MICELLIZATION OF HOMOGENEOUS NON-IONIC DETERGENTS

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Received 10th February, 1961

The preparation and purification of a homologous series of alkyl hexaoxyethylene glycol monoethers is described. The micellization of these materials in aqueous solution has been investigated by means of surface tension and light scattering measurements. On the basis of the former measurements it is concluded that the energetics of micelle formation are governed by the partial dehydration of the monomers as they aggregate. The turbidities of the micellar solutions have been shown to be markedly dependent on traces of ionic surface-active agents; these appear to form mixed micelles with the nonionic detergent and thereby impose a weak charge.

Non-ionic detergents of the alkyl polyoxyethylene glycol monoether type are generally prepared commercially by the condensation of ethylene oxide with alcohols, to yield a product in which the hydrophilic portion has a Poisson distribution of chain lengths.¹ To obtain specific isomers of this type, it is necessary to synthesize them unambiguously. These compounds are of interest in their surface-active behaviour since they supply information complementary to that obtained with conventional ionic detergents and, because of their non-ionic character, are more amenable to theoretical treatment. This paper describes the preparation of a homologous series of alkyl hexaoxyethylene glycol monoethers (RE₆) and an investigation of the micellization of these materials in aqueous solutions, using surface-tension and light-scattering measurements.

Several previous studies on non-ionic detergents in aqueous media have been carried out using the latter method 2, 3 but in these cases the materials used were prepared from commercial samples and consisted of mixtures of varying hydrophilic chain lengths. The effect of fractionation upon such materials was investigated by Kushner⁴ who found a large variation in apparent micellar weights between the various fractions. The heterogeneity of the samples used has inevitably led to lack of clarity in the results. For instance, sharp breaks were not observed in the curves of turbidity against concentration in the neighbourhood of the critical micelle concentration (c.m.c.) and in some cases turbidities were found to differ according to the mode of preparation of the solutions.³ In the present work, in addition to examining the light scattered by simple aqueous solutions of the n-alkyl hexaoxyethylene monoethers, a preliminary study has been carried out on the n-dodecyl hexaoxyethylene monoether in dilute solutions of an anionic surface active agent, namely, sodium dodecyl sulphate (SDS). These measurements show that non-ionic micelles can interact with ionic surfaceactive agents to form weakly charged micelles.

EXPERIMENTAL

PREPARATION OF ALKYL HEXAOXYETHYLENE MONOETHERS

The n-butyl, n-octyl, n-dodecyl and n-hexadecyl monothers have been prepared using the Williamson ether synthesis by one or both of the two routes indicated below: 5-7

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The glycols were fractionally distilled immediately before use. The alkyl chlorides were obtained either from pure alcohols (SO₂Cl₂) or by distillation of the highest-grade alkyl chloride available, and were shown to contain only one isomer by gas-liquid chromato-graphy. n-Octyl and n-hexadecyl ethers were prepared by method (i). However, the yield from this method was small, principally because a large quantity of unsaturated hydrocarbon was also produced by dehydrohalogenation of the alkyl chloride, and with the n-octyl compound it was found difficult to separate the monoether from the unreacted glycol by distillation. Method (ii) gave better yields and was used to prepare the n-butyl, n-octyl and n-dodecyl compounds. Colourless products were obtained by fractional distillation of the reaction product from glass wool and charcoal with a 6-in. Vigreaux column in a sealed system, at a pressure of 10^{-4} to 10^{-5} cm of mercury on the high-vacuum side of the pumping unit.

PHYSICAL CONSTANTS

The general physical constants of these materials are recorded in table 1. The boiling points quoted are the distillation temperatures using the conditions described above. Molecular weights of these compounds were determined from their hydroxyl values with



wavelength (in microns)

FIG. 1.—Infra-red spectrum of n-hexadecyl hexaoxyethylene monoether, (a) freshly distilled, (b) plus a trace of water.

