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Nonionic Micelles*

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ABSTRACT

Current theories and recent results on the thermodynamics of micelle formation and the structure of micelles of nonionic surfactants in water are reviewed. The experimental results are in favor of the mass-action model of micelle formation. This model predicts the existence of micelles below the critical micelle concentration (cmc) and a gradual transition at the cmc. The cmc, as determined conventionally, depends on both the association number, N , and the equilibrium constant, nK_c , of closed association on a mole basis. Empirical relationships between N and nK_c have been found for *n*-octyl- β -D-glucoside (OG) and two nonylphenol(ethylene glycol)_x ethers (NP) at various temperatures as well as for four different ethylene glycol acrylamides (EMA)
 $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{CO} - \text{NR} - (\text{CH}_2)_{10} - \text{CO} - (\text{OCH}_2\text{CH}_2)_{15} - \text{OCH}_3$.
The equilibrium constants of association can be determined by different molecular weight methods, even in the case of polymolecular unimers. Extrathermodynamic relationships exist between the enthalpies and entropies of association.

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The micelles are spherical. Intrinsic viscosities of the micelles can be calculated from the concentration dependence of reduced viscosities, but not from extrapolation to the intercept. From the intrinsic viscosities the amount of water in the micelles can be evaluated and thus the dimensions of the micelles. The micelles of NP can be pictured as consisting of a hydrophobic core and a hydrophilic shell of interrupted helices of poly(ethylene glycol) residues. The dimensions of the OG micelles indicate a duplex micelle, i.e., a micelle with a water core.

INTRODUCTION

Monographs and research papers on emulsion polymerization rely heavily on polymerization kinetics. In contrast, the colloidal aspects of emulsion polymerization are largely neglected. Of course, all people believe in the role of micelles in emulsion polymerization: the emulsifier forms micelles which solubilize monomer. Radicals enter the micelles and start a polymerization there. Additional monomer diffuses from emulsified monomer droplets into the micelles. The micelles grow and finally become latex particles.

According to this picture, little room is left for a specific role for the emulsifier. It is merely the vehicle to solubilize the monomer and stabilize the growing micelles, the monomer droplets, and the latex particles. It is apparently widely believed that the emulsifier can exert this action only above a certain critical concentration, the so-called critical micelle concentration (cmc). It has been stated that "it is now fairly widely believed that below a critical concentration the solute is present as single molecules or ions and that above this concentration micelles begin to form" [1]. Similar statements can be found in other monographs and research papers. It has also been said that "further increases in concentration of surfactant beyond this point increase the number of micelles while the concentration of simple surfactant species remain constant" [2]. These statements imply that there are no micelles below the cmc. On the other hand, there are some findings that emulsion polymerization takes place even below the cmc [3, 4]. For instance, it has been found that "the number of particles generated in emulsion polymerization above cmc is in general one to two orders of magnitude larger than in reaction mixtures in which the initial surfactant concentration is below the cmc" [3]. It thus seems of interest to investigate what the real meaning of the cmc is.

The structure of the surfactant molecules and the structure of the micelles formed from them presents another problem. There are

qualitative findings of an influence of the chemical structure of the emulsifier on emulsion polymerization [5]. The chemical structure of the emulsifier may or may not influence the shape of the micelles. Practically all geometrical arrangements have been suggested for the shape of micelles in solution, in particular spheres, rods, disks (for nonionic micelles see, e.g., Ref. 20). Very few experiments give unequivocal information about the shape of micelles in solution. One can speculate that the shape of the micelles may influence at least the initial stages of polymerization. Indeed, it has been found that the polymerization rate depends on the number of ethylene oxide residues in nonylphenol(polyethylene glycol) ethers [14]. There are findings of an interfacial resistance by the surfactant [9-11], and theoretical considerations emphasize its role in a retardation of the polymerization [12]. On the other hand, "some authors believe that the apparent importance of emulsifier micelles in the initiation of emulsion polymerization is coincidental" [13]. The shape of micelles will thus be reviewed, too.

For theoretical and experimental reasons, the following discussion will be restricted to nonionic micelles. The association of nonionic micelles is easier to treat theoretically because of the absence of the additional association/dissociation of the ionic groups. Furthermore, the critical micelle concentrations are in general higher for nonionic detergents than for ionic surfactants. Higher cmc will allow a more complete measurement of the concentration dependence of properties (e.g., apparent molecular weights) because of the decreasing sensitivity of the methods to decreasing concentration.

THE MEANING OF THE cmc

The concentration dependence of certain properties of surfactant solutions in water is known to show a more or less pronounced "bend" at a certain "cmc", e.g., the surface tension and the electrical conductivity (ionic micelles only). The appearance of this cmc has been explained by two theories:

The pseudochemical theory of micelle formation [6] assumes an association equilibrium between N unimeric surfactant molecules (with molecular weight M_I) and N -mers with the particle weight $(M_I)_N = (M_N)$. This equilibrium can be treated by the mass law:

$$NM_I = M_N; \quad {}^nK_{I,N} = [M_N]/[M_I]^N \quad (1)$$

${}^nK_{I,N}$ is the equilibrium constant on a mole basis. A shortcoming of this theory is that it offers no explanation of why N - and only N - unimers form a micelle.

The younger theory of phase separation [7] postulates the beginning of a phase separation at the cmc. The micelles form single distinct phases, dispersed in the solution. It is difficult to see, however, why the single phases do not unite to form one big phase.

All the experimental results found thus far and reported below support the pseudochemical equilibrium theory. One can thus investigate the predictions of this theory. It is another problem, however, to show whether the model is really applicable to the experimental results.

