

Synthesis and surface active properties of long chain ether alcohol sulfates
 $R(OCH_2CHR')_iOSO_3Na^*$

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RÉSUMÉ

Des sulfates purifiés d'éther-alcool $R(OCH_2CHR')_iOSO_3Na$ ont été préparés par sulfatation des produits isolés de réaction d'oxydes d'éthylène, de propylène et de 1,2-butylène avec des alcools normaux primaires contenant 12, 14, 16 et 18 atomes de C. L'effect de la structure sur la concentration critique de micelles (CMC), le point de Krafft, la tension superficielle et le pouvoir de dispersion des savons calcaires a été examiné.

L'effet des groupes «oxyalkyl» de réduire la CMC et d'augmenter le point de Krafft est exprimé en fonction d'un nombre équivalent de groupes méthylènes.

ZUSAMMENFASSUNG

Keine Fettalkoholäthersulfate $R(OCH_2CHR')_iOSO_3Na$ wurden hergestellt durch Sulfatation von isolierten Reaktionsprodukten aus Äthylen-, Propylen- und 1,2-Butylenoxyd mit normalen primären Alkoholen mit 12, 14, 16 und 18 C. Der Einfluss der Konstitution auf die kritische Mizellkonzentration (CMC), auf Krafftpunkt, Oberflächenspannung und Kalkseifendispergiervermögen wurde gegrüft.

Der Einfluss der Oxalkylgruppen auf Verringerung der CMC und Erhöhung des Krafftpunktes wurde als Funktion einer äquivalenten Anzahl von Methylengruppen dargestellt.

SUMMARY

Purified ether alcohol sulfates $R(OCH_2CHR')_iOSO_3Na$ were prepared by the sulfation of the separated reaction products of ethylene, propylene and 1,2-butylene oxides with 12, 14, 16 and 18 C normal primary alcohols. The effect of structure on critical micelle concentration (CMC), Krafft point, surface tension and lime soap dispersing power was investigated.

The effect of oxyalkyl groups in reducing CMC and increasing Krafft point was expressed in terms of an equivalent number of methylene groups.

Introduction

Ether alcohol sulfates have been studied as a means of improving the solubility of saturated tallow alcohol sulfates (^{1, 2}). The addition of one or two oxyethyl groups to the higher alcohols results in increased solubility and retention of the good detergency characteristics of the sulfate, but further additions reduce detergency.

When propylene oxide or butylene oxide is used instead of ethylene oxide in the alkali-catalyzed reaction with a long chain alcohol, the ether alcohols formed are the less reactive secondary alcohols (³). The distribution constant, or ratio of ether alcohol reactivity to parent alcohol reactivity is 0.3 for the butylene oxide reaction, and 0.5 for propylene oxide compared to about 2 for the ethylene oxide reaction (⁴). The addition of one mole of epoxide to fatty alcohol gives a 50 % yield of the first derivative with propylene oxide and 60 % with butylene oxide, but first derivative yields from oxyethylation never exceed 30 %. Side chains resulting from propylene oxide and butylene oxide oxyalkylations have a further advantage because they lower the Krafft point of aqueous solutions. Sulfated oxyalkylation reaction mixtures which have a major portion of first derivative have surface active properties very similar to the pure first derivative ether alcohol sulfate.

The ether alcohol sulfates from ethylene oxide have been the subject of interesting structure-property studies (^{5, 6}). Using pure individual ether alcohol sulfates based on the reactions of ethylene oxide, propylene oxide, and 1,2-butylene oxide with dodecanol, tetradecanol, hexadecanol, and octadecanol, it is possible to make a systematic study of the effect of further structural variations on surface active and related properties.

Experimental

Materials

Ether alcohols were prepared by previously described methods (³). An equivalent amount of epoxide was added to the appropriate purified fatty alcohol containing 0.5 % potassium hydroxide while stirring at 180°. After neutralization of the catalyst, individual ether alcohols were distilled from the reaction mixture and redistilled to give products found to be 97-99 % pure by vapor phase chromatographic analysis. Sulfations were carried out in cold carbon tetrachloride solutions, using 10-20 % excess of chlorosulfonic acid. The sulfates were neutralized with 18 N sodium hydroxide and purified by two crystallizations from ethanol. Carbon, hydrogen, sodium and sulfur analyses agreed with theoretical values within experimental error.

Physical measurements and evaluation

A more detailed description of foam and detergency values may be found elsewhere (^{2, 3}). Critical micelle concentrations were determined by a dilution titration in the presence of 10^{-5} molar pinacyanole chloride. Values for CMC were confirmed by surface tension curves for a substantial portion of the compounds. Krafft point was taken as the temperature at which a 1 % solution becomes clear on gradual heating.

