Synthesis of Cationic Novel Bolaform Surfactant and Effect of Alkyl Group Chain Length on Polar Head Group

2. Dodecane-1,12-bis(trimethylammonium bromide)

and

Dodecane-1,12-bis(triethylammonium bromide)

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Abstract: Surfactants are organic compounds which contain hydrophobic groups acting as tail and hydrophilic groups acting as head, thus they are solved hardly in water and organic solvents. Surfactants are able to change surface energy within levels considerably. Property of surfactant comes from its double molecular structure. It means that it contains two hydrophilic and hydrophobic groups simultaneously. A novel type of surfactants known as bolaform is studied and synthesized in this paper. Bolaforms have two polar head groups connected via a poly methylen chain. They are categorized into anionic, cationic and non ionic depending on the head group's charge. Micelle extraction of metallic ions, using as molecules sensitive to light and usage in synthesis of mesoporous silica structure for different applications such as in catalysts are among bolaforms' applications. Structural formula of synthesized kinds with the same spacer and different heads is as follows. Bolaform A with structural formula of Br⁻(CH₃)₃N⁺(CH₂)₁₂ N⁺(CH₃)Br⁻ with side branches of methyl in head group and bolaform B with structural formula of Br⁻(CH₃ CH₂)₃N⁺(CH₂)₁₂ N⁺(CH₃ CH₂)₃Br⁻ . IR and NMR identification techniques approve obtained product. Using surface tension measurement device it can be observed that synthesized bolaforms have suitable CMC (relatively low); in other words, bolaform's surfactants with long spacer have surface activity property.

Keywords: Cationic Novel Bolaform

1. Introduction

The world bolaform was originally used in relation to electrolytes in order to refer to organic molecules made up of two charged groups connected by a linear polymethylene chain. When the

polymethylene chain is sufficiently long, the bolaform electrolyte becomes a bolaform amphiphile or surfactant [1]. Bolafroms adsorb at the air-water interface but are much less efficient than the corresponding conventional surfactants in lowering the surface tension of water. The values for surface area per surfactant obtained from such polts, suggest that most bolaforms adopt a wicket-like or looped conformation at the air-water interface, with the polar groups anchored at the interface and alkanediyl chain forming a more or less wide loop in the air[2]. Findings also show that the aggregation number of bolaform micelles increases with the ionic strength of solution, it decreases when the size of the head group is increased, and increases with the carbon number of the alkanedyil group bolaform [3].

2. Experimental Section

Materials: Triethylamine for synthesis (Fluka), Ethanol Absolute (Merck)-1,12 dibromo dodecane (Merck), Trimethylamine solution 31-35 wt. % in ethanol (~4.2 M) sigma-aldrich was prepared.

Methods: The Bolaform surfactants are synthesized in the following way: First 1,12 dibromo dodecane was dissolve in ethanol and stirred for 20 minutes. Triethylamine was added in large excess to 1,12 dibromo dodecane (dissolved in ethanol) and the mixture was kept under vigorous stirring at 55C for five days, the obtained white powder was recrystallized three times from ethanol so as to obtain 1,3-bis (triethylammonium bromide)[3]. 1,12 dibromo dodecane was dissolved in ethanol and then directly add to Trimethylamine solution 31-35 wt. % in ethanol (~4.2 M) and obtain white powder after three times recrystallization in ethanol and the resultant product is called dodecane 1,12-bis (trimethylammonium bromide). In this study, dodecane 1,12-bis (trimethylammonium bromide) are called A and B, respectively.

3. Results and Discussion

¹H NMR (500 MHz, D₂O):

δ: 2.27 (18H, S), 2.36 (8H, triplet), 1.29 (16H, multiplet) for A bolaform.
δ: 1 (18H, triplet), 2.40 (12H, quartet), 2.36 (4H, triplet), 1.39 (4H, multiplet), 1.29 (12H, S), for B bolaform

IR Spectroscopy: Another method to identical structure of bolaforms is IR spectroscopy. These kinds of bolaforms have absorbance less water than the bolaforms with short length spacer. The IR spectrum of bolaform with 12 length spacer is shown in figure 1.

Surface Tension Measurement: Surface tension measurements were carried out at 298.15 K by the ring method using a Sigma 700 tensiometer under atmospheric pressure. In the Figure 2 surface tension diagram of bolaform is shown.

Table 1. Characterization of Novel Bolaform Surfactants

Bolaform names	structure	Melting point
Dodecane 1,12 bis (trimethylammonium bromide)	P N Br O O O O O O O O O O O O O O O O O O O	250°
Dodecane 1,12 bis (triethylammonium bromide)	P Br N Br O	75°-76°

Synthesis method can be seen in the following:

Synthesis method for bolaform A:

Trimethylamine solution in ethanol (~4.2 M)

Br (CH₂)₁₂ Br

55°C, stirrer during the 3 days

Synthesis method for bolaform B:

(CH₃CH₂)₃N:

Br (CH₂)₁₂ Br

55°C, stirrer during the 3 days

Br⁻(CH₃ CH₂)₃N⁺(CH₂)₁₂N⁺(CH₂ CH₃)₃Br⁻

 $Br'(CH_3)_3N'(CH_2)_{12}N'(CH_3)_3Br'$



Figure 1.IR spectra of A bolaform

The surface tension of bolaforms with long spacer has low CMC, because 12 methylene groups as spacer have hydrophobic effects and decreases CMC of bolaform.



Figure 2.surface tension diagram of bolaform A

4. Conclusions

The results show that bolaforms behave in many respects as conventional surfactants. However, they are much less efficient than conventional surfactants as far as useful properties are concerned. Being much more hydrophilic they form micelles only at high concentration. These micelles have much smaller size and solubilizing capacity than the micelles of corresponding conventional surfactants, which reduces the applicability of bolaform in the usual uses of surfactants. Nevertheless, bolaforms appear to have interesting biological properties [4]. bolaforms with long spacer are more advantageous than the bolaforms with short spacer, for example Dodecane 1,12 bis (trimethylammonium bromide) with 12 length spacer have lower CMC than the propane 1,3 bis (trimethylammonium bromide)

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