The mass law predicts an increase of both unimer concentrations, c_I , and N-mer concentrations, c_N , with increasing total surfactant concentration, c (Fig. 1). This was known to Jones and Bury [6] in the 1920s but has apparently since been forgotten. Because of the exponent in Eq. (1), a $\log c_N$ vs c plot is more appropriate than a c_N

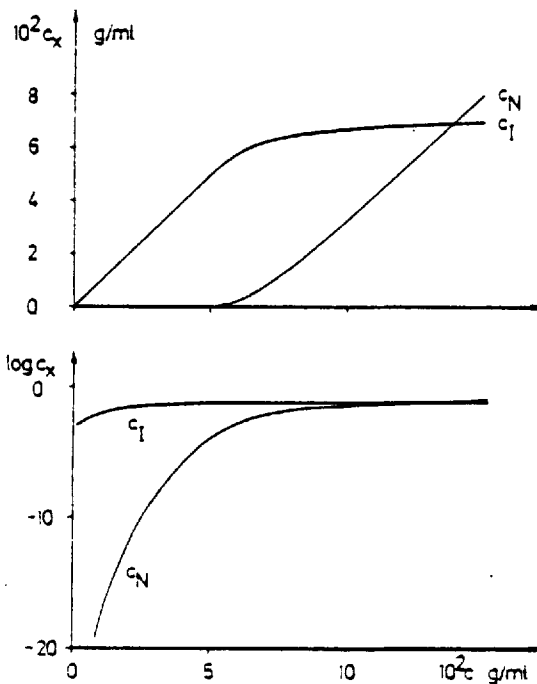


FIG. 1. Dependence of unimer concentrations, c_I , and N-mer concentrations, c_N , on total concentration, c . Calculations for $N = 20$, ${}^n K_c = 50$, and $(M_1)_n = 100$ dalton.

vs c plot [the same applies to $c_I = f(c)$]. A break is apparent only for the $c_N = f(c)$ and $c_I = f(c)$ functions. The theory thus predicts the existence of micelles below the cmc. The cmc may be identified in this context with the "break" in either the $c_N = f(c)$ or $c_I = f(c)$ functions. According to the theory, the micelles have the same structure below and above this cmc. Only the fraction of the micelles changes with the total concentration c .

Figure 1 shows that there is no sharp break in the curve, e.g., the $c_N = f(c)$ function. c_I does not become constant above the cmc but increases slowly with increasing c . Furthermore, attempts to determine cmc by extrapolating the two branches of these functions to an intercept must be highly subjective because the two branches of the $c_N = f(c)$ function above and below the cmc are not linear. The same reasoning

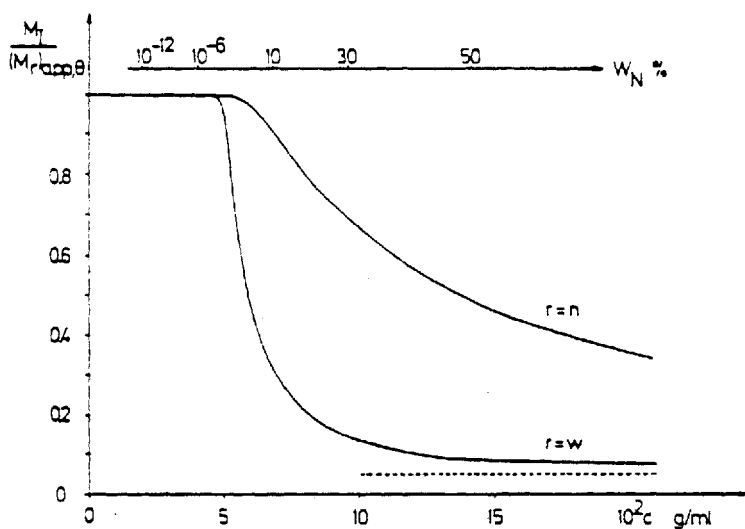


FIG. 2. Concentration dependence of normalized reciprocal apparent molecular weights $M_I / (M_r)_{app, \theta}$ in the theta state. Calculations for a closed association of molecular homogeneous unimer assuming $N = 20$, ${}^n K_c = 50$, $(M_I)_w = 100$ dalton for number-average ($r = n$) and weight-average methods ($r = w$). The weight fraction W_N of N -mers is given in per cent. (---): M_I / M_N .

applies to other plots, e.g., the concentration dependence of apparent molecular weights (Fig. 2).

Furthermore, Fig. 2 shows that number-average and weight-average molecular weight methods lead to different cmc's, which was first pointed out by Becher [8]. His approach to demonstrate this effect might be subject to criticism because he started with the assumption of a sharp onset of micelle formation on the weight fraction scale. It can be shown [19], that this assumption influences the shape of the $M_{app} = f(c)$ functions but not his main conclusion: the influence of the method on the magnitude of the cmc. In general, one would thus expect different cmc's by different methods. I know, however, of no theoretical investigation of this problem for methods other than molecular weight determinations (see Refs. 19 and 21), e.g., for surface tension and electrical conductivity.

There are thus two problems with the conventional definition of the cmc: 1) the method of determining cmc is highly subjective; 2) the result depends on the averaging of the method. Whereas the averaging problem is not serious and can be solved by adequate methods, there remains a need for a better definition of the cmc in order to avoid the subjectivity in its conventional determination.

Phillips [15] thus proposed the use of the third derivative of an ideal colligative property E with respect to concentration as a measure for the cmc. At the cmc, then, by definition

$$\left(\frac{d^3 E}{dc^3}\right)_{cmc} = 0 \quad (2)$$

"Ideal," in this context, means a solution where the second virial coefficient $A_2 = 0$. It must be mentioned that the second virial coefficient used in association studies has a different meaning from the one normally used in macromolecular science because it contains, as usual, all polymer/solvent, solvent/solvent, polymer/polymer interactions and shape factors but excludes intermolecular polymer interactions [21].

The Phillips definition of the cmc has the advantage that it is an unequivocal definition for colligative properties. The concentration dependence of these properties is—at least in principle—easily accessible. The disadvantage is that the cmc as defined by Eq. (2) depends in a very complicated manner on other than colligative properties.

