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To cite this article: Yan Min Zhang et al 2019 IOP Conf. Ser.: Earth Environ. Sci. 237 022029

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Synthesis, analysis and application of naphthalene sulfonic acid formaldehyde condensate

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Abstract: β-naphthalene sulfonic acid formaldehyde condensate is a kind of dispersant with good properties, such as wetting, emulsifying, dispersing. It is widely used as coating dispersant, dye dispersant, cement water reducer and so on. Therefore, the synthesis of naphthalene sulfonic acid formaldehyde condensate and its application performance are of great practical significance. In this paper, naphthalene sulfonic acid formaldehyde condensate was synthesized from naphthalene, concentrated sulfuric acid and formaldehyde with the ratio of naphthalene to sulfuric acid approaching 1:2, the condensation temperature ranging from 110~120℃ and the condensation time of 5.5 hours. The characteristics of groups in products were determined by IR.

1. Introduction
The trade name of naphthalene sulfonic acid formaldehyde condensate is TAMOL or NNO (NS) [1]. β-Naphthalene sulfonic acid formaldehyde condensate is an excellent variety of anionic surfactants, which has good wetting, emulsifying, dispersing, foaming and other properties. It has wide application in water reducing agent and dyestuff industry. With the increase of molecular chains of condensates, their applicability is different. Naphthalene sulfonic acid formaldehyde condensate has a remarkable effect on the diffusion of inorganic particles such as cement. In the same series of products, condensates with high degree of condensation and longer molecular chain have a better diffusion effect than condensates with low degree of condensation and shorter molecular chain. There are various analytical methods for naphthalene sulfonic acid formaldehyde condensate, such as optical density analysis, infrared spectroscopy analysis, but the effect is not very intuitive, ideal, and cannot quantify its composition. At present, naphthalene sulfonic acid formaldehyde condensate is more and more used in commercial reactive dyes abroad, but its effect on the application performance of dyes has not been systematically studied. Therefore, the analysis of naphthalene sulfonic acid formaldehyde condensate and its effect on the application performance of dyes have very good practical significance [2-4].

2. Experimental part
2.1 Reagents and instruments
Main reagents: naphthalene, formaldehyde, 98% concentrated sulfuric acid, sodium hydroxide.
Main instruments: electrothermal constant temperature vacuum drying box, electric stirrer, Fourier-
transform infrared spectrophotometer.

2.2 Experimental principle

β-Naphthalene sulfonic acid was prepared from industrial naphthalene by sulfonation at high temperature, then a small amount of isomer α-naphthalene sulfonic acid was removed by hydrolysis, the condensation reaction between β-naphthalene sulfonic acid and formaldehyde was carried out under acidic conditions. The naphthalene sulfonic acid formaldehyde condensate was prepared by neutralization of alkali [5].

The purpose of sulfonation is to replace the hydrogen on the aromatic nucleus to form sulfonic group. After sulfonation, a hydrogen atom directly connected to the carbon atom on the naphthalene nucleus is replaced by sulfonic group to form naphthalene sulfonic acid. Because two benzene rings are linked in the naphthalene molecule, the α-position electron cloud is denser and more active. The sulfonation of naphthalene is reversible, and the position of the sulfonic group is related to the external conditions. α-Naphthalene sulfonic acid is easily generated at lower temperatures (below 120 °C). β-Naphthalene sulfonic acid is easily generated at higher temperatures. Because the β position is not easy to be sulfonated, the sulfonated product of β-naphthalene sulfonic acid is stable at high temperature. The content of β-naphthalene sulfonic acid should be increased in the synthesis process [6-7].

2.3 Experimental method

2.3.1 Synthesis of β-naphthalene sulfonic acid formaldehyde condensate

The main component of naphthalene superplasticizer is β-naphthalene sulfonic acid formaldehyde condensate, which is an excellent anionic surfactant. The synthesis of naphthalene superplasticizer can be divided into four steps: firstly, industrial naphthalene is sulfonated to produce β-naphthalene sulfonic acid; secondly, a small amount of isomer α-naphthalene sulfonic acid is removed by hydrolysis; the third step is the condensation reaction of β-naphthalene sulfonic acid and formaldehyde under acidic conditions; in the fourth step, naphthalene sulfonate sodium formaldehyde condensate was prepared by neutralization of alkali [8].

(1) Sulfonated reaction

The reaction of introducing sulfonic group (—SO₃H) to organic molecules is called sulfonation. The sulfonation of naphthalene is an electrophilic substitution reaction, and the sulfonation of naphthalene at low temperature is a kinetic control reaction, which is favorable for the sulfonation group to enter the α position; the thermodynamic control reaction at high temperature is favorable for the sulfonation group to enter the β position. α-Naphthalene sulfonic acid is unstable, its space is hindered greatly which is not conducive to the condensation reaction. β-Naphthalene sulfonic acid is stable with little space barrier and favorable for condensation reaction. Therefore, α-naphthalene sulfonic acid should be removed before condensation. The reaction equation is (1):

\[
\begin{align*}
\text{α-naphthalene sulfonic acid} & \quad + \quad \text{β-naphthalene sulfonic acid} \\
\text{H}_2\text{SO}_4 & \quad \xrightarrow{160°C} \\
\text{α-naphthalene sulfonic acid} & \quad \text{β-naphthalene sulfonic acid}
\end{align*}
\]

