

## <sup>33</sup>S NMR SPECTRA OF SOME SULFONATED NAPHTHALENES, NAPHTHOLS, AND THEIR ANIONS

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The <sup>33</sup>S NMR spectra of 11 naphthalenesulfonates, 11 hydroxynaphthalenesulfonates, two dihydroxynaphthalenesulfonates, and their anions have been measured in aqueous solutions. The <sup>33</sup>S NMR chemical shifts of these compounds exhibit upfield shifts when related to ammonium sulfate as the standard. Introduction of a further sulfonic group causes a small upfield shift (up to 3 ppm). Introduction of a hydroxyl group causes a downfield shift (up to 5 ppm) unless the ring is further substituted. Formation of the anion from hydroxyl group causes an additional downfield shift (up to 6 ppm). The half-width of <sup>33</sup>S NMR signals of sulfonated naphthalenes, naphthols, and their anions vary from 10 to 400 Hz.

In spite of being a biogenic element and being contained in many organic compounds, sulfur has not yet been studied systematically by NMR spectroscopy. The reason lies in relative inaccessibility of <sup>33</sup>S NMR spectra, the relative sensitivity being  $17 \cdot 10^{-6}$  as compared with the proton. The natural abundance of the <sup>33</sup>S isotope is 0.74%. The greatest difficulties in the measurement of <sup>33</sup>S NMR spectra are due to the nuclear quadrupole moment and the therewith connected large half-widths of signals. Both the theoretical and practical aspects of measurement of <sup>33</sup>S NMR spectra were described in a recent review by Hinton<sup>1</sup>. Most available data from the region of <sup>33</sup>S NMR spectroscopy (e.g. refs<sup>2-6</sup>) are restricted to measurements of small molecules or compounds giving narrow <sup>33</sup>S NMR signals. 1- and 2-naphthalenesulfonates were reported<sup>7</sup> to be resolvable by the  $\delta(^{33}\text{S})$  chemical shifts. The aim of the present communication was to measure the <sup>33</sup>S NMR spectra of aqueous solutions of naphthalenesulfonates and hydroxynaphthalenesulfonates and to decide whether or not the data obtained can be used for determination of position(s) of one or several sulfonic groups in the naphthalene ring in the same way as the <sup>13</sup>C SCS (substituent chemical shift) of sulfonic groups in naphthalenesulfonates<sup>8</sup> or hydroxynaphthalenesulfonates<sup>9</sup> are used.

### EXPERIMENTAL

The substances studied were usual commercial products or compounds prepared by known methods<sup>10</sup>. The <sup>33</sup>S NMR spectra were measured with an AM-400 (Bruker) apparatus at

30.714 MHz. The parameters of measurements were: 90° pulse (30  $\mu\text{s}$ ), spectral width 3 000 Hz, 2K data points zero filled to 8K, exponential broadening 10–100 Hz. The substances were measured as saturated solutions in water (20%  $\text{D}_2\text{O}$ ) to stabilize the field of spectrometer. An aqueous 4M solution of ammonium sulfate placed in a coaxial capillary was used as the standard. Negative values of  $^{33}\text{S}$  NMR chemical shifts denote upfield shifts. The anions of hydroxy-naphthalenesulfonates were measured with the same samples after adjusting pH 12 by addition of a weighed amount of sodium hydroxide. The temperature of sample was determined with a thermocouple as the temperature of the gas flowing through the NMR probe.

## RESULTS AND DISCUSSION

Naphthalenesulfonic acids are strong acids completely dissociated in water, therefore their readily accessible sodium salts were used for the measurements. As the effect of concentration on the  $\delta(^{33}\text{S})$  chemical shift is negligible with e.g. sulfolane<sup>6</sup>, inorganic sulfates<sup>11</sup> as well as alkylsulfonates<sup>7</sup>, the  $^{33}\text{S}$  NMR spectra of all the substances examined were measured in saturated solutions. The  $^{33}\text{S}$  NMR chemical shifts and half-widths of signals are given in Table I. From this table it can be seen that the alpha and beta positions of the sulfonic group in naphthalene nucleus can be differentiated. Introduction of an additional sulfonic group into both the substituted and non-substituted rings causes a slight upfield shift of the  $^{33}\text{S}$  signal (see

