Adsorption Kinetics in Micellar Systems

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The kinetics of adsorption and desorption to the air/water surface in submicellar surfactant solutions has been studied by means of a dynamic technique in which the surface is subjected to small amplitude sinusoidal compression and expansion. In all cases studied so far a diffusion controlled mechanism was found, characterised by a frequency dependent surface tension variation and a phase difference between applied area change and resulting surface tension change of at most 45°. When such experiments are carried out above the critical micellar concentration a characteristically different behaviour is observed with a much steeper frequency dependence of the surface tension change and with phase differences between 45 and 90°.

Experiments of this type, carried out for solutions of some nonionic surfactants can be quantitatively interpreted on the basis of a model in which the diffusional exchange of monomers between surface and bulk and the exchange between monomers in the intermicellar solution and micelles are consecutive processes. It is shown that establishment of micellar equilibrium under certain conditions can be a fairly slow process with relaxation times of the order of seconds, although the actual exchange of monomers with micelles could well be several orders of magnitude faster.

Some implications of the presence of micelles on the general nature of dissipative processes near a surface are discussed.

The resistance of fluid surfaces against deformation is an important factor in processes such as foaming, emulsification, liquid drainage from solids, and extraction. A measure for the resistance against compressional or dilational deformation is given by the surface dilational modulus

$$\varepsilon = \mathrm{d}\gamma/\mathrm{d}\ln A. \tag{1}$$

This parameter, when measured in a small amplitude surface deformation experiment, should be expressed as a complex number

$$\varepsilon \equiv |\varepsilon| \exp(\mathrm{i}\psi) \tag{2}$$

as relaxation processes, such as diffusion of surfactant between bulk and surface, cause phase shifts between surface tension change and imposed area change.

Measurements on a number of submicellar surfactant solutions[1, 2] have shown that for all these systems a complete description of the dilational surface behaviour could be based upon a knowledge of an equilibrium surface equation of state combined with a diffusion exchange mechanism of surfactant monomers between the surface under deformation and the bulk solution. All these systems showed similar frequency dependences for $|\varepsilon|$ as well as for ψ. At high frequency, $|\varepsilon|$ approaches an upper limiting value and ψ becomes zero. At low frequency ψ approaches a limiting value of 45° and the slope in a log $|\varepsilon|$ against log frequency plot tends to 0.5.

Above the critical micellar concentration of surfactant solutions, apart from the diffusional relaxation process between surface and bulk, micellar relaxation below the surface also has to be taken into account. Any change in subsurface monomer concentration resulting from surface area changes is bound to disturb the monomer–

micelle equilibrium and hence will set in motion a process of micellisation or demicellisation.

Evidence for the qualitative effect of the presence of micelles on surface dilational properties has been given previously.[2] The phase angle ψ reaches values between 45° and 90°, and the slope in log $|\varepsilon|$ against log ω plots exceeds the value of 0.5.

In this paper is presented a first attempt at reaching a quantitative theory describing surface dilational properties in micellar systems. One problem is that, although much work has been carried out on micellisation kinetics in bulk solutions,[3-11] no clear picture has emerged on its most likely mechanism. However, the different models used all lead to roughly similar relaxation time against concentration relationships and this warrants the adoption of a rather arbitrary model for the purpose of the present paper.

Finally, the relation between increased phase angles in micellar systems on the one hand and dissipative processes leading to shock absorption and protection of thin liquid films in foams on the other are discussed.

EXPERIMENTAL

METHOD

The method used for the measurement of surface dilational properties has been described previously.[2] Briefly, an enclosed part of a surfactant solution's surface area is subjected to periodic compression and expansion of small amplitude and the ensuing variation of surface tension is measured. Conditions are chosen such that the surface deformation can be considered uniform [12] over the enclosed area. The surface dilational modulus is then characterised by an absolute value, that is the ratio between amplitudes of surface tension change $\Delta\gamma$ and fractional area change $\Delta A/A$, and by an angle ψ reflecting the phase difference between surface tension change and imposed area change.

Experiments were carried out at different frequencies of surface deformation, ranging between 10 and 0.05 cycles per minute. However, for the micellar systems in general only results at frequencies above 0.2 cycles per minute were sufficiently accurate for further analysis.

