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A comparison of the properties of a polyoxyethylated nonionic detergent and its sulphate in colloidal systems

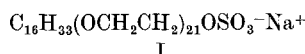
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With 7 figures and 3 tables

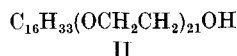
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A number of reports have been published on the surface activity and micellar properties of polyoxyethylated detergents which have a terminal sulphate group (1-7). These deal mainly with compounds having short oxyethylene chains and none include a comprehensive comparison of the physico-chemical behaviour of the sulphated compound with the parent nonionic detergent in a range of systems.

In order to determine the effect of sulphation on the properties of a widely used long chain nonionic detergent, we have prepared the sulphate (I) of cetomacrogol 1000 (II).



I
Cetomacrogol sulphate



II
Cetomacrogol 1000

We have compared the behaviour of the two compounds in aqueous solution and as suspending agents and stabilizers of oil-in-water and water-in-oil emulsions. The sulphate group has been found to have considerable effects on these properties, not always in the direction predicted from the behaviour of the shorter chain length compounds.

Experimental

Materials. Cetomacrogol sulphate (*polyoxyethylene glycol 1000 monocetyl ether sulphate*). Sulphation of the nonionic cetomacrogol was effected by dropwise addition of chlorosulphonic acid in a 2:1 molar ratio to the detergent solution in ethanol-free chloroform. After stirring at room temperature for 2-3 h the reaction mixture was neutralized with 6N methanolic NaOH and evaporated to dryness. The residue was dissolved in benzene, centrifuged to remove insoluble inorganic

salts and chromatographed on acidic alumina (*Woelm*) using 30:1 benzene:methanol as eluent. Cetomacrogol sulphate was obtained in low yield because of the difficulty in separation from unreacted cetomacrogol. Separation by means of ion-exchange resins (8) proved unsuccessful, probably due to sulphate elimination.

Assay of the chromatographed product by titration with N/100 cetyl pyridinium bromide according to the method of Barr et al. (9) indicated percentage purity of 98.4%.

Cetomacrogol 1000 BPC was used as received from Macarthy's Limited, Romford, Essex. Estimation of the ethylene oxide content by the method of Siggia et al. (10) indicated 21 ethylene oxide groups per molecule.

Chlorobenzene was monochlorobenzene (BDH), twice distilled before use. The fraction used had $n_D^{20} = 1.5248$.

Attapulgit was activated attapulgit (Pharmasorb, Jelonite Ltd.) with a stated average particle size of 2.9 μ .

Emulsions were prepared by ultrasonic dispersion under standardized conditions. The emulsions were stored in glass and sized microscopically at intervals and the results treated as described before (11). All emulsions had a phase volume of 10% w/v and contained 1% w/v surfactant. The surfactants were dissolved initially in the aqueous phase.

Viscosity measurements were made using an Ostwald viscometer of 2ml capacity (sulphate solutions) and a suspended-level dilution viscometer of 5 ml capacity (nonionic solutions) at $25^\circ \pm 0.01^\circ$.

Surface tension measurements were carried out with a *Wilhelmy* plate apparatus using a conventional torsion balance. All quoted results are equilibrium values obtained after ageing of the solutions at $25 \pm 0.1^\circ\text{C}$.

Interfacial tension measurements were made using a suspended-drop method with an apparatus based on the design of Andreas, Hauser and Trucker (12) and described before (11).

Emulsion stability: Assessment of the stability of the emulsions was carried out microscopically, following procedures outlined before (11). Results obtained from plots of the logarithm of the number of globules (in an arbitrary constant volume of emulsion) against time (seconds) are quoted in terms of rates of coalescence (K , sec^{-1}).

Zeta potential measurements. Electrophoretic mobilities (u) of the emulsion globules were measured at room temperature using a Zeta-Meter (Zeta Meter Inc., New York). 1 ml of emulsion was added to the diluent (35 ml) and the mean velocities determined from not less than ten separate runs. The zeta potential (ζ) of

the droplets in presence of the sulphated compound was calculated from the standard equation

$$u = \frac{\epsilon \zeta}{4 \pi \eta} \quad [1]$$

where ϵ = dielectric constant, and η is the viscosity of the medium in centipoise. In the case of the nonionic-stabilized emulsion the equation

$$u = f(Ka) \frac{\epsilon \zeta}{4 \pi \eta} \quad [2]$$

was used because Ka was of the order of 7 (K = reciprocal Debye-Huckel length in cm^{-1} and $a = 1 \times 10^{-8}$ cm). $f(Ka) = 0.762$ (13).

