Phenolic Aminosulfonate Surfactants

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A series of new phenolic amino sulfonates has been prepared from mono- and dialkylphenols, formaldehyde, and N-methyltaurine by the Mannich condensation. From monoalkylphenols either mixtures of mono- and disubstituted products or completely disubstituted materials were obtained. Surface-active properties, of which lime soap dispersant activity is notable, were summarized for these products.

THE MANNICH reaction involves an active hydrogen component, such as a phenol, a carbonyl compound, commonly formaldehyde, and an amine (1). The use of this reaction to prepare surfactants directly has apparently been limited to nonionics from phenols, formaldehyde, and hydrophobic polyamines (2). Amines prepared from alkylphenols, formaldehyde, and lower dialkylamines have also been quaternized to obtain cationic surface-active agents (3). A class of sequestering agents has been obtained from iminodiacetic acid, phenols, and formaldehyde (4).

The present work involved the use of N-methyltaurine as an amine in the Mannich synthesis and has given a new type of anionic or, more properly, ampholytic phenolic aminosulfonate surfactant. No previous reference to this type of Mannich reaction has been discovered. The synthetic aspects will be discussed first, then the surface-active characteristics of the products will be considered.

Synthesis

The reaction may be represented as follows, assuming that the monoalkylated phenols are principally *para* isomers:
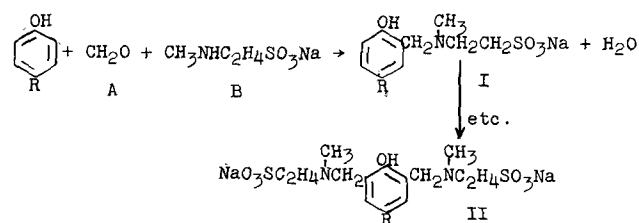
The reaction has been carried out by heating the reactants in aqueous ethanol at about 80°C. Since only open *ortho* or *para* positions are substituted in the Mannich reaction, products of types I and II are predicted. Experimentally, mixtures are produced even though only equivalent amounts of formaldehyde and N-methyltaurine are used. It has usually not been possible to separate the pure I and II; however careful purification of the total product by recrystallization, followed by elemental analysis, permitted calculation of the conversions to I and II in the cases of commercial nonyl- and dodecylphenols as typical of higher monoalkylphenols. The results are summarized in Table I. These products are clearly mixtures of side-chain and position isomers, as expected from commercially available starting-materials.

From the data it is clear that an excess of both reagents A and B must be used to obtain satisfactory conversions of the phenol. Also appreciable amounts (33%) of II (R = C_9H_{19}) were obtained even with

TABLE I
Monoalkylphenols with Formaldehyde (A) and N-Methyltaurine (B)

Run	R	Molar ratio, to RC_6H_4OH		Conversions, %, on RArOH	
		A	B	I	II
1[a]	C_9H_{19}	1.0	1.0	31[b]	33[b]
2[a]	C_9H_{19}	1.5	1.2	30[b]	52[b]
3	$C_{12}H_{25}$	1.1	1.1	60[c]	31[d]
4	$C_{12}H_{25}$	2.5	2.5	....	86[c]

[a] In Runs 1 and 2 (A) was added to a hot solution of the phenol and B; in all other runs a "stock solution" of A and B was pre-mixed (see text), stored, and used in the desired ratio to phenol.
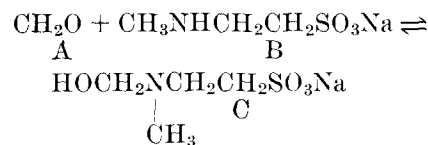[b] As a mixture, crystallized but not separated into components.
[c] As a solvent-purified gum.
[d] Crystallized, essentially pure.

