

Surface tension and cloud point changes of polyoxyethylenic non-ionic surfactants during autoxidation

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Changes in the surface tension-concentration curves of the non-ionic surfactant cetomacrogol, a polyoxyethylenic (POE) hexadecyl ether containing about 24 ethylene oxide (EO) groups, have been examined during autoxidation of aqueous solutions. The curves exhibit decreases in cmc values and changes in the slopes below and above the cmc which lead to the loss of the sharp break characteristic of micelle-formation. There is also a progressive decrease in the cloud point during autoxidation. Surface tensions and cloud points of a series of known POE hexadecyl ethers containing from 10 to 60 EO units have been measured and related to the number of EO units present. From these data, it is apparent that autoxidation of cetomacrogol is accompanied by degradation of the POE chain rather than the hydrocarbon chain, the number of EO units lost up to the time at which the solution becomes turbid being about 14. The significance of such measurements is discussed in relation to the detection of decomposition and pending rapid decomposition in synthesized and commercial surfactants.

Peroxidation readily occurs during the storage of long chain alkyl polyoxyethylene derivatives used as surfactants (Hamburger, Azaz & Donbrow, 1975). Apart from the appearance of peroxides, chemical changes were observed indicative of degradation of the molecules.

Chain-shortening would be expected to influence a number of physical properties of the system both in its micellar and monomeric state, in particular the surface activity. Loss of polyoxyethylenic (POE) groups would be expected to lead to a fall and loss of hydrocarbon groups to a rise in critical micelle concentration (cmc) (Elworthy & Macfarlane, 1965; Becher 1967).

The cloud point temperature, indicative of aggregative phase changes resulting from desolvation of the POE chain by heat, would be expected to fall with POE chain degradation but rise with alkyl chain shortening.

In the present work, the form of the surface tension—concentration curves is studied with the object of identifying the type of breakdown from changes in the slopes and in the cmc. The decomposing surfactant is the hexadecyl derivative containing 24 POE groups, cetomacragol, which is compared with related hexadecyl surfactants of varying POE chain length used as reference substances for estimation of the change in chain length of the cetomacrogol. Parallel changes observed in the cloud point of the cetomacrogol are used in conjunction with data measured on the reference substances to confirm the picture of the degradation emerging from the surface tension and chemical data.

MATERIALS AND METHODS

Substances

Hexadecyl POE derivatives containing 10, 14, 16, 24, 30, 45, 60 ethylene oxide groups per molecule (average numbers) were supplied by Glover's Chemicals Ltd., Wortley Low Mills, England, from their Texofors A series. This series included the model substance used in the autoxidation studies, cetomacrogol 1000 B.P.C.

Samples were selected for use in which there was no evidence of autoxidation, as shown by two criteria (a) the pH of 1% solutions, which lay between 6 and 7, (b) the peroxide number which was zero, measured by the ultraviolet spectrophotometric method developed for use in non-ionic micellar systems (Azaz, Donbrow & Hamburger, 1973).

Surface tension was measured using a Fisher semi-automatic Surface Tensiometer Model 21 by the method of Mittal (1972) using the correction factor of Zuidema & Waters (1941). Mittal's precautions were essential for obtaining reproducible results.

Determinations of the *cloud point* (Schott, 1969), *Peroxide Number* and *pH* were made as in the previous work (Hamburger & others, 1975). The method used for effecting the autoxidation was one allowing free access of air during storage without loss of solvent by evaporation, and is described by Hamburger & others (1975).

RESULTS AND DISCUSSION

Surface tension—concentration curves obtained by dilution of 3% cetomacrogol solution which had been stored at 50°, with or without copper sulphate (10^{-4}M) added as catalyst, indicated that surface properties were changing during storage of the solutions. Examples selected to show the progress of the change are shown in Fig. 1 A, B.