Results

Surface tension results for the sulphated compound in water and in 0.02 M NaCl are shown in fig. 1 and data calculated from this

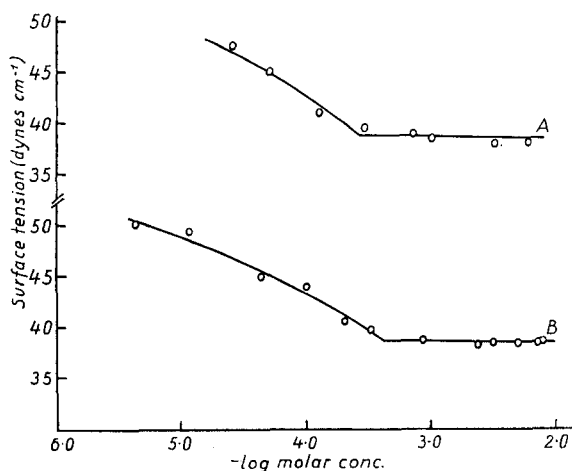


Fig. 1. Plots of surface tension vs log molar concentration for cetomacrogol sulphate at 25°C in A: 0.02 M NaCl and B: H₂O

graph are collected with information on the properties of cetomacrogol in table 1. From these it is apparent that the introduction of the sulphate group into the cetomacrogol molecule results in a lowering of the critical micellar concentration (CMC) and an increase in surface activity. The results indicate that

the addition of the sulphate group has made the molecule more hydrophobic, which is an unexpected result. This is not the trend obtained by sulphation of a shorter chain nonionic, C₁₆H₃₃(OCH₂CH₂)₇OH, as can be seen from table 1. It appears from the viscosity results shown in fig. 2 that the effect of sulphation on the cetomacrogol is one of decreased hydration.

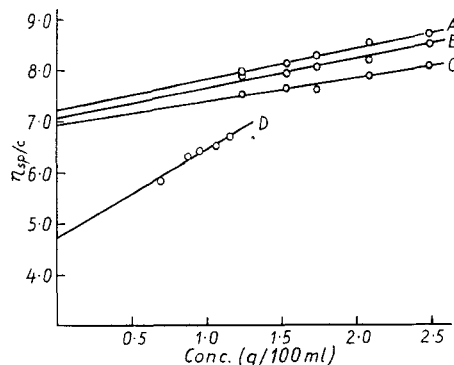


Fig. 2. Reduced viscosity at 25°C of cetomacrogol in A: H₂O, B: 2.5% NaCl, C: 5.0% NaCl and D: cetomacrogol sulphate in H₂O

The hydration (ω) of cetomacrogol was estimated from its limiting viscosity number (η), assuming micellar sphericity using the equation

$$(\eta) = 2.5 (\bar{V} + \omega V_1^0). \quad [3]$$

A value of approximately 2g water per g of detergent was calculated using an assumed partial specific volume, \bar{V} , of unity. As the contribution of the electroviscous effect to the intrinsic viscosity of the sulphate solutions is not known, only a maximum hydration can be calculated. An intercept of 4.70 corresponds to a hydration of 0.88 g/g detergent which is close to the value expected from a hydration of two water molecules per ether oxygen and 6–8 per SO₄⁻ group. Sodium chloride decreases the hydration of the nonionic slightly (see fig. 2) while 0.1 M NaCl salts out the sulphated compound at room temperature.

Table 1. Surface activity and CMC values of nonionic and sulphated analogues

Compound	Limiting surface tension (dynes cm ⁻¹)	Area/molecule (Å ²)	CMC (M/l)	Interfacial tension (dynes cm ⁻¹)	Ref.
C ₁₆ H ₃₃ (OCH ₂ CH ₂) ₇ OH	33	44	1.74 · 10 ⁻⁶	—	(24)
C ₁₆ H ₃₃ (OCH ₂ CH ₂) ₇ SO ₄ ⁻ Na ⁺	44	68	12.2 · 10 ⁻⁶	—	(3)
C ₁₆ H ₃₃ (OCH ₂ CH ₂) ₂₁ OH	41.2	120	5 · 10 ⁻⁵	5.0 (1.0%) 7.0, 0.1%	This work and (13)
C ₁₆ H ₃₃ (OCH ₂ CH ₂) ₂₁ SO ₄ ⁻ Na ⁺	38.6	125	3.33 · 10 ⁻⁶	6.4 (1.0%) 7.7, 0.1%	This work and (13)

