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Synthesis and Surface Activity of Novel Triazole-based Cationic Gemini Surfactants

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Abstract: The synthesis and surfactant activities of two new cationic gemini surfactants containing triazole compound as spacer were described. Their critical micelle concentrations (CMC), which are 1.8×10^{-4} mol/L and 3.9×10^{-4} mol/L respectively, are much lower than that of conventional surfactant cetyltrimethyl ammonium chloride (CTAC). In addition, compared with some gemini surfactants containing phenylene, xylylene and stilbenyl as spacer, this new kind of surfactants has good solubility in water at room temperature because of containing more hydrophilic groups or atoms in molecules.

Keywords: Gemini surfactant, cationic surfactant, critical micelle concentration, triazole, synthesis.

Gemini surfactants, which contain two hydrophilic groups and two hydrophobic groups in the molecule, are considered as a new generation of surfactants. These surfactants are about 3 orders of magnitude more efficient at reducing surface tension and more than 2 orders of magnitude more efficient at forming micelles than conventional surfactants[1].

During recent years, many gemini surfactants have been synthesized, and a considerable number of investigations have been reported on their unusual physico-chemical properties, including their high surface activity, unusual changes of viscosity with an increase in surfactant concentration, unusual micelle structure, aberrant aggregation behavior, and stronger interaction with oppositely charged surfactants[2-9]. To our knowledge, some gemini surfactants containing phenylene, stilbenyl and xylylene as spacer are water-insoluble at room temperature[1, 6]. As a result, they can not be applied at room temperature or lower temperature. On the other hand, there are no reports on gemini surfactants based on triazole compounds till now. However, surfactants based on heterocyclic compounds should have good solubility in water at room temperature because they contain some hydrophilic atoms such as N, S and O. In addition, they can be applied to form micelles, micromulsion and vesicles more efficiently in membrane mimetic chemistry than conventional surfactants.

In this paper, we describe gemini surfactants based on 1, 2, 4-triazole compounds. Synthetic route and the structure of these triazole-based cationic gemini surfactants **A**

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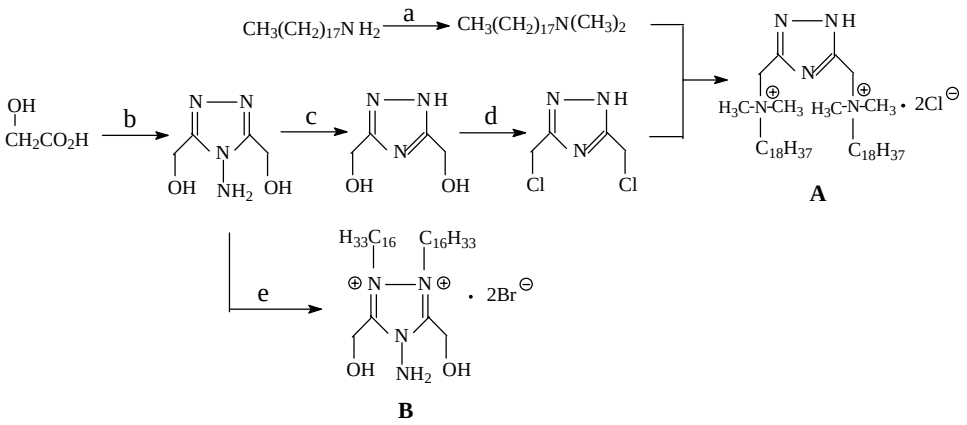
and **B** are shown in **Scheme 1**.

Scheme 1 The synthetic route to gemini surfactants **A** and **B**



Reagents: (a) HCHO/HCO_2H; (b) $NH_2NH_2 \cdot H_2O$; (c) $NaNO_2$ /HCl; (d) $SOCl_2$; (e) $CH_3(CH_2)_{15}Br$.

Surfactant **A** was synthesized from 3, 5-bis (chloromethyl)-1, 2, 4-triazole (2.0 g, 12 mmol, synthesized according to reference 10) and N, N-dimethyloctadecylamine (14.3 g, 48 mmol) in 100 mL of absolute ethanol under reflux with stirring for 48 h. After rotary evaporation of the solvent, a waxy product was obtained. Then 15 mL of distilled water was added, and the mixture was heated to ~50°C. The precipitate was filtered off, and the filtrate was concentrated. After nearly complete evaporation of the water, 30 mL of acetone was added, and the mixture was heated till it was clear. The solution was cooled in a refrigerator overnight. The precipitate was filtered and three times recrystallized from acetone-ethanol mixtures, and the desired product was obtained as a white solid[12] (3.3 g, 36%).

