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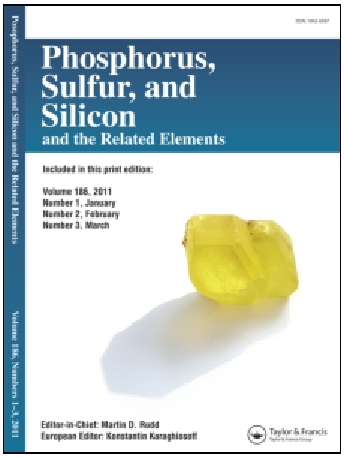

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# Synthesis and Structural Elucidation of Sulfonated Naphthalene-Formaldehyde

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*The synthesis, characterization, structural elucidation, and application of the dispersant obtained from the condensation of β-naphthalene sulfonic acid and formaldehyde are reported. The one-pot synthesis from naphthalene, sulfuric acid, and formaldehyde leads to reproducible polymers with 13 and 14 naphthalene nuclei. The $^1H$ and $^{13}C$ NMR spectra in $D_2O$ (representative spherical shape) and DMSO (representative rod-like shape) are reported. The belching technique led to excellent super pure material.*

**Keywords** Auxiliaries dispersing; belching technique; dispersing agent; β-naphthalene sulfonic acid; polymer with formaldehyde (NSC)

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## INTRODUCTION

During the past few years, commercial applications of water-soluble macromolecules, particularly as dispersing agents and surface modifiers, have been introduced in the textile, pharmaceutical, and other related industries.[1–10] The use of insoluble dyestuffs in textile processes has become a common practice in recent years. Due to the lack of the solubility of such compounds in aqueous systems, dispersing agents often are used to increase the dispersion of such suspensions.

Formaldehyde condensate of β-naphthalene sulfonate first appeared in the industry in 1913 in a patent of BASF.[11] Since then, it has been widely used for different purposes such as effective dispersant for dyes and pigments, as an emulsifier for synthetic rubbers, as leather tanning agents, or pulp rheology on the grindability of coals.[12] A detailed

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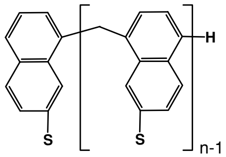

n = number of nuclei
s = sulfonate group

**FIGURE 1** Structure formula proposed for the commercially available formaldehyde condensate with $\beta$-naphthalene sulfonic acid.

investigation on the composition and physicochemical properties of this compound confirmed that it is a polynuclear macromolecule, with properties in aqueous solutions that vary depending on the number of naphthalene nuclei in the molecule. Although these products, which became known as the Tamol types, have been in use for a very long time, their constitution is not yet completely known. The formula in Figure 1 indicates schematically the assumed structure.

## RESULTS AND DISCUSSION

The degree of condensation of the commercial products presumably ranges between 2 and 10 naphthalene nuclei. The quantitative distribution of the condensates, however, varies depending on the condensation during manufacture. However, the yield of conversion for the crude mixture published in the patenting process is less than 75 %. Recently, analysis of sulfonated naphthalene-formaldehyde condensates by ion-pair chromatography and their quantitative determination from aqueous environmental samples were reported.[13] In recent articles, Wolf et al.[13] described the development of an ion-pair solid-phase extraction (IPE) and an ion-pair chromatography (IPC) procedure with fluorescence detection for the quantitative analysis of sulfonated naphthalene-formaldehyde condensates (SNF), which provides full resolution of SNF up to a degree of condensation $n = 5$ and partial resolution up to $n = 15$.[14] In this context, here we present two clear routes for the reproducible synthesis of this auxiliary dispersing agent. The first route involves sulfonation of naphthalene under strong acidic conditions fallowed by the condensation of the resulting product with formaldehyde (Figure 3). A different approach is provided by the reaction of $\beta$-naphthalene sulfonic acid with formaldehyde under weak or neutral conditions. The FT-IR spectra of the product synthesized by us were identical to that of commercial standard NSC, which has been prepared by the patent procedure of BASF.[11] In our hands, the yield

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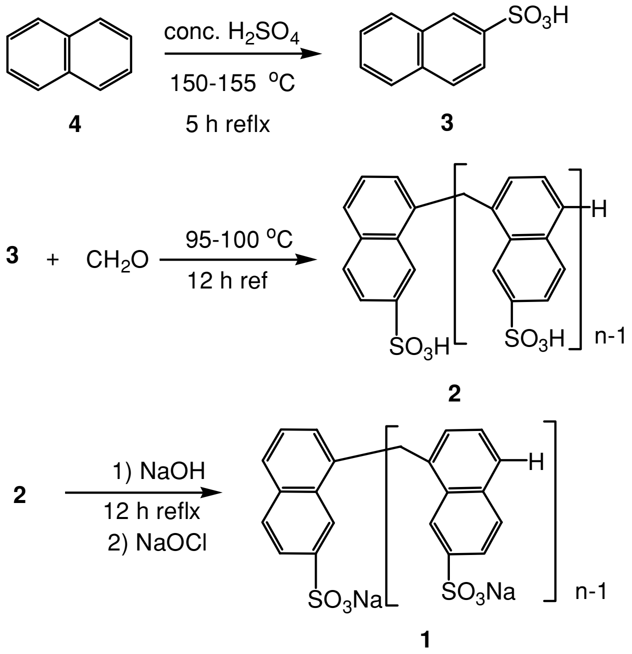

**FIGURE 2** Synthetic sequences for the formation of formaldehyde condensate of $\beta$-naphthalene sulfonate **1**.

of conversion for pure NSC with $n = 13$ has been increased to 93.5 %. Examination of a model of NSC by MM2 calculations indicated the dot surface, shown in Figure 2.

