Synthesis of Amphoteric Sulfonic Ionic Liquid Surfactant and Measurement of Its Surface Properties

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Abstract. Three kinds of amphoteric sulfonic ionic liquid surfactants were synthesized in this paper. Their functional group structures were characterized by infrared spectrometer. The surface properties of them were studied. The results show that the functional group structures of all three products conform to the structure characteristics of amphoteric sulfonic ionic liquid surfactants. The shorter the long chain alkyl carbon chain is, the closer the arrangement of surfactant on the gas-liquid surface will be, and the higher the efficiency in reducing the surface tension.

1. Introduction
Alkaline/Surfactant/Polymer (ASP) is one of the tertiary oil recovery methods with the most application prospect, which can improve the recovery ratio by more than 20%. As one of the three elements, the surfactant can directly affect the interfacial tension and oil displacement efficiency of the oil and water system. At present, sulfonate surfactant is one kind of anionic surfactants with the largest production and most extensive usage [1-2]. But its composition is complicated, the directional synthesis is difficult, and there is a quality stable problem, which makes its R&D and mass production difficult. However, ionic liquid has the modifiable anionic and cationic structure. We can design a kind of ionic liquid with certain functional group, some special functions and a specific task according to actual requirements, which is functional ionic liquid. By combining the sulfonate and ionic liquid surfactant, a new amphoteric sulfonic ionic liquid surfactant can be made, which will break a new path in the use of sulfonic compounds and amphoteric surfactant, and provide a new idea for tertiary oil recovery.

2. Experiments
2.1. Experimental reagents and instruments
With imidazole as the rest of the industrial grade reagent, anhydrous ethanol, chloroform, 2- bromide bromoethylamine hydrobromide, 1- twelve bromo alkane, 1- acrylonitrile, bromodecane, methanol, 1- fourteen alkyl bromide, isopropanol, chlorosulfonic acid, anhydrous magnesium chloride was of pure chemical reagents.

The instruments used are mainly Bruker-Tensor 27 Fourier transform infrared spectrometer, DF-101S thermal heating magnetic stirrer (Yingyuyuhua Instrument Plant in Gongyi City), FD-1201 rotary evaporator (Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd.), and so on.

2.2. Experimental Step
(1) Synthesize the three kinds of amphoteric sulfonic ionic liquid surfactants: C₁₀, C₁₂ and C₁₄ amphoteric sulfonic ionic liquid surfactants, and infrared characterization.
(2) Measure the surface properties of all three kinds of amphoteric sulfonic ionic liquid surfactants.

3. Experimental Results and Discussions

3.1. Synthesis and Characterization

3.1.1. Contents of Synthesis. A certain amount of N-methyl imidazole, acrylonitrile and methanol were added to three bottles which were installed in thermometer and reflux condenser tube, and the control reaction temperature was 55~60°C, and thermostatically stir for 24 hours. After reaction, remove the methanol and the leftover acrylonitrile by the rotary evaporator. Then the liquid is transferred to the already installed thermometer and condenser tube and the nitrogen device 250mL four mouth flask, and add the 1- bromodecane and excess isopropanol to the flask, and stir with back flow for 24 hours under the environment of nitrogen and at 60~65°C. After the reaction is over, add certain dosage of chloroform into the liquid, and then put the obtained liquid into a sodium hydroxide solution with the mass fraction of 15%. Stir the liquid with back flow for 3 hours under room temperature, put the liquid into a separating funnel for standing and layering, remove the lower water layer, wash the chloroform layer with deionized water for 5 times, remove the chloroform by the rotary evaporator[3,4], and then a pale yellow oily dope can be obtained.

The long chain imidazole synthesized in the previous step is dissolved in a suitable amount of isopropanol, then a certain amount of isopropanol and 2- bromo ethylamine hydrobromide are added to the four flask of 250mL, and nitrogen protection is done at the mouth of the flask, and the thermometer return condenser is installed, maintain the pressure between 65 and 70°C, and react for 24 hours. After reaction, hot wash the reactant by concentrated potassium hydroxides solution, adjust the pH value to 7, suck filtration, discard the solid residue, add absolute ethyl alcohol to the remaining liquid, separate out the residual potassium bromide precipitation, rotary evaporate at 70°C, vacuum drying for 4 hours, and finally obtain the yellow oily dope which is brominated 1-ethyl amino-3-decyl imidazole.

