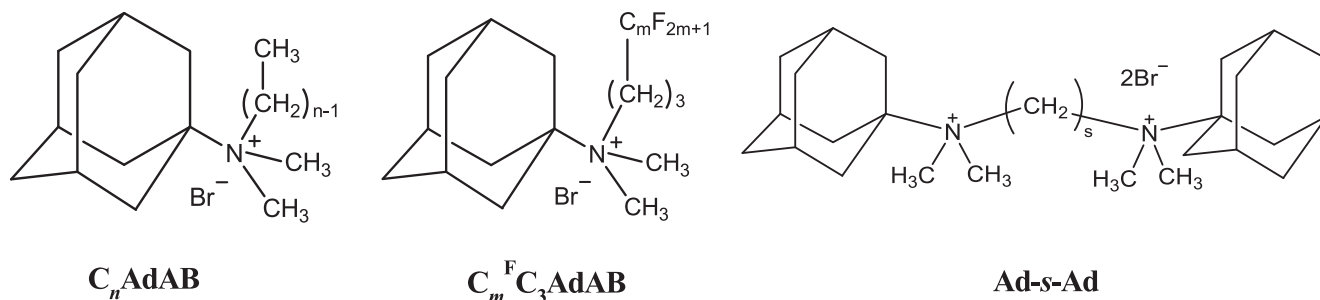
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**Fig. 1** Chemical structures of adamantane containing quaternary ammonium salt-type cationic surfactants: hydrocarbon-based single-chain type  $C_n$ AdAB ( $n = 8, 10, 12, 14, 16$ ), fluorocarbon-based single-chain type  $C_m^F C_3$ AdAB ( $m = 4, 6, 8$ ), bola type Ad-s-Ad ( $s = 10, 12$ ).

enza A virus. In addition, its indications have been expanded thanks to patients with Parkinson's disease that improved during clinical trials. Currently, it is also being used as a brain metabolic stimulant for cerebral infarction patients and as a dementia therapeutic. However, there have been almost no studies investigating surfactants with structures possessing an adamantane skeleton and both hydrophilic and hydrophobic parts in a molecule. By adding hydrophilic and hydrophobic parts to adamantane (which is hydrophobic), its solubility in water is improved, and because properties of adamantane and surfactants are both present, its use in a wide range of fields is expected.

In this study, a new quaternary ammonium salt-type cationic surfactant having an adamantane skeleton (hydrocarbon-based single-chain type  $C_n$ AdAB ( $n = 8, 10, 12, 14, 16$ ), fluorocarbon-based single-chain type  $C_m^F C_3$ AdAB ( $m = 4, 6, 8$ ), bola type Ad-s-Ad ( $s = 10, 12$ ); **Fig. 1**) were molecularly designed and synthesized. Their physicochemical properties in an aqueous solution were examined by changing the chain length. In addition, the effects of the hydrophobicity, rigidity and bulkiness of adamantane were examined by comparing it with those of conventional cationic surfactants.

## 2 EXPERIMENTAL PROCEDURES

### 2.1 Materials

1-Aminoadamantane was kindly supplied by Idemitsu Kosan Co. Ltd (Osaka, Japan). *n*-Octyl bromide, *n*-decyl bromide, *n*-dodecyl bromide, *n*-tetradecyl bromide, *n*-hexadecyl bromide, 1,10-dibromodecane, and 1,12-dibromododecane were purchased from Tokyo Chemical Industry Co. Ltd (Tokyo, Japan). 3-(Perfluorobutyl)propanol, 3-(perfluorohexyl)propanol, and 3-(perfluorooctyl)propanol were purchased from Daikin Ind. Ltd (Osaka, Japan). Methanol, ethanol, 2-propanol, acetone, ethyl acetate, hexane, diethyl ether, acetonitrile, formic acid (85%), formaldehyde solution (37%), tetrahydrofuran (THF), methanesulfonic anhydride, ethyldiisopropylamine, magne-

sium sulfate (anhydrous), NaOH, 1 M HCl, H<sub>2</sub>SO<sub>4</sub> were obtained from Wako Pure Chemicals Ind. Ltd (Osaka, Japan). Lithium bromide was purchased from Sigma-Aldrich Co. LLC (United States). All chemicals were of reagent-grade purity and used without further purification.

### 2.2 Synthesis of *N,N*-dimethyl-*N*-alkyladamantylammonium bromide ( $C_n$ AdAB)

1-Aminoadamantane (1.0 equiv.) dissolved in methanol was added slowly to a stirred mixture solution of 37% formaldehyde (4.0 equiv.) and formic acid (3.0 equiv.) at room temperature, and the mixture was stirred and refluxed for 12 h. After the solvent was removed by evaporation, water was added to the residue, and pH of the solution was adjusted to 1–2 by 1 mol dm<sup>-3</sup> HCl. The solution was concentrated by evaporation, and the residue was washed repeatedly first with hexane, and then ethyl acetate, and dried by vacuum, giving *N,N*-dimethylaminoadamantane hydrochloride as white solids. The structure was checked by <sup>1</sup>H NMR (JEOL JNM-EX 400 MHz). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS): δ 1.67–1.76 (q, 6H, <sup>4,6,9</sup>CH<sub>2</sub>), 2.05 (s, 6H, <sup>2,8,10</sup>CH<sub>2</sub>), 2.27 (s, 3H, <sup>3,5,7</sup>CH), 2.69–2.71 (d, 6H, -N(CH<sub>3</sub>)<sub>2</sub>).

The product obtained was added to 200 mL of methanol containing 8 g NaOH, and the solution was stirred while heating for 2 h. After the solvent was removed by evaporation, ethyl acetate was added to the residue, and the solution was filtered to remove the inorganic salt formed. The removal of the ethyl acetate yielded *N,N*-dimethylaminoadamantane as yellow viscous solids; the product was vacuum-dried overnight. The yield was 84%.

