



Synthesis and properties evaluation of sulfobetaine surfactant with double hydroxyl



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ABSTRACT

A series of sulfobetaine surfactants {N-[(3-alkoxy-2-hydroxy)propoxy] ethyl-N,N-dimethyl-N-(2-hydroxy)propyl sulfonate} ammonium chloride were synthesized with raw materials containing linear saturated alcohol, N,N-dimethylethanolamine, sodium 3-chloro-2-hydroxyl propane sulfonic acid and epichlorohydrin. The molecule structures of sulfobetaine surfactants were characterized by FTIR, ¹HNMR and elemental analysis. Surface tension measurements can provide us information about the surface tension at the CMC (γ_{CMC}), pC_{20} , Γ_{max} and A_{min} . The pC_{20} values of sulfobetaine surfactants increase with the hydrophobic chain length increasing. A_{min} values of the surfactants decrease with increasing hydrophobic chain length from 10 to 14. The critical micelle concentration (CMC) and surface tension (γ_{CMC}) values of the sulfobetaine surfactants decrease with increasing hydrophobic chain length from 10 to 16. The lipophilicity of surfactant was enhanced with the increase of the carbon chain, however, the ability of anti-hard water was weakened. The minimum oil/water interfacial tension of four kinds of sulfobetaine surfactants is 10^{-2} – 10^{-3} mN/m magnitude, which indicates that the synthesized bis-hydroxy sulfobetaine surfactants have a great ability to reduce interfacial tension in the surfactant flooding system. The surface tension (γ_{CMC}) values of synthesized surfactants were lower compared with conventional anionic surfactant sodium dodecyl sulfonate.

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1. Introduction

Alkylbenzene sulfonate surfactant and mahogany sulfonate and surfactant are usually used in combination flooding. Surfactant is generally used as a wetting, leveling and dispersing agent. They are also one of the main components in cosmetics, creams, gels, etc [1,2]. Surfactant constitutes the most important component of the detergent component, and its divided into four groups based on the charge of the molecular chain; anionic, cationic, zwitterionic and non-ionic. Ionic surfactants account for two-thirds of all the surfactants, and the anions account for more than 90% of all the ionics. Surfactants are used in textiles, food, polymers, cosmetics, pesticides and paper industry. Anionic surfactants with high foaming ability are widely used in the production of toothpaste, shampoo and many industrial detergents. Cationic surfactants are widely used in various industries of the textile softening agent, dispersing agent, emulsifier, wetting agent, disinfectant and preservative [3,4].

Zwitterionic surfactants containing positive and negative charge head groups are interesting molecules because they have many unique properties. Which are widely used as detergents in daily life, and applied to industrial production of oil field as flooding agents and oilfield fracturing fluids [5–8]. Anionic and nonionic surfactants are widely used in tertiary oil recovery. However, these kinds of surfactants are not suitable for high temperature and high salt reservoir conditions. The various parameters of the surfactant, such as charge and alkyl terminal length, can affect the performance of the surfactant [9]. Critical micelles concentration (CMC) value is an important index to judge the performance of surfactant aqueous solution. The formation of micelles can enhance the solubility of insoluble molecules in water, which is of great importance in various industrial processes [10].

Betaine amphoteric monomer is a broad application of a functional monomer, such as tri[(N-alkyl-N-ethyl-N-sodiumcarboxymethyl)-2-ammonium bromide ethylene] amine was synthesized by us [11]. Betaine amphoteric surfactants generally formed by the polymerization activity olefin bond portion and betaine pendant moiety of a neutral zwitterionic characteristics [12–17]. Betaine

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amphoteric surfactant has good stability in acid and alkali environment and its solubility is less affected by the electrolyte and pH [18]. In addition, betaine amphoteric surfactant has a strong anti-hard water and performance good compatibility and synergy combined with anionic surfactant [19,20]. Betaine amphoteric surfactant has excellent performance for Enhanced Oil Recovery (EOR) [21]. However, few research is available for sulfobetaine with two hydroxyl groups. Therefore, a series of dual hydroxy sulfobetaines with different the number of carbon atoms in the hydrophobic chain were synthesized by us.

