A Study of the Surface Activity of Tertiary Alcohol Sulfates

T. ZIMAITY, A. SAMMOUR and E. AFSAH,
Chemical Department, Ministry of Industry, Cairo, United Arab Republic

Abstract

A number of tertiary alcohols were prepared by the action of a series of Grignard reagents on ethyl oleate. The tertiary alcohols were converted to alkyl sulfates by reaction with sodium chlorosulfonate. The surface active properties of the prepared sodium alkyl sulfates were studied in relation to the length of the branched chain and the bulkiness of the charged head of the surfactants.

Introduction

Sodium alkyl sulfates of primary and secondary alcohols have been studied extensively as surface active agents. It has been stated that higher tertiary alcohols suitable for sulfation to surface active agents have been made by treating a fatty acid ester, such as ethyl oleate, or a glyceride, such as palm oil, with a Grignard reagent (1). However, no data or chemical studies have been given because the original source of this work was a British patent.

In the present work, the long chain tertiary alcohol sulfates were studied as surface active agents. For this purpose, a number of tertiary alcohols corresponding to oleic acid were synthesised by the action of Grignard reagents on ethyl oleate. They have the general formula: $CH_3(CH_2)_7CH{=}CH(CH_2)_7CR_2OH$, where R = CH_3 (I), C_2H_5 (II), n-C_3H_7 (III), $CH(CH_3)_2$ (IV), n-C_4H_9 (V), $C(CH_3)_3$ (VI), phenyl (VII) and benzyl (VIII) radicals. The products were obtained in high yields and are listed in Table I.

The alcohols obtained were converted into the corresponding sodium alkylsulfate, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CR_2OSO_3Na$, by the action of sodium chlorosulfonate (2–4), to avoid the attack on the double bond or the formation of olefinic hydrocarbons when sulfuric acid or chlorosulfonic acid is used or both. The products obtained are listed in Table II.

The surface activity of the sodium alkylsulfates (IX-XIV) were studied and compared with the primary oleyl alcohol sulfate, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OSO_3Na$.

Experimental Procedures

Preparation of Unsaturated Tertiary Alcohols Corresponding to Oleic Acid From Ethyl Oleate

A series of Grignard reagents were prepared, using, in each case, 0.34 g magnesium and 0.34 mole of each of the following alkyl halides in 100 ml dry ether: CH_3I, C_2H_5I, n-C_3H_7I, $(CH_3)_2CHBr$, n-C_4H_9I, $(CH_3)_3C$ Cl, C_6H_5Br, and $C_6H_5CH_2Cl$. A solution of 52.76 g (0.17 mole) ethyl oleate in 200 ml dry ether was added gradually. The reaction was completed by boiling under reflux for 2 hr, then cooled and poured with stirring into a mixture of 50 g ice and 100 ml 4 N sulfuric acid. The ether layer was separated, washed with water, 5% sodium bicarbonate solution, and finally with water. Then it was dried over anhydrous sodium sulfate. The products were obtained by evaporating ether under reduced pressure.

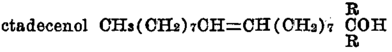
Sulfation

Sulfation was carried out using sodium chlorosulfonate prepared by the reaction of sodium chloride and chlorosulfonic acid in equimolecular amounts (3,4). Five grams of sodium chlorosulfonate were added in small amounts with stirring to the solution of the tertiary alcohol (10 g) in 20 ml cold carbon tetrachloride, and the temperature was not allowed to exceed 25 C. The mixture was diluted with cold ethanol and neutralized with sodium hydroxide solution. Inorganic impurities were removed by filtration and the organic unreacted materials were removed by repeated extraction with petroleum ether. The pure sodium alkyl sulfate was kept as an aqueous solution, as it has been found to be highly hygroscopic. The solution of the product was completed to a known volume and checked for the exact concentration by evaporation to dryness of a known volume. The products were analysed for sodium and sulfur and the results are shown in Table II.

The sulfation products of compounds VII and VIII gave unreliable values for sodium and sulfur. Therefore, they were excluded from our study on surface activity.