Octyl, decyl, dodecyl, tetradecyl, or hexadecyl bromide (2.0 equiv.) was added to a stirred solution of *N,N*-dimethylaminoadamantane (1.0 equiv.) dissolved in acetonitrile. The mixtures were refluxed for over 20 h. After the solvent was evaporated under reduced pressure, the residue was washed repeatedly first with hexane, and then ethyl acetate, and recrystallized several times from 2-propanol (ethanol for hexadecyl) to give *N,N*-dimethyl-*N*-alkyladamantylammonium bromide  $C_n$ AdAB ( $n = 8, 10, 12, 14, 16$ ) as white solids. The yields were 48%, 71%, 94%, 84%,

and 39% for C<sub>8</sub>AdAB, C<sub>10</sub>AdAB, C<sub>12</sub>AdAB, C<sub>14</sub>AdAB, and C<sub>16</sub>AdAB, respectively. The structures were checked by <sup>1</sup>H NMR and elemental analysis (Perkin-Elmer 2400II CHNS/O). <sup>1</sup>H NMR (CDCl<sub>3</sub> TMS): C<sub>8</sub>AdAB; δ 0.85–0.90 (3H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.27–1.38 (10H, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>5</sub>-CH<sub>2</sub>-), 1.72 (6H, <sup>4,6,9</sup>CH<sub>2</sub>), 1.83–1.89 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 2.13–2.14 (6H, <sup>2,8,10</sup>CH<sub>2</sub>), 2.40 (3H, <sup>3,5,7</sup>CH), 3.14 (6H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.24–3.30 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>). C<sub>10</sub>AdAB; δ 0.85–0.90 (3H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.26–1.37 (14H, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>7</sub>-CH<sub>2</sub>-), 1.72 (6H, <sup>4,6,9</sup>CH<sub>2</sub>), 1.82–1.87 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 2.14–2.15 (6H, <sup>2,8,10</sup>CH<sub>2</sub>), 2.39 (3H, <sup>3,5,7</sup>CH), 3.13 (6H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.25–3.30 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>). C<sub>12</sub>AdAB; δ 0.86–0.90 (3H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.25–1.38 (18H, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>9</sub>-CH<sub>2</sub>-), 1.72 (6H, <sup>4,6,9</sup>CH<sub>2</sub>), 1.82–1.87 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 2.12–2.13 (6H, <sup>2,8,10</sup>CH<sub>2</sub>), 2.40 (3H, <sup>3,5,7</sup>CH), 3.14 (6H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.25–3.29 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>). C<sub>14</sub>AdAB; δ 0.86–0.90 (3H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.26–1.37 (22H, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>11</sub>-CH<sub>2</sub>-), 1.73 (6H, <sup>4,6,9</sup>CH<sub>2</sub>), 1.83–1.89 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 2.13–2.14 (6H, <sup>2,8,10</sup>CH<sub>2</sub>), 2.40 (3H, <sup>3,5,7</sup>CH), 3.14 (6H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.24–3.29 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>). C<sub>16</sub>AdAB; δ 0.86–0.90 (3H, CH<sub>3</sub>-CH<sub>2</sub>-), 1.25–1.38 (26H, CH<sub>3</sub>-(CH<sub>2</sub>)<sub>13</sub>-CH<sub>2</sub>-), 1.73 (6H, <sup>4,6,9</sup>CH<sub>2</sub>), 1.82–1.88 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 2.13–2.14 (6H, <sup>2,8,10</sup>CH<sub>2</sub>), 2.40 (3H, <sup>3,5,7</sup>CH), 3.14 (6H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.24–3.29 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>). Elemental analysis: C<sub>8</sub>AdAB; Calcd for C<sub>20</sub>H<sub>38</sub>NBr: C, 64.50; H, 10.28; N, 3.76. Found : C, 64.57; H, 10.93; N, 3.68. C<sub>10</sub>AdAB; Calcd for C<sub>22</sub>H<sub>42</sub>NBr: C, 65.98; H, 10.57; N, 3.50. Found : C, 65.69; H, 10.97; N, 3.49. C<sub>12</sub>AdAB; Calcd for C<sub>24</sub>H<sub>46</sub>NBr: C, 67.27; H, 10.82; N, 3.27. Found : C, 67.29; H, 10.88; N, 3.32. C<sub>14</sub>AdAB; Calcd for C<sub>26</sub>H<sub>50</sub>NBr: C, 68.39; H, 11.04; N, 3.07. Found : C, 68.24; H, 10.96; N, 3.03. C<sub>16</sub>AdAB; Calcd for C<sub>28</sub>H<sub>54</sub>NBr: C, 69.39; H, 11.23; N, 2.89. Found : C, 69.16; H, 11.14; N, 2.83.

### 2.3 Synthesis of *N,N*-dimethyl-*N*-(3-perfluoroalkyl)propyladamantylammonium bromide (C<sub>*m*</sub><sup>F</sup>C<sub>3</sub>AdAB)

The compounds of 3-(perfluorobutyl)propyl, 3-(perfluorohexyl)propyl and 3-(perfluorooctyl)propyl bromide were synthesized by the corresponding 3-(perfluoroalkyl)propanol and methanesulfonic anhydride, ethyldiisopropylamine in THF according to reference<sup>8)</sup>.

3-(Perfluorobutyl)propyl, 3-(perfluorohexyl)propyl or 3-(perfluorooctyl)propyl bromide (1.0 equiv.) was added to a stirred solution of *N,N*-dimethylaminoadamantane (1.0 equiv.) dissolved in acetonitrile. The mixtures were refluxed for over 40 h. After the solvent was evaporated under reduced pressure, the residue was washed repeatedly first with hexane, and then ethyl acetate, and recrystallized several times from acetone or (2-propanol for 3-perfluorohexyl) to give *N,N*-dimethyl-*N*-(3-perfluoroalkyl)propyladamantylammonium bromide C<sub>*m*</sub><sup>F</sup>C<sub>3</sub>AdAB (*m* = 4, 6, and 8) as white solids. The yields were 23%, 32%, and 33% for C<sub>4</sub><sup>F</sup>C<sub>3</sub>AdAB, C<sub>6</sub><sup>F</sup>C<sub>3</sub>AdAB, and C<sub>8</sub><sup>F</sup>C<sub>3</sub>AdAB, respectively. The structures were checked by <sup>1</sup>H NMR and ele-