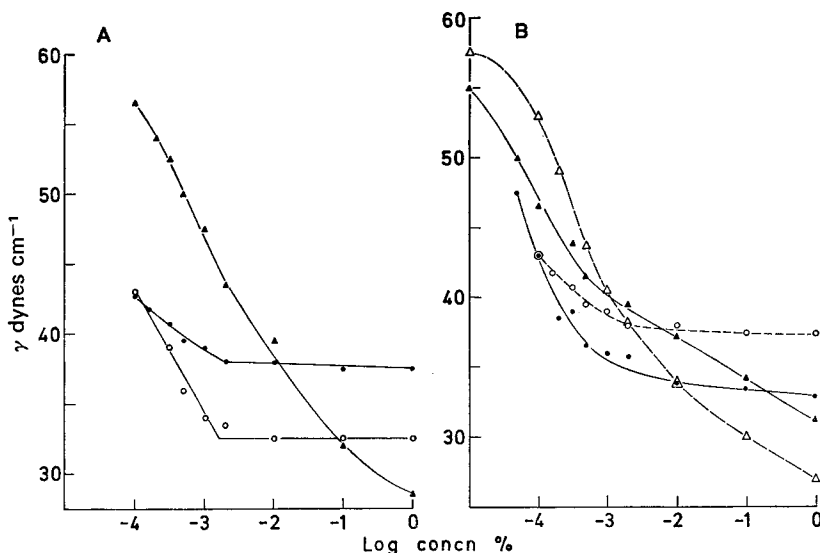


FIG. 1. A. Changes in the surface tension—log concentration curves of cetomacrogol solution (3%) on storage at 50°, measured at 0 or 1 day ●—●, 10 days ○—○, 69 days ▲—▲.

B. Changes in the surface tension—log concentration curves of cetomacrogol solution (3%) containing CuSO_4 10^{-4}M on storage at 50°, measured at 0 days ○—○, 1 day ●—●, 20 days ▲—▲, 60 days △—△.

In the absence of catalyst, the characteristic surface tension—concentration curve of fresh cetomacrogol showing the expected sharp break at the cmc, is still obtained for several days but after about a week the curvature in the cmc region has increased. The cmc falls in value, becoming at the same time more difficult to determine with accuracy. Within about 60 days the slope above the cmc has increased significantly and the distinctive point representing micelle-formation has almost disappeared. The general form of the curve at this stage approaches that of a Gibb's equation plot for a water-soluble organic substance having a structure favouring adsorption at the air-water interface, and forming an expanded film at low surface pressures.

With catalyst present, there are similar changes but the rate of change is greater, being detectable within the first few days, and reaching the terminal stages earlier. The catalyst does not itself affect the surface tension—concentration curve of a freshly-prepared cetomacrogol solution which has not undergone oxidation.

Typical values of the cmc and the slopes above the cmc, are given in Table 1 (Columns 3 and 4). These support the above observations and suggest that the ultimate disappearance of the break is a result mainly of the large increase of slope above the cmc.

Table 1. *Changes in cetomacrogol solution properties during exposure of 3% solution to oxidation at 50°.*

Period of exposure (days)	γ 1% (dynes cm^{-1})	$dy/d \log c^*$ above cmc	-log cmc % units	P.N.	pH	KOH 0.1N (ml g^{-1} cet.)	Cloud** point °C	EO units	
								Ex γ 1%	Ex C.P.
(a) No catalyst added									
0	38.0	0	2.7	0	6.80	<0.2	89.0		
10	37.6	0.25	2.9	0	7.00	0.3	89.0		
16	37.1	0.4	3.3	0	7.11	0.35	88.9		
57	29.5	3.0	—	0	2.84	8.10	71.2		
69	28.9	—	—	69	2.18	—	—		
(b) Catalysed by CuSO_4 (10^{-4}M)									
0	38.0	0	—	—	—	—	89.0	22	22
1	35.0	0.8	3.2	20	4.23	0.45	88.8	15	21
4	34.5	—	3.3	40	2.85	2.10	86.4	14	17
8	—	—	—	—	—	—	86.1	—	16
14	34.0	—	5.7	—	2.68	3.00	84.2	13	15
20	32.0	1.8	—	3	2.7	4.10	82.9	11	14
25	31.0	—	—	—	—	—	72.3	10.5	12
57	28.2	—	—	0	2.84	7.25	68.5	10	11
60	29.5	3.4	—	0	2.28	—	—	—	—

* Units γ dynes cm^{-1} (or mN m^{-1}), c % w/v.

** 3% solution with M NaCl .

Surface tension—concentration curves were measured similarly on freshly-prepared solutions of a series of POE ethers of *n*-hexadecanol for which the mean chain lengths were known and these are shown in Fig. 2. It is observed that as the hydrophobic properties of the surfactant increase, the sub-cmc slope increases which, on the basis of the Gibb's equation, indicates a higher surface concentration of monomers. The slope values range from 6.0 for the 60 EO compound to 20 for the 14 EO compound, measured from the linear section of the surface tension, γ (dynes cm^{-1}) against $\log c$ (c % w/v) plots just below the cmc. Furthermore, the slope above the cmc lies close

