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Synthesis of novel quaternary ammonium surfactants containing adamantane

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Abstract

A series of novel quaternary ammonium surfactants containing adamantane were designed and synthesized from 1-adamantanecarboxylic acid. The structures of target surfactants were confirmed by ^{1}H NMR, elements analysis and FTIR. Surface properties of these surfactants were investigated. Due to the lipophilicity of adamantane, the critical micelle concentration (CMC) and C_{20} values of the synthesized quaternary ammonium surfactants are lower than that of conventional quaternary ammonium surfactants.

Keywords: Adamantane; Synthesis; Quaternary ammonium surfactants; 1-(Alkyldimethylammoniamethyl) adamantane bromide

Quaternary ammonium compounds (QACs) are an important branch of surfactants that have unique qualities that make them attractive for investigation. QACs have been proved to be useful in a variety of applications, including the following: such as detergents, disinfectants, antistatic agents and fabric softeners [1–3]. Benzalkonium bromide (dodecyldimethylbenzylammonium bromide), for example, is currently utilized for disinfectants in hospital and a high-efficiency algaecide in seawater [4–5].

Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a very symmetric tricyclic hydrocarbon with three fused chair-form cyclohexane rings in a diamond lattice structure. The particular structure of adamantane imparts many useful chemical and physical properties, such as extreme lipophilicity, good thermal and oxidative stabilities, low surface energy, and innocuity, *etc*. [6–8]. Amino derivatives of adamantane, such as aminoadamantanes which are known to have interesting biological properties, are used medically to treat influenza [9]. Incorporation of adamantyl groups into the molecular structure of surfactants will take advantage of the special properties of the adamantane structure. The benefits of adamantane lipophilicity may exhibit low CMC value [10–12]. However, nowadays a little study focuses on the surfactants containing adamantane.

In this paper, we successfully synthesized a series of quaternary ammonium surfactants containing adamantane, 1-(alkyldimethylammoniamethyl) adamantane bromide from 1-adamantanecarboxylic acid. The synthetic procedure sketch is shown in Scheme 1.

Firstly, 1-adamantanyl-*N*,*N*-dimethylcarboxamide (**2**) was synthesized by modification of published literature procedures [13]. The mixture of 1-adamantanecarbonxylic acid (56 mmol) and $SOCl_2$ (80 mmol) was stirred for 3 h at

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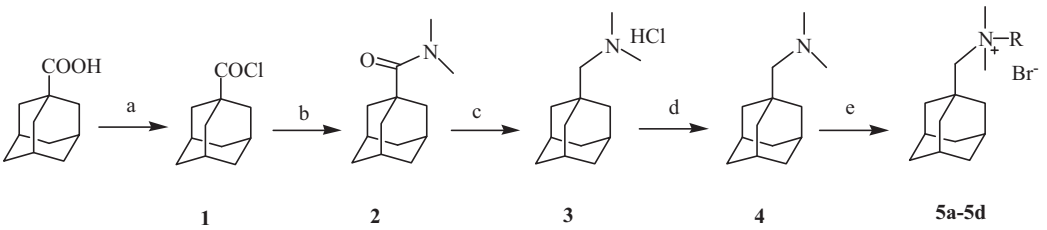

Scheme 1. The synthesis of compounds **5a–5d**. Condition and regent: (a) $SOCl_2$, 80 °C, 3 h, 99%; (b) TEA, $HN(CH_3)_2$.HCl, CH_2Cl_2, r.t., 12 h, 79%; (c) i: $LiAlH_4$, dry THF, reflux, 20 h, ii: 2 mol/L HCl, 77% in two steps; (d) 2 mol/L NaOH; and (e) RBr, isopropanol, reflux, 48 h, 26−43%.

80 °C, and became transparent. The excess $SOCl_2$ was removed by distilling to give compound **1**. Then to a stirring suspension of dimethyl amine hydrochloride salt (86 mmol) and triethylamine (TEA) (180 mmol) in CH_2Cl_2 (50 mL) was added into the solution of the compound **1** (55 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The resulting solution was stirred at r.t. for 12 h, and then the solution was washed by dilute hydrochloric acid and brine. The combined organic layers were dried ($MgSO_4$), and concentrated to give a light yellow crystalline solid. The solid was purified by column chromatography (ethyl acetate:hexanes = 1:1) to give compound **2** as a colorless crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.717 (br s, 6H), 2.019 (br s, 9H), 3.053 (br s, 6H).

N,*N*-Dimethyl-1-aminomethyladamantane hydrochloride (**3**) was synthesized by the reduction of compound **2** using $LiAlH_4$ in dry THF and then hydrochlorination with ice cold 2 mol/L HCl. Compound **3** was recrystallized from methanol/acetone to give white crystals, ^{1}H NMR (300 MHz, D_2O): δ 1.546–1.554 (m, 6H), 1.591–1.691 (m, 6H), 1.931 (br s, 3H), 2.832 (s, 6H), 2.865 (m, 2H). Then compound **3** was neutralized by 2 mol/L NaOH (25 mL) to give compound **4** as a colorless transparent liquid.