mental analysis. <sup>1</sup>H NMR (CDCl<sub>3</sub> TMS): C<sub>4</sub><sup>F</sup>C<sub>3</sub>AdAB; δ 1.67–1.79 (6H, <sup>4,6,9</sup>CH<sub>2</sub>), 2.14 (6H, <sup>2,8,10</sup>CH<sub>2</sub>), 2.28–2.33 (2H, C<sub>4</sub>F<sub>9</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 2.43 (3H, <sup>3,5,7</sup>CH), 2.47–2.49 (2H, C<sub>4</sub>F<sub>9</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 3.14 (6H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.68–3.74 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>). C<sub>6</sub><sup>F</sup>C<sub>3</sub>AdAB; δ 1.67–1.78 (6H, <sup>4,6,9</sup>CH<sub>2</sub>), 2.16 (6H, <sup>2,8,10</sup>CH<sub>2</sub>), 2.28–2.34 (2H, C<sub>6</sub>F<sub>13</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 2.41 (3H, <sup>3,5,7</sup>CH), 2.46–2.50 (2H, C<sub>6</sub>F<sub>13</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 3.14 (6H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.67–3.71 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>). C<sub>8</sub><sup>F</sup>C<sub>3</sub>AdAB; δ 1.67–1.79 (6H, <sup>4,6,9</sup>CH<sub>2</sub>), 2.14 (6H, <sup>2,8,10</sup>CH<sub>2</sub>), 2.28–2.33 (2H, C<sub>8</sub>F<sub>17</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 2.42 (3H, <sup>3,5,7</sup>CH), 2.46–2.49 (2H, C<sub>8</sub>F<sub>17</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 3.14 (6H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.67–3.73 (2H, -CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>). Elemental analysis: C<sub>4</sub><sup>F</sup>C<sub>3</sub>AdAB; Calcd for C<sub>19</sub>H<sub>27</sub>NF<sub>9</sub>Br: C, 43.86; H, 5.23; N, 2.69. Found : C, 44.03; H, 5.09; N, 2.87. C<sub>6</sub><sup>F</sup>C<sub>3</sub>AdAB; Calcd for C<sub>21</sub>H<sub>27</sub>NF<sub>13</sub>Br: C, 40.66; H, 4.39; N, 2.26. Found : C, 40.40; H, 4.47; N, 2.44. C<sub>8</sub><sup>F</sup>C<sub>3</sub>AdAB; Calcd for C<sub>23</sub>H<sub>27</sub>NF<sub>17</sub>Br: C, 38.35; H, 3.78; N, 1.94. Found : C, 38.53; H, 3.84; N, 2.06.

### 2.4 Synthesis of 1, *n*-bis(*N,N*-dimethyladamantylammonium)alkane bromide (Ad-*s*-Ad)

*N,N*-Dimethylaminoadamantane (3.0 equiv.) was added to a stirred solution of 1, 10-dibromodecane or 1, 12-dibromodecane (1.0 equiv.) dissolved in acetonitrile. The mixtures were refluxed for over 40 h. After the solvent was evaporated under reduced pressure, the residue was washed repeatedly first with hexane, and then ethyl acetate, and recrystallized several times from mixtures of hexane and ethanol to give 1, *n*-bis(*N,N*-dimethyladamantylammonium)alkane bromide Ad-*s*-Ad (*s* = 10 and 12) as white solids. The yields were 84% and 63% for Ad-10-Ad and Ad-12-Ad, respectively. The structures were checked by <sup>1</sup>H NMR and elemental analysis. <sup>1</sup>H NMR (CDCl<sub>3</sub> TMS): Ad-10-Ad; δ 1.40–1.45 (12H, -N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-), 1.71 (12H, <sup>4,4',6,6',9,9'</sup>CH<sub>2</sub>), 1.91–1.95 (4H, -N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-), 2.12 (12H, <sup>2,2',8,8',10,10'</sup>CH<sub>2</sub>), 2.38 (6H, <sup>3,3',5,5',7,7'</sup>CH), 3.14 (12H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>-), 3.36–3.41 (4H, -N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-). Ad-12-Ad; δ 1.32–1.41 (16H, -N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-), 1.71 (12H, <sup>4,4',6,6',9,9'</sup>CH<sub>2</sub>), 1.88–1.93 (4H, -N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-), 2.13 (12H, <sup>2,2',8,8',10,10'</sup>CH<sub>2</sub>), 2.38 (6H, <sup>3,3',5,5',7,7'</sup>CH), 3.14 (12H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>-), 3.36–3.41 (4H, -N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>-). Elemental analysis: Ad-10-Ad; Calcd for C<sub>34</sub>H<sub>62</sub>N<sub>2</sub>Br<sub>2</sub>: C, 62.00; H, 9.49; N, 4.25. Found : C, 61.59; H, 10.26; N, 4.18. Ad-12-Ad; Calcd for C<sub>36</sub>H<sub>66</sub>N<sub>2</sub>Br<sub>2</sub>·0.5H<sub>2</sub>O: C, 62.15; H, 9.71; N, 4.03. Found : C, 61.90; H, 10.54; N, 4.01.

### 2.5 Measurements

All adamantane containing quaternary ammonium salt-type cationic surfactant solutions were prepared using Milli-Q Plus water (resistivity = 18.2 MΩ cm), and the mea-

measurements were performed at 25°C (35°C for C<sub>16</sub>AdAB and 60°C for C<sub>8</sub><sup>F</sup>C<sub>3</sub>AdAB).

### 2.5.1 Electrical conductivity

The electrical conductivity measurements were performed with a CM-30R TOA electrical conductivity meter to determine Krafft temperature ( $T_K$ ) and critical micelle concentration (CMC).

*a. Krafft temperature ( $T_K$ ).* A clear aqueous solution of adamantane containing cationic surfactant (0.20 wt%) was prepared by dissolving in hot water, and placed in a refrigerator at  $\sim 5^\circ\text{C}$  for at least 24 h, where the precipitation occurred. The temperature of the precipitated system was then raised gradually under constant stirring, and the conductance ( $\kappa$ ) was measured by raising range of 0.5 to 2.5°C. The  $T_K$  was obtained as the temperature where the  $\kappa$  and temperature plots showed an abrupt change in slope. The temperature in solution is maintained by circulating temperature-controlled water, and the reproducibility of  $T_K$  measurements was within  $\pm 0.1^\circ\text{C}$ . For cationic surfactants with no precipitate when kept at  $\sim 5^\circ\text{C}$ , the  $T_K$  was determined as  $< 5^\circ\text{C}$ .

*b. Critical micelle concentration (CMC).* To obtain CMC of adamantane containing cationic surfactants, the conductance ( $\kappa$ ) of the solution was recorded at various concentrations by adding surfactant solution adjusted to the concentration of above the CMC in 50 mL of water. The CMC was determined from the breakpoint of the conductivity versus concentration plot.