A and B equivalent to the phenol. Comparing Runs 1 and 2, a fair conversion is obtained in either case, but conversion to II is increased about 60% by a 20% excess of B. A large excess (150%) of A and B gives good conversion to II (R = t-$C_{12}H_{25}$). The results seem entirely consistent with the fact (1) that alkyl substitution facilitates the reaction and with the suggestion, for which some qualitative evidence was noted in this work, that the Mannich reaction is reversible or at least that a redistribution may occur. Some of these products gave clear dilute aqueous solutions which slowly became turbid; from some mixtures, small quantities of viscous oils, probably impure methylenediphenols, were separated.

Although the reaction can be carried out conveniently by adding formaldehyde to the phenol and N-methyltaurine in solution, most of this work utilized a "stock solution" of equimolar quantities of the carbonyl and amine reagents. This procedure is not only convenient but has a theoretical basis in that these are known to condense, producing an N-methylol derivative of type C, which may be the interme-

$$CH_2O + CH_3NHCH_2CH_2SO_3Na \rightleftharpoons$$
$$\quad A \qquad\qquad\qquad B$$
$$HOCH_2NCH_2CH_2SO_3Na$$
$$\quad | \qquad\qquad C$$
$$\quad CH_3$$

diate in some types of Mannich reaction (1,5). The stock solution may be stored indefinitely if carbon dioxide is excluded.

In order to obtain monosubstituted products (III) a series of dialkylphenols was studied. These were prepared by alkylation of phenol or, in one case, o-cresol, with olefins (BF_3 catalyst) and are principally 2,4-dialkylphenols. The reaction occurred at
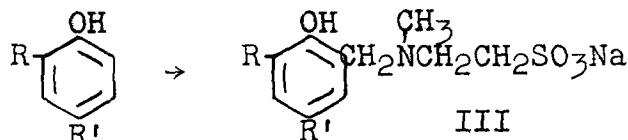
least as readily as with monoalkylphenols, giving both gums and crystalline products. Again purification proved difficult, and in most instances even recrystallized products had low carbon contents and usually

high sulfur and nitrogen values, suggesting that the excess N-methyltaurine or derived methylenebis(N-methyltaurine) formed salts or mixed crystals with the products. In several cases fractional recrystallization of the crystalline products gave two crops: one essentially insoluble in hot solvents (Insol., isopropyl alcohol or mixtures with small volumes of methanol) and the other soluble (Sol.) in the hot solvent but crystallizing when the solution was cooled. The results are given in Table II.

TABLE II

Dialkylphenols → III

Run	R	R'	Molar ratio, A+B	Conv. %	Recryst., % conv.	
					Sol.	Insol.
5	C_9H_{19}	C_9H_{19}	1.2	95[c]	....	....
6	CH_3	C_9H_{19}	1.12	98[c]	....	....
8[a]	sec.-C_5H_{11}	sec.-C_5H_{11}	1.2	100[c]	....	....
9[b]	C_5H_{11}	C_5H_{11}	1.2	59[d]	....	....
10[b]	C_5H_{11}	C_5H_{11}	1.2	....	29[d]	25[d]
11[e]	C_6H_{13}	C_6H_{13}	1.2	100[c]	....	....
12[f]	C_6H_{13}	C_6H_{13}	1.2	70[d]	....	....
13[g]	C_6H_{13}	C_6H_{13}	1.2	59[d]	....	....
14[h]	C_5H_{11}	C_5H_{11}	1.03	....	61[c]	32[d]
15[i]	C_5H_{11}	C_5H_{11}	1.03	....	35[d]	44[d]
16	CH_3	CH_3	1.11	90[d]	....	....

[a] Source, Sharples brand, Pennsalt Chemicals Corporation.
[b] Source, Koppers Company; in run 10, redistilled before use.
[c] Solvent-purified gums, containing small excess N-methyltaurine values.
[d] Crystallized as a mixture containing small N-methyltaurine values.
Sources: Phenol was dialkylated (see experimental part) with [e] 1-hexene; [f] 4-methyl-1-pentene; [g] 2-methyl-1-pentene; [h] 2-pentene; [i] 2-methyl-2-butene.