In the present investigation, the four kinds of betaine amphoteric surfactants were synthesized with raw materials and their structure were characterized by FTIR, ¹HNMR and elemental analysis. The effect of surface activity, foaming property, γ_{CMC} , CMC, pC_{20} , Γ_{max} , A_{min} , the emulsifying property, hard water tolerance and interfacial tension were investigated.

2. Experimental section

2.1. Materials

Lauryl alcohol, tetrabutyl ammonium bromide (TBAB), tetradecyl alcohol, cetyl alcohol, toluene, epichlorohydrin, sodium hydroxide, *N,N*-Dimethylethanolamine, sodium 3-chloro-2-hydroxyl propane sulfonic acid, dichloromethane, calcium chloride, hydrochloric acid and ethanol were purchased from Kelong Ltd, Chengdu, China. All of which were in analytical grade.

2.2. Analytical methods

The structures of product were characterized by FTIR (Nicolet6700, America), ¹H-Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker (Wissembourg, France) AR × 400 spectrometer (400 MHz) and Element analyses were determined by Costech ECS 4010 (HNSO analyzer, Italy). Surface tension (γ_{CMC}) was measured with JK99B automatic tensiometer by the hanging ring method at 298.15 K. According to GB/T 7462-94, the emulsification property was determined by measuring the time of bleeding 10 mL water from the aqueous solutions of surfactants with various concentration. The foaming property was measured with ROSS-Miles pour-foaming apparatus. Interfacial tension (IFT) were determined with TX500C spinning drop IFT apparatus.

2.3. Synthesis and characterization

Four kinds of sulfobetaine surfactants were synthesized through three steps by following Schemes 1–3.

2.3.1. Synthesis of the intermediate long chain alkoxy glycidyl ether

In the first step, 150 mL petroleum ether as solvent was added to a three-neck flask of 500 mL. Then, a total of 0.25 mol of aliphatic alcohol and 0.40 mol of sodium hydroxide (NaOH) together with 0.01 mol of tetrabutyl ammonium bromide (TBAB) were added to the solvent by agitation at 30 °C. Then, 0.50 mol epichlorohydrin

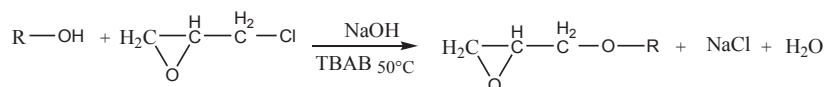
was added dropwise in 0.5 h under agitation. Then the reaction was carried out at 50 °C for 5 h. After naturally cooled to room temperature, the mixture was filtrated to remove impurities (NaOH, NaCl, and TBAB). Finally, the solvent was removed by rotary vacuum distillation to get pure alkoxy glycidyl ether. The yields of long chain alkoxy glycidyl ether (10-a, 12-a, 14-a, 16-a) were 93 wt%, 91 wt%, 88 wt% and 83 wt%, respectively. The structures of product were characterized by FTIR, ¹HNMR and elemental analysis. FTIR: The resolution, scan's numbers and detector are 4, 32 and DTGS KBr, respectively. 2925.31 cm^{-1} ($\nu_{\text{C-H}}$), 1461.75 cm^{-1} ($\nu_{\text{C-H}}$), 1110.29 cm^{-1} and 1257.42 cm^{-1} ($\nu_{\text{C-O}}$). ¹HNMR (CDCl_3): $\delta = 0.842$ (t, 3H, $-\text{CH}_3$), $\delta = 1.106$ – 1.335 (m, methylene in alkane, $-\text{C}(\text{CH}_2)_{n-2}\text{C}-$), $\delta = 3.107$ – 3.346 (m, 2H, $-\text{CH}_2-\text{O}-$). Elemental analysis: 10-a Calculated for $\text{C}_{13}\text{H}_{26}\text{O}_2$ C, 72.90%; H, 12.15%; O, 14.95%; Found C, 72.98%; H, 12.26%; O, 15.12%. 12-a Calculated for $\text{C}_{15}\text{H}_{30}\text{O}_2$ C, 74.38%; H, 12.40%; O, 13.22%; Found C, 74.40%; H, 12.54%; O, 13.75%. 14-a Calculated for $\text{C}_{17}\text{H}_{34}\text{O}_2$ C, 75.56%; H, 12.59%; O, 11.85%; Found C, 75.58%; H, 12.63%; O, 12.16%. 16-a Calculated for $\text{C}_{17}\text{H}_{38}\text{O}_2$ C, 68.46%; H, 12.75%; O, 10.74%; Found C, 68.48%; H, 12.80%; O, 11.06%.