### 2.5.2 Surface tension

Surface tension measurements were performed with a Krüss K100 tensiometer using the Wilhelmy plate technique. To obtain an equilibrium surface tension value, sets of measurements were performed until the change in the surface tension was less than 0.01 mN m<sup>-1</sup> every 60 s. The CMC and the surface tension at CMC ( $\gamma_{\text{CMC}}$ ) were determined from the breakpoint of the surface tension versus the logarithm of the concentration curve. In most cases, the surface excess concentration ( $\Gamma$ ) in mol m<sup>-2</sup> and the area occupied by molecule ( $A$ ) of the adamantane containing cationic surfactants at the air–water interface were calculated using the following Gibbs adsorption isotherm equations<sup>9)</sup>:

$$\Gamma = -\frac{1}{iRT} \frac{d\gamma}{d\ln C} \quad (1)$$

$$A = \frac{1}{N_A \Gamma} \quad (2)$$

where  $\gamma$  represents the surface tension in mN m<sup>-1</sup>,  $R$  the gas constant (8.31 J mol<sup>-1</sup> K<sup>-1</sup>),  $T$  the absolute temperature,  $i$  the number of species,  $C$  the cationic surfactant concentration,  $(d\gamma/d\ln C)$  the slope below the CMC in the surface tension plots, and  $N_A$  Avogadro's number. We use  $i = 2$  for C<sub>*n*</sub>AdAB and C<sub>*m*</sub><sup>F</sup>C<sub>3</sub>AdAB, and  $i = 3$  for Ad-*s*-Ad in this study, possibly involved assuming complete dissociation, from the electrode potential measurement for

bromide counterion. The Gibbs free energy of micellization and adsorption ( $\Delta G_{\text{mic}}^\circ$  and  $\Delta G_{\text{ads}}^\circ$ , respectively) of the surfactants could be obtained from the following equations<sup>9)</sup>:

$$\Delta G_{\text{mic}}^\circ = RT(1 + 2\beta) \ln \left( \frac{\text{CMC}}{55.3} \right) + 2RT\beta \ln 2 \quad (3)$$

$$\Delta G_{\text{ads}}^\circ = \Delta G_{\text{mic}}^\circ - \frac{\pi_{\text{CMC}}}{\Gamma} \quad (4)$$

where  $\beta$  is the apparent degree of counterion binding to the micelle/solution interface calculated from  $\beta = 1 - \alpha$ . Here,  $\alpha$  is calculated as the ratio of the slopes above and below the CMC in the electrical conductivity measurements.  $\pi_{\text{CMC}}$  denotes the surface pressure at the CMC ( $\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}$ ),  $\gamma_0$  is the surface tension of water, and  $\gamma_{\text{CMC}}$  is the surface tension of the surfactant solution at the CMC. The pC<sub>20</sub> value, which is often used to estimate the adsorption and aggregation properties of surfactants, represents the efficiency of adsorption at the air/water interface<sup>9)</sup>. Here, C<sub>20</sub> represents the compound concentration required to reduce the surface tension of water by 20 mN m<sup>-1</sup>. The larger the value of pC<sub>20</sub>, the greater the tendency to adsorption at the air–water interface exhibited by the surfactant. The CMC/C<sub>20</sub> ratio represents the effectiveness that can be correlated with structural factors regarding the adsorption and micellization processes<sup>9)</sup>. The larger the value of the CMC/C<sub>20</sub> ratio, the greater the tendency of the surfactant to adsorb at the interface, relative to its tendency to form micelles.

## 3 RESULTS AND DISCUSSION

### 3.1 Krafft temperature

The Krafft temperature ( $T_K$ ) of an ionic surfactant corresponds to its solubility in water and can be defined as the melting point.  $T_K$  can be easily determined by measuring the variation in electrical conductivity with temperature. **Figure 2** shows a typical curve of conductance versus temperature for C<sub>14</sub>AdAB and C<sub>16</sub>AdAB at a concentration of 0.20 wt%. The conductance rapidly increases with an increase in temperature because of the gradual dissolution of the surfactant, and then slowly increases as a result of the increase in ionic mobility.  $T_K$  is taken as the temperature at which the conductance versus temperature plot shows a breakpoint<sup>10, 11)</sup>, as indicated by the arrows in the curve in **Fig. 2**. As the solutions were clear and showed no visible precipitates when kept at  $\sim 5^\circ\text{C}$  for at least 24 h, the  $T_K$  value for the surfactants was estimated to be  $< 5^\circ\text{C}$ . The  $T_K$  values for C<sub>*n*</sub>AdAB, C<sub>*m*</sub><sup>F</sup>C<sub>3</sub>AdAB, and Ad-*s*-Ad are listed in **Table 1**, along with those of the corresponding conventional cationic surfactants of alkyltrimethylammonium bromide (C<sub>*n*</sub>TAB)<sup>12)</sup>. As expected,  $T_K$  for C<sub>*n*</sub>AdAB and C<sub>*m*</sub><sup>F</sup>C<sub>3</sub>AdAB increased with an increase in the hydrocarbon and fluorocarbon chain length, thereby causing the hydrophobic interactions to increase as well. The  $T_K$  values for C<sub>*n*</sub>AdAB

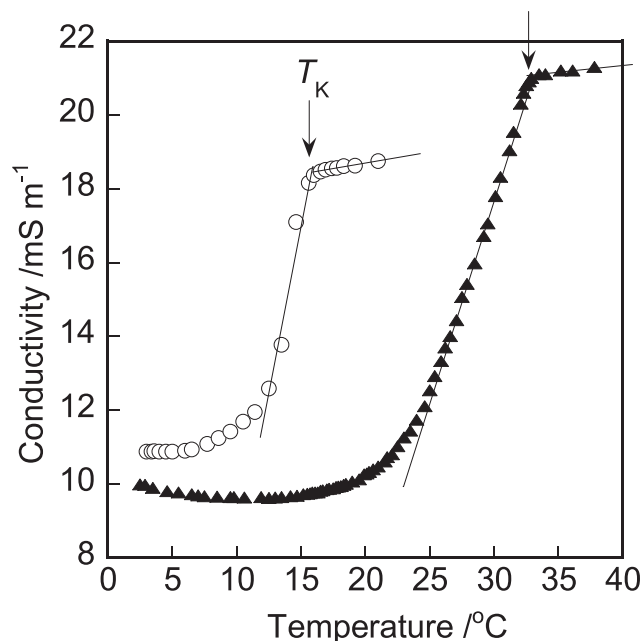


Fig. 2 Variation in electrical conductivity with temperature in surfactant solution for  $C_n$ AdAB at 0.20 wt%:  $\circ$ ,  $n = 14$ ;  $\blacktriangle$ ,  $n = 16$ . The arrow indicates the Krafft temperature  $T_K$ .

with  $n = 14$  and  $16$  were higher than those of  $C_n$ TAB, due to the hydrophobicity of adamantane. The  $T_K$  values for bola-type surfactants with adamantyl groups at each alkyl chain terminal (Ad-*s*-Ad) were  $< 5^\circ\text{C}$  for spacer chain lengths of  $s = 10$  and  $12$ . The bola-type surfactants showed high solubility in water, since they possess two quaternary ammonium-salt hydrophilic groups despite the two adamantane skeletons.

