Relaxation Phenomena after an Area Strain on the Adsorbed Surfaces of Aqueous Solutions of Poly(oxyethylene) Dodecyl Ethers

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The relaxations were observed after suddenly dilating or compressing the equilibrium surfaces of aqueous solutions of poly(oxyethylene) dodecyl ethers, $C_{12}H_{25}(OC_2H_4)_nOH$ (n=5 and 7), at 303 K. The relaxation is expressed as the Maxwell model, with a Hookean surface-area modulus and a Newtonian surface-area viscosity, if the absolute value of an area strain is less than 0.3. The surface-area modulus is dependent upon the amount of surfactant molecules adsorbed in the surface, Γ, regardless of the sign of the area strain. The relaxation time, τ_c, in the case of compression is dependent on Γ, and τ_d in the case of dilation depends on the monodispersed concentration of the surfactant in the bulk solution, C. The surface dilational viscosity, $\eta_{\mathrm{D}}^{\mathrm{A}}$, has a maximum around the concentration at which the surface reaches the saturated adsorption. The rate constants for the adsorption and desorption were estimated by determining empirically the functions of $1/\tau_d$ and $1/\tau_c$ with respect to C and Γ respectively.

The rheological properties, especially the resistances against an area strain, of an interface containing adsorbed surfactants have been pointed out as important factors in stabilizing some dispersions through the resistance against the rupture of the interface.[1,2] In a previous paper[3] there has been proposed a concept that a liquid surface with adsorbed surfactant molecules behaves as a two-dimensional open system, in which the number of surfactant molecules changes during the processes, involving some area strains. Thus, when the surface is dilated, an adsorption of surfactant molecules proceeds from the bulk solution to cover the lack in the surface. On the other hand, when the surface is compressed, an excess of surfactant molecules desorbs into the bulk solution. It is the purpose of the present paper to determine quantitatively both the surface-area modulus and the surface-area viscosity of the surface adsorbed with surfactants and, further, relate them to the molecular behavior characterized by the two-dimensional open system. For this purpose, measurements were made of the stress relaxation, with the area strain kept constant, either positive or negative, after suddenly dilating or compressing the surface in equilibrium with the bulk solution at a constant temperature of some nonionic surfactants. That is, the system was simple as possible.

Experimental

The nonionic surfactants, poly(oxyethylene) dodecyl ethers $C_{12}H_{25}(OC_2H_4)_nOH$ (n=5 and 7), were kindly provided by Nihon Surfactant Kogyo K.K.; they had a purity above 99% and no distribution of polymerization in the hydrophilic part, as verified by gas chromatography.[4] The solvent was obtained by distilling the alkaline permanganate solution in ion-exchanged water after refluxing for 15 h.

An equilibrium surface was obtained by filling a Langmuir-type trough with a solution, maintaining the temperature constant at 303 K, after sweeping the surface 6 times in 1 h with three glass barriers coated with paraffin; the trough was then allowed to stand for *ca.* 15 h. The area, A_0, of the equilibrium surface was changed suddenly to another area, A, by moving one of the two barriers which had confined the area. As the result, the surface underwent an area strain, $\Delta A/A$ ($\Delta A = A - A_0$). According to the direction of the movement of the barrier, the surface was either dilated or compressed, the sign of area strain being positive or negative. When the area strain was maintained constant, the surface pressure, π, which had deviated as a result of the sudden change in the area, converged gradually to the equilibrium value, π_e. Such phenomena were measured by the Wilhelmy method using a torsion balance with a glass plate.[5] The surface pressure was determined at a precision within ±0.05 mN m^{-1}, particularly by controlling the level of the surface to avoid any changes in the position of the plate due to the change in the surface level which accompanies the movement of the barrier.