(2) Hydrolysis reaction

A part of α-naphthalene sulfonic acid is inevitably produced during sulfonation, which is not conducive to condensation reaction. Therefore, the sulfonic group on the α position can be removed by hydrolysis reaction, that is the hydrolysis reaction can be carried out at a reasonable temperature. Generally more than 120 °C, β-naphthalene sulfonic acid is stable, while α-naphthalene sulfonic acid is easy to decompose. The reaction equation is (2):
(3) Condensation reaction

Generally speaking, the reaction of low molecular compounds interacting to form polymers and removing small molecules at the same time is called polycondensation reaction, the product is called polycondensation. In the process of condensation polymerization, different low condensation polymers are gradually reduced to synthesize polymer compounds. The reaction equation of β-naphthalene sulfonic acid with formaldehyde is (3):

$$\beta\text{-naphthalene sulfonic acid formaldehyde condensate}$$

(4) Neutralization reaction

Excess sulfuric acid is present in both sulfonation and polycondensation reactions. These residual sulfuric acid and the alkyl sulfonic acid produced by the reaction are neutralized into salts by alkali in the final stage of synthesis. The neutralization reaction equation is (4):

2.4 Experimental steps

Naphthalene (30 g) was added to a three-necked flask and heated to 137 ℃. At the same time, the mixture was stirred with an electric stirrer. The 98% concentrated sulfuric acid of 14.5 mL was added to the flask, 30min added (speed is too fast or temperature rises suddenly, the mixture was easy to burst and spray). The temperature was raised to about 160 ℃ and the constant temperature reaction lasted 180 minutes. Then the temperature was reduced to about 140 ℃ and 4.5mL distilled water was used to hydrolyze 20min. When the temperature is 110 ℃, adding formaldehyde 10.6 mL, the reactor at constant temperature for 330 minutes, cooling down after reaction, neutralization with sodium hydroxide to pH=7 ~ 8, that is β-naphthalene sulfonic acid sodium formaldehyde condensate [9-10].

2.5 Infrared spectroscopic analysis of β-naphthalene sulfonic acid sodium formaldehyde condensate

A small amount of the synthesized product was refined in an agate mortar. The naphthalene sulfonic acid sodium formaldehyde condensate was compressed into transparent tablets according to the conventional solid sample infrared testing method. Infrared spectrum detection was carried out on the Fourier infrared spectrophotometer [9,11].
Figure 1 IR spectrogram of β-naphthalene sulfonic acid sodium formaldehyde condensate

Table 1 Infrared spectrum analysis

| Vibration frequency /cm⁻¹ | Group                     | Vibration form         |
|---------------------------|---------------------------|------------------------|
| 3442cm⁻¹                  | -OH                      | stretching vibration   |
| 908cm⁻¹                   | -CH₂⁻                    | stretching vibration   |
| 3037cm⁻¹                  | C-H in naphthalene ring   | stretching vibration   |
| 892cm⁻¹                   | -H on naphthalene ring    | bending vibration      |
| 2725cm⁻¹                  | Two adjacent -H on naphthalene ring | bending vibration |
| 1357cm⁻¹-972cm⁻¹          | -SO₃H                    |                        |

3. Results and discussion

The synthesis of β-naphthalene sulfonic acid formaldehyde condensate is mainly affected by naphthalene aldehyde ratio, reaction temperature and reaction time.

(1) The amount of formaldehyde will affect the condensation products. When the ratio is too small, some formaldehyde volatilization makes the reaction incomplete enough. The ratio is too large, side reactions are prone to occur. It is impossible to synthesize high molecular weight formaldehyde condensates.

(2) Naphthalene sulfonation is a reversible reaction, its products are related to external conditions. The main product is α-naphthalene sulfonic acid at low temperature (35-90°C), and the same reaction mixture mainly produces β-naphthalene sulfonic acid at high temperature (160-165°C). Therefore, in order to obtain the β-naphthalene sulfonic acid, the sulfonation temperature should be controlled at around 160°C. Formaldehyde has low boiling point, it is easy to volatilize, so the condensation temperature is controlled at 110°C.

(3) The sulfonation reaction time is too long, the sulfonation probability increases; the sulfonation time is too short, the sulfonation reaction is incomplete, the yield of β-naphthalene sulfonic acid is not high. The sulfonation time should be controlled for 3 hours, the condensation time is about 6 hours.
4. Conclusion

(1) Naphthalene reacts with concentrated sulfuric acid to form β-naphthalene sulfonic acid at high temperature. The reaction is intense and the temperature is not easy to control. There are side reactions. Polysulfonation and sulfones may be formed, which affect the purity of the product.

(2) In the condensation of β-naphthalene sulfonic acid with formaldehyde, the acidity of the system has a great influence on the condensation degree. The low acidity is unfavorable to the sulfonation reaction. The high acidity is easy to cause the explosive polymerization, the high viscosity produces caking, and the water solubility is poor. The naphthenic acid ratio of 1:2 was used to synthesize the condensation product of β-naphthalene sulfonic acid formaldehyde condensate.

Acknowledgment

This work was supported by the University Project of Gansu Province (2017A-095) and the 13th Five-Year Period Education Plan of Gansu Province (GS [2017] GHB0360)

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