TABLE I

The  $^{33}\text{S}$  NMR chemical shifts and half-widths of NMR signals of sulfonated naphthalenes in water (20%  $\text{D}_2\text{O}$ ) at 298 K. The values of signal half-widths are given with the accuracy of  $\pm 10\%$

Position of sulfonic group	$\delta(^{33}\text{S})$	$w_{1/2}$ , Hz
1	–15.3	16
2	–11.5	13
1,4	–18.5	48
1,5	–16.0	32
1,7	–12.0(7)	20
	–15.9(1)	24
2,6	–12.8	26
2,7	–12.5	35
1-Nitro-4,8	–15.8 <sup>a</sup>	360
2-Nitro-4,8	–18.5 <sup>a</sup>	240
1,3,7	–12.7	60
	–14.0 <sup>a</sup>	220
1,3,5	–14.1 – –16.9 <sup>b</sup>	215

<sup>a</sup> A common signal; <sup>b</sup> a broad signal with a plateau.

TABLE II

The  $^{33}\text{S}$  NMR substituent chemical shift (SCS) of sulfonic group of naphthalene-X-sulfonates due to introduction of additional sulfonic group into the position Y

Y	$^{33}\text{S}$ SCS	
	X = 1	X = 2
4	-3.2	—
5	-0.7	—
6	—	-1.3
7	-0.6	-1.0
8	—	-0.5

TABLE III

The  $^{33}\text{S}$  NMR chemical shifts and half-widths of signals of 1-hydroxynaphthalene-X-sulfonates in water (20%  $\text{D}_2\text{O}$ ) at 298 K. The  $w_{1/2}$  values are given with the accuracy of  $\pm 10\%$ . The values in parentheses correspond to the anions of the substances measured at pH 12

X	$\delta$	$w_{1/2}$ , Hz
2	-9.3 <sup>a</sup>	32 <sup>a</sup>
4	-13.5 (-11.4)	65 380)
5	-14.0 (-12.7)	34 (33)
8	-10.4 (-8.2)	30 (115)
3,6	-11.1 (-11.4)	200 (200)
3,8	-13.1(3) -11.9(8) (-9.3) <sup>b</sup>	42 100 (250)
4,8	-14.2(4) -11.9(8) (-8.9) (-6.2) (-8.3) <sup>a,b</sup>	25 150 (170) (400) (35) <sup>a</sup>

<sup>a</sup> Measured at 340 K; <sup>b</sup> a common signal.

TABLE IV

The <sup>33</sup>S NMR chemical shifts and half-widths of signals of 2-hydroxynaphthalene-X-sulfonates in water (20% D<sub>2</sub>O) at 298 K. The  $w_{1/2}$  values are given with the accuracy of  $\pm 10\%$ . The values in parentheses correspond to the anions of the substances measured at pH 12

X	$\delta$	$w_{1/2}$ , Hz
1	-10.6	280
6	-11.5 <sup>a</sup>	7 <sup>a</sup>
	(-10.0) <sup>a</sup>	(36) <sup>a</sup>
7	-10.4	120
	(-8.0)	<i>b</i>
6,8	-12.7(6)	26
	-16.5(8)	40
	-13.2 <sup>c</sup>	19 <sup>c</sup>
	-16.7 <sup>c</sup>	40 <sup>c</sup>
	-13.4 <sup>a</sup>	19 <sup>a</sup>
	-16.9 <sup>a</sup>	29 <sup>a</sup>
	(-11.7) <sup>a</sup>	(6) <sup>a</sup>
	(-15.3) <sup>a</sup>	(11) <sup>a</sup>

<sup>a</sup> Measured at 360 K; <sup>b</sup> a very broad signal; <sup>c</sup> measured at 330 K.

TABLE V

The <sup>33</sup>S NMR substituent chemical shifts (SCS) of sulfonic group of naphthalene-X-sulfonates due to introduction of a hydroxyl group into the position Y

Y	<sup>33</sup> S SCS	
	X = 1	X = 2
1	—	2.2
2	4.7	—
3	—	5.0 <sup>a</sup>
4	1.8	-0.9 <sup>a</sup>
5	1.3	0.4
6	—	-1.2 <sup>b</sup>
7	-1.2 <sup>b</sup>	1.1
8	4.9	—

<sup>a</sup> Calculated from the shifts of dihydroxynaphthalenedisulfonates (Table VI) and 2,7-naphthalenedisulfonate; <sup>b</sup> calculated from the shifts of 2-hydroxynaphthalene-6,8-disulfonate and corresponding naphthalenesulfonate.