Surfactant **B** was obtained by reacting 4-amino-3, 5-bis (hydroxymethyl)-1, 2, 4-triazole (0.71 g, 5 mmol) with cetyl bromide (6.1 g, 20 mmol) in 80 mL of absolute ethanol under reflux for 48 h. After the reaction mixture was concentrated to 30 mL and cooled to room temperature, the precipitate was filtered and washed with hexane (5 mL) and ether (5 mL). Finally it was three times recrystallized with acetone to give a white solid[12] (2.9 g, 77%).

The surface tension and CMC of A and B

The surface tensions were determined by Krüss DSA10-MK2 Drop Shape Analysis System and the temperature was maintained precisely at 25°C. **Figure 1** shows plots of the surface tension *vs* log molar concentration of gemini surfactants **A** and **B**.

CMC values of each surfactant given according to the break points in **Figure 1** are shown in **Table 1**. Conventional surfactant cetyltrimethyl ammonium chloride (CTAC) was used as a control compound in our experiments. According to **Table 1**, CMC

values of gemini surfactants **A** and **B** are 1.8×10^{-4} mol/L and 3.9×10^{-4} mol/L respectively, and CMC of conventional surfactant CTAC is 1.3×10^{-3} mol/L. Clearly, CMCs of these gemini surfactants are much lower than that of CTAC. In addition, compared with some gemini surfactants containing phenylene, xylylene and stilbenyl as spacer, gemini surfactants **A** and **B** have good solubility in water at room temperature because of more hydrophilic atoms or groups in their molecules.

Figure 1 Plots of surface tension *vs* log molar concentration (**A** and **B**)

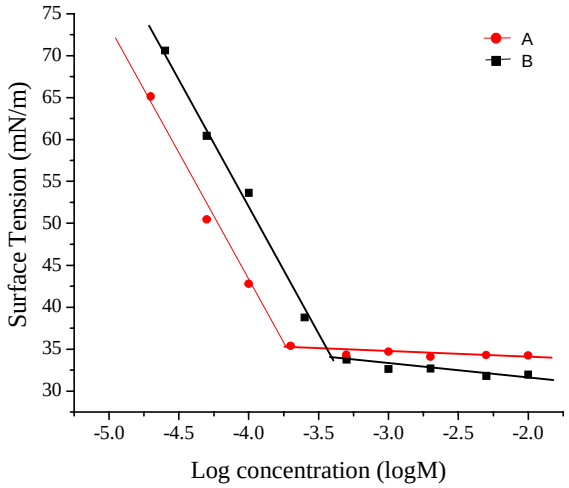


Table 1 CMC values and surface tension of gemini surfactants at 25°C

R	**A**	**B**	CTAC
CMC (mmol/L)	0.18	0.39	1.3 (30°C) [11]
γ_{CMC} (mN/m)	35.49	34.06	——

Acknowledgments

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12. **A**: m.p. 115-117°C. IR (KBr, cm^{-1}): 2850, 1674, 1468, 1379, 1106, 1012. ^{1}H-NMR (300MHz, $CDCl_3$, δppm): 0.89 (t, 6H, $-CH_3$), 1.26 (m, 64H, $-(CH_2)_{16}-$), 1.82 (m, 4H, $CH_3(CH_2)_{16}CH_2-$), 3.60 (s, 12H, $-N(CH_3)_2$), 4.42 (s, 1H, >NH), 4.88 (d, 4H, triazole-CH_2-). Anal. Calcd. for $C_{44}H_{91}N_5Cl_2$ (%): C, 69.47; H, 11.97; N, 9.21. Found: C, 69.32; H,12.01; N,9.36. **B**: m.p. 87-88°C. IR (KBr, cm^{-1}): 3319, 3265, 1635, 1568, 1468, 2849. ^{1}H-NMR (300MHz, DMSO-d_6, δppm): 0.87 (t, 6H, $-CH_3$), 1.25 (m, 56H, $-(CH_2)_{14}-$), 1.81 (m, 4H, $CH_3(CH_2)_{14}CH_2-$), 4.34 (d, 4H, triazole-CH_2-), 5.12 (t, 2H, -OH), 5.62 (s, 2H, $-NH_2$). Anal. Calcd. for $C_{36}H_{74}N_4O_2Br_2$ (%): C,57.45; H,9.57; N,7.45. Found: C,57.36; H,9.33; N,7.59.

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