Study on Naphthalene Sulfonic Acid Formaldehyde Condensate by Ultraviolet Absorption Spectrum

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Abstract: Naphthalene sulfonic acid formaldehyde condensate is a kind of surfactant with excellent performance, which is widely used in printing, dyeing, cement, paint and other industries. There are various analytical methods for naphthalene sulfonic acid formaldehyde condensate, such as optical density analysis, electrophoresis, chromatographic analysis and spectral analysis. A series of formaldehyde condensates were synthesized from naphthalene, formaldehyde solution and concentrated sulfuric acid solution. The products were qualitatively analyzed by infrared and ultraviolet absorption spectra.

1. Introduction
The general formula for the structure of naphthalene sulfonic acid formaldehyde condensate is as follows:

\[
\text{H} \left[ \begin{array}{c} \text{CH}_2 \\ \text{SO}_3\text{H} \\ \text{SO}_3\text{H} \end{array} \right]_{n=1} \text{Naphthalene sulfonic acid formaldehyde condensate}
\]

Naphthalene sulfonic acid formaldehyde condensate is abbreviated as NS. It has been an important anionic surfactant in industry. It has been widely used in printing and dyeing, leather making, cement, rubber, paint, oil field mud treatment and other industries. With the dramatic increase of synthetic fibers, as the main additives of synthetic fibers dyes, the demand for naphthalene sulfonic acid formaldehyde condensate has increased dramatically, and its position in the additive industry has become more important [1].

Naphthalene sulfonic acid formaldehyde condensate is a high molecular compound. Its dispersion performance is closely related to its degree of polymerization. The degree of polymerization is too low or too high, its dispersion effect is poor. According to the current application practice, the products with low degree of polymerization (n=1-3) are mainly used as diffuser in textile printing and dyeing industry, while the products with medium degree of polymerization (n=6-12) are mainly used as superplasticizer for concrete. The products with high degree of polymerization (n≥15) can be used as additives for coal water slurry and extra-strong concrete. The different degree of polymerization has a great influence on its application performance. Therefore, improving the degree of polymerization of products can improve the quality parameters and expand its application fields. In this experiment, industrial naphthalene, concentrated sulfuric acid, formaldehyde and liquid alkali were used as the main raw materials. The reaction principle, synthesis process and application development of sulfonation, hydrolysis and condensation processes were re-explored in detail, so as to make the synthesis process more perfect [2-3].
2. Experimental part

2.1. Synthesis of naphthalene sulfonic acid formaldehyde condensate

2.1.1. Synthetic raw materials
Naphthalene (analytical purity), concentrated sulfuric acid (98%), formaldehyde solution, NaOH solution, CaCO₃ (analytical purity)

2.1.2. Synthesis process
The synthetic methods of naphthalene sulfonic acid formaldehyde condensate at home and abroad can be roughly divided into three steps. Firstly, industrial naphthalene is sulfonated at high temperature to produce β-naphthalene sulfonic acid. Secondly, removal of a small amount of isomer α-naphthalene sulfonic acid by hydrolysis. Then, β-naphthalene sulfonic acid and formaldehyde are condensed under acidic conditions, naphthalene sulfonic acid formaldehyde condensate was synthesized by acid-alkali neutralization.

12.8g refined naphthalene (0.1mol) was weighed and heated in four flasks. When the temperature rose above 130℃, 98% sulphuric acid (about 7ml, 0.13mol) was slowly dripped into the four flasks. After adding acid, the temperature continued to rise to 160-162℃ and kept constant for 2 hours. Then the temperature was lowered to 110℃, 4-5 ml distilled water was added, 2-3 drops of solution were extracted under stirring, and the total acidity was determined. The total acidity was controlled between 28%—32% by adding sulphuric acid. 10 ml (0.3 mol) 37% formaldehyde solution was slowly dripped between 80 - 90℃, heated to 95-100℃, stirred for 5-6 hours at constant temperature, added 30 ml hot water, stirred to dissolve completely, added 3.6 g (about 0.09 mol) sodium hydroxide concentrated solution, then slowly added calcium carbonate powder wet with water bubbles, stirred at the same time, until no bubbles were produced. The pH value was determined at about 7, filtered, collected filtrate, concentrated. Light brown powder can be obtained by drying and grinding [4-6].