2.3.2. Synthesis of tertiary amine

In the second step, *N,N*-Dimethylethanolamine (0.80 mol) dissolved in ethanol was added into a three-necked flask with a reflux condenser under agitation. Then the prepared glycidyl ether (0.20 mol) and sodium ethoxide (4 mmol) as the catalyst were added dropwise into this three-necked flask and had reacted for 10 h at 80 °C. The solvent and the excess of *N,N*-Dimethylethanolamine were evaporated to get pure linear alkoxy tertiary amine. The yields of long chain alkoxy glycidyl ether (10-b, 12-b, 14-b, 16-b) were 88 wt%, 85 wt%, 83 wt% and 81 wt%, respectively. The structures of product were characterized by FTIR, ¹HNMR and elemental analysis. FTIR: The resolution, scan's numbers and detector are 4, 32 and DTGS KBr, respectively. 2929.40 cm^{-1} ($\nu_{\text{C-H}}$), 3306.74 cm^{-1} ($\nu_{\text{O-H}}$), 1115.01 cm^{-1} ($\nu_{\text{C-O}}$), 1141.54 cm^{-1} ($\nu_{\text{C-N}}$). ¹HNMR (CDCl_3): $\delta = 0.842$ (t, 3H, $-\text{CH}_3$), $\delta = 1.135$ – 1.380 (m, methylene in alkane, $-\text{C}(\text{CH}_2)_{n-2}\text{C}-$), $\delta = 3.160$ – 3.435 (m, 2H, $-\text{CH}_2-\text{O}-$), $\delta = 6.104$ – 6.085 (m, 1H, $\text{O}-\text{CH}(\text{OH})-$), $\delta = 4.362$ (s, 1H, $\text{O}-\text{CH}(\text{OH})-$), $\delta = 2.882$ – 3.268 (s, 6H, $\text{N}^+(\text{CH}_3)_2-$). Elemental analysis: 10-b Calculated for $\text{C}_{17}\text{H}_{37}\text{O}_3\text{N}$ C, 67.33%; H, 12.21%; N, 4.62%; Found C, 67.35%; H, 12.33%; N, 4.68%. 12-b Calculated for $\text{C}_{19}\text{H}_{41}\text{O}_3\text{N}$ C, 68.88%; H, 12.39%; N, 4.23%; Found C, 68.91%; H, 12.42%; N, 4.31%. 14-b Calculated for $\text{C}_{21}\text{H}_{45}\text{O}_3\text{N}$ C, 70.19%; H, 12.53%; N, 3.90%; Found C, 70.25%; H, 12.58%; N, 4.12%. 16-b Calculated for $\text{C}_{23}\text{H}_{49}\text{O}_3\text{N}$ C, 71.32%; H, 12.66%; N, 3.62%; Found C, 71.36%; H, 12.74%; N, 3.71%.

2.3.3. Synthesis of four model betaine amphoteric surfactants {*N*-[(3-alkoxy-2-hydroxyl)propoxy]ethyl-*N,N*-dimethyl-*N*-(2-hydroxyl)propyl sulfonate} ammonium chloride ($R = \text{C}_{10}\text{H}_{21}$, $\text{C}_{12}\text{H}_{25}$, $\text{C}_{14}\text{H}_{29}$, $\text{C}_{16}\text{H}_{33}$)

In the third step, the target products four model betaine amphoteric surfactants were synthesized with sodium 3-chloro-2-hydroxyl propane sulfonic acid as sulfonating agent in a 500 mL three-neck glass reactor. A total of 0.10 mol tertiary amine was added to the reactor, taking into account the solubility of the



Abbreviation 10-a, 12-a, 14-a, 16-a.

Scheme 1. Synthesis of long chain alkoxy glycidyl ether ($R = \text{C}_{10}\text{H}_{21}$, $\text{C}_{12}\text{H}_{25}$, $\text{C}_{14}\text{H}_{29}$, $\text{C}_{16}\text{H}_{33}$).

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