

THE CRITICAL MICELLE CONCENTRATION OF ETHER ALCOHOL SULFATES, $R(OC_2H_4)_iOSO_3Na^1$

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The critical micelle concentration (c.m.c.) of sodium hexadecyl and octadecyl ether alcohol sulfates ($R(OC_2H_4)_iOSO_3Na$, $i = 1, 2, 3, 4$) was measured by surface tension, dye titration and conductance methods. In moles per liter $\times 10,000$ the values were 2.1, 1.2, 0.7, 0.8 in the hexadecyl series and 1.9, 0.8, 0.5, 0.4 in the octadecyl series, respectively. Although solubility as measured by the Krafft point increased with the number of ethenoxy groups, the c.m.c. decreased; apparently as a result of the combined effects of increased hydrophilicity and greater chain length.

Sulfated ether alcohols are surface active agents of increasing importance for detergent and allied uses. In a previous report³ we have shown that sodium salts of sulfated ethenoxytated tallow alcohols with low ethenoxy content are considerably more soluble than the corresponding alcohol sulfates and have similar surface active properties. It seems desirable therefore to study the effect of ethenoxylation on fundamental solution properties such as critical micelle concentration (c.m.c.) for this class of compounds.

The commercial method for preparing ether alcohols, *i.e.*, the reaction of ethylene oxide with an appropriate fatty alcohol, results in a mixture, $R(OC_2H_4)_nOH$, where n is known only as an average value. This study is concerned with chemical individuals where n becomes i , or a specific integer, prepared through the Williamson synthesis from known purified starting materials.

Experimental

Ether Alcohol Sulfates.—Ether alcohols of known composition were prepared from the alkyl bromide and a glycol by a method described to us by Wrigley.⁴ The pure ether alcohols were sulfated in a manner similar to that described elsewhere.⁵ A 15% excess of chlorosulfonic acid was added

dropwise to a stirred solution of 0.1 mole of ether alcohol in 150 ml. of chloroform cooled in an ice-bath at 10–20°. When the addition was completed the reaction mixture was allowed to warm to room temperature and stirring was continued for an hour. After chilling again to 10°, 100 ml. of absolute methanol was added and the solution was neutralized with 18 *N*. sodium hydroxide. The product was crystallized and filtered from the reaction mixture, redissolved in hot absolute ethanol, insoluble inorganic salt was filtered from the hot solution and the product was recrystallized from the filtrate at room temperature. In some instances a second recrystallization from absolute alcohol was required. Carbon, hydrogen, sulfur⁶ and sodium analyses of the first three members of each series were found to be within 0.3% of the theoretical value. The compound containing four ethenoxy groups was somewhat more difficult to purify.

Surface Tension.—The duNoüy tensiometer was used to measure surface tension. Since little change was observed with temperature variation over a limited range, measurement was made at room temperature, $25 \pm 1^\circ$. Appropriate corrections⁷ were applied to the readings to obtain surface tension in dynes per centimeter. Figure 1 is a surface tension *versus* $\log C$ plot for the ether alcohol sulfates derived from hexadecanol and Fig. 2 is a similar plot for the ether alcohol sulfates derived from octadecanol. The solutions were allowed to age one hour prior to measurement and measurements were repeated until four identical values were obtained. Since Nutting and co-workers⁸ have shown that most of the change of surface tension with time, for sodium alkyl sulfates, occurs within 2 to 60 minutes, the values reported may be considered to be very nearly true equilibrium values.

Dye Titration.—Pinacyanole chloride was used as described by Corrin, Klévans and Harkins.⁹ Five ml. of a

(1) Presented at the Meeting in Miniature of the Central Pennsylvania Section, American Chemical Society, University Park, Pa., March 15, 1958.

(2) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(3) R. G. Bistline, Jr., A. J. Stirton, J. K. Weil and E. W. Maurer, *J. Am. Oil Chemists' Soc.*, **34**, 516 (1957).

(4) A. N. Wrigley, Ph. D. Dissertation, Temple University, 1958.

(5) J. K. Weil, A. J. Stirton and E. W. Maurer, *J. Am. Oil Chemists' Soc.*, **32**, 148 (1955).

(6) Microanalysis for C, H and S performed by Miss Laverne Scroggins.

(7) W. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.*, **52**, 1751 (1930).

(8) G. C. Nutting, F. A. Long and W. D. Harkins, *J. Am. Chem. Soc.*, **62**, 1496 (1940).

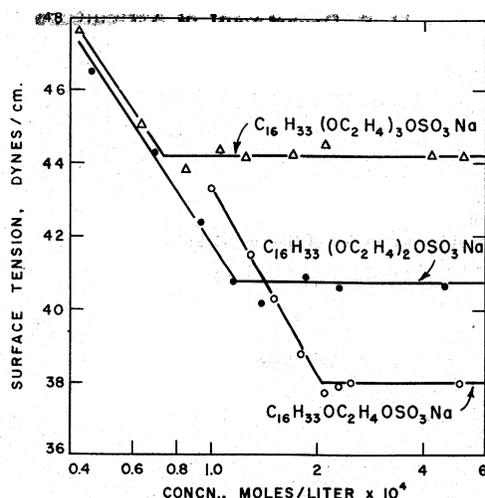


Fig. 1.—Surface tension versus logarithm of concentration in moles per liter for aqueous solutions of ether alcohol sulfates from hexadecanol.