TABLE I

1,1-Dialkyloctadecenol

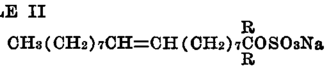


$CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{R}{\underset{R}{C}}OH$

Compound	R	bp C/mm Hg	Refractive index, nD20 C	Formulas	Analyses Found	Analyses Required
I	CH_3	168–70/2	1.4596	$C_{30}H_{40}O$	C,80.90 H,13.51	81.01 13.60
II	C_2H_5	208–10/2	1.4623	$C_{22}H_{44}O$	C,81.50 H,13.40	81.41 13.66
III	C_3H_7(n)	205–8/2	1.4629	$C_{24}H_{48}O$	C,81.34 H,13.50	81.74 13.72
IV	C_3H_7 (iso)	180–2/1.5	1.4543	$C_{24}H_{48}O$	C,82.50 H,13.42	81.74 13.72
V	C_4H_9(n)	230–6/3	1.4635	$C_{26}H_{52}O$	C,82.50 H,14.20	82.03 13.77
VI	C_4H_9 (tertiary)	220–5/4	1.4605	$C_{26}H_{52}O$	C,81.96 H,13.82	82.03 13.77
VII	C_6H_5	236–8/1	1.5359	$C_{30}H_{44}O$	C,85.60 H,10.50	85.65 10.54
VIII	$CH_2C_6H_5$	280–2/2	1.5201	$C_{32}H_{48}O$	C,77.69 H, 9.64	77.37 9.74

TABLE II

Sodium 1,1-dialkyloctadecenylsulfate



$CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{R}{\underset{R}{C}}OSO_3Na$

Compound	R	Per cent yield	Formula	Per cent sodium		Per cent SO_3	
				Found	Required	Found	Required
IX	CH_3	80	$C_{20}H_{40}SO_4Na$	6.00	5.77	20.00	20.10
X	C_2H_5	80	$C_{22}H_{44}SO_4Na$	5.24	5.39	18.69	18.77
XI	C_3H_7(n)	80	$C_{24}H_{48}SO_4Na$	4.90	5.06	17.61	17.62
XII	C_3H_7(iso)	60	$C_{24}H_{48}SO_4Na$	5.00	5.06	17.59	17.62
XIII	C_4H_9(n)	80	$C_{26}H_{52}SO_4Na$	4.58	4.77	16.56	16.59
XIV	C_4H_9(tertiary)	60	$C_{26}H_{52}SO_4Na$	4.62	4.77	16.58	16.59

Surface Active Properties

Surface activity and related properties are shown in Table III. Critical micelle concentration (cmc) was determined by plotting log concentration in moles per liter against the surface tension as dynes per centimeter (5), foam height by the Ross-Miles test (6), calcium stability by a modified Hart method (7). Wetting properties were measured by Draves Clarkson test (8) using 5 g cotton skein and a 1.5 g hook. Detergency was measured as the increase in reflectance (ΔR), after washing two 3 × 4 in. swatches of standard soiled cotton cloth in 200 ml 0.25% detergent solution, in the wash wheel worked at 40 cycles/min at 60 C for 20 min.

Discussion

The values for Krafft point show that the compounds are completely soluble in water.

Sodium tertiary alcohol sulfates have higher values of cmc than the corresponding sodium primary alcohol sulfate (Table III). This is in agreement with the results of other investigators who showed that cmc increases with branching on the hydrophobic chain (11,12). However, there is only a slight difference between the values of our compounds. The three compounds X, XII and XIV, could be considered as derived from compound IX, by substitution of the hydrogen atoms of the two branched methyl groups with CH_3 groups, so the bulk of the charged head is increased. The four compounds give the same cmc value. Klevens (13) shows that values of cmc are not changed by substitution near the hydrophilic head, with one, two or three groups, even as large as hydroxyethyl in place of amine hydrogen in cationic surfactants. He shows that the increased bulkiness of the charged head, caused by the introduction of these groups, has a disruption effect on the micelle which negates the influence of the branched chain. Since the cmc depends on chain length, all the compounds were expected to give nearly the same values and this agrees with the results obtained.

The wetting time determined according to Draves (8) gave quite duplicable results within limited sinking time ranges. Below 5 sec, the timing is necessarily inaccurate; and above 3 min, results are difficult to duplicate. Results show that wetting time decreases with increasing concentration. A maximum wetting time of 180 sec was attained at the concentration of 0.0625% for all compounds. It was observed that at any concentration, the increase in wetting time is proportional to the increase in chain length of the two branched chains at the terminal carbon atom bearing the active groups as in compounds IX, X and XI. However, this increase did not extend to compound XIII, for which the wetting time fell to a lower value. This may be due to the structure of this compound, in which the hydrophilic group lies at the end of a C 18 chain and at the middle of a C 9 chain, each of which is capable of surface activity.

