The Role of the Cationic Group in Anionic Detergents

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It seems that sodium salt of alkyl sulfate has been extensively studied, while little data are known concerning organic salts of alkyl sulfate. It is therefore thought to be of interest to investigate the effect of the substitution of the cationic group attached to the hydrophilic portion of the detergent molecule. Such effcts should be studied both surface-chemically and from the viewpoint of bulk properties.

Materials used for those investigations were, as sulfate type, triethanolamine dodecyl sulfate (TDS), morpholine DS (MDS), pyridine DS (PDS), and sodium DS. As sulfonate type, triethanolamine alkyl benzene sulfonate (TABS) and sodium salt of the same sulfonate (SABS) were used.

Experimental

Materials.—All dodecyl sulfates were synthesized from dodecyl alcohol, chlorosulfonic acid and the corresponding base. The way of synthesis and the identification of product was given in detail previously[1].

Alkyl benzene, the raw material for the sulfonated detergent was the product of Oronite Chemical Co. and was redistilled at 130~136°C/3 mmHg. It was sulfonated with pure chlorosulfonic acid, at an equimolar ratio assuming the alkyl chain of the alkane to be mainly isododecyl, and neutralized either with aqueous sodium hydroxide or triethanolamine. The analysis of SABS showed that the amounts of unreacted alkane and inorganic material were less than 1.5%, respectively.

Measurements.—Monolayer experiments were carried out with the use of a Wilhelmy-type surface balance and surface tension was measured with DuNuoy's instrument. Foaming power was measured, at 40°C throughout, by Ross-Miles method[2,3], apparent viscosity was measured, at 30°C, with a modified Couette type rotational viscometer. Because of their extremely high solubility, the yield of TDS and PDS decreased considerably in the process of purification and we could not carry out whole-scale solubility measurements. Therfore, a Kraft point conventionally determined by dye color change[4] was adopted as a measure of solubility, since this method requires only a very small amount of the sample. It appeared that the Rhodamine 6G used for this purpose fortunately gave a clear color change at the K. P.

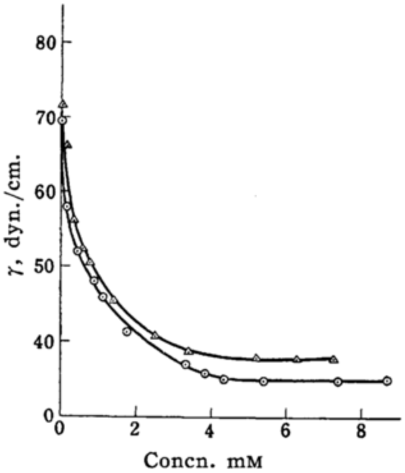

Fig. 1. Surface tension of organic DS.
—⊙— MDS 40°C
—△— TDS 33°C

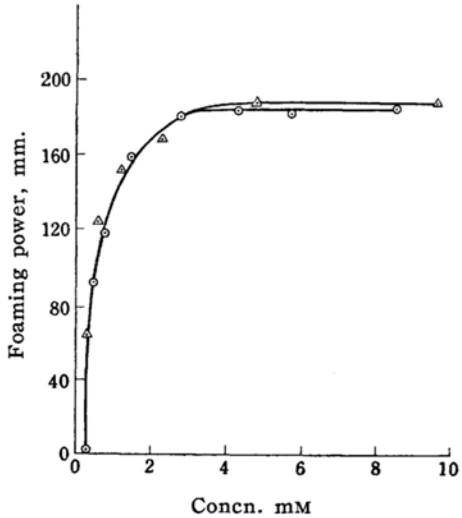

Fig. 2. Foaming power of TDS and MDS.
—⊙— MDS
—△— TDS 40°C

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[1] M. Kashiwagi, This Bulletin, **31**, 667 (1958).
[2] M. Kashiwagi, ibid., **29**, 193 (1957).
[3] M. Kashiwagi, ibid., **30**, 572 (1957).
[4] K. Ino, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 165 (1958).

Results

1) **Substitution of the Cationic Group in Sulfate Portion.**—(*A*) *Surface Chemical Properties.* — (*1*) *Surface area.* — Surface areas of MDS, TDS and PDS on the substrate of 25% ammonium sulfate are calculated from $F-A$ curve and a surface equation of their state[5] developed by Pethica, $F(A-A_0)=nkt$, where A_0 refers to the surface co-area of the hydrophilic group in the molecule and n is a constant. A_0 is thus calculated to be 34 Å^2/mol., identical for all three DS', between the surface areas of 70 Å^2/mol. and 40 Å^2/mol. and, at 40 Å^2/mol., changes to 17 Å^2/mol. which corresponds to the cross-sectional area of the hydrocarbon chain. Those values of A_o are in excellent agreement with those of SDS[5]. The reason for this coincidence is now ascribed to the shielding effect of ammonium ions fully present in bulk phase since the colloidal electrolyte of the detergent may be considered to be equally accessible to both ammonium and organic cations.