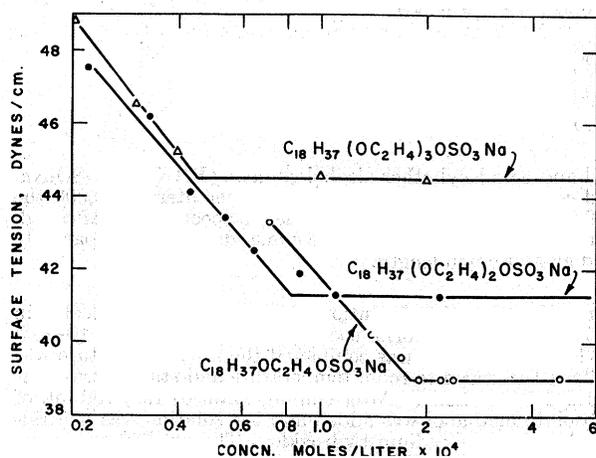


Fig. 2.—Surface tension versus logarithm of concentration in moles per liter for aqueous solutions of ether alcohol sulfates from octadecanol.

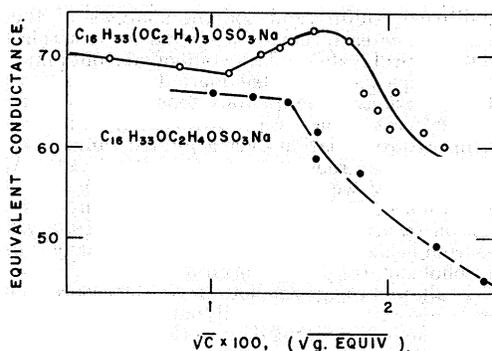


Fig. 3.—Variation of equivalent conductance with concentration of sodium hexadecyloxyethyl sulfate and sodium hexadecyloxyethoxyethoxyethyl sulfate at $25.00 \pm 0.05^\circ$.

solution of 10^{-5} molar pinacyanole containing about twice the critical concentration of surface active agent was titrated with a solution containing only 10^{-5} molar pinacyanole. The c.m.c. was calculated from the titration required to obtain a visible color change from blue to purple.

Conductance.—A Leeds and Northrup conductivity

(9) M. L. Corrin, H. B. Klevens and W. D. Harkins, *J. Chem. Phys.*, **14**, 480 (1946).

bridge operating at 1,000 cycles was used to measure conductance at $25 \pm 0.05^\circ$. A Jones cell, Leeds and Northrup type A,¹⁰ having a cell constant of 0.050 ± 0.001 was used for all measurements. Surfactants were dissolved in water which had been passed through a column of Amberlite MB-1¹⁰ to reduce specific conductance to $0.53-0.56 \times 10^{-6}$ mho, and values were corrected by subtracting the solvent conductance. Resistances above 10,000 ohms were determined by connecting a 10,000 resistance in parallel with the unknown. Figure 3 shows the conductance curve for sodium hexadecyloxyethyl sulfate [$C_{16}H_{33}OC_2H_4OSO_3Na$] and sodium hexadecyloxyethoxyethoxyethyl sulfate [$C_{16}H_{33}(OC_2H_4)_3OSO_3Na$].

Krafft Point.—The Krafft point, which is significant with respect to synthetic detergents as well as soaps, was used as a measure of the comparative solubility of the eight compounds. It was determined as the temperature at which a uniform 1% dispersion changed sharply to a clear solution on gradual heating.¹¹ The cloud point, or the temperature at which a clear 1% solution became turbid on gradual cooling, is less reproducible, but it is more important in defining the lowest temperature which may be used in the c.m.c. measurements.

Discussion of Results

Table I lists the c.m.c. for the ether alcohol sulfates at 25° , the Krafft points and cloud points and the c.m.c. for sodium hexadecyl sulfate at 30° . Since the Krafft points of sodium hexadecyl sulfate and sodium octadecyl sulfate are above room temperature we have no comparable c.m.c. for sodium octadecyl sulfate; and it was necessary to base the value for sodium hexadecyl sulfate on surface tension measurements at 30° . The agreement with Powney and Addison¹² may be regarded as acceptable when allowances are made for differences in temperature and for differences in the minimum observed. Generally good agreement is apparent in comparing the c.m.c. determined by dye titration, conductance and surface tension methods. The methods showed least agreement in the case of sodium octadecyloxyethyl sulfate, probably because the temperature of measurement was below the cloud point and the clarity of the detergent solution used for dye titration could not be assured.