MATERIALS

The preparation, purity and surface chemical properties of the nonionic compounds $C_{12}E_6$ and $C_{14}E_6$ have been described previously.[2]

The sulphobetaine, hexadecyldimethylammoniopropanesulphonate (HDPS) was prepared by reacting in ethyl acetate γ-propane sultone with 99.5 % pure hexadecyldimethylamine. The compound was recrystallised once from isopropyl alcohol and twice from a 2 : 1 (v/v) acetone+isopropanol mixture. Purity was 100 %, according to mass spectrometry. The compound had a Krafft point at 29°C. After heating concentrated solutions to well above this temperature, metastable solutions could be maintained at lower temperatures for at least a day without any sign of precipitate formation. Experiments on HDPS solut tions were carried out at 22, 28 and 35°C. At the two temperatures below the Krafft pointhe surface dilational behaviour of the metastable solutions was not found to be different from that at 35°C.

None of the compounds displayed a minimum in their surface tension at the c.m.c., indicating a high degree of surface chemical purity.

Water distilled from alkaline permanganate was used to prepare all solutions. Its surface tension at 25°C was 72.25 mN m^{-1}.

RESULTS

Detailed data on equilibrium and dynamic surface properties of the nonionic compounds are given in ref. (2).

Fig. 1 shows the surface tension behaviour around the c.m.c. for the HDPS at three different temperatures. The c.m.c. appears to be virtually temperature-independent.

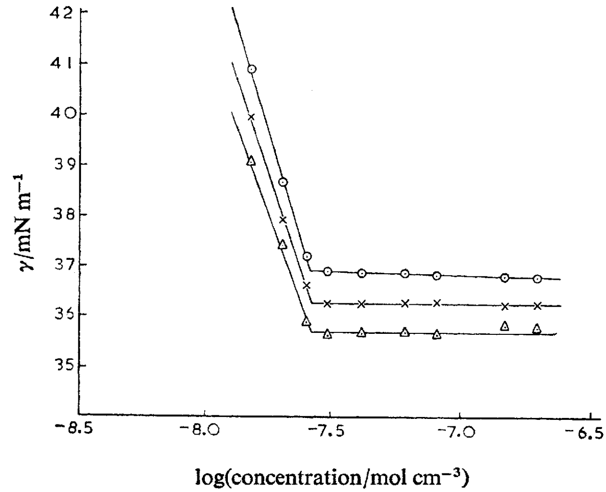

Fig. 1.—Surface tension of HDPS solutions in the neighbourhood of the c.m.c. ○, 22°C; ×, 28°C; △, 35°C.

The dynamic dilational behaviour for HDPS solutions below the c.m.c. did obey the simple diffusion exchange mechanism just as did the nonionic compounds described in ref. (2). No details of the analysis will be given here. The resulting parameters are summarised in table 1.

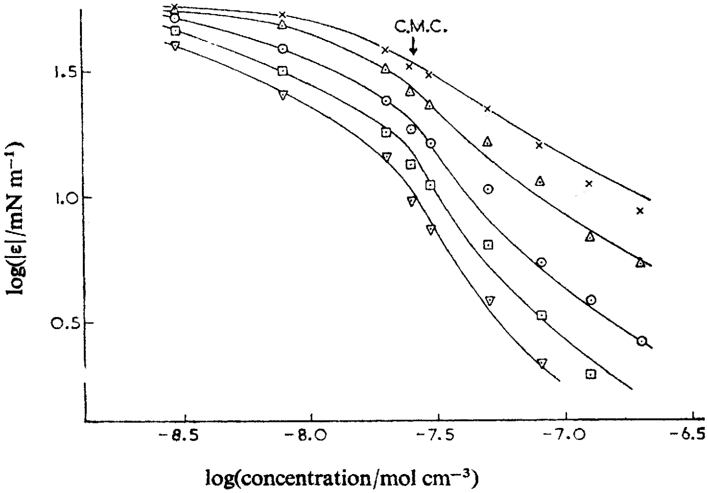

Fig. 2.—Surface dilational modulus for HDPS solutions at different frequencies, as a function of concentration: ×, 10 c.p.m.; △, 5 c.p.m.; ○, 2 c.p.m.; □, 1 c.p.m.; ▽, 0.5 c.p.m. Temperature 28°C. Drawn lines, theory.