Because surfactants form micelles in aqueous solution at temperatures above  $T_K$ , the measurements discussed below were performed at  $35^\circ\text{C}$  for  $C_{16}$ AdAB,  $60^\circ\text{C}$  for  $C_8^F C_3$ AdAB, and  $25^\circ\text{C}$  for the others.

### 3.2 Critical micelle concentration (CMC)

The electrical conductivities of the adamantane containing cationic surfactants were determined as a function of

the concentration, and are plotted in Figs. 3(a) to (e). The conductivity increased linearly with an increase in concentration, and then increased slowly at the breakpoint, which corresponds to the CMC. Table 2 summarizes the CMC values and the degree of ionization for a micelle ( $\alpha$ ) for  $C_n$ AdAB,  $C_m^F C_3$ AdAB, and Ad-*s*-Ad, as obtained from the conductivity plots. The values of CMC and  $\alpha$  were affected by the hydrocarbon chain length, fluorocarbon chain length, and spacer chain length of the surfactants. Similar to the case of conventional surfactants, the CMC of  $C_n$ AdAB decreased with an increase in the hydrocarbon chain length. It is generally known that the CMC decreases logarithmically as the carbon number ( $n$ ) in the hydrocarbon chain of a homologous series increases, and the relation can be expressed by the so-called Kleven's equation as

$$\log \text{CMC} = A - Bn \quad (5)$$

where  $A$  and  $B$  are constants specific to the homologous series at constant temperature, pressure, and other parameters. The plots of hydrocarbon chain length against the logarithm of the CMC of the adamantane-containing cationic surfactants  $C_n$ AdAB are compared with the corresponding surfactants  $C_n$ TAB in Fig. 4. Here, we used the equation without considering the measurement temperature for  $C_{16}$ AdAB. A linear relationship between the logarithm of CMC and the hydrocarbon chain length for the  $C_n$ AdAB surfactants was observed, as well as that of conventional surfactants. The  $B$  value was estimated to be  $0.32$  for  $C_n$ AdAB, which was quite close to that ( $0.31$ ) for  $C_n$ TAB<sup>13</sup>. This indicates that for cationic surfactants, the variation in CMC with the hydrocarbon chain length is not affected by the adamantyl group and its bulky structure. The surfactant  $C_8$ AdAB with  $n = 8$  deviated from this straight line. This may also be due to its short hydrocarbon chain, resulting in insufficient micelle formation. The CMC values for the adamantane-containing  $C_n$ AdAB surfactants were one-half of those for the corresponding  $C_n$ TAB surfactants with the same number of carbons in the hydrocarbon chain. This shows that  $C_n$ AdAB surfactants have a low CMC due to the hydrophobicity of the adamantane skeleton.

On the other hand, a unique behavior was observed for

Table 1 The values of Krafft temperature  $T_K$  ( $^\circ\text{C}$ ) for the adamantane containing cationic surfactants.

	$n = 8$	$n = 10$	$n = 12$	$n = 14$	$n = 16$
$C_n$ AdAB	$< 5$	$< 5$	$< 5$	16.1	33.3
$C_n$ TAB <sup>a</sup>	$< 0$	$< 0$	$< 0$	$\sim 0$	24.9
	$m = 4$	$m = 6$	$m = 8$		
$C_m^F C_3$ AdAB	$< 5$	$< 5$	58.7 <sup>b</sup>		
	$s = 10$	$s = 12$			
Ad- <i>s</i> -Ad	$< 5$	$< 5$			

<sup>a</sup> Reference 12, <sup>b</sup> at 0.050 wt%.