Results and Discussion

The relations of the surface pressure, π, with the time, t, after sudden area strains are shown in Fig. 1 when, for example, the surface of a solution of 3.56×10^{-2} mol m^{-3} of n=5 is dilated with various proportions. As may be seen in the figure, π converges to an equal value if the area strain does not exceed 0.67. The converged value was regarded as the equilibrium surface pressure, π_e, of the surface at that temperature. The stress corresponding to the area strain at time t is the

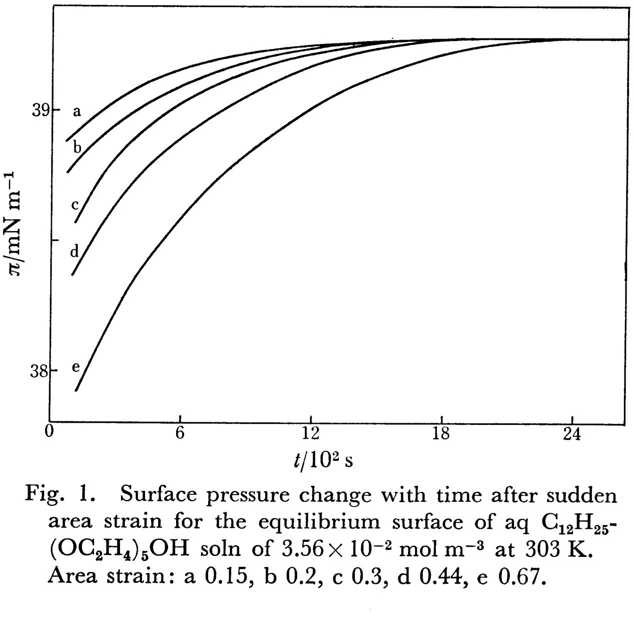

Fig. 1. Surface pressure change with time after sudden area strain for the equilibrium surface of aq $C_{12}H_{25}(OC_2H_4)_5OH$ soln of 3.56×10^{-2} mol m^{-3} at 303 K. Area strain: a 0.15, b 0.2, c 0.3, d 0.44, e 0.67.

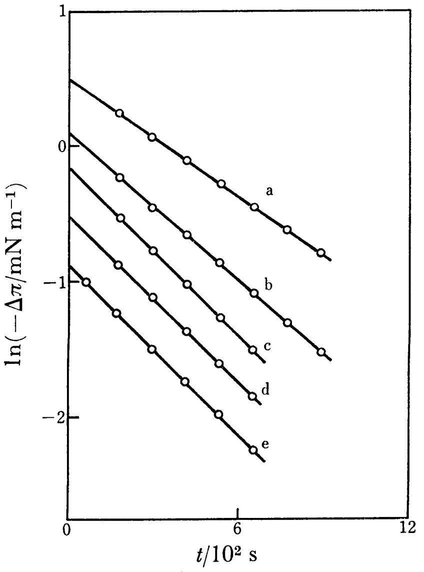

Fig. 2. Stress relaxation plots for the curves in Fig. 1.

difference in the surface pressure from the equilibrium value, $\Delta\pi=\pi-\pi_e$, which has the sign opposite to the strain; it is negative in the case of the dilation and positive in the compression.

The curves in Fig. 1 show the stress relaxation when the area strain is kept constant. The natural logatithm of the absolute value of the stress, which is estimated from the curves in Fig. 1, decreases linearly with time t, as is shown in Fig. 2. The relations between $\Delta\pi$ and t can be expressed by

$$\Delta\pi = K\exp(-t/\tau) \tag{1}$$

for each area stress, where K is the initial stress and τ is the relaxation time; these values are obtained from the value extrapolated to $t=0$ and the slope of the straight line in Fig. 2 respectively.

Equation 1 corresponds correctly to the relaxation of the Maxwell model with the surface-area modulus, ε^A, and the surface-area viscosity, η^A, when the model undergoes a constant area strain, $\Delta A/A$.[6] Accordingly, K, τ, ε^A, and η^A are connected with each other by

$$K = -\varepsilon^A(\Delta A/A), \tag{2}$$

and

$$\tau = \eta^A/\varepsilon^A. \tag{3}$$

Since K has the sign opposite to $\Delta A/A$, as has been mentioned above, ε^A is always positive. Both ε^A and η^A can be obtained from the measured K and τ by applying Eqs. 2 and 3. As a result of repeated measurements of the surfaces with an equal bulk concentration, as is shown in Fig. 3, it may be concluded that both ε^A and η^A are independent of the area strain, $\Delta A/A$; they are, therefore, Hookean and Newtonian respectively if the area strain is less than 0.3. Only if the absolute value of the area strain does not exceed 0.3 were ε^A and η^A confirmed to be Hookean and Newtonian for any surface under investigation, with either the dilation or compression of the surface.

