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Structure of a Nekal-type Surfactant A—Commercial Twitchell Reagent “Idrapidsalter”—*₁

Shunroku KANNO*, Akira SUZUKI**, Hajime BABA*, and Yasuo HANZAWA*

* Department of Applied Chemistry, Faculty of Engineering, Yamagata University
(3-16, Jōnan 4-chōme, Yonezawa-shi, Yamagata-ken)

** Present address: Takemoto Oil & Fat Co., Ltd.
(2-5, Minato-machi, Gamagōri-shi, Aichi-ken)

The structure of a Nekal-type surfactant, which was prepared by sulfonation in the β -position of naphthalene followed by alkylation with isopropyl alcohol, was determined on the basis of an analysis on an NMR spectrum of its sulfonamide derivative. The pattern of the NMR spectrum observed in the lower magnetic field than 7 ppm (δ) showed characteristic substitutions of the alkyl and sulfonic acid groups on the naphthalene nucleus. From these results, this sulfonic acid was identified as 1,4-diisopropyl-6-naphthalene sulfonic acid.

From reasons based on their synthetic procedures, the Nekal-type commercial surfactants have been usually considered as mixtures of various homologues and/or isomers of alkyl-naphthalene-sulfonate¹⁾, and works on determining structures of these compounds were, with a few exception²⁾, scarcely found within the limits of the authors' investigation. Marimon *et al.*³⁾ recently reported, on the basis of their chromatographical behavior, that technical samples of sodium propyl-naphthalene-sulfonate were composed of several components with different degree of sulfonation and alkylation.

Previously, Kanno⁴⁾ reported from the results of instrumental and elemental analyses on the potassium salt of the main component of “Idrapidsalter”^{*2}, a commercial Twitchell reagent, that this was identified as potassium diisopropyl-naphthalenemonosulfonate, and also that IR, UV, and NMR spectra, and X-ray diffraction pattern of this compound agreed with the corresponding properties of potassium diisopropyl-naphthalene- β -monosulfonate prepared by the procedure described by Lederer⁵⁾.

With regard to the structure of the compound synthesized in such a way, Meyer *et al.*²⁾ estimated

that the main component of this product was identified as sodium 1,6-diisopropyl-naphthalene 3(or 7)-sulfonate from the results of investigations on its several derivatives.

In the present paper, the authors confirmed that the structure of the fore-going diisopropyl naphthalene- β -mono sulfonic acid was represented as 1,4-diisopropyl-naphthalene-6-sulfonic acid, on the basis of the NMR spectrum of the sulfonamide derivative.

1 Experimental

1.1 Measurements

The mp was uncorrected. The IR spectrum was recorded on a Hitachi EPI-S2 spectrometer (NaCl prism). The NMR spectrum was determined at 90 MHz with a Hitachi R-22 High Resolution NMR spectrometer in deuterochloroform solution using tetramethylsilane as an internal standard. Their chemical shifts were presented in terms of δ -values: s, singlet; d, doublet; d-d, double doublet; sept, septet.

1.2 Preparation of Potassium Diisopropyl naphthalene- β -mono sulfonate

Diisopropyl-naphthalene- β -monosulfonic acid was prepared in accordance with the Lederer's procedure⁵⁾.

Naphthalene (192 g, 1.5 mol) was sulfonated in the β -position, in the usual way, with concn-

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trated sulfuric acid (192 g, 2 mol) at 170~180°C. After the sulfonation was over, the reaction mixture was diluted with concentrated sulfuric acid (150 g), and then a cooled mixture of isopropyl alcohol (189 g, 3.15 mol) and concentrated sulfuric acid (300 g) was added drop by drop into the sulfonated mixture at 120~130°C under refluxing and vigorous stirring. Alkylation was continued for 2 h, then the reaction mixture was settled. After a separated sulfuric acid layer was removed, the reaction product was dissolved in diethyl ether, and then the ether solution was washed several times with 6 N sulfuric acid. The sulfonic acid dissolved in the ether solution was extracted with water, and subsequently neutralized with 25% potassium hydroxide aqueous solution. Potassium diisopropyl naphthalene- β -monosulfonate, colorless scales, was crystallized out from the aqueous solution, filtered off, and then recrystallized three times from water. Yield 59 g (13% based on naphthalene, 30.7% for the crude potassium salt).

1.3 Preparation of Diisopropyl naphthalene- β -mono sulfonic Acid

An aqueous solution of barium chloride (7.4 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}/100\text{ ml H}_2\text{O}$) was poured into a hot solution of the potassium salt (2.0 g/1000 ml H_2O) under vigorous stirring. After the reaction mixture was cooled to room temperature, the precipitated barium sulfonate was filtered off, recrystallized twice from water, and then dried under reduced pressure. Yield 77%, colorless needles.

The powdered barium sulfonate (14 g) was added to 1 N sulfuric acid (70 ml), and the mixture was stirred for 1 h at 60°C, and then produced barium sulfate was filtered off. The filtrate was made up to ca. 12 N, on sulfuric acid, with concentrated sulfuric acid, and then the produced sulfonic acid was extracted with diethyl ether. After the ether was distilled off, recovered colorless crystals were recrystallized twice from a benzene-petroleum ether (bp 40~60°C) mixture (1:1, vol/vol). Yield 50%, colorless plate, mp 101~102°C (no lit.).