Table 2. Rates of coalescence of emulsions stabilized with 1% cetomacrogol sulphate (I) and 1% cetomacrogol (II)

Emulsion	Emulsifier	Rate of coalescence (sec ⁻¹)
Chlorobenzene-in-water	I	$5.2 \cdot 10^{-7}$
	II	$0.9_3 \cdot 10^{-7}$
Water-in-chlorobenzene	I:II = 10:1	$3.5 \cdot 10^{-7}$
	I	$0.3_0 \cdot 10^{-7}$
	II	× ×

× × Breakdown too rapid for assessment.

Table 2 shows the results of the emulsion stability studies. The sulphated compound is a less efficient stabilizer of chlorobenzene-in-water emulsions; a 10:1 sulphate: non-ionic mixture has intermediate stabilizing

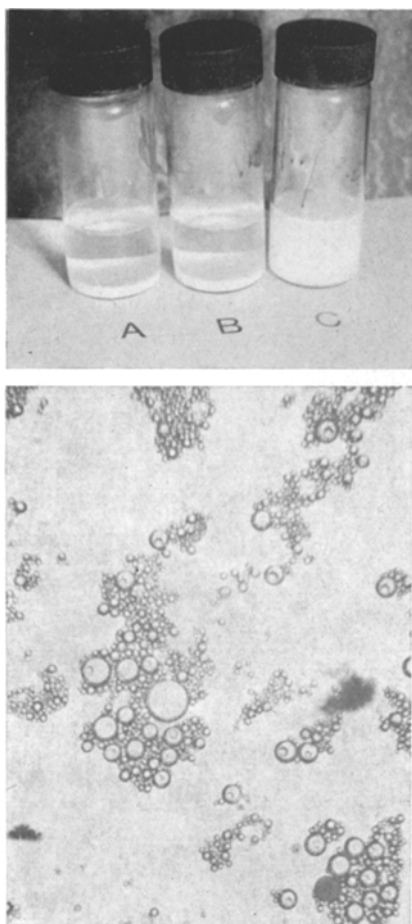


Fig. 3. Upper photograph shows emulsions of chlorobenzene-in-water (A and B) containing cetomacrogol sulphate and (C) containing cetomacrogol. B is stabilized by a 1:10 nonionic-sulphate mixture (see table 2). The clearing of the supernatant is the result of flocculation, which can be seen in the photomicrograph (lower photograph) of a chlorobenzene emulsion stabilized with 1% cetomacrogol sulphate

properties. Conversely the sulphate is a more effective stabilizer of water-in-chlorobenzene emulsions. Cetomacrogol is a very ineffective stabilizer of w/o emulsions, as expected from its HLB value of 16. Calculation of HLB values using tables of group contributions is suspect when polyoxyethylated compounds are being compared, as differing degrees of hydration alter the hydrophilic properties. The HLB of the sulphated detergent calculated in this manner is 45 and hence it would not be expected to be an efficient o/w stabilizer according to HLB predictions (14). The interfacial tension between chlorobenzene and water in the presence of the sulphate is $6.4 \text{ dynes cm}^{-1}$ (mNm^{-1}) compared with 5 dynes cm^{-1} (mNm^{-1}) for the nonionic. Differences in stability therefore cannot be attributed to differences in interfacial tension.

Rapid settling and clearing of the supernatant was noted in the o/w emulsions stabilized by the ionic detergent (fig. 3A) due to flocculation of the oil globules (fig. 3B). The sulphate behaves as a true ionic detergent in its effect of increasing the electrophoretic mobility of the chlorobenzene droplets (fig. 4) while the nonionic decreases electrophoretic mobility. At the concentrations employed in the o/w emulsions the electrophoretic mobilities were $-7.5 \mu\text{sec}^{-1}/\text{Vcm}^{-1}$ and $-1.3 \mu\text{sec}^{-1}/\text{Vcm}^{-1}$ for the ionic and nonionic emulsions which correspond to zeta potentials of -96 and -23 mV respectively. [Because of the shortage of the ionic detergent the result at the highest concentration (1%) was extrapolated from 4 results at lower concentrations.] The foam