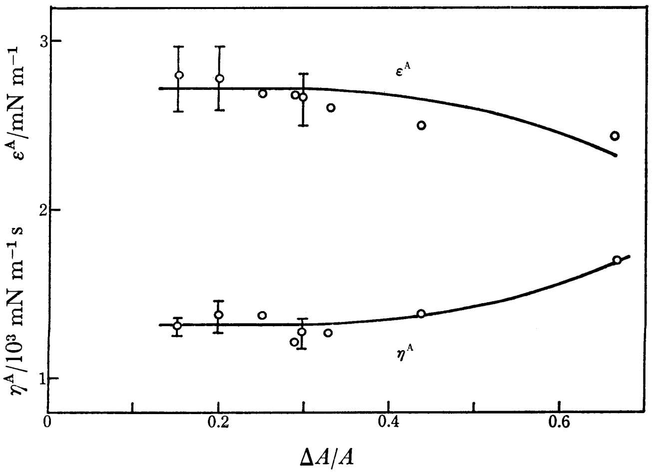

Fig. 3. Surface-area modulus ε^A and surface-area viscosity η^A vs. area strain plots for $C_{12}H_{25}(OC_2H_4)_5OH$ soln of 3.56×10^{-2} mol m^{-3}.

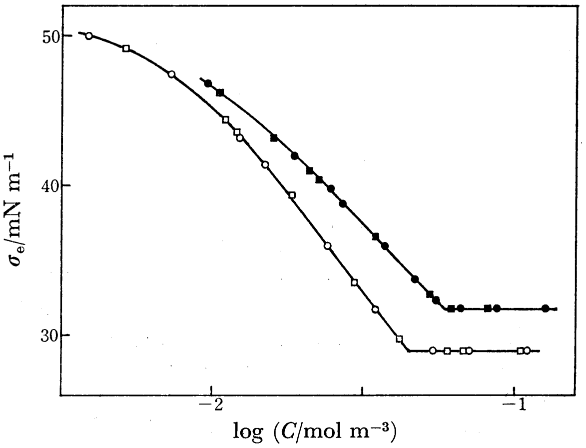

Fig. 4. Equilibrium surface tension vs. log concn plots for aq $C_{12}H_{25}(OC_2H_4)_nOH$ soln.

n: 5 7

○ ●: dilation

□ ■: compression

The equilibrium surface tension, σ_e, which was estimated by subtracting the converged surface pressure, π_e, in the relaxation curve from the surface tension of pure water at 303 K, 71.15 mN m^{-1}, [7] is plotted against the logarithm of concentration, C, in Fig. 4. All the plots fall on a single curve for $n=5$ and 7, whether π_e is measured by means of the dilation or the compression of the surface. This means that the measured relaxation process is a process approaching a final state, irrespective of the dilation or compression, *i.e.*, it is approaching a true equilibrium state. The concentrations at the break points, corresponding to the critical micelle concentration, CMC, are 4.5 and 5.9×10^{-2} mol m^{-3} for $n=5$ and 7, smaller than the values at 6.8 and 6.9×10^{-2} mol m^{-3} at 278 K measured by Ohba and Takahashi for the same substances,[4] but the differences are not so great in the surface tension. The CMC value for $n=5$ determined by van Voorst Vader *et al.*[8] is 12×10^{-2} mol m^{-3}, far larger and rather close to the value found by our preliminary experiments using the drop-weight method. These facts indicate that the break point on the surface tension vs. log C curve, corresponding to the CMC, has a tendency to be smaller in concentration as the surface tension approaches the equilibrium value.