1.4 Preparation of Diisopropyl naphthalene- β -monosulfonamide

The diisopropyl naphthalene- β -monosulfonic acid (2g) was heated at 95~98°C with phosphorpen-ta-chloride (4 g) on a water-bath. The reaction product was poured into water, then extracted

with diethyl ether. The diisopropyl naphthalene- β -monosulfonyl chloride, recovered from the ether solution, was converted to the sulfonamide by heating with ammonium carbonate (2 g). The produced sulfonamide was extracted with benzene, and then recrystallized from a benzene-*n*-hexane mixture (1:1, vol/vol). Yield 72%, colorless needles, mp 181.0~181.5°C (lit. 179~180°C²³). Found: C, 65.08%; H, 7.63%; N, 4.78%; mol. wt. (Rast), 296. Calcd. for $\text{C}_{18}\text{H}_{21}\text{O}_2\text{NS}$: C, 65.95%; H, 7.21%; N, 4.81%; mol. wt. 291. IR spectrum (KBr disc): $\nu_{\text{N-H}}$ 3342 and 3259 cm^{-1} , $\nu_{\text{S=O}}$ 1300 and 1172 cm^{-1} . NMR (δ , in CDCl_3): 1.40 ppm (isopropyl CH_3 , 12 H, d, $J=7.0\text{ Hz}$), 3.76 ppm (isopropyl CH, 2 H, sept, $J=7.0\text{ Hz}$), 5.15 ppm (NH_2 , 2 H, s), 7.50 ppm (arom H, 2 H, s), 7.90 ppm (arom H, 1 H, d-d, $J=9.3$ and 2.0 Hz), 8.25 ppm (arom H, 1 H, d, $J=9.3\text{ Hz}$), and 8.78 ppm (arom H, 1 H, d, $J=2.0\text{ Hz}$).

2 Result and Discussion

As melting ranges of the diisopropyl naphthalene- β -monosulfonic acid, reproduced by way of the barium salt, and its sulfonamide were considerably narrow (101~102 and 181.0~181.5°C, respectively), the well-known fact, that the Nekal-type surfactants may be mixtures of several homologues and/or isomers, should be doubtful. This study was undertaken to determine the chemical structure of the fore-going diisopropyl naphthalene- β -monosulfonic acid by means of analyzing the NMR spectrum of the sulfonamide derivative.

The NMR spectrum (Fig.-1) shows the presence of isopropyl methyl (doublet ($J=7.0\text{ Hz}$) at 1.35 and 1.42 ppm, 12 H), isopropyl methine (septet ($J=7.0\text{ Hz}$) at 3.5~4.0 ppm, 2 H), amino group in the sulfonamide group (comparatively broad singlet at 5.15 ppm, 2 H), and

Fig.-1 The 90 MHz NMR spectrum of the diisopropyl naphthalene- β -monosulfonamide, with sweep width 800 Hz and sweep time 200 s (in CDCl_3).

five ring-protons of naphthalene (lower magnetic field than 7 ppm).

Although, Meyer *et al.*²⁾ had offered such a structure as previously described on the sodium salt of this sulfonic acid, the pattern of the NMR spectrum presented in this paper was quite different than that expected from the structure proposed by them.

As it is anticipated that the singlet peak at 7.50 ppm is attributable to the presence of two structurally equivalent ring-protons, these protons should be attached to equivalent positions on the nucleus without the sulfonyl group. In this instance, it is reasonable to consider that each of the two isopropyl groups, introduced into the naphthalene nucleus following to the sulfonation, has to be substituted in the both α -positions of the same nucleus, as is described in the Bordwell's work⁶⁾, because it seems, usually, to be difficult to substitute these groups in mutually adjacent β -positions of the nucleus, on the basis of their own steric effect.

From the results of these considerations and the following analyses on the NMR spectrum, this compound was reasonably identified as 1,4-diisopropyl-naphthalene-6-sulfonamide; that is,

(1) The structurally equivalent protons in the 2- and 3-positions were found as a singlet, corresponding to two protons, at 7.50 ppm as described above. This peak was observed at the highest magnetic field in the ring-proton region, because these protons were in the β -positions of the naphthalene nucleus, and, moreover, were adjacent to the electron-releasing isopropyl groups⁷⁾.

(2) The doublet ($J=2.0$ Hz) at 8.78 ppm were able to be assigned to the proton in the 5-position, coupled with the *meta*-proton (7-position), because these peaks appeared in the

lowest magnetic field in this spectrum, as the result that the proton in this position joined at the α -position of the nucleus, and, furthermore, was adjacent to the strongly electron-withdrawing sulfonyl group⁷⁾.

(3) Peaks owing to the proton in the 7-position were found at 7.90 ppm as double-doublet ($J=9.3$ and 2.0 Hz, respectively) ascribed to couplings with the both *ortho*- and *meta*-protons (8- and 5-positions, respectively).

(4) The doublet ($J=9.3$ Hz) at 8.25 ppm were assigned to the proton in the 8-position coupled with the *ortho*-proton (7-position).

Consequently, it was recognized that the main component of the Nekal-type surfactant, prepared by means of the procedure described above, was identified as 1,4-diisopropyl-naphthalene-6-sulfonic acid and/or its salts.

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