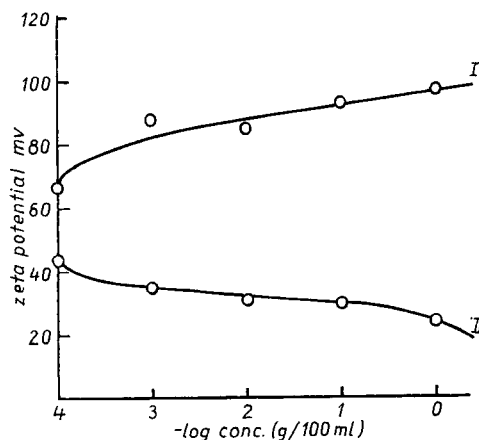


Fig. 4. Change of zeta-potential with concentration of surfactant for chlorobenzene globules in aqueous solutions of (I) cetomacrogol sulphate and (II) cetomacrogol

stability of aqueous sulphated cetomacrogol is less than that of the parent nonionic as indicated by the results shown in fig. 5, in agreement with the emulsion stability results. Preliminary results with suspensions of attapulgit confirm two trends observed in other systems i.e. flocculation in the presence of the sulphate and sensitivity of the sulphate to NaCl. More rapid clearing

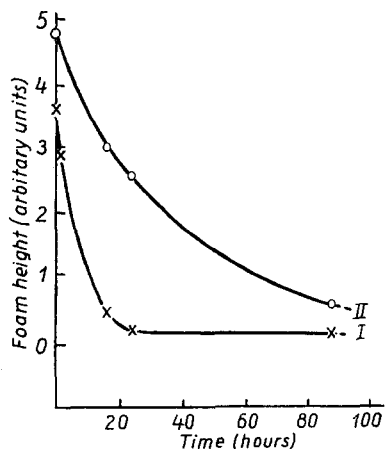


Fig. 5. Foam height of aqueous solutions of I: 0.01% cetomacrogol sulphate and II: 0.01% cetomacrogol as a function of time, determined from photographs of the foams produced in 10 ml. volumetric cylinders

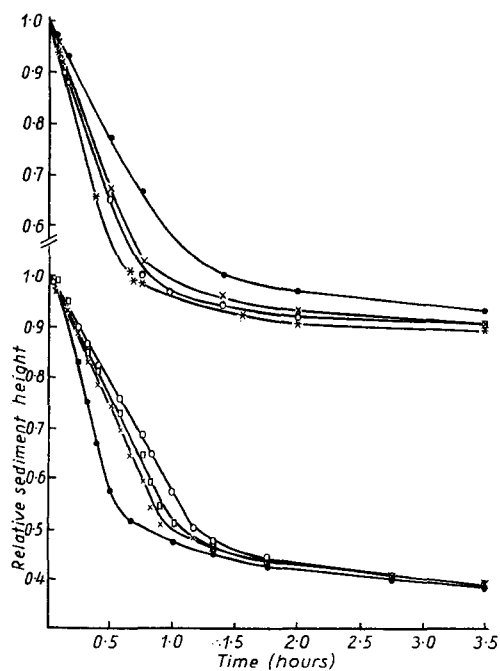


Fig. 6. Sedimentation behaviour as a function of time for Attapulgit in (●) 0.5% cetomacrogol sulphate, (×) 0.01% cetomacrogol sulphate, (○) 0.5% cetomacrogol (*) H₂O and (□) 0.1 M NaCl. Upper figure is data for salt-free surfactant solutions. Lower figure refers to surfactant in 0.1 M NaCl

of the supernatant was noted in the presence of sulphate when compared with an equal concentration of cetomacrogol, and also slower settling of the sediment to a slightly higher final sediment volume. These signs are all qualitative indications of flocculation (15). On the addition of 0.1 M salt to the system the sedimentation curves of nonionic and ionic systems are reversed (see fig. 6) perhaps an indication of the salting out of the sulphate.