Watterson and Elias [19] thus suggested the use of the third derivative of the unimer or N -mer concentration with respect to concentration as a definition of cmc:

$$-d^3 c_I/dc^3 = d^3 c_N/dc^3 = 0 \quad (3)$$

For the molar concentration $[M_1]_{cmc}$ of the unimers at the cmc, they

obtained a very simple relationship between $[M_I]_{\text{cmc}}$, the association number N , and the molar equilibrium constant nK_o of the open association (to be more exact: end-to-end open association, see Ref. 22)

$$[M_I]_{\text{cmc}} = \left(\frac{N-2}{N^2(2N-1)} \right)^{\frac{1}{(N-1)}} \left(\frac{1}{{}^nK_o} \right) = f(N)/{}^nK_o \quad (4)$$

where the equilibrium constant nK_o is related to the molar equilibrium constant nK_c of the closed association via

$${}^nK_c = ({}^nK_o)^{N-1} \quad (5)$$

For infinitely high association numbers, Eq. (4) approaches

$${}^nK_o = 1/[M_I]_{\text{cmc}} \quad \text{for } N \rightarrow \infty \quad (6)$$

The function $f(N)$ has values of $f(N) = 0.91$ for $N = 100$ and $f(N) = 0.95$ for $N = 200$. In the limit of $N \rightarrow \infty$, $f(N)$ approaches 1. At infinite high association numbers the equilibrium constant of open association can thus be calculated from the molar unimer concentration at cmc (see the similar conclusion for the Phillips definition of the cmc [15, 16]).

As has been shown above, the cmc is by neither definition the concentration at which the first micelles appear. The cmc is thus of phenomenological importance only, i.e., it shows the concentration where a sufficient micelle concentration has been built up to be detected by the method used.

This means that the cmc cannot be used to make any predictions about processes happening above and below the cmc. For instance, it is in general not permissible to calculate heats of micellization from the temperature dependence of the cmc because the cmc depends not only on the equilibrium constants but on the association number N as well (see Refs. 19 and 21). Only in the case of very high N can the cmc be used to calculate thermodynamic quantities [15, 16, 19]. Both the equilibrium constant of association and the association number can vary with temperature which has been found for water solutions of *n*-octyl- β -D-glucoside [23] and two nonylphenol (poly(ethylene glycol)_x)ethers [24].

It is, however, of interest that there are relationships between the association numbers and the equilibrium constants of association for the two

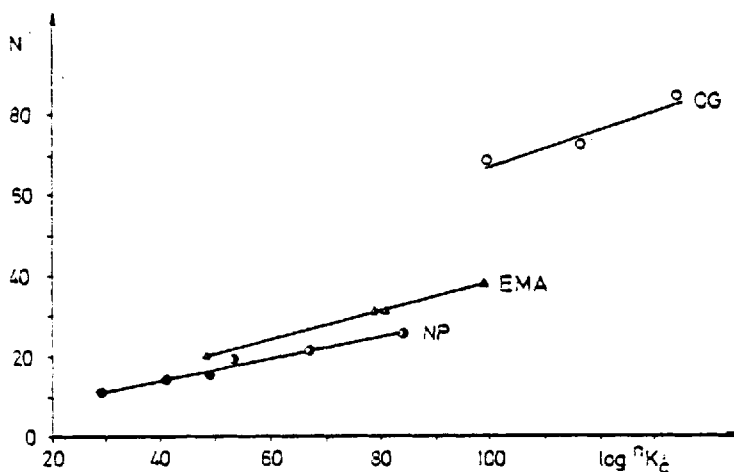


FIG. 3. Dependence of association number N on the logarithm of the equilibrium constant nK_c of association for *n*-octyl- β -D-glucoside (OG) in water at different temperatures (\circ), for ethylene glycol methacryl amides $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{NR}-(\text{CH}_2)_{10}-\text{CO}-(\text{OCH}_2\text{CH}_2)_x-\text{OCH}_3$ (EMA) with different alkyl groups R at 40°C (Δ), and for nonylphenol(ethylene glycol)_{*x*} ethers (NP) in water at different temperatures for $x = 42$ (\blacktriangleright) and 62 (\bullet) (data from Refs. 23, 24, and 37).

different types of surfactants (Fig. 3). It remains to be shown how this interdependence is related to the chemical structure of the surfactant molecules and/or the physical structure of the micelles. No sufficient experimental data are available at present for a hypothesis.

THE THERMODYNAMICS OF MICELLE FORMATION

All the conclusions drawn thus far are based on the predictions of the mass-action model. Yet to be shown is that this model is really applicable to the study of micelles in solution. Because there are two variables (N and nK_c) in this model, both have to be determined in order to demonstrate the applicability of the model. A scan of the literature shows some determinations of N , but none of the equilibrium constant. The feelings of some prominent workers in this field have recently been expressed in an

authoritative text [25]: "However, for the model to be of any use, the K values for each equilibrium must be known, and there is at present no means available of finding them." This statement is false.

The mass-action model predicts an influence of the association number N and the equilibrium constant nK_c of association on the concentration dependence of apparent molecular weights in the theta state. It should thus allow the determination of N and nK_c from this concentration dependence, and exactly this has been done in a recent series of papers by Elias and co-workers [23, 24]. In order to determine the equilibrium constant, the whole concentration envelope of apparent molecular weights must be determined, especially at low concentrations. This is easier done with number-average molecular weight methods than with weight-average methods. Furthermore, only certain surfactants with a sufficiently high cmc can be investigated because of the limits of sensitivity of the present methods.

Typical examples of the concentration dependence of apparent number-average molecular weights of two nonionic surfactants are shown in Fig. 4. In both cases the curve drawn corresponds to the best

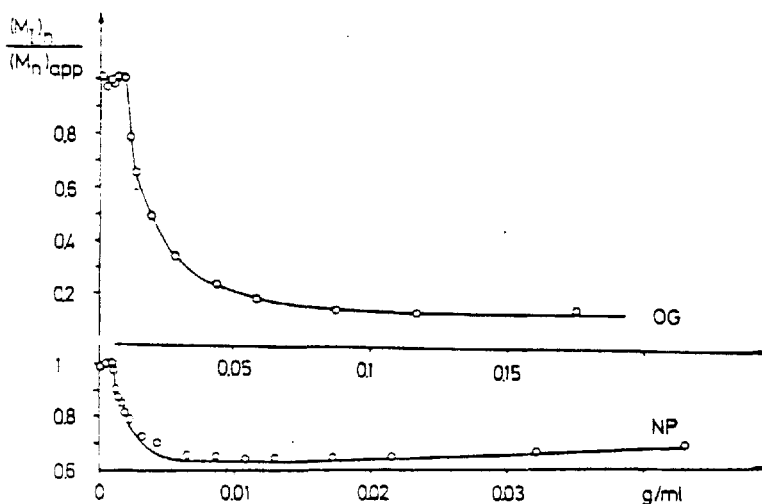


FIG. 4. Concentration dependence of normalized reciprocal apparent number-average molecular weights at 20°C of *n*-octyl- β -D-glucoside (OG) and a nonylphenol(ethylene glycol)₄₂ ether (NP) in water (data from Refs. 23 and 24).