2.1.3. Standard spectrogram

Fig. 1 Standard IR diagram of naphthalene sulfonic acid formaldehyde condensate

2.2. Determination of naphthalene sulfonic acid formaldehyde condensate by infrared spectroscopy

2.2.1. Experimental preparation
Take 20g dry KBr powder and 1-2 g dry sample, grind them evenly in agate mortar, put them into the pressing die, exhaust, press the sheet, and then put the pressed sheet into the light path. The infrared spectra of the samples were plotted with KBr tablets as reference (Fig. 2). The scanning range is 400-4000cm⁻¹ and the resolution is 2.4cm⁻¹. The infrared spectra of the sample naphthalene sulfonic acid formaldehyde condensate is as follows:
2.2.2. Analysis of Infrared Spectrum

Naphthalene sulfonic acid formaldehyde condensate was successfully synthesized by condensation of naphthalene sulfonic acid with formaldehyde. After the condensation reaction, the naphthalene sulfonic acid formaldehyde condensate was analyzed by Infrared Spectrometry, and the peak area was compared.

The infrared spectra of naphthalene sulfonate condensates are shown in Fig. 2. Compared with the standard spectra, the infrared spectra of naphthalene sulfonate condensates have 12 distinct absorption peaks, which can be used to infer the composition of naphthalene sulfonate condensates:

1. There is a strong and wide absorption peak at 3431 cm\(^{-1}\). The peak height is 52. The functional groups may be alcohols and phenols, because alcohols and phenols have absorption peaks in the range of 3400-3200 cm\(^{-1}\), and the absorption peaks are O-H stretching vibration.

2. There is a strong peak at 3053 cm\(^{-1}\). The peak height is 75. The functional groups may be characteristic peaks of proteins and polysaccharides, because proteins and polysaccharides have absorption peaks in the range of 3000-2500 cm\(^{-1}\). It's the C-H stretching vibration.

3. There is a small absorption peak at 2920 cm\(^{-1}\). Its peak height is 81, which may be alkanes. There are absorption peaks in the range of 2960-2850 cm\(^{-1}\) for alkanes.

4. There is an obvious main absorption peak at 1593 cm\(^{-1}\). Its peak height is 81. The functional group may be olefin, because the absorption peak of olefin is 1680-1580 cm\(^{-1}\), which is C = C stretching vibration.

5. There are two small absorption peaks at 1503 cm\(^{-1}\) and 1384 cm\(^{-1}\). The peak heights are 72 and 68. The functional groups may be alkanes, because the absorption peaks of alkanes are in the range of 1465-1340 cm\(^{-1}\) and bending vibration.

6. A single absorption peak appeared at 1188 cm\(^{-1}\), 1107 cm\(^{-1}\) and 1051 cm\(^{-1}\). The peak heights are 6, 21 and 24. The functional group may be sulfonate, because the absorption peak of sulfonate is 1300-1000 cm\(^{-1}\), which is S=O stretching vibration.
(7) A strong absorption peak appeared at 827 cm\(^{-1}\), 740 cm\(^{-1}\) and 686 cm\(^{-1}\). The functional group may be haloalkanes [6-7].

In conclusion, compared with the standard spectra of naphthalene sulfonic acid formaldehyde condensate, the synthesized substance may be naphthalene sulfonic acid formaldehyde condensate.

2.3. Determination of naphthalene sulfonic acid formaldehyde condensate by Ultraviolet Spectroscopy

2.3.1. Experimental preparation

According to the requirement of ultraviolet spectroscopy, standard solution with concentration of 10\(^{-3}\) mol/l was disposed. Pour the solution into a colorimetric dish. The solution was scanned and measured by ultraviolet spectroscopy. If the scanning range is too high or too low or too wide in the spectrum, the solution should be diluted or reconstituted, and the wavelength and absorbance should be fine-tuned. The ultraviolet spectra are as follows.

![UV diagram of different concentrations of NS](image)

Draw a linear chart based on the coordinates of concentration and maximum absorbance. Coordinates are (1×10\(^{-5}\), 0.4112), (50×10\(^{-5}\), 0.4990), (250×10\(^{-5}\), 0.5522), (500×10\(^{-5}\), 0.7482).

![Linear absorption diagram of NS with different concentrations](image)

2.3.2. Analysis of Ultraviolet Spectrum

Ultraviolet spectroscopy is due to the transition of valence electrons in the molecule under the action of incident light. When a sample is irradiated by a continuous light wave in a certain wavelength range, the
photons of a certain wavelength are absorbed, which changes the transmitted light intensity. Thus, an absorption spectrum consisting of absorption lines is produced. The absorption spectrum of the tested compound can be obtained by taking the wavelength as the abscissa and the absorbance as the longitudinal coordinate.