Discussion

To obtain a clear picture of the effect of sulphation on the properties of nonionic detergents, we must consider the behaviour of the whole series. In fig. 7 the CMC and surface tension values for cetomacrogol sulphate are compared with similar data for other sodium hexadecyloxyethylene sulphates and it is clear that the explanation of Weil, Bistline & Stirton (5) is largely correct. That is, increasing the polyoxyethylene chain length of the sulphated detergent results in a progressively more nonionic character. The CMC falls as the charged head group loses its

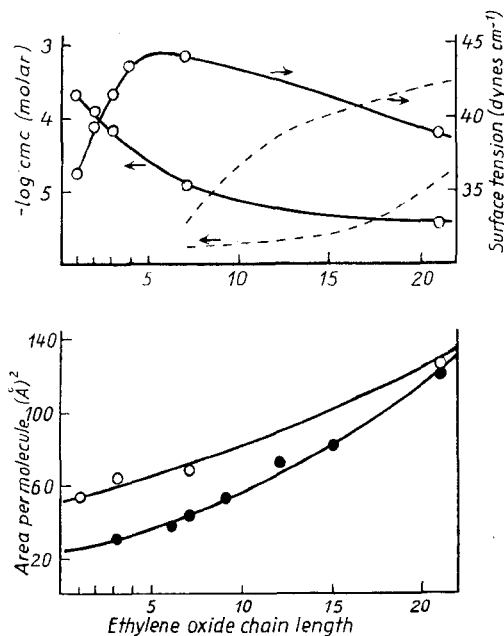


Fig. 7. Upper figure. CMC and surface tension data for sulphated cetyl ethers as a function of ethylene oxide chain length illustrating the trend towards the nonionic values (dashed lines) at higher ethylene oxide chain lengths. Lower figure. Variation of area per molecule as calculated using equation [9] of (○) the sulphated cetyl ethers and (●) the nonionic analogues as a function of ethylene oxide chain length. Data taken and calculated from references (3), (5), (24) and present work

influence. Similar behaviour has been reported for sodium dodecyl oxyethylene sulphates, the CMC decreasing from a value of $4.6 \cdot 10^{-3}$ mole/l for $E = 1$ (2) to $6.0 \cdot 10^{-5}$ mole/l for $E = 17.5$ (7). The latter value is similar to that of the nonionic analogue (between the values of $8.2 \cdot 10^{-5}$ and $8.4 \cdot 10^{-5}$ moles/l quoted (16) for $E = 14$ and $E = 28$ respectively at 25°). Fig. 7 also indicates an increase in surface tension with increasing E , as in the nonionic series, up to maximum at $E = 6$ and then a decrease towards the nonionic value. Hence, up to $E = 6$ the decrease in CMC with increasing E is not evidence of increasing hydrophobicity but is indicative of the diminishing influence of the charged group in retarding micelle formation. Hence a calculation of the free energy decrease as a function of E is misleading unless the contributions of hydrophobic bonding ($\Delta G_{H\phi}$), the hydrophilic ethylene oxides (ΔG_{EO}) and the electrostatic contribution of the $\text{SO}_4^- \text{Na}^+$ (ΔG_{el}) are distinguished. We can write

$$\Delta G_m = \Delta G_{H\phi} + \Delta G_{EO} + \Delta G_{el}. \quad [4]$$

For a C_{16} chain the first term is constant at -10.6 Kcal mol^{-1} (16 times $1.1 kT$), Heusch (17) shows that, for a number of nonionic polyoxyethylated nonyl phenols $\Delta G_{EO}/E = +0.033$ Kcal mole^{-1} . An estimate of the maximum ΔG_{el} for the present series of sulphates can be obtained from the experimental ΔG_m of $\text{C}_{16}\text{H}_{33}\text{SO}_4\text{Na}$ which has a value of -7.0 Kcal mole^{-1} (see below). As $E = 0$ for this compound, $\Delta G_{el} = -7.0 - (-10.6) = +3.6$ Kcal mole^{-1} . In the absence of added electrolyte and at sufficiently low concentrations ΔG_{el} is given (18) as

$$\Delta G_{el} = \frac{Ne^2}{Db} \quad [5]$$

for a micelle containing N monomers, where D = dielectric constant of the medium, b is the micellar radius and e the protonic charge. Thus assuming a reasonably constant N , ΔG_{el} would be proportional to $1/b$, and hence we have a means of estimating the values of ΔG_{el} for other members of the series. An experimental value of b is available for $E = 7$ only (3), values for the other sulphated compounds were calculated from

$$b = b_{\text{hydrocarbon}} + b_{\text{peg}} + b_{\text{SO}_4^-}. \quad [6]$$

The radius of the hydrocarbon core, $b_{\text{hydrocarbon}}$, of the $\text{C}_{16}\text{H}_{33}(\text{OCH}_2\text{CH}_2)_7\text{SO}_4\text{Na}$ micelle has been estimated as 2.2 nm (3) and this value was used throughout. The

contribution of the sulphate group, $b_{\text{SO}_4^-}$, was taken as 0.4 nm. Values for the radius of the polyoxyethylene region, b_{peg} , are dependent on the extension of the oxyethylene chain and could only be estimated with any certainty for the short chain compounds, hence ΔG_m could not be calculated for cetomacrogol sulphate.