TABLE 1

compound	temp./°C	$10^8 \times$ monomer concentration/mol cm^{-3}	$\omega_{\bullet}$/s^{-1}	D_0/cm^2 s^{-1}	ε_0/mN m^{-1}	τ_0/s
$C_{12}E_6$	25	6.6	1.35	4×10^{-6}	50	0.0046
$C_{14}E_6$	25	0.525	0.145	4×10^{-6}	60	0.025
HDPS	22	2.55	0.615	3.5×10^{-6}	65	0.18
HDPS	28	2.55	0.725	4.0×10^{-6}	65	0.13
HDPS	35	2.55	0.813	4.5×10^{-6}	65	0.037

Fig. 2 and 3 show the behaviour of the absolute value of the modulus $|\varepsilon|$ for HDPS solutions in the c.m.c. region at 28 and 35°C respectively, while fig. 4 and 5 reproduce similar data [2] for the nonionic compounds $C_{12}E_6$ and $C_{14}E_6$.

Finally fig. 6 illustrates the behaviour of the phase shift ψ for HDPS at 28°C.

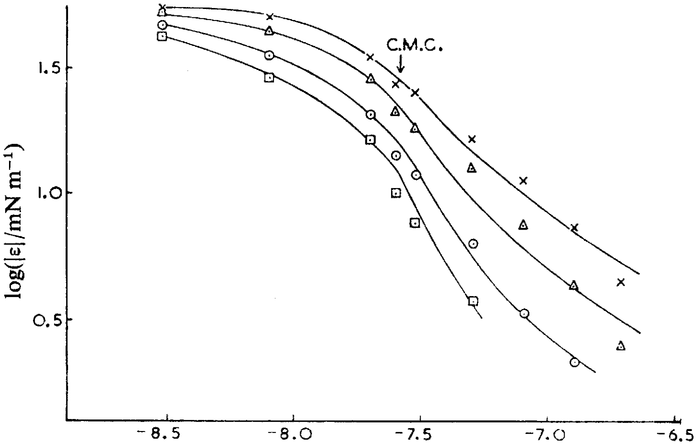

FIG. 3.—As fig. 2. Temperature 35°C.

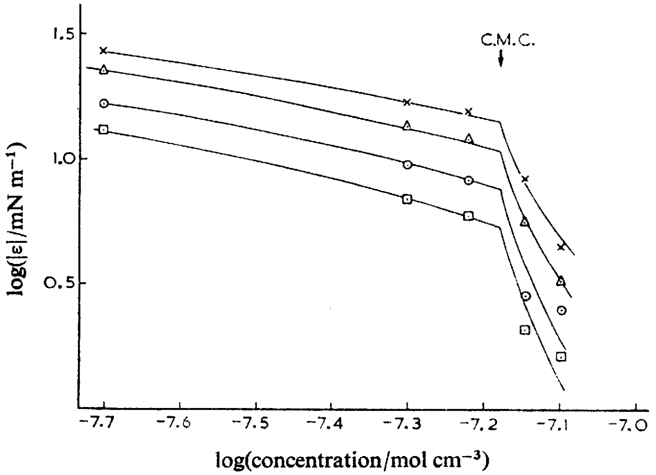

FIG. 4.—As fig. 2, data for dodecyl hexaethylene glycol ($C_{12}E_6$). Temperature 25°C.

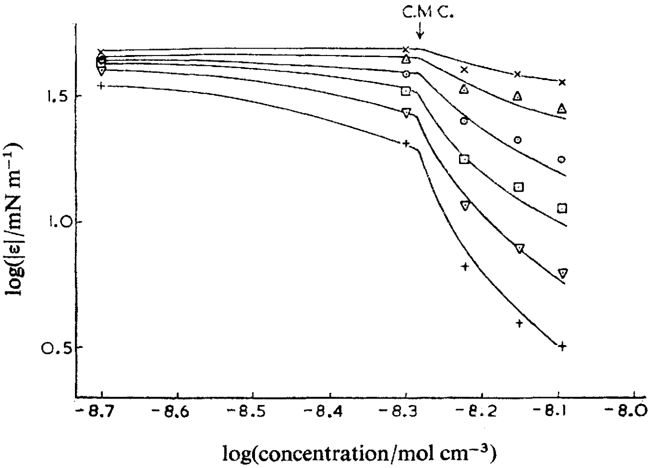

FIG. 5.—As fig. 2, data for tetradecyl hexaethylene glycol ($C_{14}E_6$). Temperature 25°C.

