

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DAVIDSON COLLEGE]

## Surface Activity of the Sodium Sulfonates of Some Di-*n*-alkoxybenzenes. I. 1,4-Di-*n*-alkoxybenzenes

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Received August 29, 1956

A series of 1,4-di-*n*-alkoxybenzenes were prepared and sulfonated, and the sulfonates were identified by the titration of their *p*-toluidine salts. The surface tension of the Na-sulfonates was determined at 25° by means of a Du Noüy tensiometer.

In connection with an investigation of the relationship of position isomerism with surface activity a series of 1,4-di-*n*-alkoxybenzenes were prepared and sulfonated. The sulfonates were identified by the titration of their *p*-toluidine salts.<sup>1</sup>

Hartley has described the preparation of a number of di-*n*-alkoxybenzenes and their sulfonates.<sup>2</sup> In a second study he discussed their surface activity but did not treat of the 1,4-di-*n*-alkoxybenzene sulfonates.<sup>3</sup> The surface tension of solutions of the sodium sulfonates was determined at 25° by means of a Du Noüy tensiometer.

### EXPERIMENTAL

*The Di-n-alkoxybenzenes.* A series of these ethers from 1,4-dimethoxybenzene through 1,4-di-*n*-octoxybenzene was prepared by the Williamson reaction from Eastman Kodak 1,4-dihydroxybenzene and the appropriate alkyl halides obtained from Columbia Organic Chemicals Co. The recovery of the di-*n*-alkoxybenzenes from the reaction mixture was accomplished by adding water to dissolve the sodium bromide and extracting the mixture with petroleum ether. The petroleum ether extract was treated with 10% NaOH to remove any unreacted 1,4-dihydroxybenzene. The solvent was removed by distillation and the 1,4-di-*n*-alkoxybenzene recovered by crystallization from ether and ethanol. The seven known compounds recovered were of high purity with sharp melting points checking with those in the literature. Of this series, one member, 1,4-di-*n*-heptoxybenzene, m. p.<sup>4</sup> 57.6–58°, yield 27%, is new.

*Anal.* Calcd. for C<sub>20</sub>H<sub>34</sub>O<sub>2</sub>: C, 78.36; H, 11.19. Found: C, 78.27; H, 10.97.

*Sulfonation of the Di-n-alkoxybenzenes. (I–VIII).* The di-*n*-alkoxybenzene (0.1 mole) was dissolved in 250 ml. of CCl<sub>4</sub> and cooled to 0°. The solutions were stirred during the addition of 0.1 mole of ClSO<sub>3</sub>H from a dropping funnel. The addition being made at such a rate that the temperature did not rise above 5°. After 3 hr. of stirring the mixture was allowed to reach room temperature and neutralized with 0.1 mole Na<sub>2</sub>CO<sub>3</sub> solution. The aqueous layer was separated from the CCl<sub>4</sub> layer. In the case of the Na-salts of 1,4-dimethoxybenzene sulfonate (I), 1,4-diethoxybenzene sulfonate (II), 1,4-di-*n*-propoxybenzene sulfonate (III), and 1,4-di-*n*-butoxybenzene sulfonate (IV) the salts were recovered by evaporation of the aqueous layer and extraction of the solids with EtOH. The salts were crystallized from the EtOH, dried, and washed with ether.

The Na-salts of 1,4-di-*n*-pentoxybenzene sulfonate (V) and 1,4-di-*n*-hexoxybenzene sulfonate (VI) appeared in both layers. The aqueous layers were treated as in I–IV. The salts were crystallized from the CCl<sub>4</sub> layer, and recrystallized

from alcohol, dried, and washed with ether. The salts of 1,4-di-*n*-heptoxybenzene sulfonate (VII) and 1,4-di-*n*-octoxybenzene sulfonate (VIII) appeared almost exclusively in the CCl<sub>4</sub> layer and were recovered as were V and VI. The Na-sulfonates were identified by titration of the *p*-toluidine salts.<sup>1</sup> The yields obtained and the melting points of the *p*-toluidine salts are recorded in Table I.

TABLE I  
YIELDS OF NA-SULFONATES OF 1,4-DI-*n*-ALKOXYBENZENES AND MELTING POINTS OF *p*-TOLUIDINE SALTS

	Compound Na-Sulfonate of	Yield, %	M.P. of <i>p</i> - Toluidine Salt (Corr.)
I	1,4-Dimethoxybenzene	41.6	202 –203°
II	1,4-Diethoxybenzene	46.39	195 –195.6°
III	1,4-Di- <i>n</i> -propoxybenzene	30.00	172 –172.8°
IV	1,4-Di- <i>n</i> -butoxybenzene	76.4	170.5–171.6°
V	1,4-Di- <i>n</i> -pentoxybenzene	80.0	170 –171°
VI	1,4-Di- <i>n</i> -hexoxybenzene	79.1	166 –167°
VII	1,4-Di- <i>n</i> -heptoxybenzene	89.6	164 –165°
VIII	1,4-Di- <i>n</i> -octoxybenzene	35.0	160 –161°