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Immediately after chilling to effect a slight turbidity. Lime soap dispersing power was determined by the method of Borghetty and Bergman (9). Surface tensions measurements were made with the DuNoüy tensiometer.

Results and Discussion

The critical micelle concentration values for this group of ether alcohol sulfates and alcohol sulfates are listed in Table 1. The insertion of an oxyalkyl group between the hydrophobe and the ionic head of an alkyl sulfate might be expected either to reduce the CMC because the total chain has been lengthened (7), or to raise the CMC because oxyalkyl groups tend to contribute hydrophilic nature to the surfactant. We have found that oxyethyl groups (8), and to a greater extent oxypropyl and oxybutyl groups (3), reduce the critical micelle concentration but these reductions are less than might be expected from a consideration of their chain length alone.

Although a quantitative treatment of these effects is difficult we shall attempt to relate the net effect to changes in the hydrophobic chain.

The logarithm of the critical micelle concentration has been plotted against length of the hydrophobic chain for each of the ether alcohol sulfate series. Figure 1 gives examples of the plots showing that the slopes of all of the lines are parallel, following the relationship $\log \text{cmc} = A - BN$ (7). By measuring the horizontal distance between curves (dotted line) one can compare the effect of the alkyl chain and the oxyalkyl chain in lowering the critical micelle concentration.

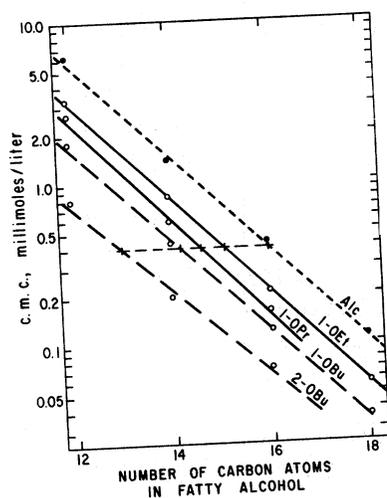


Fig. 1. Logarithm of cmc vs. number of C atoms in fatty alcohol for Na alkyl sulfates and related ether alcohol sulfates.

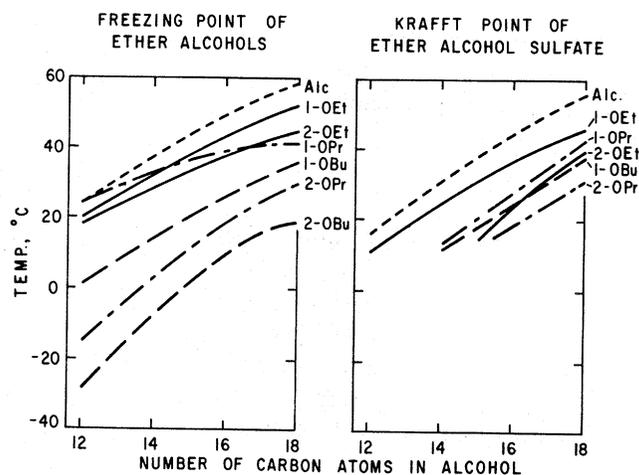


Fig. 2. Freezing point of ether alcohols and Krafft point of ether alcohol sulfates vs. number of C atoms in fatty alcohol.

Methylene group equivalent

Oxyalkyl Group	One Group	Two Groups
—OCH ₂ CH ₂ —	0.9	1.4
—OCH ₂ CH(CH ₃)—	1.4	2.2
—OCH ₂ CH(C ₂ H ₅)—	1.8	3.0

It is interesting to note that successive additions of oxyalkyl groups give less lowering of CMC than the first. Tokiwa (5) showed that affinity of the oxyalkyl groups for water increases as the oxyalkyl groups are removed from the competition of the sulfate group. Thus it might be expected that the oxyalkyl groups further removed from the sulfate would be more hydrophilic and hence lower the critical micelle concentration to a lesser extent.

Krafft (10) found that a relationship exists between the melting point of a fatty acid and the cloud point for solutions of the sodium soap. By measuring the clarification temperature, Demarcq and Dervichian (11) found an even closer correspondence. A survey of the melting points of the ether alcohol sulfates recorded in Table 1 shows no particular relationship to the Krafft point for 1% aqueous solutions. Melting of the sulfates appear to fall into groups determined by their oxyalkyl substitution: 177-195° for alcohol sulfates, 123-166° for monoxyethylated compounds, 116-136° for dioxyethylated compounds, 131-142° for monoxypropylated compounds, 69-88° for monoxybutylated compounds, etc., with no sharp melting point for any of the compounds.