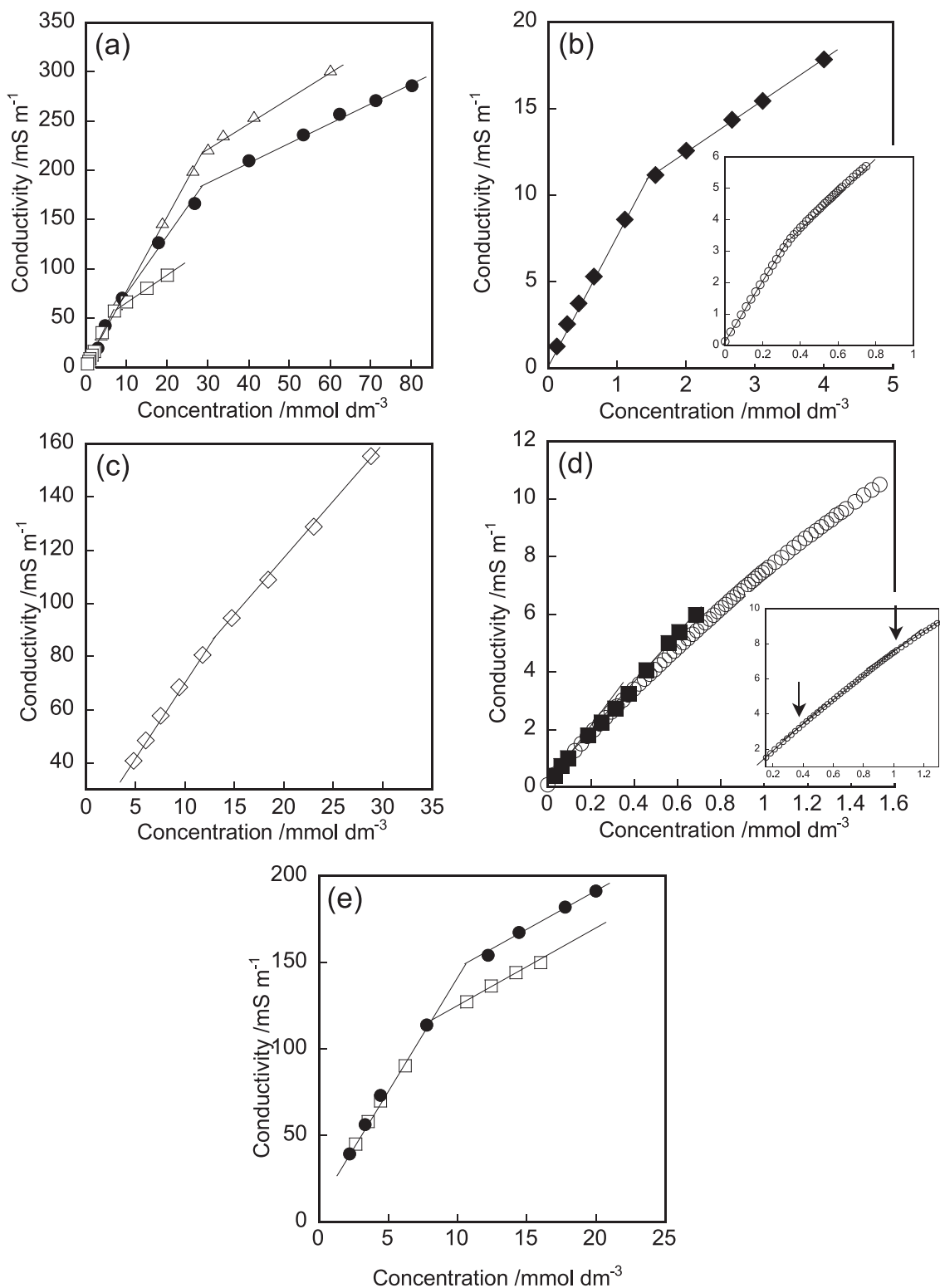


Fig. 3 Variation in electrical conductivity with surfactant concentration for (a)  $C_n\text{AdAB}$ :  $\triangle$ ,  $n=8$ ;  $\bullet$ ,  $n=10$ ;  $\square$ ,  $n=12$ , (b)  $C_n\text{AdAB}$ :  $\blacklozenge$ ,  $n=14$ ;  $\circ$ ,  $n=16$ , (c)  $C_m^F C_3\text{AdAB}$ :  $\diamond$ ,  $m=4$ , (d)  $C_m^F C_3\text{AdAB}$ :  $\circ$ ,  $m=6$ ;  $\blacksquare$ ,  $m=8$ , (e) Ad-s-Ad:  $\bullet$ ,  $s=10$ ;  $\square$ ,  $s=12$ .

**Table 2** The values of CMC, degree of ionization ( $\alpha$ ), surface tension at the CMC ( $\gamma_{\text{CMC}}$ ), surface excess concentration ( $\Gamma$ ), area occupied per molecule ( $A$ ), efficiency of adsorption ( $pC_{20}$ ), effectiveness for adsorption and micellization process ( $\text{CMC}/C_{20}$ ) and standard free energies of adsorption and micellization ( $\Delta G_{\text{ads}}^{\circ}$ ,  $\Delta G_{\text{mic}}^{\circ}$ ) for the adamantane containing cationic surfactants obtained from the electrical conductivity and the surface tension plots.

Surfactant	CMC (mmol dm <sup>-3</sup> )		$\alpha$	$\gamma_{\text{CMC}}$ (mN m <sup>-1</sup> )	$10^6\Gamma$ (mol m <sup>-2</sup> )	$A$ (nm <sup>2</sup> /molecule)
	conductivity	surface tension				
C <sub>8</sub> AdAB	27.1	–	–	–	1.76	0.943
C <sub>10</sub> AdAB	28.8	28.5	0.345	37.8	1.90	0.876
C <sub>12</sub> AdAB	6.45	5.71	0.318	38.1	2.36	0.704
C <sub>14</sub> AdAB	1.43	1.81	0.366	38.0	1.62	1.03
C <sub>16</sub> AdAB	0.357	0.358	0.580	39.6	1.78	0.932
C <sub>4</sub> <sup>F</sup> C <sub>3</sub> AdAB	10.5	–	0.723	–	–	–
C <sub>6</sub> <sup>F</sup> C <sub>3</sub> AdAB	0.978	–	–	–	1.98	0.839
C <sub>8</sub> <sup>F</sup> C <sub>3</sub> AdAB	0.0524	–	0.862	–	–	–
Ad-10-Ad	10.1	10.3	0.345	55.4	0.36	4.58
Ad-12-Ad	8.86	9.25	0.315	49.5	1.17	1.42

**Table 2** Continued.

Surfactant	$pC_{20}$	CMC / C <sub>20</sub>	$\Delta G_{\text{ads}}^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta G_{\text{mic}}^{\circ}$ (kJ mol <sup>-1</sup> )
C <sub>8</sub> AdAB	1.78	–	–	–
C <sub>10</sub> AdAB	2.27	5.26	–40.6	–22.5
C <sub>12</sub> AdAB	2.85	4.06	–42.1	–27.8
C <sub>14</sub> AdAB	3.55	6.37	–50.8	–29.9
C <sub>16</sub> AdAB	4.09	4.45	–47.2	–29.0
C <sub>4</sub> <sup>F</sup> C <sub>3</sub> AdAB	–	–	–	–
C <sub>6</sub> <sup>F</sup> C <sub>3</sub> AdAB	3.78	–	–	–
C <sub>8</sub> <sup>F</sup> C <sub>3</sub> AdAB	–	–	–	–
Ad-10-Ad	1.48	0.310	–71.2	–25.3
Ad-12-Ad	2.21	1.52	–45.6	–26.4

the C<sub>m</sub><sup>F</sup>C<sub>3</sub>AdAB surfactants with fluorocarbon chains. The C<sub>4</sub><sup>F</sup>C<sub>3</sub>AdAB showed a clear breakpoint, which was assumed to be the CMC, in the conductivity plot (Fig. 3(c)). However, the C<sub>6</sub><sup>F</sup>C<sub>3</sub>AdAB showed two breakpoints (Fig. 3(d), open circles); the first breakpoint is derived from the formation of ion-pairs between the ammonium headgroup and the bromide ion, while the second breakpoint corresponds to the CMC<sup>14, 15</sup>. The former may also be derived from the formation of small aggregates such as dimers and trimers. The C<sub>8</sub><sup>F</sup>C<sub>3</sub>AdAB showed slightly breakpoint, which was taken as the CMC, in the plot (Fig. 3(d), solid squares), despite the poor solubility in water.

For the bola-type Ad-*s*-Ad surfactants, the breakpoints taken as the CMC were obtained from the conductivity plot. The CMC decreased with an increase in the spacer chain length from 10 to 12, because of the increased hy-

drophobicity. The bola-type surfactants could easily form micelles at low concentrations, because of the interaction of the hydrophobic chain and the curved chain between the ammonium headgroups, thus resulting in decreased CMC. Further, for *s* = 12, the CMC of the adamantane-containing bola-type Ad-*s*-Ad surfactant was approximately 2/5 of that for the corresponding non-adamantane-containing surfactant with the same carbon number in the hydrocarbon chain (20–30 mmol dm<sup>-3</sup>)<sup>16</sup>. This observed CMC behavior is similar to the trend exhibited by conventional hydrocarbon-type surfactants, as described above.