a reproducibility of about ± 1 %. The high experimental value obtained for the hexaoxyethylene glycol may be ascribed to a small quantity of water, and in general, it was found that the lower members of this series were extremely hygroscopic. This is confirmed by the infra-red spectra of these materials. The spectrum from a freshly distilled sample of the hexadecyl compound is extremely well resolved (fig. 1a) but the addition of a trace of water to the material modifies it considerably (fig. 1b). The spectrum shown in fig. 1b is similar to the spectra obtained from the lower members of the series; the water modifies the infra-red spectrum and the hygroscopic nature of the lower members eliminates the possibility of a spectrum of the type seen in fig. 1a being obtained.

compound		HE	CrEe	C.E. (i)	CoEc (ii)	CraEe	C16E6
		0	0420			-12-0	-10-0
molecular) calc.	282	338	394	394	450	506
weight	from -OH value	290	335	391		454	506
b.p.	$(10^{-4} - 10^{-5} \text{ cm})$	190	160	205	205	225	235
m.p. (°C)	3.5	-1.6	8.8	9.0	25.2	38.3
C	theory	51.0	56.9	60.9	60.9	64·0	66•4
	found	51.1	57.0	61.2	60.6	63.8	66.5
H	theory	9.0	10.1	10.7	10.7	11.1	11.5
	found	8.9	10.1	10.8	10.4	1 0 ·9	11.6
n_D^{40}		1.4569	1.4444	1.4462	1.4463	1.4483	1.4507

TABLE 1.—PHYSICAL PROPERTIES OF NON-IONIC COMPOUNDS

PURIFICATION

Despite the precautions taken to ensure that pure compounds were obtained by this synthesis and the fact that the analyses indicated that the material was at least 99% pure, some samples gave a small minimum (<1 dyne) in the surface tension against log concentration $(\gamma/\log c)$ curve; this is often indicative of a trace of impurity. In general, these compounds appear to be particularly prone to oxidation. Simply leaving a pure sample of the butyl compound in a desiccator for several months caused a carbonyl peak to develop at 5.8 μ in the infra-red spectrum, which was not present initially, and heating on a steam bath produced larger quantities of the carbonyl compound in the other members of this series. It seemed possible therefore that the oxidation products were not all entirely removed by subsequent distillation. The impurity was successfully removed by chromatographic separation using a method based on that devised by Kelly and Greenwood.⁸ Samples were eluted with a chloroform+acetone mixture on a silica gel column (containing ca. 13 % H₂O). For the butyl and octyl compounds 80:20 chloroform+ acetone and for the n-dodecyl and n-hexadecyl compounds 90:10 chloroform+acetone were found convenient. A minor peak containing the impurity preceded the major component in the chromatograph. The infra-red spectrum of the impurity showed a strong carbonyl peak at 5.8 μ which was undetectable in the starting material, and an approximate estimate from the chromatographs suggested it constituted about 0.5 % of distilled material. To remove small quantities of the column material washed through with the monoether (which imparted a very slight colour), the middle cut of the main peak from the chromatogram was carefully distilled in a small bulb, when colourless products were obtained. The purity of the sample thus obtained was confirmed by chromatographic analysis of 0.1 to 0.3 g of specimens on a similar column taking special care to dry and distil the solvents, to ignite the silica to 500°, and to rehydrate it before When these precautions were taken the chromatographed material remained use. colourless after careful evaporation of the solvents under reduced pressure. The residues from the evaporation were dissolved in a standard quantity of water and the refractive index measured with a Rayleigh interferometer. Only one peak was obtained when the interferometer reading was plotted against the volume of eluate to give the chromatogram; these samples gave no detectable minima in the γ against log c curves.

SODIUM DODECYL SULPHATE

Dodecyl sulphuric acid was prepared by the chlorosulphonation of fractionally distilled lauryl alcohol, which had been shown to contain only one isomer by gas-liquid chromatography. The sodium salt was obtained by neutralization of the reaction mixture with A.R. caustic soda. After repeated recrystallizations from ethanol and water the sodium dodecyl sulphate was freed from traces of lauryl alcohol by extraction of a 50/50ethanol+water solution with $60-80^{\circ}$ petroleum ether as described by Harrold.⁹

EXPERIMENTAL TECHNIQUES

SURFACE TENSION MEASUREMENTS

The critical micelle concentrations (c.m.c.) of the octyl, dodecyl and hexadecyl compounds were determined at 25° by measuring the γ against log c curves in an air thermostat $(\pm 1^{\circ})$ using a Du Nouy tensiometer.¹⁰ This method cannot be considered to give results of high precision in view of the fact that the surface is not strictly in equilibrium with the

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saturated atmosphere, but for the purpose of simply determining the c.m.c. it may be considered adequate. To determine the change in c.m.c. of the dodecyl compound with temperature, a drop volume apparatus was used. An Agla syringe was held in a saturated atmosphere and the equipment immersed in a water thermostat (\pm ·05°). The apparatus was calibrated with benzene and water ¹¹ in the range 15-35°; the accuracy of the measurements was \pm 0·2 %.