The conductance curves of Fig. 3 show a considerable difference between the conventional shape for sodium hexadecyloxyethyl sulfate and that for sodium hexadecyloxyethoxyethoxyethyl sulfate. McDowell and Kraus¹³ have shown increases above the c.m.c. for cationic surfactants with bulky groups at the hydrophilic end which are the same as that shown here by the compound with three ethenoxy groups. Thus we may determine the c.m.c. of the more highly ethenoxyated members of the series from the point where conductance increases rather than from the usual decrease. The conductance curve for sodium hexadecyloxyethoxyethyl sulfate, [$C_{16}H_{33}(OC_2H_4)_2OSO_3Na$] lies between the two curves shown on Fig. 3 and shows a smaller downward inflection at the c.m.c.

On first consideration it might be expected that ether alcohol sulfates with higher ethenoxy content would have higher c.m.c. values as a result of an

(10) Reference to a manufactured product does not constitute recommendation by the U. S. Dept. of Agriculture over similar products not mentioned.

(11) M. Démarcq and D. Dervichian, *Bull. soc. chim.*, **12**, 939 (1945).

(12) J. Powney and C. C. Addison, *Trans. Faraday Soc.*, **33**, 1243 (1937).

(13) M. J. McDowell and C. A. Kraus, *J. Am. Chem. Soc.*, **73**, 2173 (1951).

TABLE I
SOLUTION PROPERTIES OF ETHER ALCOHOL SULFATES

Compound	C.m.c., moles/l., 25°, × 10,000 Conductance method	Surface tension method	Dye titration method	Kraft point 1% concn.	Cloud point, 1% concn.
$C_{16}H_{33}OSO_3Na$		4 ^a		45°	30°
$C_{16}H_{33}OC_2H_4OSO_3Na$	2.34	2.1	2.2	36°	12°
$C_{16}H_{33}(OC_2H_4)_2OSO_3Na$	1.34	1.2	1.4	24°	8°
$C_{16}H_{33}(OC_2H_4)_3OSO_3Na$	1.23	0.7	1.0	19°	0°
$C_{16}H_{33}(OC_2H_4)_4OSO_3Na$		0.8	1.0		<0°
$C_{18}H_{37}OC_2H_4OSO_3Na$		1.9	1.1	46°	30°
$C_{18}H_{37}(OC_2H_4)_2OSO_3Na$		0.8	0.7	40°	19°
$C_{18}H_{37}(OC_2H_4)_3OSO_3Na$		0.5	0.5	32°	12°
$C_{18}H_{37}(OC_2H_4)_4OSO_3Na$		0.4	0.4	18°	12°

^a Measurements at 30°.

increase in the hydrophilic nature of the compound. It was rather surprising then to find that as ethenoxylation was increased, the first three members of both ether alcohol sulfate series showed a small but definite decrease in c.m.c.

Klevens¹⁴ has shown that the entire chain length rather than the length of the hydrophobic portion determines the c.m.c. of common anionic detergents; *e.g.*, "thus a C_{13} fatty acid, a C_{12} sulfonate, and a C_{11} sulfate all have c.m.c. values in the same range." Specifically the addition of a hydrophilic oxygen atom between a carbon atom and a sulfur atom of an alkyl sulfonate does not cause an increase but rather a decrease in c.m.c., similar to that produced by a methylene group in the same position. If this relationship would hold for the ether alcohol sulfates, however, a much greater decrease in c.m.c. with ethenoxylation would be shown, *i.e.*, a decrease by a factor of eight for each ethylene oxide unit.

It seems apparent that the end result in this case is a combination of two or more effects which result in slight decreases in critical micelle concentration with increased ethenoxy content. Since generally low values have been recorded for the c.m.c. of non-ionic type surfactants^{15,16} this decrease may be explained by a decrease in anionic properties with

a corresponding increase in non-ionic properties as ethenoxy content is increased. Further evidence for this transition toward non-ionic properties is found in the abnormal shape of the conductance curve of the more highly ethenoxyated materials above the c.m.c. which indicates an increase in bulk at the hydrophilic end.

The c.m.c. decreases with increase in the number of ethenoxy groups from 0 to 1 to 2 to 3, but the difference in c.m.c. between compounds with 3 and 4 groups is in doubt. Examination of higher members of the series would be required to establish the trend; however, purification difficulties increase with the number of ethenoxy groups.

It is interesting to observe, from Figs. 1 and 2, that surface tension values below the c.m.c. for either the hexadecyl or octadecyl series, fall on a common line for the series, within experimental error. In each case the c.m.c. is determined by the intersection of a common line with the horizontal line of surface tension values. Thus members of either series with higher surface tension at the higher concentration have lower c.m.c.

Preliminary observations by the dye titration method showed that sulfated ethenoxyated tallow alcohols $R(OC_2H_4)_nOSO_3Na^3$ with an average value of about $n = 2$ had nearly the same c.m.c. as that for the corresponding pure compound, $i = 2$.

Acknowledgment.—The authors are indebted to A. N. Wrigley for advice and assistance in preparing the ether alcohols.

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(15) M. Cohen, *Mem. services, chim. état*, **36**, 93 (1951).

(16) L. Hsiao, H. N. Dunning and P. B. Lorenz, *THIS JOURNAL*, **60**, 657 (1956).