The fractionally crystallized products are mainly of interest in connection with evaluation data. However it is apparent that excellent conversions can be realized with small excesses of the reagents even when considerable manipulation was involved in the separations. All products are considered to be mixtures of isomers, both position and side-chain.

An attempt to use an hydrophobic aldehyde (n-decanal, 2,4-dimethylphenol, and N-methyltaurine) in place of formaldehyde gave an intractable mixture.

Surface-Active Characteristics

These materials were evaluated as surfactants and especially as lime soap dispersants by the standard methods described by Harris (6). The data are tabulated, according to the designations of the previous tables, in Table III.

The data are remarkable mainly in their broad ranges although clearly excellent surfactants can be prepared by this method. It appears that a single alkyl group in the phenol cannot be larger than C_{12} unless two solubilizing groups are to be introduced (Runs 3,4). With two alkyl groups the upper limit in size lies between C_6 and C_9 in each. No completely consistent correlations are evident in the data. The better lime soap dispersants do show a lack of foam stability, even in soft water; products of Runs 11 and 14 are poor dispersants however and also show this instability. Fractionated products (Runs 10,14,15) show no definite trends in properties although the soluble fractions are as good as, and better than in two cases, the insolubles as dispersants.

Although cotton detergencies were determined for most of these products, the data are not presented because they are generally inferior to commercially available formulations.

It is interesting to speculate on the mechanism of the lime soap dispersant activity of this class. An hypothesis, which is in agreement with this data, is pictured as follows:

IV   V
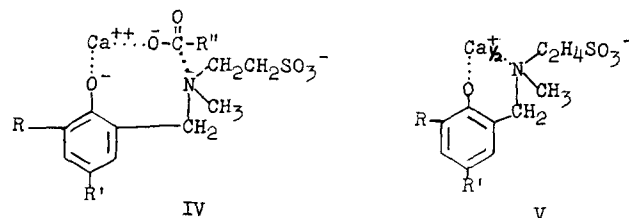
A "mixed salt" may be stabilized by the nitrogen by interaction with the carbonyl as in IV. If R is large, micelle formation might be expected to occur and the superiority of small branched alkyl groups could then be due to their weak micelle-forming characteristics since further agglomeration would result in "curd" formation. Chelation, though probably minor, may also play a part, as depicted in V. In any case, two methyl groups (Run 16) are not effective, indicating that surface activity is required and that IV does not completely explain the effectiveness of these types.

TABLE III

Surface-Active Properties, 25°C.

Run-type	Surface tension,[a] DuNuoy, sec., 0.25% dynes/cm.	Wetting,[b] Draves, sec., 0.125%	Lather,[c] cm., Ross-Miles, 0.1% solution, 50°C. Hardness				Lime soap dispersion[d]
			50 p.p.m.		300 p.p.m.		
			At once	5 min.	At once	5 min.	
1—I, II	33	17	15.6	15.4	19.5	19.5	>80
2—I, II	33	30	16.0	16.0	19.5	19.4	80
3—I	39	>180	1.7	1.1	Insol.	Insol.	>80
4—II	35.5	53	18.6	18.0	13.6	13.6	40
5—III	38.5	>180	12.5	12.3	0	0	>80
6—III	35.5	16	16.3	13.9	4.7	3.9	40
8—III	36	10	14.2	2.0	17.0	6.8	20
9—III	32.5	5.7	18.1	8.8	19.1	18.8	20
10—III Insol	....	......	......	......	......	......	40
10—III Sol	....	......	......	......	......	......	40
11—III	32.5	134	16.0	15.3	1.6	Trace	>80
12—III	30	13	20.7	20.7	2.9	2.7	60
13—III	....	......	......	......	......	......	60
14—III Insol	36	11	16.5	3.7	19.1	16.1	>80
14—III Sol	39	15	14.3	1.8	17.6	10.4	80
15—III Insol	....	5	13.0	0.9	18.4	17.6	40
15—III Sol	....	4	11.6	1.6	18.6	8.2	20
16—III	....	......	......	......	......	......	>80

[a] Ref. 6, pp. 31–33.
[b] Ref. 6, pp. 40–41.
[c] Ref. 6, pp. 47–49.
[d] Ref. 6, pp. 35–36; no attempt was made to obtain data below 20, considered excellent.

