MONOSULFONATION of

R. Norris Shreve and John H. Lux[1]
PURDUE UNIVERSITY, LAFAYETTE, IND.

► ► ► **The sulfonation of 2-methylnaphthalene with a small excess of sulfuric acid has been studied, and the positions of the entering sulfonic acid groups were found to be mainly the 8 position at 40° C., the 6 position at 90–95° C., and the 7 position at 160° C. Many derivatives of the sulfonic acids were made and their possible uses**

THE purpose of this investigation was to discover and develop possible uses for 2-methylnaphthalene through sulfonation and further reaction products. 2-Methylnaphthalene is a product of coal tar distillation and has recently became more available at higher purity as a result of improvements in the tar separation processes. 2-Methylnaphthalene occurs in coal tar to the extent of 1.5 per cent (*10*) and in petroleum fractions of about the kerosene range to the extent of 1.5–2.0 per cent (*5*).

Wendt (*12*) first sulfonated 2-methylnaphthalene in 1892 and reported that sulfonation occurred even at room temperatures; however, he was unable to identify any products. Years later in 1925 Dziewoński, Schoewóna, and Waldmann (*1*) sulfonated 2-methylnaphthalene at 90° to 100° C.; they obtained 2-methylnaphthalene-6-sulfonic acid in good yields and identified it by conversion to 2-methyl-6-naphthol. Dziewoński and Wulffsohn (*2*) in 1929 sulfonated 2-methylnaphthalene with chlorosulfonic acid in nitrobenzene at 30° to 40° C. and obtained 2-methylnaphthalene-8-sulfonic acid, but reported no other isomer. Later Vesely and Pac (*8*) sulfonated with chlorosulfonic acid in carbon tetrachloride at −5° C. and reported a 25 per cent yield of 2-methylnaphthalene-8-sulfonic acid and a 7 per cent yield of 2-methylnaphthalene-1-sulfonic acid. Vesely and Strusa (*9*) also prepared another derivative of 2-methylnaphthalene by treating Tetralin with bromine, magnesium, and dimethyl sulfate which gave a mixture of 5- and 6-methyl-Tetralin. Sulfonation of the latter gave 6-methyl-Tetralin-7-sulfonic acid which was converted to the corresponding tetrahydronaphthalene derivatives.

Plan of the Investigation

The raw material for the sulfonation was white, solid 2-methylnaphthalene (melting point 32.5° C.) of about 98.5 per cent purity which is now available commercially. This compound was sulfonated in four different ways. Sulfonation at 40° C. gave mainly 2-methylnaphthalene-8-sulfonic acid; at 90–95° C., 2-methylnaphthalene-6-sulfonic acid; and at 160° C., 2-methylnaphthalene-7-sulfonic acid. As it was desired to make derivatives containing functional groups on the same ring as the methyl group, the opposite ring was hydrogenated. The ring without the methyl group was no longer aromatic, and any sulfonation that took place was on the ring containing the methyl group to give 6-methyl-Tetralin-7-sulfonic acid.

The sulfonation products were isolated by precipitation of the barium salts. The use of calcium salts was tried, but they could not be obtained in so good a crystal form as the barium salts. Also, the advantage of the greater solubility of the calcium salts was outweighed by the difficulties of handling their slimy condition.

Three methods for the production of sodium salts from barium salts were tried. The first, by means of the reaction

$$Ba(SO_3CH_3C_{10}H_6)_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaSO_3CH_3C_{10}H_6$$

was chosen because nearly quantitative yields of the sodium salts were obtained. Later it was found that yields from the reaction

$$Ba(SO_3CH_3C_{10}H_6)_2 + Na_2CO_3 \longrightarrow BaCO_3 + 2NaSO_3CH_3C_{10}H_6$$

were also almost quantitative, and since sodium carbonate is less expensive its use was more desirable. The use of the barium salts necessitates the handling of large volumes of solutions. Much time and heat are also required for the concentration and crystallization of these solutions. With these in mind and to achieve economy, the reaction

$$CH_3C_{10}H_6SO_3H + NaCl \longrightarrow HCl + CH_3C_{10}H_6SO_3Na$$

was investigated for each of the four sulfonic acids reported. The reaction proved valuable for the preparation of the ordinary sodium salts but did not seem applicable to the making of sodium 6-methyl-1,2,3,4-tetrahydronaphthalene-7-sulfonate because of its much greater solubility. Another case where it was not advisable to prepare the sodium salts direct was that of the sulfonic acid made at low temperatures—namely, sodium 2-methylnaphthalene-8-sulfonate. Here it was found that the other isomer formed in the reaction could not be separated by recrystallization of the sodium salts. If the presence of another isomer is not a great disadvantage—i. e., for wetting agents—the direct method may be used even for the sodium salt of the 8-sulfonic acid.

