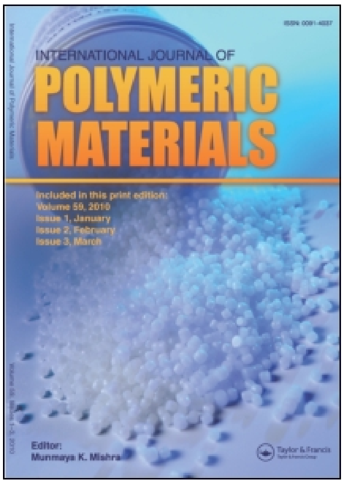

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Synthesis and Structural Elucidation of NSC Auxiliary Dispersing Agents

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The synthesis, characterization, structural elucidation, and application of the dispersant (NSC) obtained from condensation of β-naphthalene sulphonic acid and formaldehyde are described. The one pot process from naphthalene, sulphuric acid, and formaldehyde leads to reproducible condensate products with $n = 13$ *and 14 naphthalene nuclei. The* ^1H *and* ^{13}C *NMR spectra were recorded in* D_2O *(representative spherical shape) and DMSO (representative rod-like shape). Bleaching leads to the recovery of excellent super pure material.*

Keywords: auxiliary dispersing, bleaching, dispersing agent, β-Naphthalene sulphonic acid poly with formaldehyde (NSC)

INTRODUCTION

During the past years, commercial applications of water-soluble macromolecules have been introduced, particularly as dispersing agents and surface modifiers in the textile, pharmaceutical, and other related industries [1–9].

An application of insoluble dyestuffs in textile processes has become a common practice in recent years. Usually, due to the lack of the solubility of these compounds in aqueous systems, dispersing agents are used for increasing the dispersion of such suspensions.

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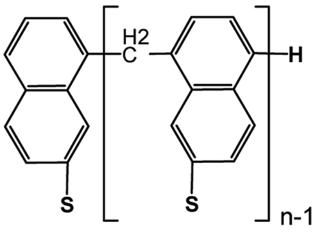
Formaldehyde condensate of β-naphthalene sulphonate first appeared in industry in 1913 by the patent issued for BASF [10]. Since then, it has been widely used in many ways such as effective dispersant for dyes and pigments, as an emulsifier for synthetic rubbers, as leather tanning agent in pulp rheology, and in pulverizing of coals [10]. A detailed investigation on the composition and physicochemical properties of the compound confirmed that it is a polynuclear macromolecule with properties in the aqueous solutions that vary, depending on the number of 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 below in Figure 1 indicates schematically the assumed structure.

The degree of condensation of the commercial products presumably lay at 2 to 10 naphthalene nuclei. The quantitative distribution of the condensates, however, varies depending on the conditions of manufacture. However, published patents indicate a conversion yield for crude mixtures of less than 75%. In the present study the conversion yield for pure NSC with $n = 13$ has been increased to 93.5%. Examination of the MM2 model of NSC indicates the Dot surface (Figure 2).

This article presents a contribution to the synthesis of NSC dispersing agent. At this report, two clear ways to employ for the reproducible synthesis of this auxiliary dispersing agent are described. First, sulfonation of naphthalene in strong acidic condition and then condensation of the resulted products with formaldehyde. A different approach is the reaction of β-naphthalene sulphonic acid with formaldehyde in weak acidic or neutral condition. The FT-IR spectra of the synthesized NSC were identical to that of commertical standard NSC, which had been prepared by the patent issued to BASF.



n = number of nuclei
S = sulphonate group

FIGURE 1 Structure formula proposed for the commercially available formaldehyde condensate of β-naphthalene sulfonic acid.

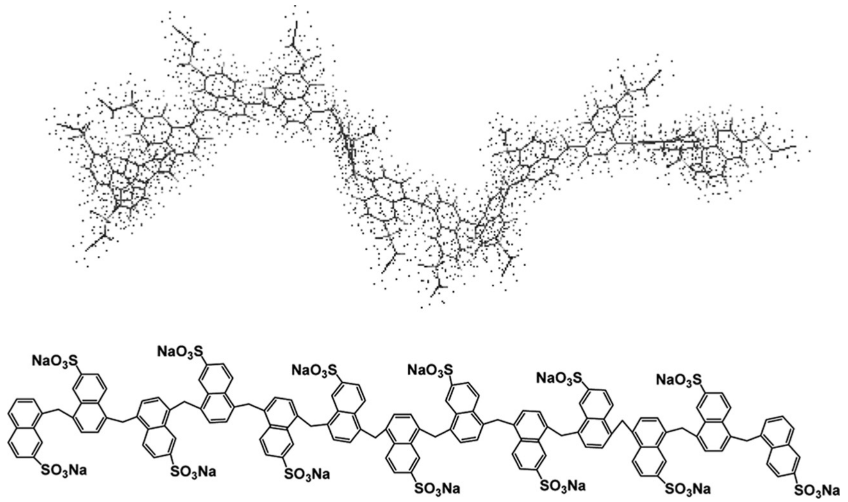


FIGURE 2 Dot surface MM2 model's of synthesized NSC (CS Chem 3D Ultra).