curve fit using the model of closed association and an iteration procedure. Several observations may be made with regard to these curves:

1. The curve fit is better for the *n*-octyl- β -D-glucoside than for the nonylphenol[poly(ethylene glycol)]ether. The reason is very probably the molecular weight distribution of the latter surfactant (*n*-octyl- β -D-glucoside is molecular homogeneous). As has been recently shown by Solc and Elias [22], the following simple relationships exist between the number-average molecular weight $(M_N)_n$ of the *N*-mer, the number-average molecular weight $(M_I)_n$ of the unimer, the weight-average molecular weight $(M_I)_w$ of the unimer and the association number *N*:

$$(M_N)_n = N(M_I)_n \quad (7)$$

$$(M_N)_w = (M_I)_w + (N - 1)(M_I)_n \quad (8)$$

From Eqs. (6) and (7) we obtain

$$\frac{(M_N)_w}{(M_N)_n} = 1 + \frac{1}{N} \left(\frac{(M_I)_w}{(M_I)_n} - 1 \right) \quad (9)$$

If *N* is high, even a very broad molecular weight distribution [in terms of $(M_I)_w/(M_I)_n$] would not show up in polydispersity of the micelles (Fig. 5). An $(M_N)_w/(M_N)_n < 1.05$ is hardly detectable by the present molecular weight techniques. For *N* = 20, $(M_I)_w/(M_I)_n$ can thus be as big as 2. Most technical nonionic surfactants have $(M_I)_w/(M_I)_n$ of less than 2.

The determination of *N* by weight- and number-average molecular weight methods should thus give the same figure, even in the case of polymolecularity of the surfactants. At the limit of high concentrations, both $(M_w)_{app}/(M_I)_w$ and $(M_n)_{app}/(M_I)_n$ will thus lead to the same *N*. However, at finite concentrations an error is introduced if one applies equations derived for a molecular-homogeneous surfactant to a poly-molecular one because the method averages over both the unimers and *N*-mers. This will cause a deviation from the curve fit in the S-shaped region of the concentration envelope of the apparent molecular weights.

2. At least for the nonylphenol[poly(ethylene glycol)]ether, the values of $(M_I)_n/(M_I)_{n,app}$ do not level off at high concentrations. Instead, they pass through a weak minimum with increasing concentration

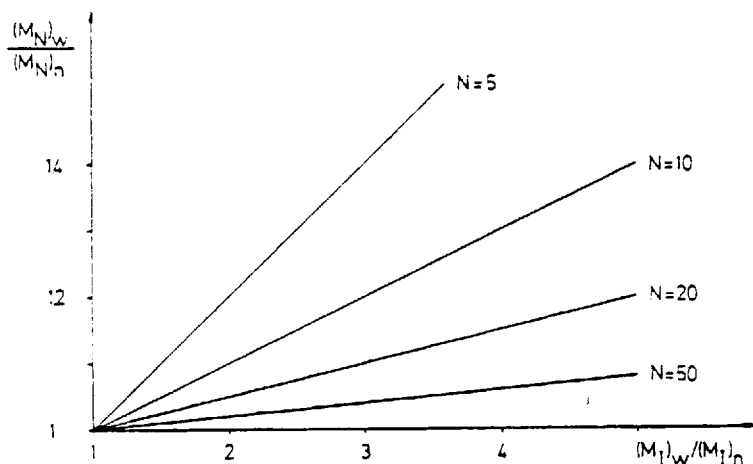


FIG. 5. Dependence of the polydispersity of the micelles [as expressed by $(M_N)_w/(M_N)_n$] on the polymolecularity of the unimers [as expressed by $(M_1)_w/(M_1)_n$] for different association numbers N .

and increase again. A similar behavior has been found recently and was interpreted as a change of association number N with concentration [39]. In our model, however, N is considered to be constant and independent of concentration. Curves with a minimum are typical for a positive second virial coefficient which has to be considered in the iteration procedure. As a consequence, the apparent levelling-off reported in some published papers will then lead to a too low association number. For the examples shown in Fig. 4, one would assume an association number of approximately 10 for the *n*-octyl- β -D-glucoside from mere inspection of the diagram whereas the computer calculation shows the true association number to be 83.5! For the nonylphenol[poly(ethylene glycol)ether] the corresponding figures are about 1.6 (from the diagram) and 21.6 (computer). The discrepancy is caused by both the existence of positive virial coefficients and the very slow approach of $(M_1)_n/(M_n)_{app,\theta}$ with c toward $1/N$.

3. The curves fulfill the predictions of the mass-action models quantitatively. They show the typical S-shape with a "sharp" break at low concentration and smooth transition at higher concentration. If the mass-action model is valid, one would expect to get the same association numbers and equilibrium constants from different molecular weight averaging methods. This prediction has been tested for the *n*-octyl- β -D-glucoside and two nonylphenol[poly(ethylene glycol)]ethers

at different temperatures using vapor pressure osmometry (giving number averages) and light scattering and ultracentrifugation (both giving weight averages). As can be seen from Table 1, the agreement is very good in all cases. We can thus conclude that the mass-action model is indeed adequate to describe the micellization of nonionic surfactants.