The apparatus for the sulfonations consisted of a 500-ml. three-neck flask equipped with a mercury-seal motor-driven stirrer, 360° C. thermometer, and dropping funnel.

Barium 2-Methylnaphthalene-8-sulfonate

To 0.5 mole (71 grams) of 2-methylnaphthalene were added dropwise 71 grams of concentrated (93 per cent) sulfuric acid with stirring. The reaction was allowed to proceed for 8 hours, the temperature being maintained at 40° C. by a water bath. At the end of that time the reaction mixture was

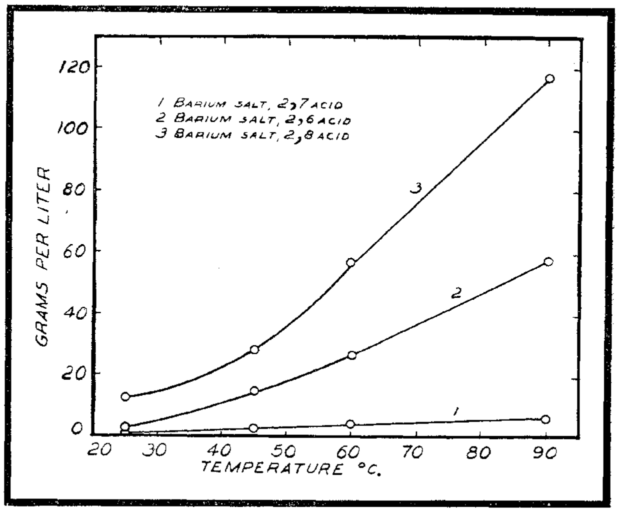

Figure 1. Variation in Solubility of Barium Salts with Temperature

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[1] Present address, Carbide Carbon Chemicals Corporation, South Charleston, W. Va.

2-METHYLNAPHTHALENE

studied, since 2-methylnaphthalene is now available commercially.

The most promising of these derivatives appear to be the sodium salts which have good wetting properties and are easily made. It was found that the derivatives could be made in existing industrial equipment with little difficulty.

diluted to a volume of about 0.5 liter by pouring it into cold water. On standing, the unsulfonated 2-methylnaphthalene collected in a cake on top of the solution and was easily removed. There remained in suspension in the solution a small amount of sulfone which was formed during the reaction. When filtered the sulfone was obtained as a small white cake. (A more accurate analysis of the hydrocarbon and sulfone was obtained by treating the mixture with excess concentrated sulfuric acid, diluting, and filtering.) The solution was then heated to boiling and neutralized while hot with barium oxide. The barium sulfate formed in the reaction was removed by filtration and washed with 500-ml. portions of boiling water until no separation of the barium 2-methylnaphthalene-8-sulfonate took place on cooling. The washings were then added to the filtrate, and the resulting solution was made slightly acidic with acetic acid. The resultant solution of barium sulfonate was clarified by absorbent charcoal if it was dark and then concentrated to 2000 ml. On cooling, barium salts of the sulfonic acids crystallized out and were filtered from the solution. Concentration of the solution yielded a second crop of crystals which were recrystallized before being added to the first crop. Since there was a difference in solubility between the two fractions of barium salts, it was obvious that more than one isomer was present, and the presence of a small amount of the 6 isomer was detected.

In a saturated solution of the 2,8 barium salt the 2,6 barium salt was completely salted out. This means that, in order to separate the two isomers, one need only dissolve the salt mixture in water, evaporate the solution to the point at which it is saturated with respect to the more soluble 2,8 barium salt, allow crystals of the 2,6 isomer to form, and filter this 2,6 isomer from the mixture. Since the amount of the 2,6 isomer at 40° C. is about 13 grams per 100 grams of mixture, the point to which the solution must be concentrated is easily estimated.

The solubility of the barium salt of the pure 2,8-sulfonic acid is shown in Figure 1 and Table I. This barium salt, formed at low temperatures, is the most soluble of the isomers, which is an aid in its purification by recrystallization. Also the low-temperature sulfonic acid is hydrolyzed by live steam, as would be expected for an alpha acid.

The results given for the amounts of salts formed are figured on the dry basis although the barium salts crystallize with water attached. An example is the barium salt of 2,8-sulfonic acid which analyzed $Ba(SO_3CH_3C_{10}H_6)_2.3H_2O$. Results in several low-temperature sulfonations are given in Table II.