It is well known that foaming is one of the most conspicuous properties of surface active agents. Foam is considered to be a gas-in-liquid system in which bubbles of gas are dispersed more or less stably in a continuous liquid phase (14). The foam volume and its stability is a measure of the foaming power of the surfactant. The foam height values of all compounds are lower than that of the sodium oleyl sulfate. In relation to chemical structure, the foam height decreases with increasing length of the branched chain. The increased bulkiness of the charged head causes a marked decrease in foam height as shown in compounds IX, X and XII.

Studying detergency involves numerous factors and full control over every factor cannot be attained. Only cotton detergency was carried on in the present

TABLE III

Surface Active Properties

Compound	R	Krafft point,[a] C	Critical micelle concentration, mmoles/liter	Wetting time 0.25%, 25 C, sec	Foam height[b] 0.25%. 60 C, mm distilled water	Detergency, 60 C, ΔR		Calcium stability 25 C ppm $CaCO_3$
						0.25% Distilled water unbuilt	0.05% + 0.2% Builder, 300 ppm built[c]	
IX	CH_3	Clear at zero	3.98	32.2	195	10	7	303
X	$CH_3 \cdot CH_2$		4.26	49	165	8	11	284
XI	n-C_3H_7		2.95	73	135	5	7.5	297
XII	$(CH_3)_2CH$		3.98	21	105	10	6.5	303
XIII	n-C_4H_9		3.16	43.6	110	5	4.7	353
XIV	$(CH_3)_3C$		3.98	29.8	135	18	10.7	429
Sodium oleyl sulfate			0.29[d]	......	240[e]	23	27	920[e]

[a] Temperature at which a 1% dispersion became a clear solution on gradual heating.
[b] Stable foam, Ross-Miles test (6).
[c] Builder composition: 55% $Na_5P_3O_{10}$, 24% Na_2SO_4, 10% $Na_4P_2O_7$, 10% Na metasilicate, 1% carboxy methyl cellulose.
[d] Reference 9.
[e] Reference 10.

work. The time, temperature and degree of agitation, which are the most important variable physical factors in detergency, were controlled. The results of detergency power reflect the poor detergency of all the compounds, both as built and unbuilt samples in soft and hard water, compared to detergency power of sodium octadecenyl sulfate. Many investigators show that sodium salts of branched-chain fatty acids have lower detergency compared to those of normal fatty acids (12). The same results were obtained in alkyl sulfates, alkane sulfonates and dialkyl benzene sulfonates in which detergency decreased by branching (15).

The calcium ion stability values are nearly of the same order for all compounds. However, all compounds under study are less stable than the corresponding sodium octadecenyl sulfate.

REFERENCES

1. Schwartz, A.M., and J.W. Perry, "Surface Active Agents," Interscience Publishers, Inc., New York, 1949, p. 63; British Patent 422,804.
2. Schwartz, A.M., and J.W. Perry, Ibid. p. 58.
3. Metzger, A., (Bohme Fettchemie, G.M.B.H.), German Patent 639,625, Dec. 10, 1936; Chem. Abstr. 31: 3938 (1937).
4. Snoddy, A.O., and W.S. Martin, British Patent 479,482 (1938); Chem. Abstr. 32: 5109 (1938).
5. Osipow, L.I., "Surface Chemistry, Theory and Industrial Applications, "Reinhold Publishing Corp., New York, 1963, p. 188; C.P. Roe and P.D. Brass, JAOCS 76: 4703 (1954).
6. Ross, J., and G.D. Miles, Oil Soap 18: 99 (1941).
7. Wilkes, B.C., and J.N. Wickert, Ind. Eng. Chem. 29: 1234 (1937).
8. Draves, C.Z., and R.G. Clarkson, Amer. Dyest. Rep. 20: 201 (1931).
9. Weil, J.K., A.J. Stirton and E.B. Leardi, AOCS 44: 522 (1967).
10. Weil, J.K., A.J. Stirton and F.D. Smith, Ibid. 42: 873 (1965).
11. Hartly, G.S., Trans. Faraday Soc. 37: 130 (1941).
12. Nevolin, F.V., T.G. Tipisova and A.D. Petrov, Maslob. Zhir. Prom. 28: 15 (1962); Chem. Abstr. 57: 15263 (1962).
13. Klevens, H.B., JAOCS 30: 74 (1953).
14. Nieven, W.W., "Fundamentals of Detergency," Reinhold Publishing Corp., 1950, p. 82.
15. Hoelbel, H., D. Klamann and P. Kurzendoerfer, Proceedings of the International Congress on Surface Activity, 1960; Chem. Abstr. 57: 3581 (1967).

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