As in the case of the fatty acid-soap relationship these compounds show a correspondence between the freezing points of the ether alcohols and the Krafft point of the ether alcohol sulfate solutions. Figure 2 shows plots of the freezing points of ether al-

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TABLA

Structure R(OCH ₂ CHR') _i OH		Ether Alcohol Sulfate, R(OCH ₂ CHR') _i OSO ₃ Na					
R	(OCH ₂ CHR') _i	Freezing Point of Alcohol, °C	Melting Point, °C	Krafft Point, °C	Lime Soap Dispersing Power, %	Critical Micelle Concentration millimoles/l	Surface Tension dynes/cm, 1% Solution
C ₁₂ H ₂₅	None	24	190-95	16	30	6.32	49 ^c
C ₁₂ H ₂₅	OC ₂ H ₄	20	143-146	11	7	3.31	36
C ₁₂ H ₂₅	(OC ₂ H ₄) ₂	19	126-136	< 0	5	2.58	40
C ₁₂ H ₂₅	OCH ₂ CH(CH ₃)	24	137-142	< 0	14	2.69	—
C ₁₂ H ₂₅	[OCH ₂ CH(CH ₃) ₂	-15	87-93	< 0	6	1.54	—
C ₁₂ H ₂₅	OCH ₂ CH(C ₂ H ₅)	1	77-82	< 0	10	1.80	—
C ₁₂ H ₂₅	[OCH ₂ CH(C ₂ H ₅) ₂	-28	liq.	< 0	10	0.80	—
C ₁₄ H ₂₉	None	38	182-183	30	19	1.39	36
C ₁₄ H ₂₉	OC ₂ H ₄	32	146-150	25	7	0.85	38
C ₁₄ H ₂₉	(OC ₂ H ₄) ₂	29	130-134	< 0	5	0.68	40
C ₁₄ H ₂₉	OCH ₂ CH(CH ₃)	33	139-140	14	8	0.58	—
C ₁₄ H ₂₉	[OCH ₂ CH(CH ₃) ₂	3	82-87	< 0	9	0.36	—
C ₁₄ H ₂₉	OCH ₂ CH(C ₂ H ₅)	14	74-76	13	9	0.43	39
C ₁₄ H ₂₉	[OCH ₂ CH(C ₂ H ₅) ₂	-8	liq.	< 0	9	0.20	36
C ₁₆ H ₃₃	None	49	186-190	45	—	0.42	35 ^a
C ₁₆ H ₃₃	OC ₂ H ₄	43	161-166	36	3	0.22	38
C ₁₆ H ₃₃	(OC ₂ H ₄) ₂	37	116-119	24	3	0.14	41
C ₁₆ H ₃₃	OCH ₂ CH(CH ₃)	39	131-133	27	8	0.16	37
C ₁₆ H ₃₃	[OCH ₂ CH(CH ₃) ₂	19	81-84	19	7	0.076	39
C ₁₆ H ₃₃	OCH ₂ CH(C ₂ H ₅)	26	84-88	23	9	0.12	37
C ₁₆ H ₃₃	[OCH ₂ CH(C ₂ H ₅) ₂	10	liq.	21	8	0.061	38
C ₁₈ H ₃₇	None	58	177-178	56	—	0.11	41 ^a
C ₁₈ H ₃₇	OC ₂ H ₄	52	123-125	46	9	0.056	39 ^a
C ₁₈ H ₃₇	(OC ₂ H ₄) ₂	45	119-121	40	7	0.040	41
C ₁₈ H ₃₇	OCH ₂ CH(CH ₃)	41	134-137	43	8	0.114	35 ^a
C ₁₈ H ₃₇	[OCH ₂ CH(CH ₃) ₂	30	80-82	31	7	0.045	39
C ₁₈ H ₃₇	OCH ₂ CH(C ₂ H ₅)	36	69-73	38	10	0.035	39
C ₁₈ H ₃₇	[OCH ₂ CH(C ₂ H ₅) ₂	19	35	24	11	0.035	35

a. Temperature at which 1% solution becomes clear on gradual heating.

b. Percent agent required to maintain 1% calcium oleate in suspension.

c. Concentration below the cmc.

d. Run on a supercooled solution.

cohols and Krafft points of ether alcohol sulfates. The monoxyethylated series show the greatest correspondence, freezing points of the ether alcohols being 6-9° higher than the Krafft point. Fatty alcohols melted 2 to 8° above the Krafft points of their sulfate solutions. Although there is a general relationship between Krafft point and freezing point of the ether alcohols, variations in slope of the curves result in a changing increment between the values.