Finally, a series of 1-(alkyldimethylammoniamethyl) adamantane bromide (**5a–5d**) were synthesized by quaternization of compound **4** with *n*-bromoalkanes. For instance, the 1-(octyldimethylammoniamethyl) adamantane bromide was synthesized as follows. The solution of 1-bromooctane (13 mmol) in isopropanol was added to a stirred solution of compound **4** (10 mmol) in isopropanol, the mixture was refluxed for 48 h. Then the resulting mixture was concentrated. The residue was washed several times with diethyl ether (3 × 30 mL) to give a colorless crystalline solid. Then the solid was recrystallized from THF and purified by column chromatography (dichloromethane:-methanol:ammonia = 15:1:0.01) to give compound **5a** as colorless crystals. **5b**, **5c** and **5d** were synthesized v*ia* similar procedures. The results of compounds **5a–5d** are listed in Table 1.

Table 1
The results of compounds **5a–5d**.

Compound	R	Yield	^{1}H NMR (300 MHz, $CDCl_3$): δ	Elements analysis (%, calcd.)	FTIR (KBr, cm^{-1}): ν
5a	$-C_8H_{17}$	43%	0.858–0.902 (t, 3H), 1.269–1.362 (m, 10H), 1.702–1.725 (m, 8H), 1.828–1.835 (m, 6H), 2.053 (br s, 3H), 3.324 (s, 2H), 3.482 (s, 6H), 3.619–3.676 (t, 2H)	C, 65.27(65.09); H, 10.43(10.48); Br, 20.68(20.55); N, 3.62(3.88).	2904, 2848, 1632, 1486, 1469, 1458, 1105, 933.
5b	$-C_{10}H_{21}$	39%	0.855–0.900 (t, 3H), 1.258–1.361 (m, 14H), 1.713–1.733 (m, 8H), 1.810–1.833 (m, 6H), 2.061 (br s, 3H), 3.320 (s, 2H), 3.476 (s, 6H), 3.615–3.671 (t, 2H)	C, 66.64(66.90); H, 10.70(10.63); Br, 19.28(19.05); N, 3.38(3.42).	2904, 2849, 1631, 1477 1469, 1457, 1103, 932.
5c	$-C_{12}H_{25}$	35%	0.854–0.898 (t, 3H), 1.250–1.366 (m, 18H), 1.712–1.731 (m, 8H), 1.808—1.834 (m, 6H), 2.059 (br s, 3H), 3.314 (s, 2H), 3.470 (s, 6H), 3.609–3.664 (t, 2H)	C, 67.85(67.98); H, 10.93(10.87); Br, 18.05(17.87); N, 3.16(3.28).	2905, 2849, 1631, 1477 1469, 1457, 1103, 984.
5d	$-C_{16}H_{33}$	26%	0.854–0.898 (t, 3H), 1.250–1.358 (m, 26H), 1.699–1.722 (m, 8H), 1.769–1.832 (m, 6H), 2.052 (br s, 3H), 3.322 (s, 2H), 3.482 (s, 6H), 3.615–3.672 (t, 2H)	C, 69.85(70.08); H, 11.32(11.27); Br, 16.02(15.71); N, 2.81(2.94).	2916, 2849, 1631, 1469, 1457, 1103, 984.

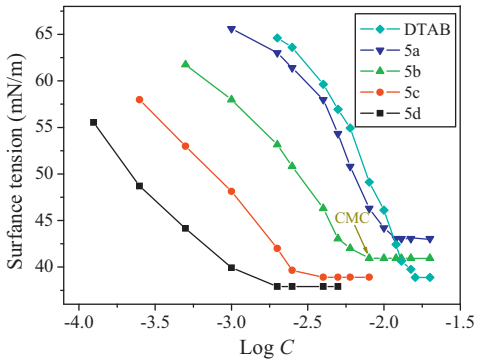

Fig. 1. Surface tension of aqueous **5a**–**5d** and DTAB solutions at 25 °C.

Table 2
Value of the CMC, γ_{CMC} and C_{20} for surfactants **5a**–**5d**.

Surfactants	CMC (mol/L)	γ_{CMC} (mN/m)	C_{20} (mol/L)
5a	12×10^{-3}	43.053	5.62×10^{-3}
5b	8×10^{-3}	40.953	2.40×10^{-3}
5c	4×10^{-3}	38.906	5.01×10^{-4}
5d	2×10^{-3}	37.902	2.24×10^{-4}
$C_{12}H_{25}N^{+}(CH_3)_3\ Br^{-}$ (DTAB)	16×10^{-3}	38.894	6.61×10^{-3}

1. Surface tension and CMC

The surface tension of aqueous solutions (γ) was measured by KSV Sigma 700 tensiometer at 25 °C. This tensiometer works based on the Wilhelmy plate method. The surface activity of target compounds **5a**–**5d** has been compared with conventional surfactant DTAB (dodecyltrimethylammonium bromide), which was purchased from Aladdin-reagent (China). Fig. 1 shows the surface tension of aqueous solutions of **5a**–**5d** and DTAB. The critical micelle concentration (CMC) and surface tension at the CMC (γ_{CMC}) were determined from the break point of the surface tension versus logarithm of concentration curve. The concentration values of the surfactants in the aqueous phase that produces a 20 mN/m reduction in the surface tension of the solvent (C_{20}) were got from Fig. 1. The results were showed in Table 2. The CMC and γ_{CMC} of DTAB were 16×10^{-3} mol/L and 38.894 mN/m, which were similar with literature [14]. Compared with DTAB, the surfactants **5a**–**5d** have lower CMC and C_{20} values, which may be resulting from the lipophilicity of adamantane.

In summary, a series of novel quaternary ammonium surfactants containing adamantane can be synthesized from 1-adamantanecarboxylic acid. These surfactants exhibit the lower CMC and C_{20} values.

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