(*2*) *Surface tension.* — Surface tension vs. concentration curves of both TDS and MDS are shown in Fig. 1, from which values of CMC are determined to be 0.004 M for both detergents. The CMC value of SDS is known to be about 0.007 M[6]. This value (0.004 M) is the same in the order of magnitude, but somewhat smaller than that of SDS. This small discrepancy may be ascribed both to the relatively large size of the counter ion[7,8] and the greater ions degree of hydration of these ions[9].

(*3*) *Foaming power.*—Foaming power vs. concentration curves of TDS and MDS are shown in Fig. 2, from which values of CMC for both detergents can be determined[2] to be 0.004 M and 0.003 M respectively. These values of CMC can be considered to be in good agreement with the values from surface tension measurements, as appeared in Fig. 1. Anyway, those two salts of DS exhibit approximately the same degree of foaming power, and moreover this in turn proves to be nearly equal to the foaming power of 186 mm. shown by aqueous SDS at its CMC.

(*B*) *Bulk Properties.* — (*1*) *Solubility.* — Solubility values of organic salts of DS, except for MDS, are found to be much higher than those of SDS. Solutions of both TDS and PDS at 30% remainded perfectly transparent even at 0°C, while MDS alone has very small solubility at 0°C, evidently much less than its CMC (i. e., less than 0.15%). The kraft points (K. P.) of both TDS and PDS are found to be less than 0°C, whereas the K. P. of MDS is found to be 30°C, compared with 10°C of SDS[10]. Thus a striking difference in solubility by the nature of the cationic group is observed as estimated from K. P. data.

(*2*) *Viscosity.*—Viscosity values of TDS and SDS at 30°C are listed in Table I. It is clear that SDS exhibits much higher viscosity than organic DS.

TABLE I. VISCOSITY OF TDS AND SDS AT 30°C

	10%	20%	30%
TDS	1.5 c. poise	3	5
SDS	4.5	8.5	820

(**II**) **Substitution of the Cationic Group in Sulfonate Portion.**—Foaming power of TABS in a standard condition (0.25%, 40°C) is 193 mm., while that of SABS under the same conditions is found to 196 mm. in the Ross-Miles unit. Those values nearly equal each other. The relation is, however, quite different in solubility. TABS dissolves in the amount of 80%, at 0°C, while the solubility of SABS is found to be less than 10% at 20°C. Viscosity values at 30°C are 7 cp. at 30%, 2.5 cp. at 20%, and 1.4 cp. at 10% solutions for TABS, while the viscosity of SABS is found to be 5 cp. at 10% solution. Once again those data may be interpreted as an indication that the substitution of the cationic group in sulfonate portion does not virtually change surface chemical properties, but it does change the bulk properties.

Discussion

The results thus obtained are summarized in Table II. The value of CMC obtained for TDS and MDS, as they appeared in Table II, are in the same order but smaller than that of SDS. It has been shown that the value of CMC decreases when the counter ion becomes very large[7], or the degree of hydration of the counter ion decreases[8,9]. The

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[7] A. Cushman A. P. Brady and J. W. McBain, ibid., **3**, 425 (1948).

[8] K. Meguro and T. Kondo, private communications.

[9] K. Meguro et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1236 (1956).

[10] E. Hutchinson, *J. Phys. Chem.*, **58**, 1126 (1954).

second factor would be less effective, because CMC values of potassium, sodium and lithium salts of DS are fairly close (7~10 mM)[9].

According to Klevens, these differences may be due to minor differences in the degree of ionization of the micelles, for it has been observed that the presence in small amounts of unionized additives (unreacted alcohol for example) will markedly decrease the CMC, whereas the use of an ionized additive of an equivalent chain length and the same charge will result in little change[11]. This is true of uni-univalent electrolytes. As for a polyvalent electrolyte, valence of cation may follow the Schulz-Hardy rule in decreasing CMC[12].

TABLE II. PROPERTIES OF VARIOUS SALTS OF DODECYL SULFATE

Surface properties

	TDS	PDS	MDS	SDS
Surface area of hydrophilic group on 25% $(NH_4)_2SO_4$	34Å²/mol.	34	34	34
Foaming power (0.25%, 40°C)	188 mm.	—	184	186
CMC	4mM		3~4	7

Bulk properties

	TDS	PDS	MDS	SDS
Kraft P.	less than -5°C	less than 0°C	30°C	10°C
Estimated solubility grade	1	2	4	3
Viscosity	low	low	low	high

Summary

Various salts of dodecyl sulfate (DS) and alkylbenzene sulfonate have been investigated surface-chemically and from the viewpoint of their bulk properties. It was shown that these organic salts of DS occupy the same surface area as that of SDS, on the substrate of concentrated anmonium sulfate, independent of the nature of the cationic group attached to the sulfate anion. CMC values determined by two different methods (i. e., surface tension and foaming power) show practically the same value. These results are approximately in accord with the known principle that the number of carbon atoms in the molecule of the normal straight chain colloidal electrolyte of one particular class is the determining factor for the value of CMC, although a slight but definite shift in CMC value is observed with variation in substituting group. On the other hand, bulk properties such as viscosity and solubility are influenced remarkably by the substitution of cationic group in anionic detergents.

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11) H. B. Klevens, ibid., **14**, 742 (1946).

12) H. Lange, *Kolloid-Z.*, **121**, 16 (1951).