LIGHT SCATTERING MEASUREMENTS

The light scattering apparatus used was that previously described.¹² All determinations were made using unpolarized incident light of wavelength 5461 Å at room temperature (*ca.* 18°C). The glassware used was treated with chromic acid, washed thoroughly with tap and distilled water, rinsed with ultrafiltered water and finally flushed with a jet of acetone vapour.

All solutions were filtered through Pyrex no. 5 sintered-glass filters (pore size *ca.* 1·1 μ) under pressures of 5-10 cm of mercury. 20 ml of the clarified solution were then pipetted into the light-scattering cell; aliquots of solution were removed from the cell and solvent added until a series of solutions of different concentrations had been examined. Similarly, aliquots of solution were added to 20 ml of the clarified solvent after the solvent readings had been obtained. Each run was repeated in triplicate in such a manner that a check could be obtained on points obtained by the dilution procedure and those obtained directly on "equilibrium" filtered solutions (see Becher and Clifton ³). The concentration of each solution was determined interferometrically.

REFRACTIVE INDEX INCREMENTS

The specific refractive index increments were determined at 5600 Å (values at this wavelength are not significantly different from those at 5461 Å) using a Zeiss interferometer to determine Δn ; $\Delta n = n - n_0$, where *n* and n_0 are the refractive indices of solution and solvent respectively. For all solvents examined (water, sodium chloride solution and SDS solutions) good linear plots of Δn against concentration of the detergents were obtained; no obvious change of gradient was found with the C₈E₆ compound in the region of the c.m.c. The differential refractive index increment was found to be 0.1348 ml/g for the two compounds examined.

RESULTS

SURFACE-TENSION MEASUREMENTS

The critical micelle concentrations, as determined from the abrupt change in slope of the γ against log c curves, are recorded in table 2.

Гавle 2.—	MICELLAR	WEIGHTS	AND	C.M.C.	OF	n-ALKYL	HEXAOXYETHYLENE	MONOETHERS
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compound	micellar weight from light scattering	aggregation number	c.m.c. light scattering, M	c.m.c. surface tension, M	temp., °C for s.t. measurements
C_8E_6 (a)	12,450	32	7·6×10−3	9·8×10 ⁻³	25
(b)			16·8×10-3	9·8×10 ⁻³	25
$C_{12}E_6(c)$	84,600	188			
(<i>d</i>)	71,400	158			
(e)				10·8×10 ⁻⁵	15
(e)	71,500	158		8·7×10 ⁻⁵	25
(e)				7·2×10 ⁻⁵	35
(e)	84,000	187			
in 0·1 M NaCl					
(f)	60,000	133			
$C_{16}E_6$				1·0×10 ⁻⁶	25

The surface tension of solutions of the octyl compound came to a steady value within the time required to take a measurement but, with the dodecyl and hexadecyl compounds, time effects became noticeable at about 10^{-5} M and were excessively long at concentrations less than 10^{-6} M. A surface-ageing effect is expected in this region from a consideration of the diffusion of the molecules to the

air/water interface $^{13, 14}$ (*ca.* 3 h at 10^{-6} M). Some days were required to obtain a steady value for the surface tension of the hexadecyl compound at concentrations below the c.m.c. and hence the value obtained for this compound may be considered to be only approximate. Fig. 2 shows the surface-tension curves for the dodecyl compound at concentrations near the c.m.c. at temperatures of 15, 25 and 35°, determined using the drop volume apparatus. It can be seen that as the temperature rises the c.m.c. decreases (see table 2).