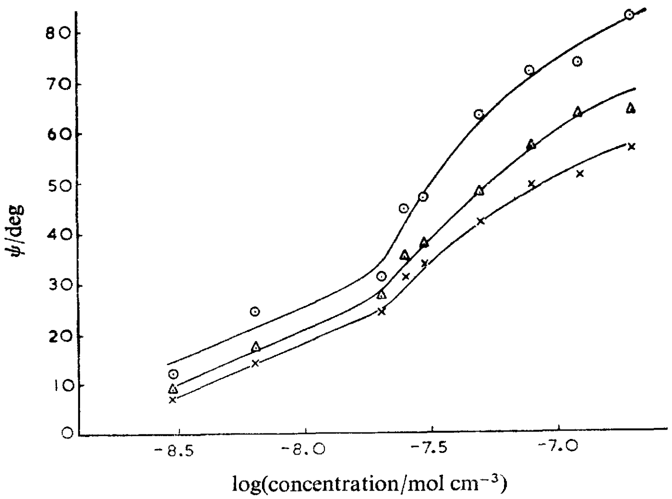

FIG. 6.—Phase angle, ψ, for HDPS at different frequencies, as a function of concentration: ×, 10 c.p.m.; △, 5 c.p.m.; ○, 2 c.p.m. Temperature 28°C.

DISCUSSION

(*a*) THE EFFECT OF MICELLAR RELAXATION ON SURFACE DILATIONAL PROPERTIES

Measurements at concentrations above the c.m.c. of the surfactants under consideration gave phase angles above 45° and slopes in $\log|\varepsilon|$ against $\log\omega$ graphs exceeding 0.5. This behaviour has been explained by a qualitative argument previously.[2] The model which we will adopt here to obtain a quantitative expression for the dilational modulus above the c.m.c. contains the following assumptions:

(i) there is no surface excess of micelles and their concentration at equilibrium is uniform right up to the air/water surface;

(ii) the intrinsic surface properties that is the surface tension, γ, the surface excess, Γ, and derived quantities such as the high frequency limiting value of the modulus $-\mathrm{d}\gamma/\mathrm{d}\ln\Gamma$[14] remain constant above the c.m.c.;

(iii) the amplitude of the applied sinusoidal surface deformation is sufficiently small to permit linearisation of the problem;

(iv) micellar relaxation takes place according to the mechanism proposed by Kreschek *et al.*,[4] in which the rate is limited by one slow decomposition step with rate constant k_2.

The first two of these assumptions seem to be plausible. Micelles, by nature can be supposed to be non surface active. Although a certain measure of desorption due to electrostatic repulsion could be expected for micelles of anionic or cationic surfactants, this does not apply to the nonionic surfactants discussed in this paper.

When the surface tension is practically concentration-independent above the c.m.c., as found for the present systems, it seems obvious that all other *intrinsic* surface properties, properties not affected by diffusion exchange with the bulk liquid, will be concentration-independent as well.

It is difficult to make predictions about the amplitude of the experiments being small enough to permit linearisation. For the systems discussed in the present paper most experiments were carried out at a relative area variation of about 5 %. Under these conditions the surface tension change resulting from a sinusoidal area change was sinusoidal as well and the dilational modulus proved to be independent of the amplitude. Both findings indicate that a linearised theory should be applicable.

The fourth assumption is the least likely to be a realistic one. However, as pointed out before, other mechanisms, such as the highly unlikely one of an α-th order reaction appear to lead to roughly the same global relaxation behaviour and it seems warranted to choose a rather arbitrary mechanism for a first exploration of the area.

By a method, similar to that used for submicellar systems, we then obtain the following expression for the surface dilational modulus (see Appendix I):

$$\varepsilon = \varepsilon_0\left[1+(1-\mathrm{i})\zeta\frac{\{(1-\mathrm{i}x)[(1+\delta(1-\mathrm{i}x)^{\frac{1}{2}})^2+\mathrm{i}k(\delta^2-1)]\}^{\frac{1}{2}}}{1-\mathrm{i}k+\delta(1-\mathrm{i}x)^{\frac{1}{2}}}\right] \tag{3}$$

where $k \equiv k_2/\omega$, $x \equiv k(1+\beta)$, $\delta \equiv [D_M/D_0]^{\frac{1}{2}}$, $\zeta \equiv (\mathrm{d}c_0/\mathrm{d}\Gamma)\sqrt{D_0/2\omega}$, $\beta \equiv \alpha^2[c_M/c_0]_{y=-\infty}$, $\varepsilon_0 \equiv -\mathrm{d}\gamma/\mathrm{d}\ln\Gamma$, $\mathrm{i} \equiv \sqrt{-1}$, with k_2 the rate constant for the slow decomposition step,[4] α the number of monomers per micelle, c_M the molar concentration of micelles, D_M the micellar diffusion coefficient, c_0 the monomer concentration at the c.m.c., D_0 the monomer diffusion coefficient, ω the angular frequency of the experiment.