Table I. Effect of Temperature on Solubility of Salts of Sulfonic Acids in Water

Isomer	Solubility, Grams/Liter 25° C.	45° C.	60° C.	90° C.
		Barium Salts		
2,8	12.1	28.0	56.9	117.2
2,6	2.01	15.1	27.3	58
2,7	0.57	2.9	4.8	6.6
		Sodium Salts		
2,8	43.2	84.1	100.4	168.0
2,6	31.0	65.3	92.1	144.0
2,7	19.0	52.9	80.0	134.6

Barium 2-Methylnaphthalene-6-sulfonate

In the sulfonation apparatus 71 grams of 93 per cent sulfuric acid were added dropwise to 71 grams of 2-methylnaphthalene maintained at 95° C. by a steam cone. At the end of 8 hours the reaction mixture was poured over 100 grams of ice and allowed to stand until the unsulfonated 2-methylnaphthalene collected on the surface. The cake of unsulfonated hydrocarbon was lifted from the surface of the solution, and the solution was filtered to remove the sulfone formed. The solution was heated to boiling and neutralized hot with barium oxide; the separation was then continued as in the previous case. On recrystallization all of the fractions had the same solubility in water. The results of several runs are given in Table III.

Table II. Sulfonation Runs at 40° C. Producing Barium 2-Methylnaphthalene-8-sulfonate[a]

Run No.	Time, Hours	Crude Ba Salt Grams	Crude Ba Salt % Converted	Unreacted Hydrocarbon Recovered Grams	Unreacted Hydrocarbon Recovered %	Sulfone Grams	Sulfone %	Pure 8 Barium Salt Grams	Pure 8 Barium Salt % Converted	Pure 8 Barium Salt % yield	Miscellaneous Isomers[b] Grams	Miscellaneous Isomers[b] %
1	4	47	32.5	46.1	65.1	...	...	...	...	..	..	...
2	4	45.1	31.1	46	64.8	...	...	...	...	..	..	...
3	6	91	62.8	...	...	...	...	...	...	..	..	...
4	6	89	61.5	24	33.8	...	...	...	...	..	..	...
5	6	89.5	61.9	24	33.8	0.8	0.9	73	50	76	12	8.3
6	6	91	62.8	24	33.8	0.7	0.8	72	50	75	16	11.1
7	8	96	66.2	...	...	...	...	...	...	..	..	...
8	8	102	70.3	...	...	...	...	...	...	..	..	...
9	8	102	70.3	20.2	28.4	1.1	1.3	76	54	75	18	12.4
10	8	100	69.0	19.8	28.0	1.2	1.4	78	54	74	17	11.7
11	8	100.5	69.2	20.3	28.6	1.1	1.3	77	53	77	18	12.4
12	24	90	62.0	0.0	0.0	26.1	36.7	...	...	..	..	...

[a] Theoretical barium content, 23.66%; analysis showed all actual values between 23.6 and 23.8%.

[b] Mixtures of 2,6 and 2,8 isomers obtained by crystallization in recovering the given amount of pure 2,8 barium salt.

Barium 2-Methylnaphthalene-7-sulfonate

This salt was prepared in the same manner as those previously described, except that the reaction was carried out at 160° C., and the mixture was poured into 250 grams of ice. The barium salt formed was recrystallized until it was white in color. It was not very soluble in hot water, so that large volumes of solutions had to be handled. Here again only one principal product was formed, as shown by the fact that a salt of only one solubility was found.

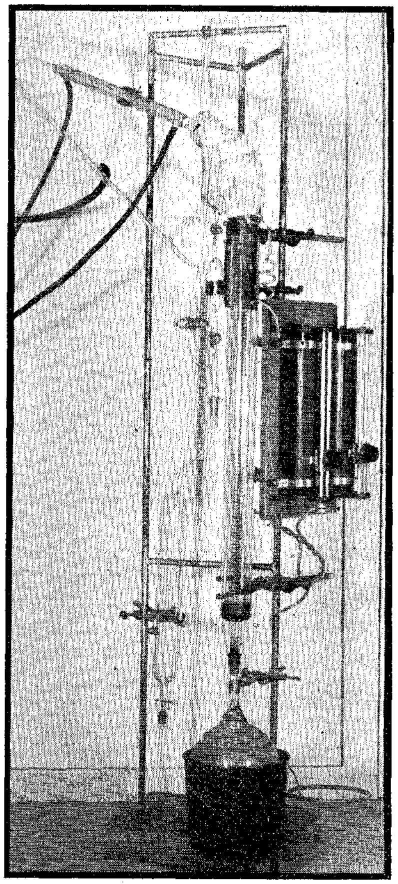


Figure 2. Lecky Distillation Column

To obtain an accurate analysis of the amount of unsulfonated 2-methylnaphthalene it had to be removed from the solution by steam distillation. Also, it was advantageous to extract the sulfone later with ether; even then a white compound was not obtained. If the latter procedure is followed, there is no point in using the 250 grams of ice mentioned above. The reaction mixture may merely be poured into cold water, allowed to stand until cool, and then filtered. This removes the sulfone, unsulfonated 2-methylnaphthalene, and other tarry by-products which are formed. If the recovery of the unsulfonated hydrocarbon is not desired, the latter method is the more desirable. The results of several runs at high temperatures are given in Table IV.