TABLE 1. Association Numbers N and Equilibrium Constants wK_c of Closed Association on a Mass Basis for *n*-Octyl- β -D-glucoside [23] and Two Nonylphenol(ethylene Glycol) $_n$ ethers [24] as Determined by Light Scattering (LS), Sedimentation Equilibrium (SE), and Vapor Phase Osmometry (VPO)

Sample	Temp. (°C)	N		log wK_c		
		LS	SE	VPO	LS	SE
<i>n</i> -Octyl- β -D-glucoside	50	72	-	154	154	-
	30	84	83	173	179	175
	20	68	-	135	144	-
Nonylphenol(ethylene glycol) $_{42}$ ether	50	25	-	79	69	-
	30	21	22	63	57	56
	20	19	-	50	51	-
Nonylphenol(ethylene glycol) $_{62}$ ether	50	15	-	43	40	-
	30	14	12	36	37	32
	20	11	-	25	28	-

Because the concentration dependence of apparent molecular weights can be described by a single equilibrium constant over the whole experimental concentration range, there is consequently a constant (standard) Gibbs free enthalpy ΔG_N of micelle formation.

Contrary to what has occasionally appeared in the literature, there is no need to assume that the enthalpy of association ΔH_N and entropy of association ΔS_N change with concentration. Both enthalpy and entropy of association are available from the temperature dependence of ΔG_N .

ΔG_N , ΔH_N , and ΔS_N all vary with temperature [23, 24]. Both enthalpy and entropy of association are positive, indicating the entropy of association as the driving force for the micelle formation. This finding can be explained [17] satisfactorily by an iceberg formation [18] around the surfactant molecules and the micelles.

The extrathermodynamic relationships between the enthalpies and entropies of association are interesting (Figs. 6 and 7). For the *n*-octyl- β -D-glucoside and the two nonylphenol[poly(ethylene glycol)] ethers two separate linear relationships each between ΔH_T and ΔS_T have been found (Fig. 6). The slope corresponds to a compensation temperature of 300° K, which is a bit suspect because it is near the average

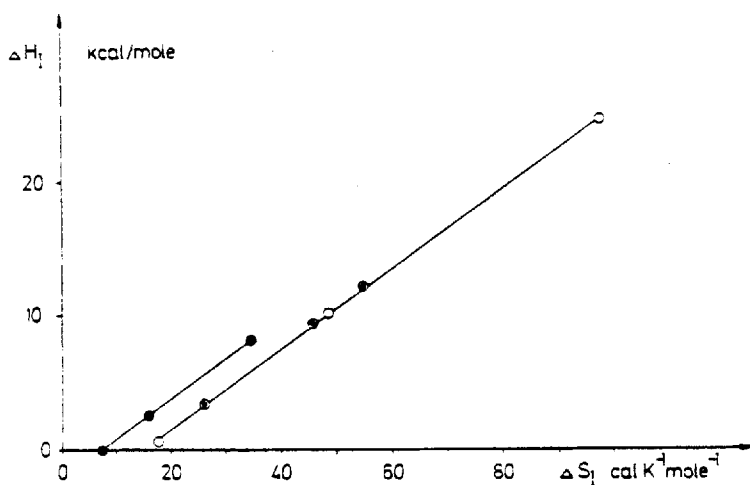


FIG. 6. Relationships between the enthalpies ΔH_T and entropies ΔS_T of association per unimer for *n*-octyl- β -D-glucoside (●) and two nonylphenol(ethylene glycol)_x ethers with $x = 42$ (○) and 62 (◉) in water at different temperatures (from Ref. 23).

temperature of the measurements. Because the temperature range is relatively narrow (293-323° K), none of the criteria worked out as a test for the reality of extrathermodynamic relationships can be applied. There are, however, arguments available in favor of extrathermodynamic relationships even if the compensation temperature is near the average experimental temperature (cf. Ref. 26).

THE SHAPE OF MICELLES

Very few methods are available for the determination of the structure of micelles. X-ray measurements require high concentrations

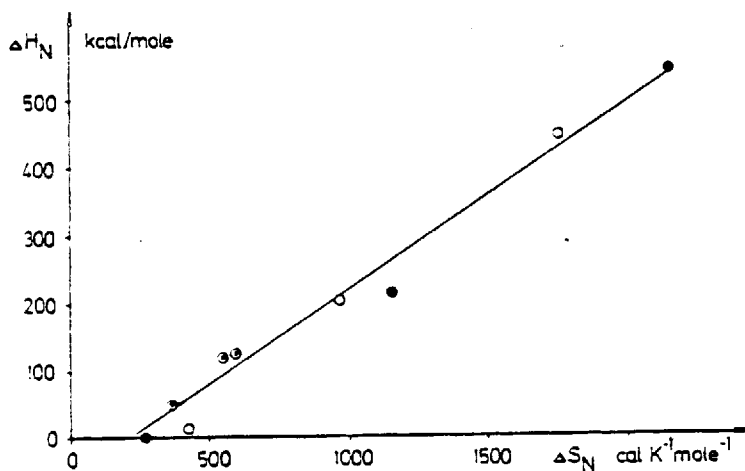


FIG. 7. Relationship between the enthalpies ΔH_N and entropies ΔS_N of association per N-mer for n-octyl- β -D-glucoside (●) and two nonylphenol(ethylene glycol) $_x$ ethers with $x = 42$ (○) and 62 (⊙) in water at different temperatures (from Ref. 23).

for sufficient intensity. It is known that the shape of micellar associations is different at high and low concentrations (see the fiber formation of soap solutions at high concentrations). One may thus suspect that x-ray measurements have been carried out in the past at too high concentrations. Any conclusions drawn from results of x-ray measurements are thus subject to criticism.

The angular dependence of reduced light-scattering intensity can be used to get information about the dimensions of micelles. The presence of small amounts of dust is a tremendous problem. It can be shown that even the finding of a correct unimer molecular weight or N-mer molecular weight is no proof of the correctness of the dimensions calculated from the angular dependence of reduced light-scattering intensity because of the different averaging for molecular weight and dimensions [24]. Furthermore, the dimensions of small micelles cannot be determined at all by light scattering. On the other hand, little use has been made of the information provided by depolarization of scattered light. A Cabannes factor of 1 indicates isotropic particles, i.e., spheres in the case of micelles.