Eqn (3) covers the general case, taking into account monomer diffusion below the surface, micellar diffusion and re-establishment of the monomer–micelle equilibrium.

The parameter x can be related to the micellar relaxation time as it would be found from bulk relaxation experiments.[4-6, 14] This time, defined by

$$\tau^{-1} = \frac{-\partial\ln\Delta c_M}{\partial t} = \frac{-\partial\ln\Delta c_0}{\partial t} \tag{4}$$

where Δc_M and Δc_0 are deviations of micellar and monomer concentrations respectively from their equilibrium values, is found for the mechanism proposed by Kreschek *et al.*[4] to obey

$$\tau^{-1} = k_2\left(1+\frac{\alpha^2 c_M}{c_0}\right) = x\omega. \tag{5}$$

In other words, values for x, to be obtained from a computer fit of experimental data to eqn (3) can be directly compared to values for $(\omega\tau)^{-1}$ such as would emerge from experiments in which the deviation from equilibrium is uniform throughout the system and in which diffusion can be ignored.

The second term inside the outer square brackets of eqn (3) can be considered as a " supply function ", F_s, which reflects the ability of surface active material to exchange between surface and bulk during an experiment with a characteristic rate of the order ω :

$$F_s = (1-\mathrm{i})\zeta\frac{\{(1-\mathrm{i}x)[(1+\delta(1-\mathrm{i}x)^{\frac{1}{2}})^2+\mathrm{i}k(\delta^2-1)]\}^{\frac{1}{2}}}{1-\mathrm{i}k+\delta(1-\mathrm{i}x)^{\frac{1}{2}}}. \tag{6}$$

The higher the value of F_s, the smaller $|\varepsilon|$ will be compared to its high frequency value ε_0. It is of interest to consider the limiting behaviour of this " supply function ", F_s, for very slow and for very fast micellisation. For the former case we have

$$F_s = (1-\mathrm{i})\zeta \tag{7}$$

as to be expected for a submicellar system.[1] Only the free monomers participate in the diffusion exchange process. For the latter case, where

$$F_s = (1-\mathrm{i})\zeta\sqrt{(1+\beta)(1+\beta\delta^2)}, \tag{8}$$

transport plays a much more important role, as the monomers in the micelles are also able to exchange with the surface. The reduction of $|\varepsilon|$ from its high frequency value can be expected to be greater, the larger the number of monomers per micelle and the larger the micellar concentration and diffusion coefficient.

It should be stressed here, that the dilational modulus above the c.m.c. only vanishes completely for an experiment at infinitely low frequency. The supply of surfactant molecules which " short-circuits " any surface tension change is always emanating from a layer of finite thickness, of the order $\sqrt{D/2\omega}$.[1]

Fig. 7 shows a typical example of the behaviour of $|\varepsilon|$ which could be expected in

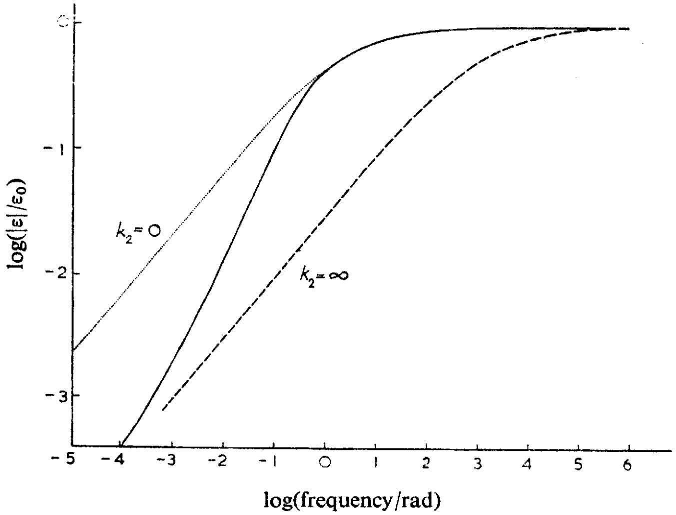

FIG. 7.—Effect of micellisation on surface dilational modulus, as predicted by eqn (3). – – –, $k_2 = \infty$; . . . . . ., $k_2 = 0$; ——, $k_2 = 0.01$. Example for $\omega_0 = 1$; $D_M/D_0 = 0.25$; $\alpha = 50$; $c_M = 0.02\,c_0$.

the above-mentioned two extreme cases. The example refers to a concentration twice the c.m.c. for a hypothetical system with 50 monomers per micelle. The upper (dotted) line gives the behaviour of $|\varepsilon|$ for a very slow micellisation reaction and the lower (dashed) one represents fast micellisation. The ratio D_M/D_0 is taken as 0.25.* It is obvious that in the frequency region where diffusion is important, the reduction of $|\varepsilon|$ is much larger in the latter than it is in the former case.