Experimental

Runs with nonylphenol, dodecylphenol, nonyl-*o*-cresol and diamylphenol, and certain other data are presented to illustrate the methods of preparation, purification, and fractionation. However, in any given case, the experimental approach will have to be adapted to the nature of the products.

Run 1. Nonylphenol,[1] 22.0 g. (0.10 mole), and 16.1 g. (0.10 mole) of sodium N-methyltaurinate as 46 g. of commercial 35% aqueous solution were mixed in 50 ml. of anhydrous ethanol and heated with stirring to 50°C. Then 3.0 g. (0.10 mole) of formaldehyde as 8.1 g. of 37% formalin was added drop by drop during 30 min. After being heated to 70° during 45 min. (a few drops added to 10–15 ml. of water gave a good-lathering, slightly turbid solution), and 25 min. of refluxing (81°, solution temperature), the mixture was dried by distillation with ethanol at the water aspirator; the ethanol was added as a necessary control of frothing.

In other runs, isopropyl alcohol was used in this drying step because of the higher water content of its azeotrope. The reaction also occurs in water alone as a solvent, but the quality of such products was not investigated in general. In all drying operations the temperature of the residues was kept below 100°, usually below 80°.

To the nearly dry residual slurry 300 ml. methanol were added; the mixture was heated to reflux and filtered to remove a small amount of inactive solid. The filtrate was again concentrated to near dryness and treated with stirring (hot) with 300 ml. of isopropyl alcohol. The solid which crystallized overnight was filtered, washed on the filter with isopropyl alcohol, and vacuum oven-dried to 55°, leaving 30.5 g. of white, caked solid. The filtrate in water was only slightly active and somewhat turbid.

The solid could not be recrystallized from aqueous alcoholic solvents without great loss and was redried at 100°/1 mm. for analysis. This and similar products had no sharp melting or decomposition point; most of them darkened, sintered, and became glasses (with bubbling) in the range from 140–210°C.

Anal. Calc'd. for $C_{19}H_{32}NNaO_4S$: C, 57.9; H, 8.19; N, 3.56; S, 8.14.

Calc'd. for $C_{23}H_{40}N_2Na_2O_7S_2$: C, 48.75; H, 7.12; N, 4.94; S, 11.32. Found: C, 51.74; H, 7.96; N, 4.21; S, 9.82.

From these data the proportions of mono- and disubstituted derivatives can be calculated, assuming that no impurities are present. The method is outlined, although it is straightforward, to illustrate the procedure which is necessary in cases in which the products cannot be separated.

The carbon and sulfur data are chosen for analysis by simultaneous equations because the ranges of nitrogen and hydrogen are too narrow with respect to probable error for reasonable significance.

Equating weights of sulfur or carbon in 100 g. of mixture of the mono- (m) and disubstituted (d) products, with the compositions found by analysis:

a) $0.0815 m + 0.1132 d = 9.82$
b) $0.5798 m + 0.4875 d = 51.74.$

Solving, from a): $d = 86.8 - 0.720 m$, and in b): $0.580 m + .4875 (86.8 - .720 m) = 51.74$, $m = 39.5$, % mono, and $d = 60.5$, % di, since (c) $m + d = 100 \times$.

¹ Source: Rohm and Haas Company.

Although one can solve a) and c) or b) and c) similarly, small errors in the analyses cause large differences in the solutions which are not considered as significant.

From these percentages the actual product contained 12.1 g. (31% conv.) I and 18.4 g. (33% conv.) II. The conversions were therefore 64% on nonylphenol and 97% on both of the other reactants.

Run 2. A similar procedure was employed, condensing 0.10 mole of the phenol with 0.12 mole of N-methyltaurine and 0.15 mole of formaldehyde in 100 ml. of ethanol (1 hr. at 75–80°).