The ΔG_m values estimated as described above are compared in table 3 with values calculated from

$$\Delta G_m = RT \ln \text{CMC} \quad [7]$$

using published CMC values. The agreement between experimental and calculated values may be fortuitous but it lends theoretical weight to the decreasing ionic character of the micelles as the hydrophilic chain is increased in length.

Table 3. Experimental and calculated Free Energies of micellization (Kcal mole^{-1})

Ethylene oxide units (E)	$\Delta G_m^{(1)}$ exptl.	Radius, b (nm) ²⁾	$\Delta G_m^{(3)}$ calculated
0	-7.0	2.6	(-7.0)
1	-7.3 ₅	3.0	-7.4 ₅
2	-7.7	3.4	-7.7 ₈
3	-8.0 ₃	3.8	-8.0 ₄
7	-9.0 ₃	5.0	-8.7 ₅
21	-9.8 ₂	—	—

¹⁾ Calculated from $\Delta G_m = RT \ln \text{CMC}$. CMC data from Weil et al. (5) ($E = 0-3$), Attwood (3) ($E = 7$), and present work ($E = 21$).

²⁾ Calculated from eq. [6].

³⁾ Calculated from

$$\Delta G_m = \Delta G_{H\phi} + E(\Delta G_{EO}/E) + \frac{\Delta G_{el}(\text{max}) \cdot 2.6}{b}.$$

Klevens' (19) equation for the CMC of an ionic detergent as a function of the total length of the amphipathic ion (δ nm) i.e.

$$\text{Log CMC} = 2.26 - 2.31 \delta \quad [8]$$

gives unrealistic values in the sulphated non-ionic series under discussion.

Areas per molecule of the sulphated detergents can be calculated in the presence of swamping neutral electrolyte from surface tension results by application of the Gibbs adsorption equation in the form

$$\Gamma = -\frac{1}{RT} \cdot \frac{d\sigma}{d \ln c} \quad [9]$$

which also can be applied to dilute solutions of ionic surfactants in the absence of neutral

electrolyte (20). The areas per molecule shown in fig. 7 for the sulphated series have been calculated from the published graphs of Weil et al. (6) and unpublished data from this laboratory. The results extrapolate to a value of 50 \AA^2 for the hexadecyl sulphate which agrees well with values quoted for alkyl sulphates at the air/water interface (21). The area of the cetomacrogol sulphate molecule is 124 \AA^2 , within experimental error of the value of 120 \AA^2 of the parent nonionic. In the presence of 0.02 M NaCl the sulphate's area is 118 \AA^2 .

Tokiwa and Ohki (1) have reported an increase of hydration with increasing oxyethylene chain length for sodium dodecyl-oxyethylene sulphates with E between 1 and 10. If a similar trend occurs in the hexadecyloxyethylene series it must be restricted to the lower members of the series since the hydration of the cetomacrogol sulphate is very much lower than that estimated for $E = 7$ (approx. $4.6 \text{ g of H}_2\text{O/g of detergent}$ [3]). It is thought that the repulsion of the terminal charged groups on the sulphated compounds results in an extension of the oxyethylene chains and a consequent mechanical trapping of water molecules. It seems unlikely, however, that repulsions between the charges could cause extension of chains 21 units in length, and the low hydration observed with cetomacrogol sulphate suggests that the sulphated polyoxyethylene chains form a more compact layer around the micelle and as such are incapable of trapping large amounts of water.

Differences in the stability of the o/w emulsions could perhaps be ascribed to differences in the hydration of the hydrophilic chains of the stabilizers. A decreased hydration would lead to a decreased entropic repulsion through its effect on the excess osmotic pressure in the overlapping region of the colliding globules (22). The case of the w/o emulsion is not as readily understood, as in both emulsions the stabilizing chain is identical. Being more hydrophobic it is possible that the sulphated compound projects further into the continuous oil phase and is also less readily desorbed into the globule than the nonionic. Both factors would contribute to increased stability.