The drawn line in fig. 7 represents the intermediate case, for $k = 10^{-2}\zeta^2$. In this case there is a transition from the dotted to the dashed curve in the frequency region where $x \approx 1$. In this region the slope in the log $|\varepsilon|$ against log ω curve, as predicted before,[2] exceeds unity.

Similar evidence, shown in fig. 8 shows that in the same frequency region the phase angle ψ exceeds the value of 45°, which was shown to be the maximum value for monomer diffusion exchange.

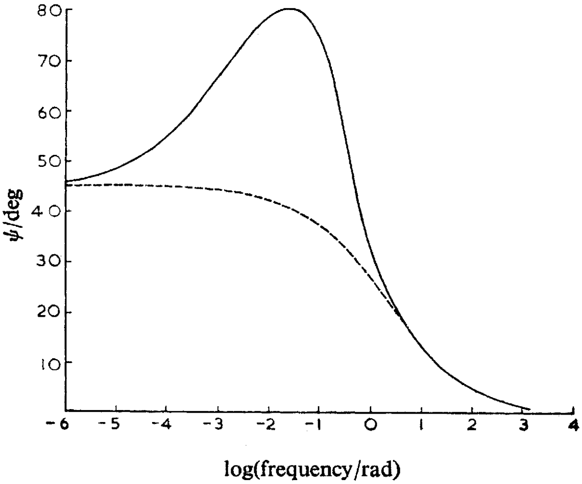

FIG. 8.—Effect of micellisation on the phase angle ψ. ---, $k_2 = 0$; ——, $k_2 = 0.01$. Further data as for fig. 7.

(b) COMPARISON WITH EXPERIMENTAL EVIDENCE

The agreement between theory, as expressed by eqn (3), and experimental evidence for the three surfactants discussed, was tested by means of a least square curve fitting programme. Apart from the values for $|\varepsilon|$ at various concentrations and frequencies, the following parameters had to be fed into this programme.

(1) The equilibrium surfactant monomer concentration at the c.m.c., c_0.

(2) The high frequency dilational modulus $\varepsilon_0 = -(\mathrm{d}\gamma/\mathrm{d}\ln\Gamma)$.

(3) The diffusion exchange parameter $\omega_0 = \omega\zeta^2 = D/2(\mathrm{d}c_0/\mathrm{d}\Gamma)^2$, both (2) and (3) at the c.m.c. The method used for obtaining the latter two parameters and for extrapolating them to the c.m.c. has been described previously.[2, 14]

(4) For all three compounds the number of monomers per micelle, α, was assumed to be 100.[15] Actually the quality of the curve fit appeared to be only very weakly

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* It has been pointed out by McQueen and Hermans[13] that the ratio D_M/D_0 should be of the order $\alpha^{-\frac{1}{3}}$. The Stokes–Einstein relation predicts an inverse proportionality between particle radius and diffusion coefficient.

dependent on α, so that it did not seem necessary to use a very accurate value for this parameter. Thus, for the parameter δ, a value of 0.465 was adopted.[13]

The concentration dependence was introduced through eqn (5), which gives, with

$$c_{\text{tot}} = c_0 + \alpha c_{\text{M}}, \tag{9}$$

$$\tau^{-1} = k_2(1-\alpha+\alpha c_{\text{tot}}/c_0) \approx -k_2\alpha+k_2\alpha c/_{\text{tot}}c_0 \equiv -\tau_0^{-1}(1+c_{\text{tot}}/c_0). \tag{10}$$

Examples of the curve fit for $|\varepsilon|$ are given by the drawn lines in fig. 2–5. Taking into consideration the large number of assumptions made and the wide range of frequencies and concentrations covered, the agreement between theory and experiment can be considered quite good.