Viscometry has been used less frequently for the determination of micelle structures. These measurements have to be carried out at very low shear rates in order to prevent the destruction of the micelles. A

Zimm-Crothers viscometer [27] has been found very useful for this purpose [30]. Viscometric measurements are normally evaluated by applying the Huggins equation

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \quad (10)$$

or similar relationships. But, in the case of closed associations, any evaluations based on this relationship are not valid (see Ref. 28). For instance, it can be shown that the extrapolation of the linear part of a $\eta_{sp}/c = f(c)$ function does not lead to the intrinsic viscosity $[\eta]_N$ of the micelles (see, e.g., Fig. 8). Instead, one has to analyze the

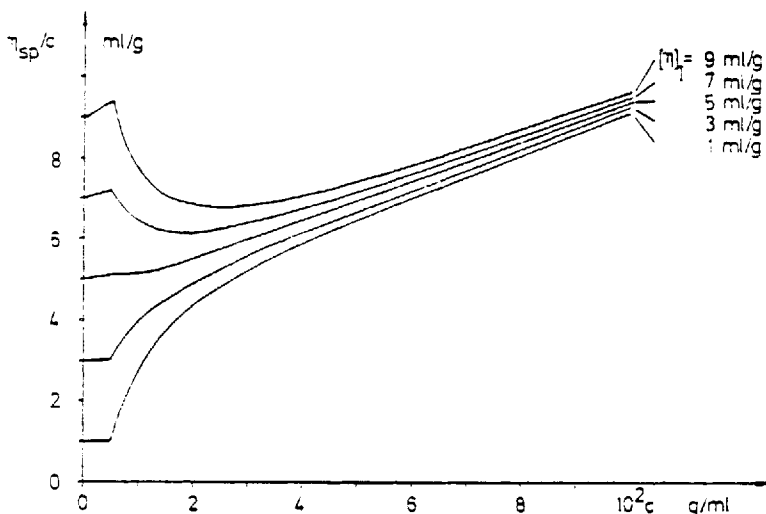


FIG. 8. Concentration dependence of reduced viscosities η_{sp}/c calculated for unimers undergoing closed associations assuming $(M_I)_n = 312$ daltons, $n = 60$, ${}^n K_c = 10^{100}$ (liter/mole)⁵⁹, $[\eta]_N = 5$ ml/g, $(k_H)_I = 1$, $(k_H)_N = 2$, and various intrinsic viscosities $[\eta]_I$ of the unimers (from Ref. 28).

function $\eta_{sp}/c = f(c)$ by an iteration procedure. In order to do this, a model with certain assumptions has to be applied. The model used for the calculation of data in Fig. 9 assumes a closed association and

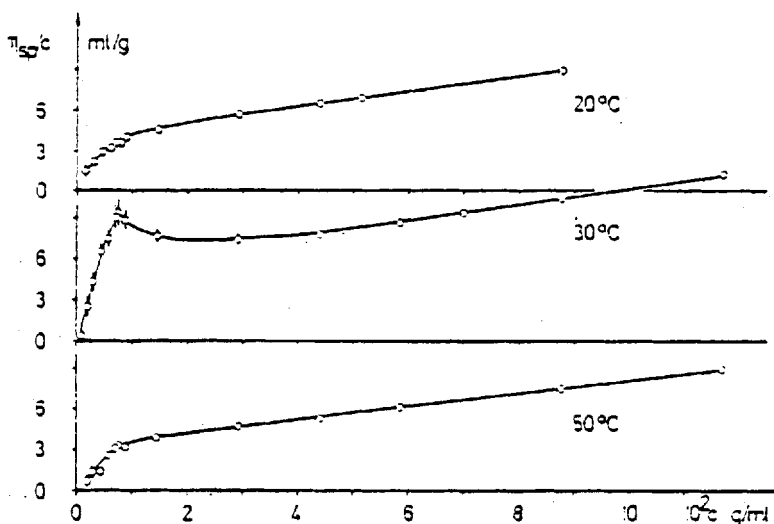


FIG. 9. Concentration dependence of reduced viscosities η_{sp}/c of n-octyl- β -D-glucoside in water at different temperatures (from Ref. 28).

the absence of thermodynamic and hydrodynamic cross-interaction of micelles and unimers. The experimental results show a striking similarity to the model curves (Fig. 9).

The model permits the evaluation of $[\eta]_N$ and $(k_H)_N$. The Huggins coefficient $(k_H)_N$ varies between 1.77 and 2.46 for n-octyl- β -D-glucoside and two nonylphenol[poly(ethylene glycol)]ethers between 20 and 50°C. No significant dependence of k_H on temperature or surfactant structure could be found. The average of 2.07 ± 0.08 agrees remarkably well with the $k_H = 2.26$ predicted for spheres [29]. We can thus assume that the surfactants investigated form spherical micelles in water.

If the micelles are spherical, dimensions can be calculated from the intrinsic viscosity $[\eta]_N$ of the micelles and the second virial coefficient of the micellar solutions. Unsolvated spheres should exhibit an intrinsic viscosity of

$$[\eta]_N = 2.5/\rho_s \quad (\text{ml/g}) \quad (11)$$

The dry surfactants possess densities ρ_2 between 1.142 and 1.196 g/ml [30]. The intrinsic viscosities of dry micelles must thus lie between 2.19 and 2.09 ml/g. Experimentally, intrinsic viscosities between 4.27 and 11.43 have been found (Table 2). The micelles, therefore,

TABLE 2. Intrinsic Viscosities $[\eta]_N$, Solvation Parameters Γ , and Radii (in Å) of Micelles

Compounds	Temp (°C)	$[\eta]_N$ (ml/g)	Γ (g water/g surfactant)	Radius from	
				$[\eta]$	A_2
n-Octyl- β -D-glucoside	50	4.27	0.83	41.6	40.3
	30	5.14	1.18	46.2	40.6
	20	5.19	1.20	26.9	36.0
Nonylphenol(ethylene glycol) _{4,2} ether	50	8.04	2.29	40.7	65.3
	30	8.29	2.41	38.8	58.0
	20	9.95	3.08	39.7	72.6
Nonylphenol(ethylene glycol) ₂ ether	50	10.12	3.23	41.9	61.0
	30	10.81	3.53	41.6	65.2
	20	11.43	3.79	39.6	62.0

must contain an appreciable amount of water, by solvation and/or by inclusion. The amount Γ of water within the micelle can be calculated from [30]

$$[\eta]_N = 2.5(\tilde{v}_2 + \Gamma\tilde{v}_1) \quad (12)$$

where \tilde{v}_2 and \tilde{v}_1 are the specific volumes of the dry surfactant and water, respectively. Specific volumes can be used instead of partial specific volumes because of the similarity of the data from density measurements of surfactant solutions and of dry surfactant [28].