Isopropyl alcohol (300 ml.) was used in the azeotropic drying step. Finally taken to near-dryness, the residue was treated with stirring with 400 ml. of methanol and was filtered hot to remove inactive salts. The filtrate again was concentrated to near-dryness, and the hot residue was stirred and treated slowly with 300 ml. of isopropyl alcohol with heating. The crystalline precipitate, after cooling, was filtered; and the cake, repeatedly washed with isopropyl alcohol and vacuum oven-dried to 45°, then weighed 41.4 g. The white solid resembled the product of Run 1; a sample was also redried for analysis.

Anal. Found: C, 50.05; H, 7.94; N, 4.71; S, 10.23.

Using the method of calculation outlined above, m = 28.5 and d = 71.5, and the weights are 11.8 g. (30% conv.) I and 29.6 g. (52% conv.) II. The values are probably somewhat high [82% conv. on nonylphenol but 112% (!) on N-methyltaurine].

Stock Solutions. To suit theoretical reasons mentioned in the discussion and to minimize drying times and reduce frothing during drying, either of two stock solutions was used in the remaining runs. A 2M solution (460 g. of 35% aqueous sodium N-methyltaurinate and 81 g. of 37% formalin—1.0 mole of each—were mixed and made up to 500 ml. with water) was convenient for volume measurements, and an even more concentrated solution containing 3.04 milliequivalents/g. (300 g. of 65% methyltaurinate, 98 g. of 37% formalin, mixed and allowed to stand overnight, then filtered) was used by weight. Approximately equal volumes of ethanol were used to make up reaction mixtures.

Run 3. Dodecylphenol (26.2 g., 0.10 mole) was heated to reflux with stirring for 2 hrs. with 55 ml. of 2M stock solution (0.11 mole) and 55 ml. ethanol. A sample was then turbid in water with good activity. After concentration and drying as usual with isopropyl alcohol, solid material deposited from this solvent was removed by filtration (slightly active).

The filtrate was concentrated to near-dryness and treated at room temperature with 300 ml. of ether. The precipitated gummy solid was filtered, washed, and dried: 18.7 g.; essentially disubstituted isomers (31% conversion).

The ethereal filtrates, taken to dryness, and the hard amber gum redried, gave 25.8 g. (59.8% conv. if pure).

Anal. Calcd. for $C_{22}H_{34}NNaO_4S$: C, 61.3; H, 7.94; N, 3.25; S, 7.43. Found: C, 62.33; H, 7.42; N, 2.49; S, 6.16.

Although the product was not pure, it did not appear to contain disubstituted products but may represent some diphenolic types. It was hexane-soluble and could not be fractionated by mixed solvent (hexane-methanol) methods.

TABLE IV

Dialkylphenols

Olefin	Olefin/ phenol	n_D^{25}	b.p.°C./mm.	Conv. % on olefin	Analyses C	Analyses H
Hexenes			Calc'd.:	$C_{18}H_{30}O$	82.3	11.52
1-Hexene	1.6	1.4948–50	120–131/0.3	26.9	82.20	11.57
4-Methyl-1-pentene	1.6	1.4937–56	125–126/0.3	36.3	82.52	11.68
2-Methyl-1-pentene	1.6	1.4993–1.5004	121–131/0.3	46.2	82.84	11.73
Pentenes			Calc'd.:	$C_{16}H_{26}O$	82.0	11.2
2-Pentene	2.0	1.4953–5	98–117/0.2	36.4	81.86	11.40
2-Methyl-2-butene	1.8	1.5040–7	103–107/0.3	42.5	81.50	11.45

Run 4. From 0.10 mole of dodecylphenol with 105 ml. of 2M stock solution and 100 ml. ethanol (2.5 hrs., 82°), after drying and diluting with isopropyl alcohol (300 ml.) then with ethanol (100 ml.) and filtering to remove inactive salts, was obtained a cream-colored tough gum: 52.4 g. (86% conversion if pure). Again analysis indicated principally disubstituted product except for the low carbon content. Excess N-methyltaurine values may have been present in the product.