Barium 6-Methyl-1,2,3,4-tetrahydronaphthalene-7-sulfonate

Hydrogenation of 2-Methylnaphthalene. Recrystallized 2-methylnaphthalene (170 ml.) and Raney nickel catalyst (20 grams) suspended in 50 ml. of 95 per cent alcohol were placed in a hydrogenation unit; hydrogen was admitted until a pressure of 1200 pounds per square inch was reached at 20° C. The shaker was started and heat was applied. When 150° C. was reached, the pressure was 1740 pounds. After 5 hours the temperature was raised to 185° C., and the reaction was allowed to proceed for another 10 hours. Then agitation was stopped, the pressure released, and the product removed. The reaction mixture was separated from the Raney nickel by filtration.

Purification and separation of the hydrocarbon mixture was carried out in the Lecky column shown in Figure 2. Fractions obtained and their boiling points at 12 mm. pressure were: 2-methyl-Decalin, 89° C.; 2-methyl-Tetralin, 101° C.; 2-methylnaphthalene, 114° C. Results are shown in Table V.

Sulfonation of 6-Methyl-1,2,3,4-tetrahydronaphthalene. One-fourth mole (36.5 grams) of the tetrahydro compound was placed in the sulfonation apparatus with 40 grams of 93 per cent sulfuric acid. The temperature was maintained at 80° C. for 4 hours, and then increased to 100° C. for 4 more hours. After sulfonation was complete, the reaction mixture was treated as the other sulfonic acids; the only variation was that the mixture was treated with benzene to extract sulfones and unsulfonated hydrocarbon rather than to allow them to settle out. No sulfone or hydrocarbon was found in the extract. Results are shown in Table V.

Sodium Salts of Methylnaphthalene Sulfonic Acids

Use of Sodium Sulfate or Carbonate. One tenth mole (57.9 grams) of the barium salt of the sulfonic acid was placed in 2 liters of water and then heated to boiling. To this was added one tenth mole of sodium sulfate (14.2 grams) or sodium carbonate (10.6 grams), and the mixture was kept in suspension by stirring. When the reaction was completed, the barium sulfate or carbonate formed was filtered from the solution. On concentration of the solution, the sodium salt of the sulfonic acid separates out. Here the reaction must be carried out with small quantities of the barium salt because of its relatively low solubility in water. The yield with sodium sulfate is practically quantitative (48.8 grams), and with sodium carbonate is slightly less (47.9 grams, 98.5 per cent).

Direct Production of Sodium Salt. The sulfonation mixture resulting from the reaction of 71 grams of 2-methylnaphthalene with 71 grams of 93 per cent sulfuric acid for 8 hours was poured into 250 ml. of water while stirring. Any sulfone or unreacted methylnaphthalene was removed at this

Table III. Sulfonation Runs at 90–95° C. Producing Barium 2-Methylnaphthalene-6-sulfonate[a]

Run No.	Time, Hours	Crude Ba Salt		Unreacted Hydrocarbon Recovered		Sulfone		Pure 6 Barium Salt		
		Grams	% converted	Grams	%	Grams	%	Grams	% converted	% yield
13	4	94	65.0	23	32	0.8	0.9	94	65.0	95.6
14	5	90	62.2	24	34	0.85	1.0	90	62.2	95.7
15	6	116	80.0	8.6	12	2.0	2.3	116	80.0	89.7
16	6	115	79.4	8.9	13	2.0	2.3	115	79.4	89.9
17	6	115	79.4	8.5	12	2.0	2.3	115	79.4	89.4
18	8	123	84.8	6.3	8.8	3.6	4.1	123	84.8	83.1
19	8	124	85.5	5.9	8.3	3.7	4.2	124	85.5	92.5
20	8	121	83.5	6.3	8.8	3.7	4.2	121	83.5	91.5
21	8	121	83.5	6.0	8.4	3.6	4.1	121	83.5	91.5

[a] Theoretical barium content, 23.66%; analysis showed all actual values between 23.7 and 23.9%; no other isomers found in this temperature range.