In principle a similar curve fit could be applied to the experimental values of the phase angle ψ. However, the experimental accuracy of this parameter at small $|\varepsilon|$ values was rather low and was therefore not used for further evaluation. In general, however, the behaviour of both $|\varepsilon|$ and ψ above the c.m.c. was as to be expected from the theory. The model used here, therefore can certainly serve as a basis for a further refinement of the picture of coupled diffusion-micellar relaxation. In the next paragraph we will discuss, on a preliminary basis, the significance of the results obtained from the least square fitting procedure.

(*c*) THE MECHANISM OF MICELLAR RELAXATION

The curve fitting programme supplies values for the characteristic relaxation times τ_0 [see eqn (10)]. They are presented in table 1, together with starting values, used for ε_0, c_0, ω_0 and the diffusion coefficient D_0.

It appears that these relaxation times are of the order of a hundredth to a tenth of a second, certainly several orders of magnitude higher than would be expected for the exchange mechanism proper between monomers and micelles.[10] Such a discrepancy has been apparent from all experiments on micellisation kinetics by various methods, except from the evidence obtained by n.m.r.[16, 17] It is of interest to note, that τ_0-values, as obtained by different techniques, including the present one, appear to increase with decreasing value of the c.m.c. The present systems have c.m.c. values (or monomer concentrations above the c.m.c.) much lower than any other system studied before in this context and they also show the highest relaxation times found so far.

This general trend suggests that the rate determining step in the process whereby micelles generate or absorb free monomers is not the micellar decomposition, but diffusional transport from or towards micelles. Such a process should proceed at a higher rate, the larger is the monomer concentration.

According to a very crude model, in which all micelles are considered stationary sources or sinks which are able to absorb or replenish all deviations from the monomer equilibrium concentration, τ_0-values could be predicted which were about 2 orders of magnitude smaller than the experimental ones. Such a model, however, can be expected to give low estimates of relaxation times for two reasons. In the first place, micelles cannot be expected to act as infinitely " deep " sinks or infinitely " high " sources. Secondly, if they were to act as such in the first instance, it would be necessary that subsequently the micellar size distribution and the total number of micelles adapt themselves such as to obey the requirements of the various monomer-micelle equilibria. Such a rearrangement of micellar size and numbers would involve a " flow " throughout the whole of the micellar size distribution, as discussed by Aniansson *et al.*[11] As this will invoke monomer diffusion over much larger characteristic distances than the average separation between two micelles, the relaxation times involved will be longer than would be expected from a simple source/sink model. The present scant knowledge of micellar size distributions does not seem to warrant a further evaluation of the model in this stage.

(*d*) THE EFFECT OF MICELLES ON DISSIPATIVE PROCESSES NEAR A SURFACE

It has been shown previously [1, 18, 19] that the lateral propagation over a liquid surface of locally applied surface tension changes strongly depends on the phase angle ψ. Such propagation is determined by the properties of longitudinal surface waves, for which the ratio between damping coefficient β_L and wavenumber κ_L is given by

$$\beta_L/\kappa_L = \tan(\pi/8+\psi/2). \tag{11}$$

This ratio determines the fraction of an initial surface tension variation which is still left after it has propagated over a distance d, equal to one wavelength:

$$|\Delta\gamma|_{d=\lambda}/|\Delta\gamma|_{d=0} = \exp(-2\pi\beta_L/\kappa_L). \tag{12}$$

For an insoluble monolayer with $\psi = 0$, this fraction is 0.075. For a micellar solution with $\psi = 80°$ it has decreased to as low a value as 3.5×10^{-6}.

In other words, the presence of micelles can cause surface tension variations to propagate over much shorter distances than would be the case below the c.m.c. This effect of two-dimensional shock-absorption may well lead to a greater stability of free thin films under dynamic conditions.

The effect of micelles on surface shock absorption is completely analogous to their effect on sound absorption.[5, 6] In both cases micellisation–demicellisation will lead to an enhanced rate of energy dissipation.

(*e*) SUMMARISING REMARKS

It has been shown in this paper how measurements of surface dilational properties carried out at various frequencies and concentrations can help to elucidate the kinetics of surfactant adsorption and desorption. When applied to micellar systems additional information can be obtained about micellar relaxation processes.

The technique used is of limited applicability. Only compounds with a fairly low c.m.c. value can be studied in this way. For surfactants with a c.m.c. of the order of 10 mmol dm^{-3} or higher, the surface tension variations would be too low to allow accurate measurements. For such systems, with small diffusion relaxation times, a high frequency surface deformation such as could be obtained by capillary waves may well be used to study adsorption and micellisation kinetics.