FIG. 2.—Surface tension against log molar concentration of n-dodecyl hexaoxyethylene monoether in water at $-\Phi - 15^\circ$, $-\Box - 25^\circ$ and $-Q - 35^\circ$.

LIGHT-SCATTERING MEASUREMENTS

The results of the light-scattering experiments are presented either in the form of τ against c curves, or in the form of $H(c-c_0)/\tau$ against $(c-c_0)$ curves. τ is the excess turbidity of the solution over that of the solvent, c the total concentration of the detergent and c_0 the c.m.c. H is an optical constant given by

$$\frac{32\pi^3 n_0^2}{3N\lambda^4} \left(\frac{dn}{dc}\right)^2,$$

where dn/dc = specific refractive index increment of the detergent, N the Avogadro number and λ the wavelength of the incident light *in vacuo*. The disymmetry ratio I_{60}/I_{120} was measured in all cases and for freshly filtered solutions was about 1.02. The depolarization ratio ρ was found to be less than 0.009 and consequently the turbidity values have not been corrected for depolarization.

n-octyl hexaoxyethylene monoether C8E6

Two preparations of this material were examined, (a) a freshly prepared material from which two separate final distillates were collected and (b), a sample which had been stored in an ampoule for 6 months. Both samples of preparation (a) yielded identical τ against c curves and the combined results are given in fig. 3. A clearly defined value was obtained for the c.m.c. and equilibrated solutions and freshly diluted solutions gave points lying on the same curve.

The (b) sample, however, on dilution of micellar solutions to concentrations below the c.m.c. gave initial turbidity readings similar to those obtained with (a) but which increased steadily with time; above a concentration of 0.6 g/100 ml, no time effects were observed. The final equilibrium values for sample (b) are plotted in fig. 3, from which it can be observed that these values are considerably greater than those for sample (a).

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The surface-tension curves of both samples (a) and (b) were identical and gave c.m.c. values of 0.39 g/ml. The c.m.c. values obtained from the τ against c curves by extrapolation to zero τ appear to be 0.30 and 0.66 g/100 ml for samples (a) and (b) respectively. A weak infra-red carbonyl band was detected in sample (b), but not in sample (a). A plot of $H(c-c_0)/\tau$ against $(c-c_0)$ is given for sample (a) in fig. 4, using the light-scattering value of 0.30 g/100 ml for c_0 .



FIG. 3.— τ against c curves for n-octyl hexaoxyethylene monoether in water, — \Box — sample (a), —O— sample (b). X, turbidity value of sample (b) immediately after diluting below the c.m.c.; ϕ , equilibrium value.



FIG. 4.— $H(c-c_0)/\tau$ against $(c-c_0)$ curve for n-octyl hexaoxyethylene monoether in water (sample (a)).

n-dodecyl hexaoxyethylene monoether $C_{12}E_6$

Four freshly prepared samples of this material were studied, (c), (d), (e) and (f). Sample (e) was also investigated in 0.1 M sodium chloride. The curve obtained was similar to that obtained in water, but the turbidities were slightly higher at equivalent concentrations. The $H(c-c_0)/\tau$ against $(c-c_0)$ curves for all four fresh samples showed slight negative curvature at low concentrations, but were horizontal above 0.4 g/100 ml (see fig. 5).

The micellar weights for the samples of n-alkyl hexaoxyethylene monoethers are listed in table 2. As expected, the size of the micelle increases with the length

of the hydrocarbon chain. The micellar weights for the $C_{12}E_6$ samples were calculated by extrapolation of the horizontal portions of the $H(c-c_0)/\tau$ against $(c-c_0)$ curves. The scatter in molecular weight for the four samples (60,000-84,600) is greater than the expected experimental error. Preliminary results suggest that this variation is caused by small changes in room temperature, and the turbidities of solutions as a function of temperature are currently being investigated.



FIG. 5.— $H(c-c_0)/\tau$ against $(c-c_0)$ curves for n-dodecyl hexaoxyethylene monoether (sample (f)) in, $- \bullet -$ water, $- \bigtriangleup - 10^{-4}$ M SDS, $- \Box - 10^{-3}$ M SDS.