Table IV. Sulfonation Runs at 160° C. Producing Barium 2-Methylnaphthalene-7-sulfonate[a]

Run No.	Time, Hours	Crude Ba Salt		Unreacted Hydrocarbon Recovered		Sulfone		Pure 7 Barium Salt			Barium Content, %[b]
		Grams	% converted	Grams	%	Grams	%	Grams	% converted	% yield	
22	4	116	79.9	8.0	11.2	4.4	5.0	116	79.9	79.9	24.5
23	4	112	77.2	8.5	11.9	4.8	5.3	112	77.9	87.2	24.5
24	4	113	78.0	8.0	11.2	4.5	5.1	113	78.0	88.0	24.5
25	6	125	86.4	2.0	2.8	5.5	6.4	125	86.4	88.7	25.0
26	6	126	86.9	1.5	2.1	6.0	6.7	126	86.9	89.0	24.9
27	6	126	86.9	2.0	2.8	6.8	6.7	126	86.9	89.6	25.0
28	8	129	89.0	None		7.8	9.0	129	89.0	89.0	25.1
29	8	130	89.5	None		7.9	9.1	130	89.5	89.5	25.2
30	8	128	88.4	None		7.5	8.5	128	88.4	88.4	24.2

[a] No other isomers found at this temperature.
[b] Theoretical barium content, 23.66%.

Table V. Results of Preparation of Barium 6-Methyl-1,2,3,4-tetrahydronaphthalene-7-sulfonate

	Run A	Run B
Hydrogenation with Raney Nickel Catalyst Using 170 Grams 2-Methylnaphthalene		
2-Methylnaphthalene recovered, grams	65	47
2-Methyl-Tetralin obtained, grams	63	86.8
2-Methyl-Decalin obtained, grams	10	7
Loss in intermediate fractions, %	30	29
Conversion to 6-methyl-Tetralin, %	36	49
Yield of 6-methyl-Tetralin, %	58	69
Sulfonation Using 36.5 Grams 6-methyl-Tetralin and 40 Grams 93% H_2SO_4 for 8 Hours		
Barium salt obtained, grams	64.0	65.5
Conversion in sulfonation, %	87.1	89.0

point either by extracting with benzene or by filtering if the temperature was kept low enough to solidify the hydrocarbon. Then the solution was poured into a salt solution of the following composition: 2,8-sulfonic acid, 200 grams sodium chloride, and 300 ml. water; 2,6- and 2,7-sulfonic acids, 150 grams sodium chloride and 300 ml. water. The resulting solutions were agitated for several hours and filtered. A second crop of crystals was obtained on the addition of more sodium chloride. The two fractions were then put together and recrystallized from water. The yields (based on hydrocarbon recovery) were 88 grams of the 2,8 sodium salt (74 per cent), 99 grams of 2,6 sodium salt (84 per cent), and 95 grams of 2,7 sodium salt (78 per cent). Figure 3 and Table I show the solubility of the sodium salts, and Figure 4 and Table VI the influence of sodium chloride on the solubility of the sodium salts.

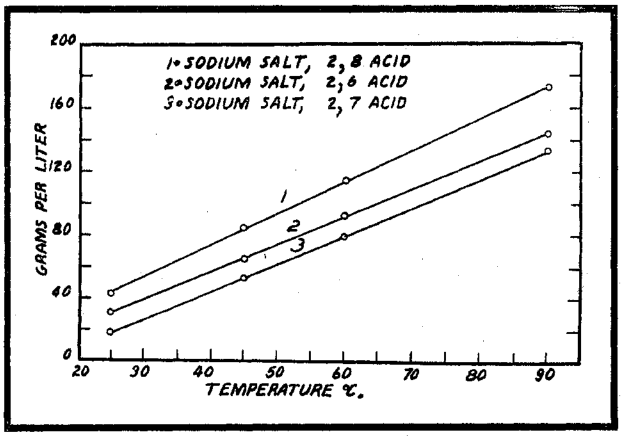


Figure 3. Variation in Solubility of Sodium Salts with Temperature

Comparison of Sulfonation Results

Tables II, III, and IV compare the effects of different variables during sulfonation. Figure 5 is a plot of data from these tables showing the variation with both time and temperature of unsulfonated 2-methylnaphthalene. The figures for naphthalene (3) are included so that inferences may be drawn as to the effect of the methyl group on the ease of substitution in the aromatic nucleus. Here, as with toluene and benzene, the aromatic compound with the methyl group is much more reactive.