To the best of our knowledge, there is no literature report on the $^1$H and $^{13}$C NMR spectra of NSC. The $^1$H NMR spectra of NSC were recorded in two different solvents: $D_2O$ and DMSO. However, these two spectra are not identical. The solubility of the condensates in water increases sharply as the number of nuclei increases. The $^1$H NMR spectrum obtained in $D_2O$ suggests a spherical shape of the molecules in water. However the $^1$H NMR spectrum of similar condensate in DMSO suggest a random rod-like shape (Figure 3 and Table I). Although formaldehyde condensates of naphthalene sulfonate belong to a relatively old generation of surfactants, they may find new fields of industrial application in the future, e.g., as precipitants for cationic substances, caking agents for basic dyes, anticaking agents for fertilizers that contain ammonium nitrate in the gypsum industry, for manufacturing of fire bricks, for agricultural formulations, and in the ceramic industry.

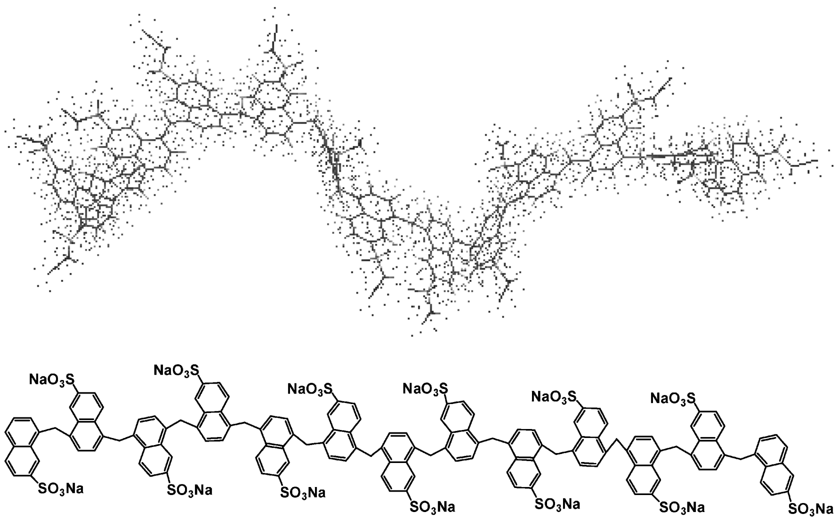

**FIGURE 3** Dot surface MM2 models of synthesized NSF (CS Chem 3D Ultra).

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## EXPERIMENTAL

Products were characterized by comparison of their physical data with those of authentic samples (IR, FT-IR, VPO, DSC, and CHNO elemental analysis). IR spectra were obtained either on a Shimadzu IR-470 or with a FT-IR–Domem instrument. NMR data were recorded in $D_2O$ and DMSOwith a Bruker Avance 500 spectrometer. $^1H$ and $^{13}C$ chemical shifts are reported in ppm ($\delta$)using TMS as internal reference. The UV/VIS and diffuse reflectance spectra (DRS) were recorded either on a Shimadzu UV-2100 instrument equipped with an integrated sphere assembly or with a DuPont-910 instrument. Vapor phase osmometry (VPO) data were obtained with a KNAUER instrument.

### Sulfonation of Naphthalene in Strong Acidic Media and Condensation with Formaldehyde; Preparation of NFC

To a 250 mL three-neck round-bottom flask equipped with a reflux condenser and a dropping funnel was added 42.5 g of naphthalene. The flask was heated to 150–155°C, and from the dropping funnel at this temperature was added dropwise 44 g of concentrated $H_2SO_4$ over a period of 30 min. The reaction mixture was allowed to stay at 150–155°C during addition of $H_2SO_4$. The resulting solution was refluxed at this temperature for 5 h. After this time, the temperature of the reaction mixture was adjusted to 90°C. To the mixture was added 24 mL of