Anal. Calc'd. for $C_{26}H_{46}N_2Na_2S_2O_7$: C, 51.2; H, 7.60; N, 4.60; S, 10.52. Found: C, 46.62; H, 7.42; N, 4.57; S, 10.52.

Run 6. This experiment illustrates the method used for the dialkylphenols, including the synthesis of a starting material which is not commercially available.

Alkylation. *o*-Cresol (187 g., 1.73 moles) containing 5 ml. of 47% BF$_3$-etherate was stirred at 30° (water-bath cooling) as 126 g. (1.0 mole) of propylene trimer were added during 30 min. After being heated at 47–55° for 5 hrs., the mixture was cooled and stirred with 30 g. of activated alumina to remove the catalyst, filtered, and fractionated in a 2-ft. "zigzag" column. The product, nonyl-o-cresol, was a colorless liquid: b.p. 117–124°/0.1–0.2 mm., n_D^{25} 1.5124; 191.0 g. (81.5% conv. on trimer). It is doubtless a mixture of isomers.

Anal. Calc'd. for $C_{16}H_{26}O$: C, 82.0; H, 11.2. Found: C, 81.84; H, 11.27.

Condensation. From 35.2 g. (0.15 mole) of the nonyl-*o*-cresol, with 85 ml. (0.17 mole) of stock solution and 85 ml. of ethanol, the cooled reaction mixture (turbid in water) was treated with 100 ml. of hexane, then with 50 ml. of water, giving a lower inactive aqueous layer (discarded). The organic layer was extracted several times with methanol, in which the active is soluble, back-extracting with hexane. [From the hexane layers oily methylene*bis*(dialkylphenol) (?), 5.0 g., n_D^{25} 1.4995, was isolated.]

The alcoholic layers were dried and finally taken to dryness from isopropyl alcohol, leaving 60.0 g. of somewhat brittle gum: 98% conversion if pure.

Anal. Calc'd. for $C_{20}H_{34}NNaO_4S$: C, 58.9; H, 8.41; N, 3.44; S, 7.87. Found: C, 57.19; H, 8.53; N, 3.48; S, 7.56.

This is one of the best analyses obtained on a dialkylphenol derivative; low carbon contents were usual, and these need not be presented in detail. The data confirmed the essential compositions and emphasized the fact that one or two elements in agreement with theory did not prove purity.

Run 10. Solvent fractionations were also carried out on a few of the crystalline dialkylphenol types. In Run 10, Koppers "diamylphenol" was redistilled and the cut boiling at 113–117°C./0.3 mm., n_D^{25} 1.5046, condensed (0.20 mole) as usual with a 20% excess of stock solution. After cooling, filtering, drying, and desalting with isopropyl alcohol (enough water was added to the hot, isopropyl alcohol (250 ml.) solution to redissolve the active slurry, leaving insoluble, inactive salts), cooling gave a gel. The gel was partially redissolved by heating the suspension in 1 liter of isopropyl alcohol and adding 100 ml. of methanol. Hot filtration and washing with the same solvent mixture and vacuum oven-drying gave 23.6 g. (29% conv.) of white-caked solid.

The filtrates, after several days, were refiltered; the cake was washed and dried, giving 20.3 g. (25% conv.). Concentration and cooling of the filtrates gave only a trace of additional solids. Similar methods were used in the other reported cases; in Run 14 the "soluble" material was a gum, turbid in water. The turbidity was greatly reduced by methanol-hexane fractionation.

Dialkylphenols. These compounds with identical (possibly isomeric) alkyl groups were prepared by alkylation of phenol, using BF$_3$ catalysis and pure olefins, mainly at 80–90°. The product mixtures were fractionally distilled to remove contaminants such as mono- and trialkylphenols. The cuts were chosen for purity rather than maximum yields.

Acknowledgments

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