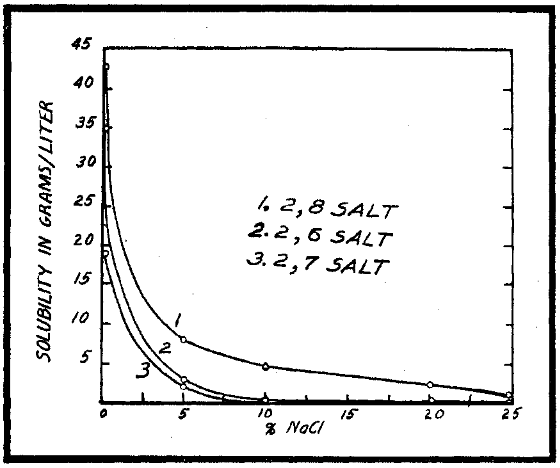


Figure 4. Effect of Sodium Chloride on Solubility of Sodium Salts of Sulfonic Acids

The sulfone formation should be noted, as these compounds may cause the loss of a large amount of hydrocarbon. Run 12, Table II, shows that 36.7 per cent of the hydrocarbon was converted to sulfone.

Derivatives of Sulfonic Acid Salts

Using methods described by Shriner and Fuson (*6*) and Groggins (*4*), sulfonyl chlorides, sulfonamides, naphthols, methyl ethers, and amino compounds were made. Table VII shows the derivatives and their melting points. All compounds except 2,7 derivatives are listed in the literature (*1, 2, 7, 8, 9*). [An exception is the 2-methyl-7-naphthylamine made from the corresponding nitro compound by Vesely and Pac (*8*). They gave the melting point as 105° C.]

Identification of Sulfonic Acids

Since the melting points are listed in the literature (*1, 2, 7, 8, 9*), no further proof is needed for any compounds except the

Table VI. Effect of Sodium Chloride on Solubility of Sodium Sulfonates in Water

NaCl, %	Solubility, Grams/Liter		
	2,8 Salt	2,6 Salt	2,7 Salt
0	43.2	31.0	19.0
5	8.1	3.0	2.0
10	4.8	0.9	0.8
20	2.3	0.7	0.5
25	0.5	0.2	0.1

Table VII. Melting Points of Derivatives of 2-Methylnaphthalene and 6-Methyl-Tetralin

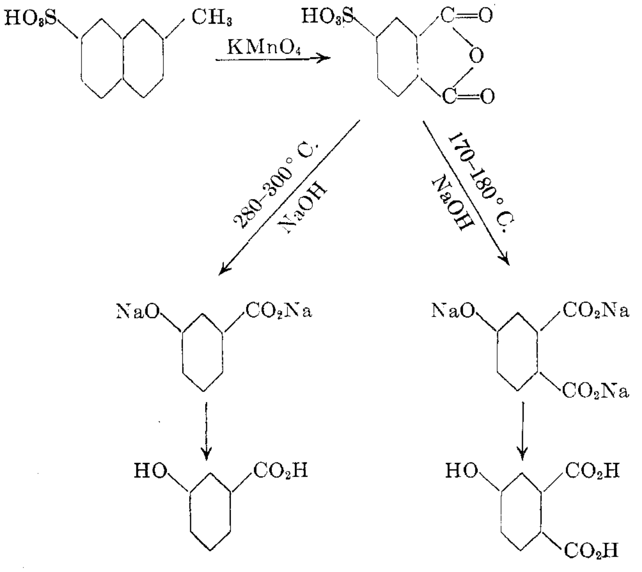
	M. P. of Derivative, ° C.				
	—SO_2Cl	—SO_2NH_2	—OH	—OMe	—NH_2
2-Methylnaphthalene					
2-Me-6-	97–8	204–5	128	79	128
2-Me-7-	63–4	163–4	101–2	78	103–4
2-Me-8-	95–6	195–6	109	41	56–7
6-Methyl-Tetralin	...	155	89	..	....

2,7 derivatives. Also, there is no record in the literature of any sulfonation of 2-methylnaphthalene at a temperature as high as 160° C. To prove the structure of the 2-methylnapthalene-7-sulfonic acid, an oxidation procedure was followed.

Oxidation of Sulfonic Acid. The barium salt of 2-methylnaphthalene-7-sulfonic acid was dissolved in water, heated to boiling, and then treated with excess sulfuric acid. The barium sulfate formed was filtered out and potassium permanganate was added. After the solution was maintained at the boiling point for 24 hours, alcohol was added to destroy excess permanganate and the solution was clarified with activated carbon. On concentration 4-sulfophthalic anhydride (as later shown) crystallizes out.

Fusion of Oxidation Product. The oxidation product was slowly added to a nickel crucible containing potassium hydroxide and sodium hydroxide, and the mixture was fused at 170–180° C. for one hour. The fusion mass was dissolved in hot water, acidified, and extracted with ether. On evaporation of the ether, 4-hydroxyphthalic acid was obtained, melting at 203–204° C. (*11*).