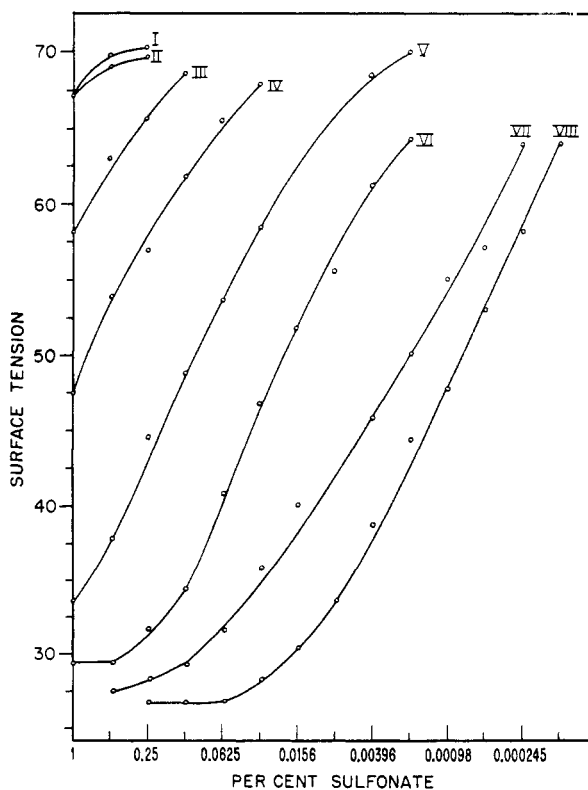


FIG. 1. THE SURFACE TENSION OF NA-SULFONATES OF 1,4-DI-*n*-ALKOXYBENZENES I–VIII AT 25° C.

- (1) L. F. Fieser, *J. Am. Chem. Soc.*, **51**, 2460, 2471 (1929).
- (2) G. S. Hartley, *J. Chem. Soc.*, 1828–34 (1939).
- (3) G. S. Hartley, *Trans. Faraday Soc.*, **37**, 130 (1941).
- (4) All melting points are corrected.

TABLE II  
SURFACE TENSION OF SOLUTIONS OF Na-SULFONATES OF 1,4-DI-*n*-ALKOXYBENZENES AT 25°

Concn., %	Compounds							
	I	II	III	IV	V	VI	VII	VIII
1.0	67.3	67.5	58.07	47.43	33.4	29.1	—	—
0.5	69.75	69.0	63.1	53.87	37.84	29.1	27.45	—
0.25	70.0	69.75	65.7	56.94	44.46	31.6	28.2	26.4
0.125			68.7	61.82	48.7	34.32	29.1	26.8
0.0625				65.45	53.6	40.72	31.4	26.8
0.0312				67.98	58.4	46.89	35.86	28.24
0.0156					<sup>a</sup>	51.8	40.3	30.4
0.0078					59.5	55.5	<sup>a</sup>	33.5
0.0039					68.7	61.08	45.9	38.8
0.0019					69.8	64.28	50.0	44.4
0.00093							55.0	47.9
0.00049							57.1	53.0
0.000245							64.0	58.4
0.000123								64.2

<sup>a</sup> Solution lost.

*Surface activity of the Na-sulfonates.* The surface tensions of aqueous solutions of I-VIII were determined at 25° using a Du Noüy tensiometer. The surface tension of the distilled H<sub>2</sub>O used in preparing the solutions was 71.42 dynes at 25°. In all cases except VII and VIII a 1% solution of the Na-sulfonate was used as initial concentration to be measured. In the cases of VII and VIII it was necessary to use initial concentrations of 0.5% and 0.25% on account of the lower solubility of these salts. After determining the surface tension of the initial solution it was diluted with an equal volume of water and the surface tension of the new solution determined. The process was continued until surface tension values obtained approached that for water.

The values obtained are recorded in Table II and are plotted in Figure 1.

*Acknowledgment.* This investigation was supported by grants from funds made available to Davidson College by E. I. du Pont de Nemours & Co., Inc., and The Monsanto Chemical Co. The author is indebted to the late Dr. R. W. Bost at whose suggestion the study was initiated.

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## Polysoaps. II. The Preparation of Vinyl Soaps<sup>1</sup>

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Received July 10, 1957

Three types of vinyl monomers, each containing a group capable of functioning as an emulsifying agent, have been prepared. An unequivocal synthesis of one of the intermediates, 10-phenylundecanoic acid, was accomplished.

In this publication we report for the first time the synthesis of vinyl monomers which also function as emulsifying agents. Although vinyl monomers which contain long chain alkyl groups are well known, there are no well defined vinyl monomers which could also be classified as good emulsifying agents. Such monomers may be called vinyl soaps. Their polymers and copolymers are thus

true polysoaps, a new type of polyelectrolyte. Of particular interest is the possibility of using vinyl soaps as the sole emulsifying agent in the emulsion polymerization of conventional vinyl monomers, with the objective of preparing a latex in which the emulsifying agent is chemically bound to the polymer. This will be reported in a future publication; the present study is concerned only with the preparation of the vinyl soaps, polymerization data being included only to demonstrate the nature of these compounds.

### DISCUSSION

From a structural viewpoint a vinyl soap would combine the functionalities of both a vinyl monomer and a soap; *i.e.*, an activated vinyl group attached to a salt of a long-chain carboxylic acid of

(1) For the first paper of this series, see S. K. Sinha, A. I. Medalia, and D. P. Harrington, *J. Am. Chem. Soc.*, **79**, 281 (1957). This work was supported by the General Latex and Chemical Corp., Cambridge, Mass.

(2) Abstracted from the thesis of H. H. Freedman, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School, Boston University. Present address, The Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.

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