To the best of the authors' knowledge there is not any literature report on the ^{1}H and ^{13}C NMR spectra of NSC. The ^{1}HNMR spectra of NSC were recorded in two different solvent systems, D_2O and DMSO. However, these two spectra are not identical. The solubility of condensates in water increases sharply as the number of nuclei increases. The ^{1}HNMR spectra obtained in D_2O suggests a spherical shape of the molecules in water. However, the ^{1}HNMR of similar condensate in DMSO suggest an extended rod-like shape (Figure 2). Although formaldehyde condensates of naphthalene sulphonate belong to a relatively old generation of surfactants, they may find new field of applications in the future, in a large number of industries as precipitants for cationic substances, caking agents for basic dyes, anti-caking agents for fertilizers that contain ammonium nitrate, gypsum industry, fire brick manufacturing, agricultural formulations, and in the ceramic industry.

EXPERIMENTAL

Products were characterized by comparison with authentic sample (IR, FT-IR, VPO, DSC, and CHNOs). IR spectra were obtained either on a Shimadzu IR-470 or FT-IR–Domem; Canada. NMR data were recorded in D_2O and DMSO Brucker Avance 500-MHz spectrometer. Chemical shifts are reported in ppm (δ) using TMS as internal reference. The UV/Vis and Diffuse Reflectance Spectra (DRS) were recorded either on a Shimadzu UV-2100 equipped with an integrated sphere assembly or DuPont-910 USA model. VPO (Vapour Phase Osmometry) were obtained on a KNAUER, Germany. All the results are tabulated in Table 1.

Sulphonation of Naphthalene in Strong Acidic Media and Condensation with Formaldehyde, Preparation of NSC 1

The procedure is shown schematically in Figure 3. To a 250 mL three-neck round bottom flask equipped with a reflux condenser were added 42.5 g naphthalene. The flask was heated to 150–155° C. To this, from an addition funnel at this temperature, were added dropwise 44 g of concentrated H_2SO_4 over a period of 30 min. The reaction mixture was kept at 150–155°C during the addition of H_2SO_4. The resulting solution was refluxed at this temperature for 5 h. Then, the temperature of the reaction mixture was adjusted to 90°C, and 24 mL CH_2O were added over a period of 30 min. Then the mixtere was refluxed at 95–100°C for an additional 12 h. After this time, the pH of the

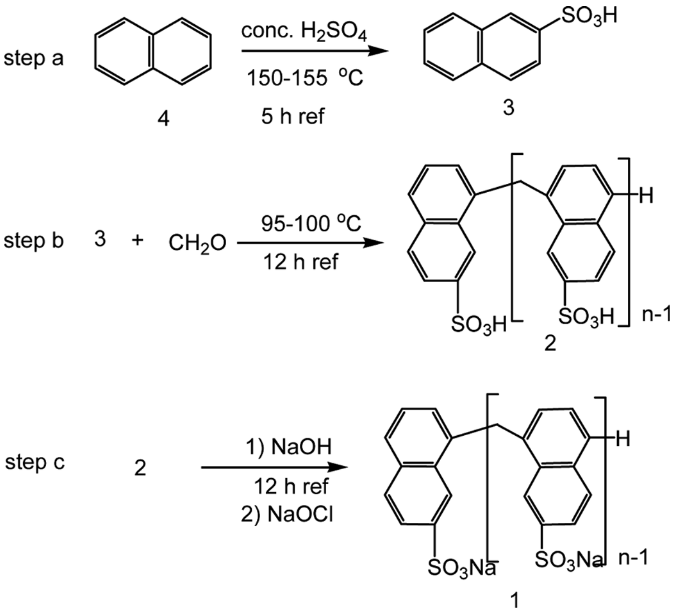


FIGURE 3 Synthetic sequence for formaldehyde condensate of β-naphthalene sulphonate 1 (NSC).