The behaviour of sample (f) was also investigated in solutions of 10^{-4} and 10^{-3} M SDS. The $H(c-c_0)/\tau$ against $(c-c_0)$ curves in 10^{-4} M SDS was very close to that obtained in water although significant deviations began to occur at the lower concentrations of $C_{12}E_6$ (fig. 5). The curve in 10^{-3} M SDS was, however, markedly different, much higher values of $H(c-c_0)/\tau$ being observed indicating either a lowering of the micellar weight or an increase in the charge of the micelle.

DISCUSSION

CRITICAL MICELLE CONCENTRATIONS

Although the c.m.c.'s determined from surface tension data were obtained primarily to establish the concentration range in which to investigate light-scattering phenomena, some deductions may be made concerning the energetics of micelle formation from these results alone. The c.m.c.'s are a factor of 100 lower than those obtained with ionic surface-active agents with the same alkyl chain. This, of course, is only to be anticipated, because these materials are essentially nonionic in character (the specific conductivities of dilute aqueous solutions are the same as the solvent) and, moreover, the hydrophilic group is about the same length as the hydrocarbon chain. Thus, there is no electrical force hindering micellization, and the methylene units in the hexaoxyethylene head group effectively increase the hydrophobic portion of the molecule.

Above the c.m.c., the activity of the species in equilibrium with the surface phase remains constant (fig. 2) and hence micellization may be considered as a phase separation. From a plot of log c.m.c. against the number of carbon atoms in the hydrophobic chain for the homologous series, a straight line resulted and from the slope it was calculated that the standard free-energy change per CH_2 group of a single molecule on micellization (using unit mole fractions as the 54

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reference states) was 1.10 kT. This agrees remarkably well with the value of $1.09 \, kT$ obtained by Shinoda ¹⁵ for fatty acid soaps and with the value of about 1 kT per CH₂ unit by Stigter and Overbeek ^{16, 17} for SDS. From the measurements of the c.m.c. as a function of temperature of the dodecyl compound it was possible to calculate the molar heat and entropy of micellization,¹⁸ namely, ΔH and ΔS . ΔH was positive and had a mean value of 5.9 kT/molecule between 15 and 35°. The increase in entropy under these equilibrium conditions was therefore 5.9 k/molecule deg. It does not seem likely that this gain in entropy is caused by the molecules being less restricted in the micelles than in water and the magnitude of ΔS strongly suggests that the energetics of micellization of these non-ionic compounds are governed almost entirely by the partial desolvation of the monomer as it enters into a micelle. Thus, it is probable that the gain in entropy results from the orientation of some or all of the water molecules in the vicinity of a single molecule (possibly in the form of an "iceberg" structure as described by Frank and Evans¹⁹) changing to a freer orientation on micelle formation.

LIGHT SCATTERING

In contrast to the non-ionic materials obtained by the purification and fractionation of commercial products, the alkyl monoethers used in the present investigation were, as far as could be detected, free of homologous contaminants and were, on the criteria of chemical analyses, extremely pure. Although weak carbonyl absorption bands were found in the old samples on examination in the infra-red, the surface-tension curves were indistinguishable from those of the fresh samples, and showed no detectable minima at the c.m.c.

It was observed by Becher and Clifton ³ that according to the mode of preparation of non-ionic detergent solutions for light scattering examination, i.e., by dilution or by filtration of equilibrated solutions, differing turbidities were obtained in the region of the c.m.c. They attributed their results to the slow breakdown of micelles when a concentrated solution was diluted. In the present work a similar time-dependence of turbidity was observed with an old C_8E_6 sample; freshly distilled samples did not show this behaviour. It seems probable, therefore, that the separation of small quantities of impurities, solubilized above the c.m.c., could account for our observations.²⁰ Moreover, it would also appear possible that these impurities arise due to slow degradation of the samples during storage.

The increase in the value of $H(c-c_0)/\tau$ observed with $C_{12}E_6$ in aqueous solutions at low concentrations (see fig. 5) has also been observed with heterogeneous non-ionic samples by Kushner and co-workers.^{2, 4} The latter workers attributed the upward trend to a change in the degree of association with concentration. Such behaviour could be explained by heterogeneity of the samples but in view of the precautions taken in the preparation of the $C_{12}E_6$ used this explanation would not seem likely in the present work. Moreover, as the results presented in fig. 5 were obtained well above the c.m.c. it seems unlikely that incomplete micellization could be responsible. Although a decrease in aggregation number with decreasing concentration seems to be the most obvious interpretation it may be significant that the upward trend was accentuated by the addition of 10^{-4} M SDS to the system, and hence could be due to traces of an ionic material. Increase of the SDS concentration to 10^{-3} M causes an overall increase in $H(c-c_0)/\tau$ and even more marked curvature at the lower concentration.