Table II). The substituent chemical shift was calculated according to Eq. (1) where NS and NDS stand for naphthalenesulfonate and -disulfonate, respectively.

$$\text{SCS} = \delta(^{33}\text{S})\text{NDS} - \delta(^{33}\text{S})\text{NS} \quad (1)$$

The effect of nitro groups cannot easily be quantified due to the signal half-width and decreasing accuracy in reading the chemical shift. For 1,7-naphthalenedisulfonate we obtained a  $^{33}\text{S}$  NMR spectrum with well-resolved signals of sulfonic groups. Their assignment is based on the analogy with the naphthalenemonosulfonates. In the case of naphthalene trisulfo derivatives the signals of individual sulfonic groups are not separated. Tables III and IV present the  $^{33}\text{S}$  NMR chemical shifts of 1-(and 2)-hydroxynaphthalene-X-sulfonates, respectively. 1-Hydroxynaphthalene-2-sulfonate and 2-hydroxynaphthalene-6-sulfonate are very little soluble in water at room temperature, hence they were measured at 340 and 360 K. The spectra of hydroxynaphthalenedisulfonates show two well-resolved  $^{33}\text{S}$  NMR signals whose assignment was based on the analogy with hydroxynaphthalenesulfonates. Introduction of a hydroxyl group into the molecule of naphthalenesulfonate causes a downfield shift in the  $\delta(^{33}\text{S})$  of sulfonic group. The results are summarized in Table V. The substituent chemical shifts (SCS) which express the upfield shift were calculated with application of the chemical shifts  $\delta(^{33}\text{S})$  of polysubstituted naphthalenes, which could affect the values. The other SCS from Table VI were calculated according to Eq. (2) where NS and NOS stand for naphthalenesulfonate and hydroxynaphthalenesulfonate, respectively.

$$\text{SCS} = \delta(^{33}\text{S})\text{NOS} - \delta(^{33}\text{S})\text{NS} \quad (2)$$

Transformation of hydroxyl group in hydroxynaphthalenesulfonates into the cor-

TABLE VI

The  $^{33}\text{S}$  NMR chemical shifts and half-widths of signals of sulfonated naphthalenediols in water (20%  $\text{D}_2\text{O}$ ) at 298 K. The  $w_{1/2}$  values are given with the accuracy of  $\pm 10\%$ . The values in parentheses correspond to the anions of the substances measured at pH 12

Compound	$\delta$	$w_{1/2}$ , Hz
3,6-Disulfo-1,8-naphthalenediol	-12.4 (-10.5)	65 (90)
3,6-Disulfo-2,7-naphthalenediol	-16.5 (-14.3)	95 (320)

responding anion causes a downfield shift in the  $^{33}\text{S}$  NMR shifts of sulfo groups by as much as 5.7 ppm (see Table III and IV).

As sulfonates are completely ionized in aqueous solutions, tetrahedral symmetry appears at the sulfur atom, which decreases the interaction of quadrupole moment and, hence, the half-widths of  $^{33}\text{S}$  NMR signals of sulfonated naphthalenes and naphthols are relatively narrow varying within tens to hundreds of Hz (see Tables I, III, and IV). Introduction of a nitro group into the naphthalene ring of 1,4-naphthalenedisulfonate increases the half-width of  $^{33}\text{S}$  NMR signal almost ten times. The transition from hydroxynaphthalenesulfonate to naphtholate is accompanied by a 3- to 6-fold broadening of the  $^{33}\text{S}$  NMR signal half-width. This, however, can be caused by the viscosity increase after addition of alkali. It is known that viscosity distinctly affects the half-widths of  $^{33}\text{S}$  NMR signals<sup>11</sup>. On the other hand, when measured at enhanced temperatures (when the viscosity is lowered) the  $^{33}\text{S}$  NMR signal of the trianion of 2-hydroxynaphthalene-6,8-disulfonic acid becomes more narrow as compared with that of 2-hydroxynaphthalene-6,8-disulfonate. The effects of anion formation and viscosity increase are antagonistic with regard to their action on the  $^{33}\text{S}$  NMR signal half-widths, the viscosity effect being predominant, which results in shortening of the relaxation times of sulfur and, hence, broadening of the  $^{33}\text{S}$  NMR lines.

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