TABLE 1 Physical Properties and Chemical Structure of Synthesized NSC

Item	Synthesized NSC
V.P.O	found 3200 g/mole, for synthesized NSC, calcd. $n = 13$; found 3440 g/mole for NSC, calcd.
MW	$n = 14$
Sulphonation degree, %	$n = 13$ found 22.5; for NSC, $n = 14$ found 27.3
CHN-O	NSC synthesized $n = 13$, found % N = 0, % C = 36.43, % H = 2.77; NSC, $n = 14$, found % N = 0, % C = 39.39, % H = 3.11
FT-IR cm^{-1}	NSC synthesized $n = 13$: 3433.33, 3066.45, 3003.2, 2921.17, 2851.5, 2345.52, 1738.25, 1624.5, 1501.93, 1447.46, 1384.21, 1352.59, 1118.05 S = O, 1119.00, 1036.69, 890.835, 821.16, 745.31, 669.47, 620.96, 561.99, 473.304 FT-IR NSC $n = 14$: 3435.5, 3056.12, 3013.32, 2912.32, 2849.32, 1597.74, 1504.97, 1443.79, 1357.58, 1488.58, 1118.18 S = O, 1037.71, 895.55, 829.14, 751.56, 681.19, 620.26, 566.74, 477.11
DSC	NSC synthesized $n = 13$, decompose > 325°C; SNC $n = 14 > 325$°C
Yield %	NSC synthesized $n = 13$, %93.5 SNC standard $n = 14$, $<$ %75
^{1}HNMR (500 MHz), δ	NSC synthesized $n = 13$: (DMSO) 9.17 s (1H), 8.7 d (2H, J = 7 Hz), 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 (3H, J = 7 Hz), 6.96 d (11H, J = 2.2 Hz), 4.86 s (22H) NSC synthesized $n = 13$: (D_2O): 9.35 (s, 2H), 9 (s, 2H), 8.8 (s, 2H) 8.76 (s, 1H), 8.70 (d, 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, 4H), 7.53 (t, 3H), 7.45 (d, 5H), 7.00 (s, 3H), 6.70 (d, 5H), 4.71(s, 22H).
^{13}CNMR (125 MHz), DMSO, δ	NSC synthesized $n = 13$: 146.9, 146.2, 145.6, 145.3, 134.2, 132.8, 131.6, 128.3, 128, 126.5, 125.6, 124.8,122.2, 122, 49.3 50,2.

resulting mixture was adjusted to pH of 8–8.5 and diluted with H_2O and 50% NaOH solution (diluted to 53% concentration of solid material). To the resulting solution was added 50 mL of commercial sodium hypochlorite (NaOCl) for Bleaching and allowed to stay at 60°C for 1 h. The solution was then spread on a glass plate and stored in the oven at 90–100°C for 2 h until 94 g of solid, were obtained. The product contains 18–20% of Na_2SO_4. For preparing of dispersions with less amount of Na_2SO_4, the temperature of solution while stirring the mixture was kept below 23°C before drying. At this stage the amount of Na_2SO_4 was found to be 0.5% at 22°C; 2.4% at 15°C and 1.6% at 10°C.

Utilizing MeOH for Decreasing the Amount of Na_2SO_4

A similar procedure as used for NSC **1** was applied, but instead of diluting to 53% concentration of solid material, 50% concentration of 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. If as an alternative, instead of 3 mL MeOH 5 mL MeOH added then after cooling and filtration, the filtrate contained 2.2% Na_2SO_4 at 10°C.

Condensation Reaction of β-naphthalene Sulphonic Acid with Formaldehyde in Neutral or weak Acidic Media

To a 250 mL three-neck round bottom flask equipped with a reflux condenser were added 13.8 g naphthalene sulphonic acid and (3 mol, 24.3 g aqueous 37% solution of formaldehyde) over a period of 68 h at 98–100°C. During the process of refluxing, a continuous addition of water made certain the reaction mixture was still homogenous. After this time the crude reaction mixture was neutralized with appropriate amount of $CaCO_3$. The viscosity of the reaction mixture was adjusted to the 6.1 cpoise (ca.12% solution). At this stage the pH of the mixture was adjusted to pH of 6.5 at 75°C by adding 3.5 mL hot water and neutralizing with sufficient solid lime (CaO). The condensate product was converted to its water soluble calcium salts. The excess H_2SO_4 resulting from the sulphonation reaction was precipitated as the corresponding $CaSO_4$. At this stage, for removing the Na_2SO_4 the reaction mixture was filtered and dried to leave a brown color powder.

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