Fusion in the same manner at about 300° C. gives *m*-hydroxybenzoic acid (melting point 201° C.) on acidification. This is an expected reaction since many phthalic acid derivatives substituted in the 4 position decarboxylate easily. The reactions were:



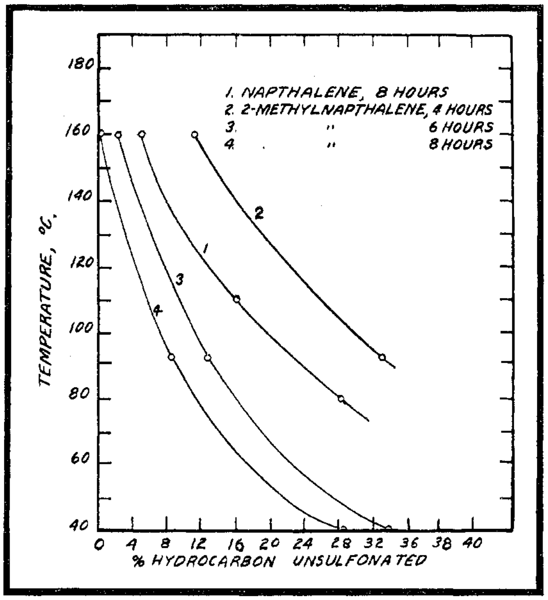


Figure 5. Effect of Temperature on Amount of Hydrocarbon Sulfonated

The 2-methylnaphthalene-6-sulfonic acid was known to be absent by comparison of solubilities (2,6 barium salt, 2 grams per liter; 2,7 barium salt, 0.57 gram per liter); therefore the 2-methylnaphthalene-7-sulfonic acid was the only compound which would give the above reactions on oxidation and fusion. This establishes the structure of the starting material as 2-methylnaphthalene-7-sulfonic acid.

Industrial Possibilities

Wetting Agent Tests. The sodium salts of the sulfonic acid were found to have wetting properties, and an attempt was made to evalulate their possibilities. Surface tension, stability, and viscosity measurements were determined, and attempts were made to apply the Draves wetting test to the compounds.

These compounds were found to be stable to both acids and bases, even in boiling solutions with concentrations as high as

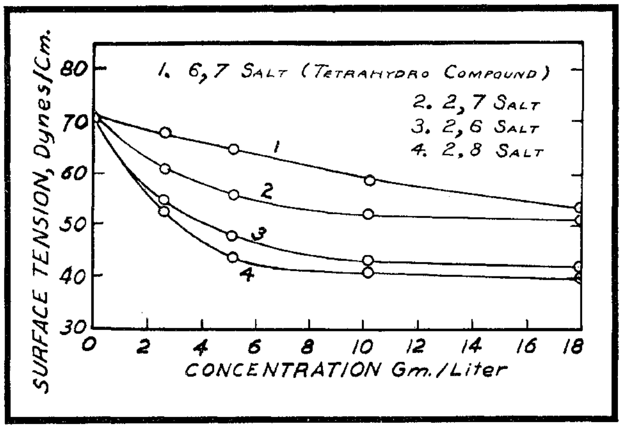


Figure 6. Surface Tensions of Solutions of Sodium Salts of the Sulfonic Acids

Table VIII. Viscosities and Densities of Aqueous Solutions of Sodium Salts of Sulfonic Acids at 25° C.

Concn., Grams/Liter	2-Me, 6-SO_3Na		2-Me, 7-SO_3Na		2-Me, 8-SO_3Na		6-Me, 7-SO_3Na[c]	
	Density[a]	Viscosity[b]	Density	Viscosity	Density	Viscosity	Density	Viscosity
0.50	0.9971	0.886	0.9981	0.876	0.9978	0.875	0.9982	0.897
1.25	0.9973	0.905	0.9983	0.903	0.9983	0.866	0.9984	0.906
2.50	0.9978	0.913	0.9984	0.926	0.9985	0.911	0.9985	0.907
3.75	0.9980	0.923	0.9986	0.936	0.9990	0.928	0.9980	0.908
5.00	0.9983	0.944	0.9990	0.942	0.9995	0.944	0.9996	0.909

[a] Gram per cc. [b] Centipoise. [c] Tetrahydro compound.

Table IX. Surface Tensions of Aqueous Solutions of Sodium Salts of Sulfonic Acids

Concn., Grams/Liter	Surface Tension, Dynes/Cm.			
	6-Me,7-SO_3Na (tetrahydro compd.)	2-Me,7-SO_3Na	2-Me,6-SO_3Na	2-Me,8-SO_3Na
2.5	67.8	61.8	55.1	53.5
5.0	64.9	56.2	47.9	43.8
10.0	68.6	53.0	43.5	41.0
18.0	53.5	51.1	41.7	39.6

15 per cent, and the wetting-out power in these concentrated solutions was increased. In addition, these compounds resisted precipitation in hard water. Viscosity and density data for dilute solutions are given in Table VIII. Surface tension measurements, made in the du Noüy tensiometer, are shown in Figure 6 and Table IX. The maximum surface tension lowering is nearly approached by one per cent solutions. The Draves test was of little use in estimating the value of these compounds.