Measurement of the horizontal increment between the curves shows that addition of one oxyethyl group lowers the Krafft point to the same extent as a reduction in 0.7 to 1.8 methylene groups. Other Krafft point reductions are 2.4 methylene group equivalents for one oxypropyl group, 3.0 for one oxybutyl group, 2.2 to 2.7 for two oxyethyl groups and 3.1 to 3.6 for two oxypropyl groups.

The effect of oxyalkylation on surface tension may also be observed from the data on Table 1. Each type of oxyalkyl insertion is responsible for a slight increase in surface tension and in most cases additional oxyalkyl substitution gives a further slight increase.

Nearly all of the ether alcohol sulfates are good lime soap dispersing agents. The first oxyalkyl substitution shows the greatest increase in lime soap dispersing properties with further increase sometimes resulting from additional substitution. Best lime soap dispersing agents are those based on hexadecanol.

References

- WRIGLEY, A.N.; STIRTON, A.J. and HOWARD, Jr., EDGAR.: *Higher Alkyl Monoethers of Mono- to Tetraethylene Glycol*. J. Org. Chem. 25, 439 (1960).
- BISTLINE, R.G., Jr.; STIRTON, A.J.; WEIL, J.K. and MAURER, E.W.: *Synthetic Detergents from Animal Fats. X. Sulfated Ethenoxylated Tallow Alcohols*. J. Am. Oil Chemists' Soc. 34, 516 (1957).
- WEIL, J.K.; STIRTON, A.J. and NÚÑEZ-PONZOA, M.V.: *Ether Alcohol Sulfates. The Effect of Oxypropylation and Oxybutylation on Surface Active Properties*. J. Am. Oil Chemists' Soc. 43, 603 (1966).
- WEIL, J.K.; STIRTON, A.J. and LEARDI, E.B.: *Ether Alcohol Sulfates from Oleyl Alcohol*. J. Am. Oil Chemists' Soc. 44, 522 (1967).
- TOKIWA, F. and OHKI, K.: *Micellar Properties of a Series of Sodium Dodecylpolyoxyethylene Sulfates from Hydrodynamic Data*. J. Phys. Chem. 71, 1343 (1967).
- GOHLKE, F.J. and BERGENHAUSEN, H.: *Alkyläthersulfat, ein ideales Tensid*. Seifen-Öle-Fette-Wachse 93, 519 (1967).
- KLEVENS, H.B.: *Structure and Aggregation in Dilute Solutions of Surface Active Agents*. J. Am. Oil Chemists' Soc. 30, 74 (1953).
- WEIL, J.K.; BISTLINE, R.G., Jr. and STIRTON, A.J.: *The Critical Micelle Concentration of Ether Alcohol Sulfates, R(OC₂H₅)₁OSO₃Na*. J. Phys. Chem. 62, 1083 (1958).
- BORGHETTI, H.C. and BERGMAN, C.A.: *Synthetic Detergents in the Soap Industry*. J. Am. Oil Chemists' Soc. 27, 88 (1950).
- KRAFFT, F.: *Über die Krystallisationsbedingungen colloidaler Salzlösungen*. Ber. 32, 1596 (1899).
- DEMARCO, M. and DERVICHIAN, D.: *Détermination des températures de clarification des solutions de savons de Li, Na, K, Rb, Cs*. Bull. Soc. Chim. 12, 939 (1945).

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DISCUSSION

Question by E.S. PATTISON:

How does the biodegradability of these ether alcohol sulfates compare with the biodegradability of the corresponding alcohols?

Answer:

Ether alcohol sulfate was found to have about the same biodegradability as alcohol sulfate when the river water die-away test was used (*J. Am. Oil Chemists' Soc.* **41**, 355-358, 1964). Using different conditions for a metabolism study (*Applied Microbiology* **16**, 48-52, 1968), the ether alcohol sulfates were not as quickly digested as the alcohol sulfates but were digested at least as rapidly as the majority of straight chain sulfonates tested.

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Question by M. MATELL:

According to fig 2 in the preprint 1-OPr derivative seems to behave a little different as to its freezing point's dependence on C-number in the alcohol. Have you any explanation to this?

Answer:

There is no explanation that we can give in answer to Dr Matell's question. Freezing point curves do not follow any relationship which can be described mathematically.