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**TABLE I Physical Properties of Synthesized NSC**

| | |
|---|---|
| V.P.O MW | found 3200 g/mol, for synthesized NSC, calcd. $n = 13$; found 3440 g/mol for NSC, calcd. $n = 14$ |
| Sulfonation degree, % | $n = 13$ found 22.5; $n = 14$ found 27.3 |
| CHN-O | $n = 13$, found N: 0 %, C: 36.43 %, H: 2.77 %<br>$n = 14$, found N: 0 %, C: 39.39 %, H: 3.11 % |
| FT-IR $\text{cm}^{-1}$ | $n = 13$: 3433, 3066, 3003, 2921, 2851, 2345, 1738, 1624, 1501, 1447, 1384, 1352, 1118 (S = O), 1119, 1036, 890, 821, 745, 669, 620, 561, 473<br>NSC $n = 14$: 3435, 3056, 3013, 2912, 2849, 1597, 1504, 1443, 1357, 1488, 1118 (S=O), 1037, 895, 829, 751, 681, 620, 566, 477 |
| DSC | $n = 13$: >325°C [dec.]; $n = 14$: >325°C [dec.] |
| Yield | $n = 13$: 93.5 %; $n = 14$: <75 % |
| $^1$H NMR (500 MHz) | $n = 13$: (DMSO) $\delta = 9.17$ (s, 1H), 8.7 (d, $J = 4.5$ Hz, 2H), 8.48 (s, 7H), 8.27–8.17 (m, 8H), 7.98 (m, 10H), 7.89 (s, 6H), 7.77 (s, 14H), 7.54 (s, 3H), 7.48 (s, 2H), 7.39 (d, $J = 7$ Hz, 3H), 6.96 (d, $J = 2.2$ Hz, 11H), 4.86 (s, 22H)<br>$n = 13$: ($D_2O$) $\delta = 9.35$ (s, 2H), 9.0 (s, 2H), 8.8 (s, 2H) 8.76 (s, 1H), 8.70 (d, $J = 4.5$ Hz, 2H), 8.61 (s, 4H), 8.54 (s, 2H), 8.39 (d, 3H), 8.28 (s, 6H), 8.24 (s, 4H), 8.00 (s, 6H), 8.04 (s, 4H), 7.99 (s, 3H), 7. 84 (s, 6H ), 7.72 (t, $J = 7$ Hz, 4H), 7.53 (t, $J = 7$ Hz, 3H), 7.45 (d, $J = 5$ Hz, 5H), 7.00 (s, 3H), 6.70 (d, $J = 7$ Hz, 5H), 4.71 (s, 22H) |
| $^{13}$C NMR (125 MHz), DMSO | $n = 13$: $\delta = 146.9$, 146.2, 145.6, 145.3, 134.2, 132.8, 131.6, 128.3, 128.0, 126.5, 125.6, 124.8, 122.2, 122.0, 49.3, 50.2 |

$CH_2O$ over a period of 30 min. Then the reaction mixture was refluxed at 95–100°C for an additional 12 h. After this time, the pH of the resulting mixture was adjusted to 8–8.5 diluting with $H_2O$ and with 50% aqueous NaOH solution. To the resulting solution was added 50 mL of commercial sodium hypochlorite (6–14% active chlorine) for belching, and the reaction mixture was allowed to stay at 60°C for 1 h. The solution was then spread on the glass plate and stored in the oven at 90–100°C for 2 h when 94 g of solid was obtained. The product contains 18–20% of $Na_2SO_4$. For the preparation of dispersions with a lower amount of $Na_2SO_4$, it is required that the temperature of solution while stirring is kept below 23°C. At this stage, the amount of $Na_2SO_4$was found 0.5 % at 22°C; 2.4% at 15°C, and 1.6 % at 10°C.

## Utilizing Methanol for Decreasing the Amount of $Na_2SO_4$

A similar procedure as used for NFC was applied, but instead of diluting to 53% concentration of the solid material, 50% concentration of the solid material was diluted with water and then 3% MeOH was added. The solution was cooled, and the precipitated $Na_2SO_4$ was removed. At this stage, the amount of $Na_2SO_4$was found to be 2.5% at 16°C and 2.2% at 10°C. Alternatively, instead of 3 mL MeOH, 5 mL of MeOH was added. Then after cooling and filtration, the filtrate contained 2.2% $Na_2SO_4$ at 10°C.

## Condensation of $\beta$-Naphthalene Sulfonic Acid with Formaldehyde in Weakly Acidic Media

To a 250 mL three-neck round-bottom flask equipped with a reflux condenser and a dropping funnel was added 13.8 g naphthalene sulfonic acid and 37% aqueous solution of formaldehyde (3 mol, 24.3 g) over a period of 68 h at 98–100°C. During reflux, water was continuously added to make certain that the reaction mixture was still homogenous. After this time, the crude reaction mixture was neutralized with an appropriate amount of $CaCO_3$. The viscosity of the reaction mixture was adjusted to 6.1 cpoise (ca. 12% solution). At this stage, the pH of the mixture was adjusted to 6.5 at 75°C by adding 3.5 mL of hot water and neutralizing with sufficient solid CaO. The product was converted to its water soluble calcium salt. The excess of $H_2SO_4$ resulting from the sulfonation reaction was precipitated as $CaSO_4$. At this stage, to remove the $Na_2SO_4$, the reaction mixture was filtrated, and the filtrate was dried to yield a brown powder.

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