The  $\alpha$  value of the micelle near the CMC can be obtained from the ratio of the plots above and below the breakpoints, indicative of the CMC, in the conductivity and concentration plots. The  $\alpha$  value reflects the ease of micelle formation in an aqueous solution; it is generally difficult to

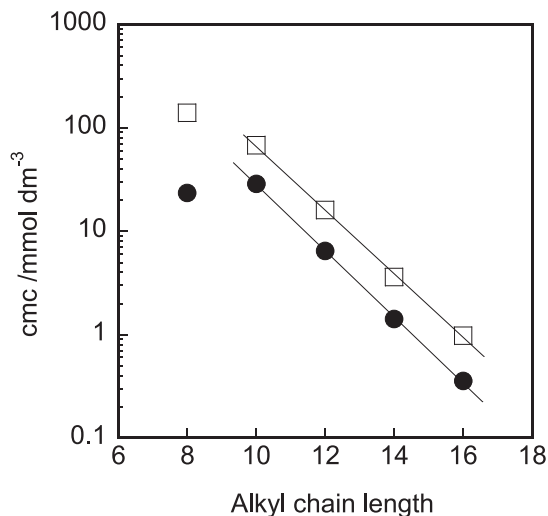


Fig. 4 Relationship between the CMC and the hydrocarbon chain length for adamantane containing cationic surfactant  $C_n$ AdAB and adamantane non-containing conventional cationic surfactant  $C_n$ TAB: ●,  $C_n$ AdAB; □,  $C_n$ TAB.

form micelles if the value is close to 1. From Table 2, the  $\alpha$  value of the hydrocarbon-type  $C_n$ AdAB drastically increases as the chain length increases from 14 to 16, whereas that of the bola-type Ad-s-Ad decreases. Thus, an increase in spacer chain length in the bola-type surfactant would easily result in micelle formation in solution because of the increased flexibility of the chain. The  $\alpha$  value for the fluorocarbon-type  $C_4^F C_3$ AdAB surfactant was much larger compared to that of hydrocarbon-type  $C_n$ AdAB surfactants. This shows that micelle formation is disadvantageous for surfactants with fluorocarbon chains because of the chain rigidity.

### 3.3 Adsorption properties at air/water interface

The surface tension of the adamantane-containing cationic surfactants was determined as a function of the concentration, and plotted in Fig. 5(a) to (c). The surface tension for  $C_n$ AdAB,  $C_m^F C_3$ AdAB, and Ad-s-Ad decreased as the concentration increased, reaching a clear breakpoint, regarded as the CMC. Table 2 summarizes the values for the CMC, surface tension at the CMC ( $\gamma_{CMC}$ ), surface

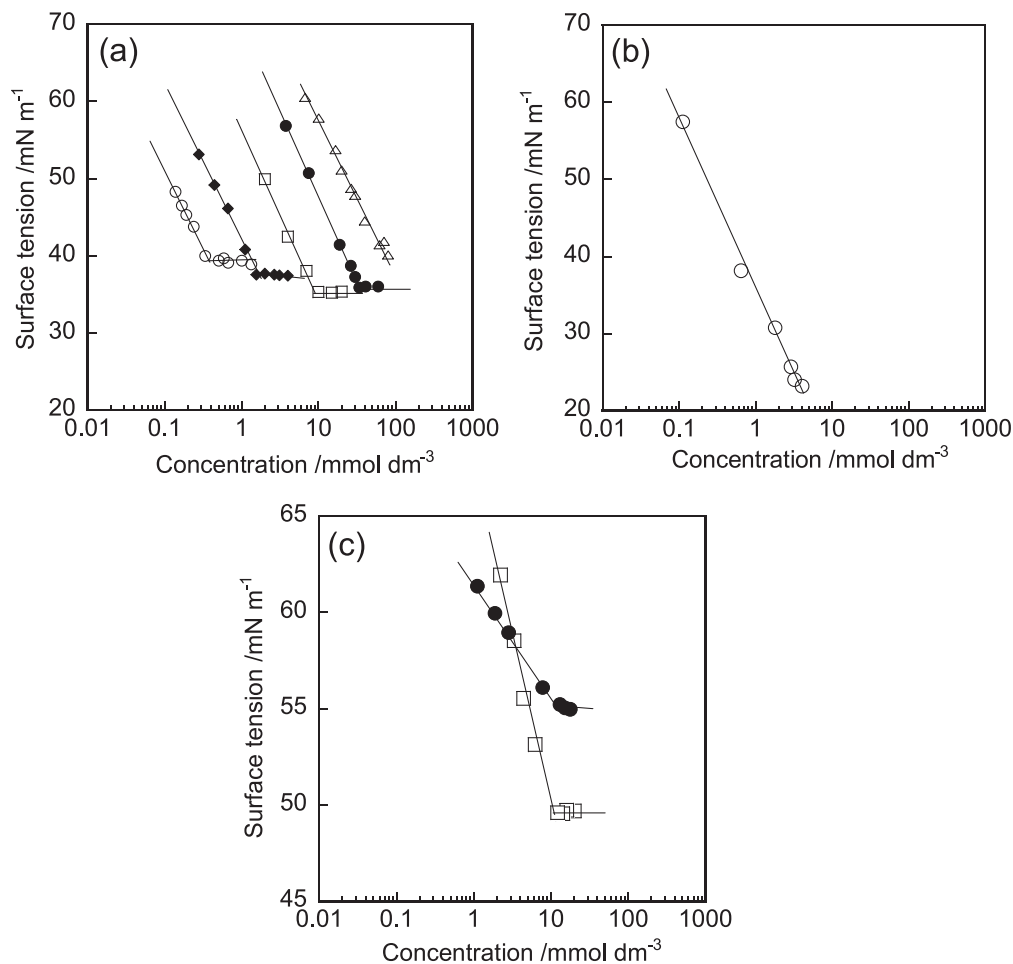


Fig. 5 Variation in surface tension with surfactant concentration for (a)  $C_n$ AdAB:  $\triangle$ ,  $n = 8$ ;  $\bullet$ ,  $n = 10$ ;  $\square$ ,  $n = 12$ ;  $\blacklozenge$ ,  $n = 14$ ;  $\circ$ ,  $n = 16$ , (b)  $C_m^F C_3$ AdAB:  $\circ$ ,  $m = 6$ , (c) Ad-s-Ad:  $\bullet$ ,  $s = 10$ ;  $\square$ ,  $s = 12$ .