The Γ -values range between 0.83 and 3.79 g water/g surfactant. The micelles must thus contain an appreciable amount of water. Because of the known association number N , radii of micelles can be calculated, assuming additivity of volumes. For n-octyl- β -D-glucoside these radii are by far higher than the length of the octyl glucoside molecule, which is 15.2 Å, if the methylene groups are assumed to be in trans-conformations. Similar results were obtained from the excluded volumes of micelles calculated from the second virial coefficients (Table 2).

Because a firmly bound water shell of 25 \AA around the exterior of the micelles is rather unlikely, we are forced to assume a water core in the interior of the octyl glucoside micelle. This water core must have a diameter of $\sim 45 \text{ \AA}$ for octyl glucoside micelles in water at 30°C . With such a large diameter it seems unreasonable to assume that all glucose residues face the exterior and all octyl group the interior exclusively. A micelle structure where the glucose groups alternate appears more reasonable (Fig. 10). This micelle structure may be called a duplex micelle.

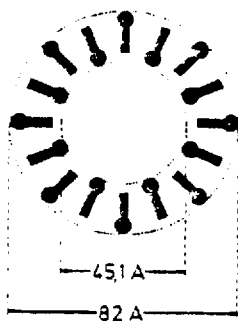


FIG. 10. Model of a duplex micelle of *n*-octyl- β -D-glucoside in water at 30°C (from Ref. 28), drawn to scale.

The situation is different for the nonylphenol[poly(ethylene glycol)]ethers. The methylene groups are probably in the all-trans-conformation, because alkanes $\text{H}(\text{CH}_2)_y\text{H}$ show this conformation in the crystalline state [31], in the melt ($y < 8$) [32], and even in aromatic solvents ($y < 16$) [33]. The ethylene oxide units are known to be in the conformation of a 7_2 -helix in the crystalline state [34] and, according to NMR measurements, are predominantly so in water solutions [35]. The maximal lengths are thus 134 \AA (42 EO units) and 191 \AA (62 EO units). These lengths are larger than the experimentally found radii (Table 2). The ethylene units must thus exist in the conformation of interrupted helices. The overall shape of the polyethylene glycol residues will thus correspond to a random coil-like structure which agrees with the conclusion drawn from the molecular weight dependence of second virial coefficients of poly(ethylene oxides) in water solutions [36].

A possible micelle structure of the nonylphenol[poly(ethylene glycol)]ethers is shown in Fig. 11. In this structure the nonyl residues form a hydrophobic nucleus, whereas the hydrophilic ethylene

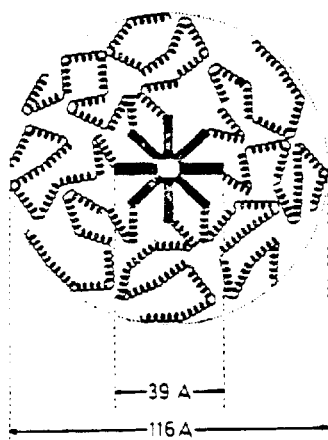


FIG. 11. Model of a micelle of nonylphenol(ethylene glycol)_{4,2} ether at 30°C in water, based on dimensions from the second virial coefficient and drawn to scale (from Ref. 28).

oxide units constitute a loose, water-filled shell. One cannot exclude, however, a duplexlike structure similar to the one proposed for the n-octyl- β -D-glucoside.

CONCLUSIONS

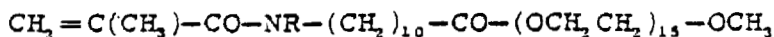
The results reported above show that under certain conditions the whole concentration dependence of apparent molecular weights can be determined. Because this concentration dependence can be analyzed for molecular homogeneous and inhomogeneous unimers, equilibrium constants of micelle formation can be determined even for small association numbers N . Thus we now have the tools to investigate the thermodynamics of formation of nonionic micelles.

The results on micelle structure are less certain. Viscosity measurements at very low shear rates seem suitable if association numbers and equilibrium constants are known. Most promising here are investigations on rigid amphipathic molecules, because of the then possible direct comparison of the calculated molecule length with the experimentally found diameter of the micelles. We have thus started to extend our investigations to other alkyl glucosides.

There remains a need for additional methods for the investigation of micelle shapes and structures. All methods must be applicable at

very dilute surfactant solutions because of the possible structural changes at higher surfactant concentrations. This rules out most of the spectroscopic methods.

Interesting in this respect are attempts to fix the structure of micelles by polymerization. This can be done if the surfactant bears a polymerizable group. We have recently prepared monomers of the acrylamide type



where R = methyl, ethyl, n-propyl, and i-propyl [37]. These compounds could be polymerized in dilute water solution above their cmc. The electron microscope examination of the polymerized micelles showed spherical entities which are apparently showing some sort of a wall (Fig. 12). Because fairly high surfactant concentrations (about 20 times cmc) have been used, these pictures can, at present, be considered only as a proof that the polymerization of micelles is possible. A quantitative examination has to await further experiments.