During the sulfonation process, weigh certain dosage of brominated 1-ethyl amino-3-decyl imidazole and methylene chloride, dissolve them at 0°C, maintain the temperature, slowly add a suitable amount of chlorosulfonic acid and dichloromethane, after reacting for 4 hours, increase to the room temperature, slowly add saturated ethanol solution of sodium hydroxide, adjust the pH to about 9, continuously react for 5 hours, and then stop the reaction. After the reaction is over, there will be a few white precipitate. After spinning dry the dissolvent dichloromethane and ethanol, some white solids will be obtained. And then, dissolve the solid by a suitable amount of aqueous solution (a few insoluble is acceptable), extract by N-butyl alcohol, combine the extract, dry by anhydrous magnesium sulfate, evaporate out the N-butyl alcohol to obtain a brown solid, and then recrystallize by ethanol to obtain a white solid which is C10 amphoteric sulfonic ionic liquid surfactant.

The preparation of C12 and C14 amphoteric sulfonic ionic liquid oil-displacing agents is the same as that of C10.

3.1.2. Product Characterization. From the following picture, we can see that 3434cm⁻¹ is the absorption peak of N-H stretching vibration. 3142cm⁻¹ shows the absorption peak of C-H stretching
vibration on imidazole ring, while 2910cm\(^{-1}\) is the position of side chain alkyl C-H stretching vibration absorption peak. The wave number 1629cm\(^{-1}\) is N-H bending vibration absorption peak at 1465cm\(^{-1}\), wavenumber imidazole ring substituents on C-H bending vibration peak shows that the wave number 1338cm\(^{-1}\) 1234cm\(^{-1}\) position is the display of C-N stretching vibration absorption peak of the imidazole ring, on display at 1156cm\(^{-1}\) is the wave number of absorption peak of stretching vibration of sulfonate groups.

The structure difference of all three products lies in the carbon number on the branch, so the infrared spectrums of the synthetic products are basically the same, which can meet the structural characteristics of amphoteric sulfonic ionic liquid surfactant of C\(_{10}\) (C\(_{12}\) and C\(_{14}\)).

![Infrared spectrum of synthetic products](image)

Figure 1. Infrared spectrum of synthetic products

3.2. Measurement of Surface Tension

In this experiment, the surface tension was measured by the drop volume method \(^{[4]}\), and the radius of long glass tube used in this method is 0.1888mm. The F value of the correction factor can be obtained by looking up in the table and the drop-weight method of water, which is 0.2759. The surface tension can be calculated by formula

$$\frac{\Delta \cdot \rho \cdot \gamma}{F \cdot g \cdot R}$$

where, \(t=25^\circ C\), \(\gamma=9.8\), and \(R=0.2053\).

By plotting a figure with the logarithmic of concentration (lgc) and the surface tension \(\gamma\), the critical micelle concentration (cmc) and the minimum surface tension (\(\gamma_{\text{cmc}}\)) can be read directly on the curve. The saturated adsorption amount (\(\Gamma_{\text{max}}\)) and the limit molecular area (\(A_{\text{min}}\)) can be calculated by using the Gibbs adsorption formula. The surface properties of all three amphoteric sulfonic ionic liquid surfactants synthesized in the experiment are listed in table 1.

| Table 1. Surface properties of all three amphoteric sulfonic ionic liquid surfactants |
|-----------------|--------|--------|--------|
| Surfactants     | C\(_{10}\) | C\(_{12}\) | C\(_{14}\) |
| cmc/mol·L\(^{-1}\) | 1.53×10\(^{-5}\) | 1.24×10\(^{-5}\) | 0.96×10\(^{-5}\) |
| \(\gamma_{\text{cmc}}\)/mN·m\(^{-1}\) | 26.86    | 27.54    | 28.89    |
| \(\Gamma_{\text{max}}\)/mmol·m\(^{-2}\) | 2.02×10\(^{-4}\) | 1.58×10\(^{-4}\) | 1.32×10\(^{-4}\) |
| \(A_{\text{min}}\)/nm\(^{2}\) | 8.22    | 10.51    | 12.58    |

It can be known from table 1 that with the increasing of the carbon chain, the concentration of critical micelle reduces, while the corresponding surface tension of the formed micelle increases, the saturation adsorption amount decreases, and the minimum molecular area increases. This indicates that the shorter the chain, the closer the arrangement of surfactant on the gas-liquid surface will be, and the higher the efficiency in reducing the surface tension.
4. Conclusion

(1) Three kinds of amphoteric sulfonates type ionic liquid surfactants of C10, C12 and C14 were synthesized, and they are confirmed as the objective products through infrared characterization.

(2) The surface properties of them are measured. With the increasing of carbon chain, the concentration of critical micelle reduces, \( \gamma_{\text{cmc}} \) increases, the saturation adsorption amount decreases, and the minimum molecular area increases.

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