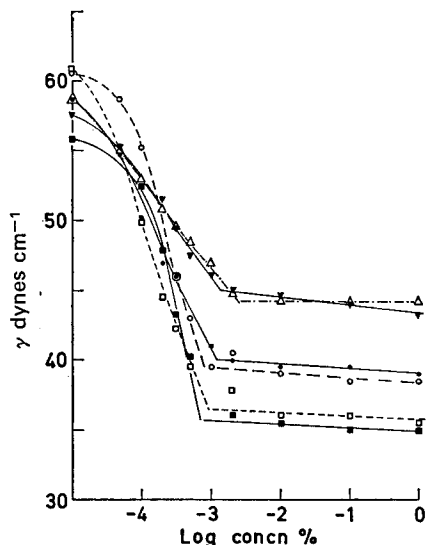


FIG. 2. Surface tension—log concentration curves of freshly prepared aqueous solutions of hexadecyl POE derivatives $C_{16}H_{33}[OC_2H_4]_mOH$, undecomposed. $m = 60$ Δ — Δ , 45 \blacktriangle — \blacktriangle , 30 \circ — \circ , 24 \square — \square , 14 \blacksquare — \blacksquare .

to zero throughout the series, the formation of the micellar phase rendering the activity of the surfactant above the cmc virtually invariant. Their sub-cmc linearity is also confined to a narrower concentration range than is the case with the higher members i.e. the surface approaches saturation at concentrations nearer to the cmc in the lower than in the higher members (Lange, 1967).

Above the cmc, the value of the surface tension is related to the number of EO groups. This is conveniently demonstrated using 1% solutions, the surface tension values for which are plotted in Fig. 3. The general trend of these results is essentially the same as that in the polyoxethylene n-dodecanols, reported by Schick (1962) and the nonyl phenol derivatives, measured by Hsiao, Dunning & Lorenz (1956). Similar slope changes above and below the cmc are also apparent from the graphs presented by Wan & Poon (1969).

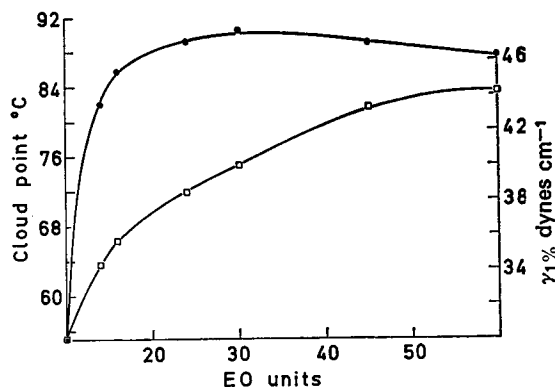
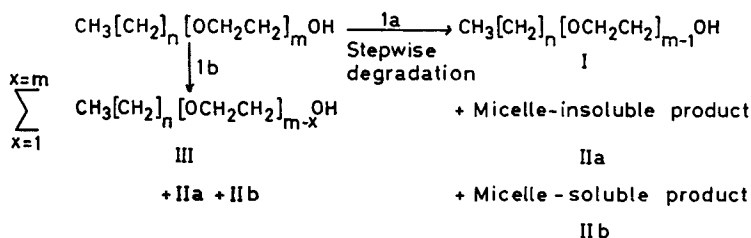


FIG. 3. Relation between EO chain length, surface tension of 1% aqueous solutions and cloud point of 3% aqueous solutions containing M NaCl for hexadecyl POE derivatives. Cloud point—EO units curve \bullet — \bullet . Surface tension—EO units curve \square — \square .

When a comparison is made of Texofors data with the cetomacrogol degradation plots, the progressive changes in form of the latter with time, and the direction of the changes in cmc and slope below and above the cmc show that there is an increase in hydrophobicity which must result from decrease of the POE chain length, and confirm that it is the POE rather than the hydrocarbon chain which is being degraded by autoxidation. Had the reverse occurred, the cmc values would have risen substantially, cmc in non-ionic surfactants being more sensitive to the length of the hydrophobic than the hydrophilic chain (Mulley, 1964; Elworthy & Macfarlane, 1965; Becher, 1967).

From the observations made at the later stages of autoxidation it seems that the fission products do not behave in accordance with reaction scheme 1a but rather in accord with scheme 1b. [This means that they do not appear to consist solely of a combination of a progressively lower member of the surfactant series (I) with respect to the shortened EO chain, accompanied by a non-surface active, micelle-insoluble, water-soluble product derived from the glycol chain end-group (IIa)].



The above is assumed as a result of a comparison of the slopes of the lower hexadecyl derivatives above the cmc and the slopes over the corresponding concentration range of the most highly degraded cetomacrogol solutions, the latter being very much larger in value. The large gradient is probably due to a continuous redistribution of surface-active compounds between micellar-phase and surface on dilution, either because micellization is occurring over a wide concentration range, as might occur if the polydispersity increases (Scheme 1b, III), or because degradation fragments (IIb) are solubilized at the higher concentrations and undergo desolubilization on dilution. This latter case would be characteristic of substances showing weak binding tendencies for the micelles such as short-chain aldehydes, fatty acids and ethers.