APPENDIX

DERIVATION OF DILATIONAL MODULUS FOR MICELLAR SYSTEMS

Variations in monomer and micelle concentration below the surface should obey the following relations:

$$\partial c_0/\partial t = -\alpha k_1 c_0^{\alpha} + \alpha k_2 c_M + D_0 \partial^2 c_0/\partial y^2 \tag{A1}$$

$$\partial c_M/\partial t = k_1 c_0^{\alpha} - k_2 c_M + D_M \partial^2 c_M/\partial y^2, \tag{A2}$$

in which k_2 can be identified with the slow step of the mechanism according to Kreschek *et al.*[4, 13]

We search for solutions of c_0 and c_M of the form

$$c_0 = (c_0)_{y=-\infty} + f_0(y)\exp(i\omega t) \tag{A3}$$

$$c_M = (c_M)_{y=-\infty} + f_M(y)\exp(i\omega t). \tag{A4}$$

For low amplitude disturbances, substitution of (A3) and (A4) into (A1) and (A2), and taking the equilibrium condition

$$(c_0)^{\alpha}_{y=-\infty} = k_2/k_1(c_M)_{y=-\infty} \tag{A5}$$

into account leads to the following differential equations:

$$f_0(y)+Pf_M(y)+Qf''_0(y) = 0 \tag{A6}$$

$$f_0(y)+Rf_M(y)+Sf''_M(y) = 0 \tag{A7}$$

where

$$P \equiv -k_2\alpha[i\omega+k_2\alpha(c_M/c_0)_{y=-\infty}]^{-1}$$

$$Q \equiv -D_0[i\omega+k_2\alpha^2(c_M/c_0)_{y=-\infty}]^{-1}$$

$$R \equiv -(k_2+i\omega)[k_2\alpha(c_M/c_0)_{y=-\infty}]^{-1}$$

$$S \equiv D_M[k_2\alpha(c_M/c_0)_{y=-\infty}]^{-1}.$$

Solutions for $f_0(y)$ and $f_M(y)$ are of the form

$$f_0(y) = E\exp(n_A y)+F\exp(n_B y) \tag{A8}$$

$$f_M(y) = M\exp(n_A y)+N\exp(n_B y) \tag{A9}$$

with for n_A and n_B those two roots of the equation

$$n^4+\frac{QR+S}{QS}n^2+\frac{R-P}{QS} = 0 \tag{A10}$$

which have a negative real part. The other two roots will not give vanishing values for f_0 and f_M at $y = -\infty$.

The constants E, F, M and N now have to be eliminated by the boundary conditions for conservation of matter at the surface. For micelles, the assumption that they are not surface active, combined with their boundary condition:

$$\frac{\partial(\Gamma_M A)}{\partial t}+AD_M\left(\frac{\partial c_M}{\partial y}\right)_{y=0} = 0 \tag{A11}$$

leads to

$$\left(\frac{\partial c_M}{\partial y}\right)_{y=0} = 0. \tag{A12}$$

Substituting this into eqn (A4) and combination with eqn (A9) gives

$$f_M(y) = M[\exp(n_A y)-n_A/n_B\exp(n_B y)]. \tag{A13}$$

An expression for the dilational modulus ε is now obtained in a way analogous to the one used in ref. (1):

$$\varepsilon = \varepsilon_0\left[1+D_0\frac{dc_0}{d\Gamma_0}\frac{n_A}{i\omega}\left\{\frac{1+(n_B/n_A)(F/E)}{1+F/E}\right\}\right]^{-1} \tag{A14}$$

The ratio F/E is found by substitution of eqn (A8) and (A13) into eqn (A6) or (A7). The resulting expression

$$(E+PM+QEn_A^2)\exp(n_A y)+(F-PM\,n_A/n_B+QFn_B^2)\exp(n_B y) = 0 \tag{A15}$$

should be valid at any value of y and therefore the coefficients of the exponential terms should each equal zero. This results in

$$F/E = -n_A/n_B\left(\frac{1+Qn_A^2}{1+Qn_B^2}\right). \tag{A16}$$

Finally, from eqn (A10) we have

$$n_A^2 n_B^2 = \frac{R-P}{QS} \tag{A17}$$

and

$$-(n_A^2 + n_B^2) = \frac{QR+S}{QS}. \tag{A18}$$

Substitution of eqn (A16), (A17) and (A18) into eqn (A14), finally gives eqn (3) for the surface dilational modulus.

Thanks are due to Mr. D. Giles for accurately performing the experiments and to Mrs. J. C. Savage for writing the least square curve fitting programme.

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