It's can be seen from Fig. 3, the ultraviolet spectra of the naphthalene sulfonic acid formaldehyde condensate show strong absorption at 210 ~ 250 nm. Indicating that there is a K absorption band, possibly containing two double bond conjugated systems. Ultraviolet spectra of naphthalene sulfonic acid formaldehyde condensate have a common absorption peak. Its wavelength is about 227 nm. The absorbance of NS at different concentrations is 0.82, 0.54, 0.49 and 0.42. With the increase of wavelength, the intensity of the peak increases first and then decreases. According to Lambert-Beer law \(A = k \times b \times c\), under the condition of constant absorbance \(A\) and sample concentration \(c\), \(k \times b\) is a fixed value. It shows that the same substance is synthesized \([8,9]\).

Fig. 4 shows that the concentration is linear with the absorbance. With the increase of the concentration, the absorbance of the solution increases. According to the analysis, the main functional groups are C = O, C = C - C = C at about 227 nm absorption peak. These absorption peaks may be characteristic peaks of naphthalene sulfonic acid formaldehyde condensate \([10]\).

3. Conclusion

(1) After analyzing the infrared spectra of naphthalene sulfonate condensates, we can deduce the possible functional groups and other components according to the peak positions of naphthalene sulfonate condensates.

(2) The results show that the ultraviolet spectra of naphthalene sulfonic acid formaldehyde condensate have good reproducibility and stability, it can be used for rapid identification of samples.

(3) By comparing the ultraviolet spectra and infrared spectra of naphthalene sulfonate condensates, we can conclude that the absorption peaks of functional groups of naphthalene sulfonate condensates can be easily determined by both spectra, and the infrared spectra of naphthalene sulfonic acid formaldehyde condensate can obtain more effective information.

(4) Ultraviolet spectra of substances reflect the characteristics of chromophores groups and assistant chromophores groups in molecules rather than the properties of the whole molecule. Therefore, the molecular structure of compounds can't be determined completely from ultraviolet spectra alone. It is necessary to cooperate with infrared spectroscopy, nuclear magnetic resonance, mass spectrometry and other methods in order to reach reliable conclusions.

Reference

[1] Han, J. J. Development and application of β-naphthalene sulfonic acid sodium formaldehyde condensate [J]. Tai hua Science and Technology, 1995(2):29-31.
[2] Che, W.C., Zhao, G.L. Synthesis of naphthalene sulfonate dispersant by raising reaction temperature [J]. Guangdong Chemical Industry, 2006, 33(2): 53-55.
[3] Si, M.Y.J., Ma, M.T. Study on Synthesis and properties of naphthalene sulfonate auxiliaries [D]. Shanghai Normal University, 2015.
[4] Wu, X.R. Structural characterization and condensation process of naphthalene sulfonic acid sodium formaldehyde condensate [D]. Zhejiang University, 2006.
[5] Nan, X.Y., Wen, W.D. Synthesis and Optical Density Analysis of naphthalene sulfonic acid formaldehyde condensate [J]. Dyes and Dyeing, 2005, 42(5): 57-59.
[6] Li, R., Liu, H.Y., Zhang. X.R., et al. Infrared spectrometric determination of nucleosome number of β-naphthalene sulfonic acid formaldehyde condensate [J]. Chemical Minerals and Processing, 2001, 30 (11).
[7] Che, W.C., Zhao, G.L. Endpoint determination of naphthalene sulfonic acid formaldehyde condensate [J]. Guangdong Chemical Industry, 2006, 33(3): 7-9.
[8] He, J. B., Deng, C.Y. Ultraviolet Spectrum Analysis of UNF Water Reducer [J]. Journal of Hefei University of Technology (Natural Science Edition), 1998(2):50-53.
[9] Xu, N., Li, Z.F., Feng, W.H. Synthesis of highly polymerized β-naphthalene sulfonic acid condensate [J]. Progress in Chemical Industry, 2003, 22(4): 395-397.
[10] Tao, C.Y., Yang, C.M., Sun, D.G., et al. Analysis of Free Formaldehyde in β-naphthalene sulfonic acid formaldehyde condensate [J]. Chemical research and application, 2009, 21(3).