The comparison of the properties of dispersions stabilized by the nonionic and ionic cetomacrogol re-emphasize the unimportance of charge (zeta potential) in the stability of these systems, a conclusion reached before (13, 23) and indicates that the properties

(e.g. hydration) of the stabilizing layers are of greater importance.

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Summary

The properties of sulphated cetomacrogol 1000 have been compared with those of the parent nonionic surfactant. The sulphate is more surface active, has a lower critical micelle concentration and is less hydrated. It is more readily salted out from solution. The sulphate is a less efficient stabilizer of chlorobenzene-in-water emulsions than the nonionic, causing flocculation, but is much more effective in stabilizing water-in-chlorobenzene emulsions. The nonionic forms more stable foams than the sulphate. The published CMC's of the sulphated cetyl ethers decrease with increase in ethylene oxide chain length, towards the region of the CMC of their nonionic analogues. This can be quantitatively explained by calculation of the electrical component of the free energy which decreases as the radius of the micelle is increased. Nevertheless from the results discussed in this paper it is apparent that even when the ethylene oxide chain is 21 units long, the sulphate groups retain some influence over the properties of the surfactant.

References

- 1) Tokiwa, F. and K. Ohki, J. Phys. Chem. **71**, 1343 (1967).
- 2) Tokiwa, F., J. Phys. Chem. **72**, 1214; 4331 (1968).
- 3) Attwood, D., Kolloid-Z. u. Z. Polymere **232**, 788 (1969); **235**, 1193 (1969).
- 4) Bistline, R. G., A. J. Stirton, J. K. Weil, and E. W. Maurer, J. Amer. Oil Chemists' Soc. **34**, 516 (1957).
- 5) Weil, J. K., R. G. Bistline, and A. J. Stirton, J. Phys. Chem. **62**, 1083 (1958).
- 6) Weil, J. K., A. J. Stirton, R. J. Bistline, and E. W. Maurer, J. Amer. Oil Chemists' Soc. **36**, 241 (1959).
- 7) Schick, M. J., J. Phys. Chem. **67**, 1797 (1963); **68**, 3585 (1964).
- 8) Gunn, M. E. and C. L. Church, Anal. Chem. **31**, 551 (1959).
- 9) Barr, T., J. Oliver, and W. V. Stubbings, J. Soc. Chem. Ind. **67**, 45 (1948).
- 10) Siggia, S., A. C. Starke, J. J. Garis, and C. R. Stahl, Anal. Chem. **30**, 115 (1958).
- 11) Elworthy, P. H. and A. T. Florence, J. Pharm. Pharmac. **19**, 140S (1967).
- 12) Andreas, J. M., E. A. Hauser, and W. B. Tucker, J. Phys. Chem. **42**, 1001 (1938).
- 13) Elworthy, P. H. and A. T. Florence, J. Pharm. Pharmac. **21**, 70S (1969).
- 14) Sherman, P., in: Emulsion Science, Ed. P. Sherman, p. 140 et seq. (London 1968).
- 15) Bell, S. H. and V. T. Crowl, in: Dispersions of Powders in Liquids, Ed. G. D. Parfitt, Chapter 5 (London 1969).
- 16) Schott, H., J. Colloid Interfac. Sci. **24**, 193 (1967).
- 17) Heusch, R., Proc. 4th Intern. Congress on Surface Activity, Gordon and Breach, Vol. 1, pp. 105-125.

18) *Emerson, M. F.* and *A. Holtzer*, J. Phys. Chem. **71**, 3320 (1967).

19) *Klevens, H. B.*, J. Amer. Oil Chemists' Soc. **30**, 74 (1953).

20) *Pethica, B. A.*, Trans. Faraday Soc. **50**, 413 (1954).

21) *Voorst Vader, F. von*, Trans. Faraday Soc. **56**, 1067 (1960).

22) *Ottewill, R. H.*, in: Nonionic Surfactants. Ed. *Schick, M.*, p. 655 (New York 1966).

23) *Elworthy, P. H.*, *A. T. Florence*, and *J. A. Rogers*, J. Colloid Interfac. Sci. **35**, 23 (1971).

24) *Elworthy, P. H.* and *C. B. Macfarlane*, J. Pharm. Pharmac. **14**, 100T (1962).

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