excess concentration ( $\Gamma$ ), occupied area per molecule ( $A$ ), parameters such as  $pC_{20}$ ,  $CMC/C_{20}$  ratio, and standard free energy of adsorption and micellization ( $\Delta G_{\text{ads}}^{\circ}$ ,  $\Delta G_{\text{mic}}^{\circ}$ ) for  $C_n\text{AdAB}$ ,  $C_m^{\text{F}}C_3\text{AdAB}$ , and Ad-s-Ad, as determined from the surface tension plots. The CMC values obtained using the two methods of surface tension and conductivity were almost the same. The  $\gamma_{\text{CMC}}$  values of  $C_n\text{AdAB}$  were almost the same as those of conventional cationic surfactants  $C_n\text{TAB}$  (37–38 mN m<sup>-1</sup> for  $n = 10$  and 12)<sup>17</sup>, whereas the  $A$  values of  $C_n\text{AdAB}$  were much larger than those of  $C_n\text{TAB}$  (0.52–0.75 nm<sup>2</sup> for  $n = 10$  and 12)<sup>17</sup>. This suggests that despite the bulky structure of adamantane, the cationic surfactants can adsorb widely and orient themselves efficiently at the air–water interface, as is known for conventional surfactants. Here, we used the equation (1) without considering the activity coefficient for  $C_{10}\text{AdAB}$  with high CMC value. The  $pC_{20}$  of  $C_n\text{AdAB}$  increased with increasing hydrocarbon chain length, indicating that the increase in chain length promotes adsorption at the air–water interface. However, the surface tension, or the surfactant adsorption efficiency at the air–water interface, did not decrease with increasing hydrocarbon chain length as described above. This suggests that adamantane-containing surfactants are strongly adsorbed at the air–water interface along the alkyl chain because of the high hydrophobicity of adamantane; however, they do not show efficient orientation until the surface tension decreases, because of the bulky adamantane structure. The  $CMC/C_{20}$  ratios of  $C_n\text{AdAB}$  were larger than those of  $C_n\text{TAB}$  (4.0–6.5)<sup>17</sup>, while the absolute values of  $\Delta G_{\text{ads}}^{\circ}$  for  $C_n\text{AdAB}$  were higher than those of  $\Delta G_{\text{mic}}^{\circ}$ . This suggests that adsorption tendencies of adamantane-containing surfactants with hydrocarbon chain at the air–water interface are higher than their tendency for micellization. This result is supported by the reduction in the surface tension and the  $pC_{20}$  parameter.

Despite  $C_8^{\text{F}}C_3\text{AdAB}$  with a fluorocarbon chain length of 8 showed poor water solubility because of its high Krafft temperature, a slight breakpoint was obtained from the conductivity plot for  $C_8^{\text{F}}C_3\text{AdAB}$  at 60°C, where the solution was clear. For  $C_6^{\text{F}}C_3\text{AdAB}$ , the surface tension decreased with increasing concentration, without reaching a clear breakpoint, and thus no CMC. However, the conductivity plot showed two slight breakpoints as described above. This difference in the CMC may come from the difference in interfacial adsorption for the surface tension method and micelle formation for the conductivity method, indicating that the adsorption and aggregation processes occur simultaneously. The aggregates may be small “pre-micelles” such as dimers or trimers. It is known that the CMC for fluorocarbon-type surfactants follows an equivalence of 1 CF<sub>2</sub> to 1.5 CH<sub>2</sub> units of hydrocarbon-type surfactants<sup>18</sup>. Therefore, it is expected that the CMC of fluorocarbon-type  $C_6^{\text{F}}C_3\text{AdAB}$  be equal to that of hydrocarbon-type  $C_{12}\text{AdAB}$ ; in other words that its alkyl carbon number

is 1.5 times the carbon number in the fluorocarbon chain, in addition to the 3 carbons from the propyl chain. In fact, the CMC was 5.71 mmol dm<sup>-3</sup>, a concentration at which the surface tension could not be measured, as the surfactant had reached its solubility limit in water. Furthermore, the  $A$  value of the  $C_6^{\text{F}}C_3\text{AdAB}$  was much larger than those of fluorocarbon-chain-containing surfactants (0.41–0.55 nm<sup>2</sup>)<sup>18</sup>. The surfactants have relatively large occupied-area values because of the bulky adamantane structure; nonetheless, they can adsorb and orient efficiently at the air–water interface, resulting a decrease in surface tension.

The CMC of bola-type Ad-s-Ad obtained by the surface tension method was very close to that measured by the conductivity method. The  $\gamma_{\text{CMC}}$  values of Ad-s-Ad were much larger than those of  $C_n\text{AdAB}$ . This low surface activity for the bola-type surfactant is caused by poor packing due to the curved orientation of the alkylene chain between the ammonium groups on the air-side. This is also supported by the small  $pC_{20}$  values. The  $\gamma_{\text{CMC}}$  of Ad-s-Ad decreases as the alkylene chain length increases from 10 to 12. This suggests that the longer the curved chain, the more the flexibility of the structure; consequently, the surfactant shows moderate close packing at the air–water interface. The occupied area was found to be quite large because of such orientations as well as the two bulky adamantane moieties.

#### 4 CONCLUSIONS

In this study, a new quaternary ammonium salt-type cationic surfactant having an adamantane skeleton in its molecules (hydrocarbon-based single-chain type  $C_n\text{AdAB}$  ( $n = 8, 10, 12, 14, 16$ ), fluorocarbon-based single-chain type  $C_m^{\text{F}}C_3\text{AdAB}$  ( $m = 4, 6, 8$ ), bola type Ad-s-Ad ( $s = 10, 12$ ); **Fig. 1**) was molecularly designed and synthesized. Its physicochemical properties in an aqueous solution were investigated, as were the effects of its hydrocarbon chain length, fluorocarbon chain length, linking chain length, and adamantane skeleton.

Although water solubility decreases due to hydrophobicity by adding an adamantane skeleton to surfactants, no significant effects on CMC, surface tension depression and adsorption at air–water interface were seen. Despite cationic surfactants having an adamantyl group have a bulky adamantane skeleton, it was found to be efficiently oriented despite slightly widened adsorption at air–water interface. Because there have been hardly any past studies on amphiphathic compounds with structures in which a hydrophilic and hydrophobic part have been added to adamantane (which is hydrophobic), and both adamantane and surfactant properties have been combined, use in a wide variety of fields is expected.

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