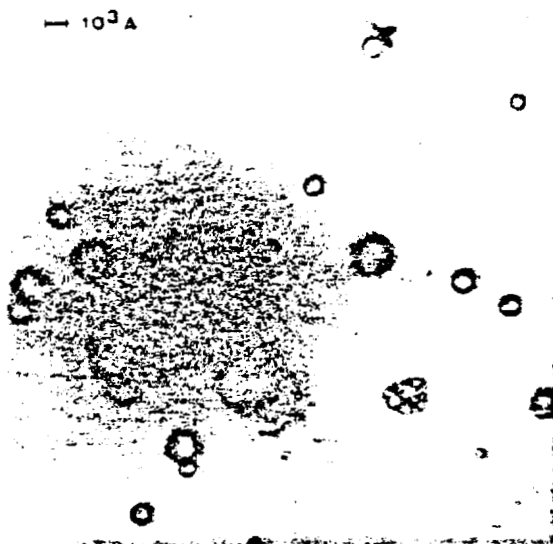


FIG. 12. Electron micrograph of polymerized micelles of $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{CO} - \text{NCH}_3 - (\text{CH}_2)_{10} - \text{CO} - (\text{OCH}_2\text{CH}_2)_{15} - \text{OCH}_3$ (from Ref. 37).

We are at present engaged in preparing glucosides containing styrene residues [38].

The investigation of the thermodynamics of micelle formation and the structure of micelles is only the first step in a better elucidation of emulsion polymerization. Little is known about the process of solubilization of monomers. Nobody knows whether the solubilization is accompanied by a change of micelle structure. There are certainly competitive equilibria between molecular dispersed surfactant molecules, empty micelles, solubilized monomer, and monomer droplets. All this is awaiting a quantitative investigation.

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REFERENCES

- [1] E. Hutchinson and K. Shinoda, "An Outline of the Solvent Properties of Surfactant Solutions," in Solvent Properties of Surfactant Solutions (K. Shinoda, ed.), (Surfactant Science Series, Vol. 2), Dekker, New York, 1967, p. 3.
- [2] J. A. Wood, J. Chem. Educ., **49**, 161 (1972).
- [3] B. M. E. Van der Hoff, "Emulsion Polymerization," in Solvent Properties of Surfactant Solutions (K. Shinoda, ed.), (Surfactant Science Series, Vol. 2), Dekker, New York, 1967, p. 293.
- [4] J. Uglestad, Lecture in Midland, Michigan, March 23, 1972.
- [5] H. Hopff and L. Fakla, Brit. Polym. J., **2**, 40 (1970).
- [6] E. R. Jones and C. R. Bury, Phil. Mag., **4**, 841 (1927).
- [7] G. Stainsby and A. E. Alexander, Trans. Faraday Soc., **46**, 587 (1950).
- [8] P. Becher, Nature, **206**, 611 (1965).
- [9] E. Hutchinson, J. Phys. Colloid Chem., **52**, 897 (1948).
- [10] F. H. Garner and A. P. Hale, Chem. Eng. Sci., **2**, 157 (1953).
- [11] B. W. Brooks, Brit. Polym. J., **2**, 197 (1970).
- [12] B. W. Brooks, Brit. Polym. J., **3**, 269 (1971).
- [13] C. P. Roe, Ind. Eng. Chem., **60**, 20 (1968).
- [14] N. Ja. Vilsanskaja and A. I. Jurzenko, Kolloid. Zh., **33**, 31 (1971).
- [15] J. N. Phillips, Trans. Faraday Soc., **51**, 561 (1955).
- [16] J. Th. G. Overbeek, Chem. Weekbl., **54**, 687 (1958).
- [17] E. D. Goddard, C. A. J. Hoeve, and G. C. Benson, J. Phys. Chem., **61**, 593 (1957).

- [18] H. S. Frank and W. W. Evans, J. Chem. Phys., **13**, 507 (1945); H. S. Frank and W. Y. Wen, Disc. Faraday Soc., **24**, 133 (1953).
- [19] J. G. Watterson and H.-G. Elias, Kolloid-Z., **249**, 1136 (1971).
- [20] M. J. Schick, S. M. Atlas, and F. R. Eirich, J. Phys. Chem., **66**, 1326 (1962).
- [21] H.-G. Elias and R. Bareiss, Chimia (Aarau), **21**, 53 (1967).
- [22] K. Šolc and H.-G. Elias, J. Polym. Sci., Part A-2, In Press.
- [23] H. R. Lässer and H.-G. Elias, Kolloid-Z., **250**, 46 (1972).
- [24] H. R. Lässer and H.-G. Elias, Kolloid-Z., **250**, 58 (1972).
- [25] D. G. Hall and B. A. Pethica, "Thermodynamics of Micelle Formation," in Nonionic Surfactants (M. J. Schick, ed.), Dekker, New York, 1967, p. 519.
- [26] R. Lumry and S. Rajender, Biopolymers, **9**, 1125 (1970).
- [27] B. H. Zimm and D. H. Crothers, Proc. Nat. Acad. Sci., **48**, 905 (1962).
- [28] J. G. Watterson, H. R. Lässer, and H.-G. Elias, Kolloid-Z., **250**, 64 (1972).
- [29] E. Guth and R. Simha, Kolloid-Z., **74**, 266 (1936); E. Guth and O. Gold, Phys. Rev., **53**, 322 (1938).
- [30] Cf., e.g., H.-G. Elias, Makromolekuele, Huethig and Wepf, Basel, 1971, p. 273.
- [31] S. I. Mizushima and T. Shimanouchi, J. Amer. Chem. Soc., **71**, 1320 (1949).
- [32] R. F. Schaufele, J. Chem. Phys., **49**, 4168 (1968).
- [33] K.-J. Liu, J. Polym. Sci., Part A-2, **5**, 1209 (1967).
- [34] H. Tadokoro, J. Chatani, N. Kobayashi, T. Yoshihara, and S. Murahashi, Rep. Progr. Polym. Phys. Japan, **6**, 303 (1963).
- [35] K.-J. Liu and J. L. Parsons, Macromolecules, **2**, 529 (1969).
- [36] H.-G. Elias and H. Lys, Makromol. Chem., **92**, 1 (1966).
- [37] U. Kammer and H.-G. Elias, Kolloid-Z., **250**, 344 (1972).
- [38] J. A. Valicenti and H.-G. Elias, Unpublished.
- [39] R. F. Balmra, J. C. Clunie, J. M. Corkill, and J. F. Goodman, Trans. Faraday Soc., **60**, 979 (1964).

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