Since cloud point, a characteristic property of non-ionic surfactants, was shown to have changed after heat-initiated autoxidation had occurred (Hamburger & others, 1975), it was measured over the period of cetomacrogol degradation at 50°. The cloud-point temperature decreased slowly in the uncatalysed system but fell rapidly and progressively when the catalyst was present (Table 1). However, the persistence of the cloud-point phenomenon to a late stage of autoxidation suggests that micelles of short POE chain surfactants still exist when the cmc is no longer detectable.

Changes in peroxide number, pH value and free acid content occurred parallel to the developments in surface tension and cloud point, and are given in Table 1. It is apparent that low values of the peroxide number do not prove non-decomposition, or that the system is a stable one, since other properties change, even during early stages of the uncatalysed reaction. The immediate rise in peroxide number in the presence of the catalyst would be in accord with elimination of the initiation stage, while the subsequent drop is associated with the low pH developed (Hamburger &

others, 1975); the free acid content increases steadily in the catalysed reaction, even though the pH shows some scatter.

The low pH and high acid value are themselves criteria for detection of the advanced stages of decomposition, at which peroxides decline and substantial amounts of acids are formed. However, while the pH is near neutrality, only the slope of the surface tension-concentration curve above the cmc indicates that there has been any alteration in the POE chain. Such evidence of early changes accords with reaction schemes proposed for the degradation of POE polymers by Crouzet & Marchal (1973) and Decker & Marchal (1973).

To estimate the degree of shortening of the POE chain, the surface tension data obtained using the reference surfactants were correlated with the corresponding data measured in the systems undergoing autoxidation. For the purpose of cross-checking, the cloud points of the reference surfactants were also measured. They are plotted in Fig. 3 together with the surface tensions of 1% solutions as a function of the number of ethylene oxide groups present. Both yield curves demonstrating a rise in the value of the property with EO content, similar to that reported for other systems (Schick, 1962; Schott, 1969, 1971). The cloud point, reproducible to within 0.5°, is sensitive to EO chain length up to about 20 EO units and the surface tension up to about 40 units.

Using these curves, the number of EO groups corresponding to the measurements obtained during the catalysed cetomacrogol autoxidation at 50° were estimated. They are listed in Table 1. There is fair agreement between the chain lengths estimated by the two methods. A similar experiment on cloud point changes at 70° using shorter time intervals, gave a non-linear decrease in cloud point with time and a linear decrease in chain length with time (Fig. 4). Under both sets of conditions, continuation of the degradation until the time at which turbidity appeared resulted in an apparent drop in POE chain length to 10 EO groups.

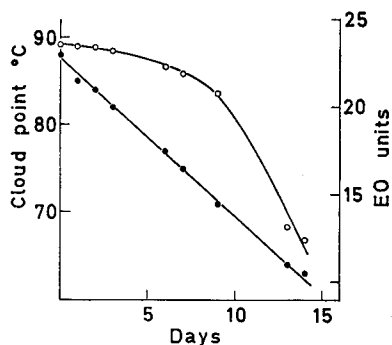


FIG. 4. Change in EO chain length with time, estimated from cloud point measurements, for cetomacrogol solution (3%) at 70°. Cloud point (3% solution with m NaCl) ○—○ EO units ●—●.

The apparent EO content obtained by these methods must be accepted with some caution, since there is little knowledge of how the properties measured are influenced by other intermediates or oxidation products which might be present at the various stages of the chain reaction. Nevertheless, the two methods measure different physical properties of the system, the surface tension data indicating an increasing

redistribution of solute material to the air/water interface and the cloud point data, a reduction in the total hydration of the hydrophilic chains. Since both are functions of the amphiphilicity albeit different ones, their agreement is probably not fortuitous.

Recognition of these changes is important particularly for commercial surfactants since they may be an indicator of when the samples are approaching the propagation stage of rapid decomposition in the classical autoxidation process, at which the shelf-life is likely to be considerably shortened and the sensitivity to autoxidative factors in storage or formulation enhanced compared to pure samples. We have also found that degradation is not prevented by storage of surfactants in the dry state under normal storage conditions.

The sub cmc slope change appears to be quite a sensitive criterion of purity, indicative of the presence of breakdown products of higher surface activity than the pure material. Its occurrence has not hitherto been recognized. Neither is it apparent from the literature whether published cmc data were obtained using surfactants which were unequivocally pure with regard to autoxidation. This could account for some of the variations in cmc values in the literature. Such changes could occur whenever a non-ionic surfactant of the polyoxyethylenic type is synthesized or isolated by a process involving the use of heat or the presence of catalysts and where the final isolation process does not remove the chain initiator, propagators or intermediates as in many classical procedures, for example that of Corkill, Goodman & Ottewill (1961), the conditions used having been shown to induce autoxidation (Hamburger & others, 1975).

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