Since in the mixed systems the concentration of SDS was maintained constant throughout the light-scattering runs, the net result in 10^{-3} M SDS over the concentration range of $C_{12}E_6$ employed is that the molar ratio of $[C_{12}E_6]/[SDS]$ varies from *ca.* 33 to 2. Thus, if the results obtained are interpreted in terms of mixed micelle formation it is apparent that a relatively large change in charge could take place. Such charge variations, in the absence of large electrolyte con-

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centrations, even at a constant micelle size, could result in large turbidity decreases and a consequent increase in $H(c-c_0)/\tau$. Also, it is not inconceivable that as the micellar charge increases, the size of the micelle decreases. However, interpretation of the rise in $H(c-c_0)/\tau$ in terms of variation in micellar weight alone in the mixed systems is difficult at the higher concentrations of $C_{12}E_6$. For example, at a $C_{12}E_6$ concentration of 1 g/100 ml the apparent micellar weight is 14,350 (aggregation number of 32) and the molar ratio of $[C_{12}E_6]/[SDS]$ is 22; thus, at approximately 1.5 dodecyl sulphate ions per micelle, it is unlikely that a drop in micellar weight would occur.

Qualitatively it would appear that the results could be explained in terms of charge effects in the following manner. If it is assumed that the charge on a micelle of the completely micellized non-ionic material is directly proportional to



FIG. 6.— HC/τ against Z curves for n-dodecyl hexaoxyethylene monoether in 10⁻³ M SDS. — $\Box - Z \times 10^2$; — $\bigcirc - Z \times 10$.

the amount of dodecyl sulphate absorbed by the micellar phase, and that the remaining sodium dodecyl sulphate functions as an ordinary electrolyte in this colloidal system, the change in turbidity may be evaluated by substitution in the Prins-Hermans²¹ equation, when taking $C = c - c_0$,

$$\frac{HC}{\tau} = \frac{1}{M} \left[1 + \frac{\alpha^2 \phi^2 Z^2 n^2(C/M)}{2Z(1-\phi)(C/m) + \alpha \phi Zn(C/M)} \right],$$

where M is the micelle molecular weight, α is the resultant degree of ionization of the micelle, ϕ the mole fraction of the ionic detergent absorbed, Z the mole ratio of ionic to non-ionic detergent, n the number of non-ionic molecules per micelle, c the weight concentration of non-ionic detergent and m the molecular weight of the monomer of $C_{12}E_6$.

Further, if it is assumed that the micelle is "dilute" with respect to dodecyl sulphate we may write M = nm and the equation reduces to

$$\frac{HC}{\tau} = \frac{1}{M} \left[1 + \frac{\alpha^2 \phi^2}{2 - (2 - \alpha)\phi} nZ \right].$$

It might be expected that both α and ϕ would be independent of Z for low values of Z and indeed the plot of HC/τ against Z shows an initial linearity (fig. 6).

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The decrease at higher values of Z may be attributed to either a reduction in the absorption of ionic detergent as the micelle charge builds up, or alternatively, an increased binding of the counter-ions which reduces the effective degree of ionization. From the gradient of the HC/τ against Z plot for low values of Z either α or ϕ may be calculated if the other is assumed. Thus, from the experimental value of the gradient (1.55×10^{-3}) , setting α and ϕ in turn equal to one, we have for $\alpha = 1$, $\phi = 0.88$, and for $\phi = 1$, $\alpha = 0.70$.

For the dilute solutions in which the ionic detergent is the minor component, the assumption of $\alpha = 1$ is probably the more correct. The reasonable value obtained for ϕ gives some support for the interpretation that the change in turbidity of the non-ionic detergent on the addition of sodium dodecyl sulphate is due almost solely to charge effects.

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