PRODUCTION. To determine the possibility of adapting the compounds made in this investigation to commercial production, runs were carried out in large sulfonation and fusion pots (Figures 7 and 8) which are similar to those used in semiworks industrial practice. A series of reactions was run on naphthalene and then on 2-methylnaphthalene, making sodium salts of sulfonic acids and naphthols, so that processes could more easily be compared. It was found that 2-methylnaphthalene sulfonic acids and derivatives could be easily produced in ordinary equipment by varying the time and temperature of the reactions.

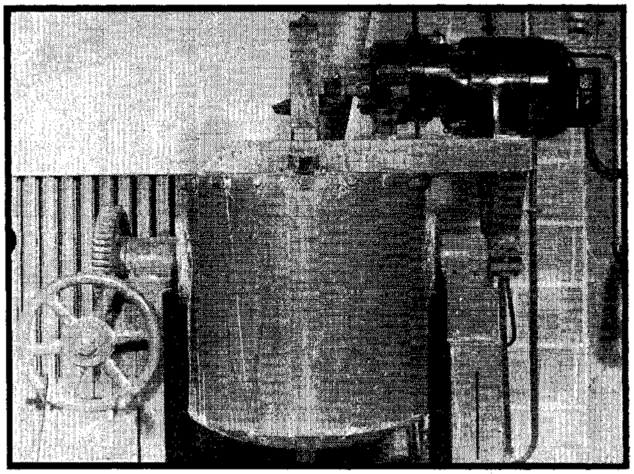


Figure 8. Fusion Pot

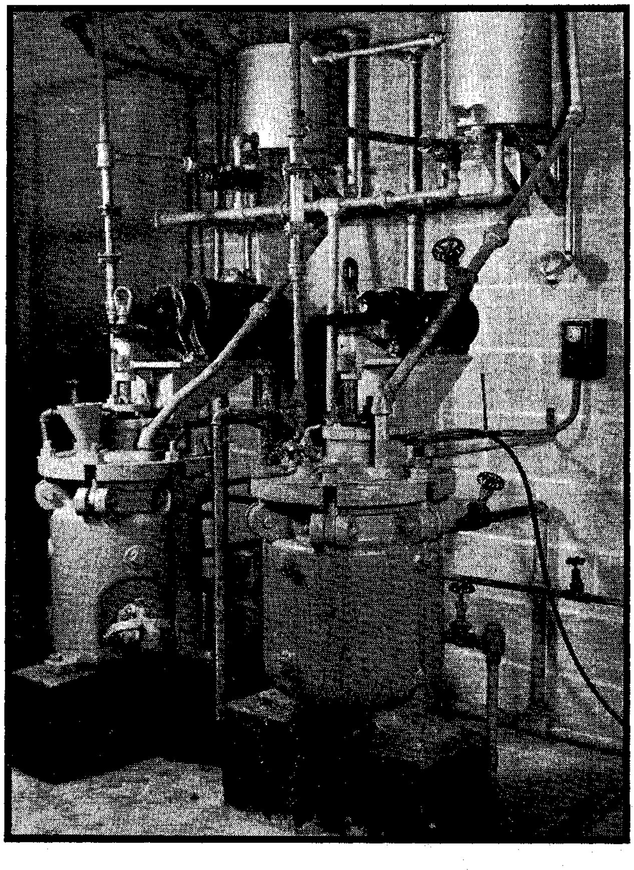


Figure 7. Sulfonator

Conclusions

1. 2-Methylnaphthalene can be sulfonated with 93 per cent sulfuric acid; sulfonation takes place in the 8 position at 40° C. (75 per cent yield), in the 6 position at 90–100° C. (90 per cent yield), and in the 7 position at temperatures above 160° C. (88 per cent yield).
2. 2-Methylnaphthalene can be hydrogenated to 6-methyl-Tetralin with hydrogen and a Raney nickel catalyst. Sulfonation of this compound gives 6-methyl-Tetralin-7-sulfonic acid.
3. Derivatives of the sulfonic acids, such as salts, sulfonyl chlorides, sulfonamides, naphthols, ethers, and amino compounds, can be made in the usual manner.
4. The sulfonic acids and their derivatives listed above can be made on a large scale by methods and apparatus now in commercial use.
5. The sodium salts of the sulfonic acids show definite wetting-out properties. They have the following advantages which may make them of use commercially: low cost, stability in dry form, resistance to precipitation in hard water,