The surface-area modulus, ε^A, increases with an

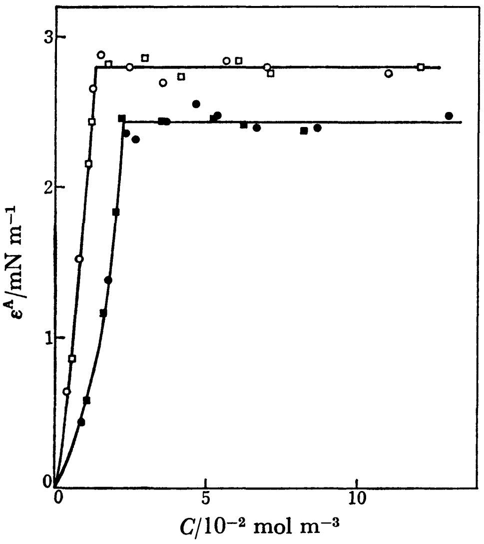

Fig. 5. Surface-area modulus *vs.* bulk concn plots. Marks are the same as in Fig. 4.

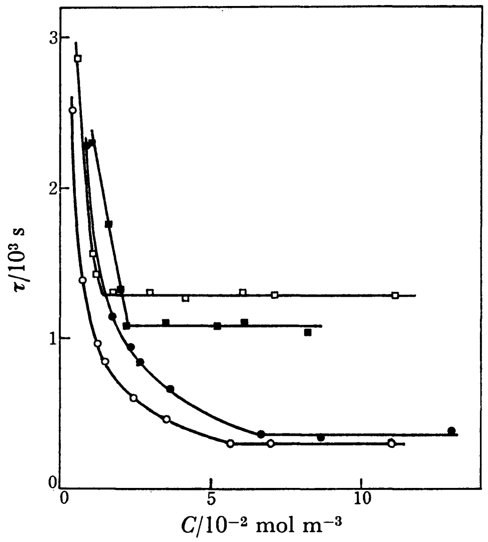

Fig. 6. Relaxation time *vs.* bulk concn plots. Marks are the same as in Fig. 4.

increase in the bulk concentration, *C*, and reaches a constant value at a concentration, shown in Fig. 5, in which the values do not differ between the cases of dilation and compression. The concentration at which ε^A becomes constant corresponds exactly to the concentration at which σ_e changes into the linear region in Fig. 4, for both $n=5$ and 7. When the Gibbs adsorption equation is applied to the curves in Fig. 4, such concentrations are found to be equal to those at which the surface is saturated with the surfactant molecules, because the amount of adsorption or surface excess is proportional to the tangent of the σ_e *vs.* log *C* curve. These facts reveal that ε^A increases with an increase in the amount of adsorption on the surface, Γ, and becomes constant when the surface is saturated, even if the concentration increases as the micelles appear in the bulk solution. ε^A can, therefore, be determined only by the state of the surface. The independence of ε^A of the dilation or compression indicates that the initial state of the surface immediately after the area strain applied is the same for both directions of the strain. Taking into account, in addition, the fact that the process converges to the same state, irrespective of the sign of the area strain, it may be concluded that the initial state corresponds to a state of the surface in the lack of surfactant molecules when dilated and to a state with an excess of them in the case of compression, and that ε^A is, therefore, equal to the reciprocal of the compressibility of the adsorbed film when it is assumed to be insoluble.[9] Thus, ε^A reflects the properties characterized by the two-dimensional closed system.

On the other hand, the relaxation time when the surface is dilated, τ_d, is significantly different from the relaxation time when it is compressed, τ_c. Both of them tend to decrease with an increase in the bulk concentration, *C*, and to attain a constant value. However, the constant value and the concentration of its attainment are quite different between τ_d and τ_c, as is shown in Fig. 6. Thus, the concentration needed for τ_c to become constant is equal to that for ε^A, at which concentration the surface is saturated. The decrease in τ_c in the lower-concentration region may, then, be attributed to the increase in the amount of adsorption on the surface with an increase in the concentration. On the other hand, the concentration at which τ_d is unchanged is in good agreement with the break point in Fig. 4, *i.e.*, the CMC, at which the monodispersed molecules are saturated in the bulk solution. τ_d is affected not by the saturation of the surface with surfactant molecules, but by the monodispersed concentration in the bulk solution.

Since τ_c and τ_d depend only upon the amount of adsorption of the surfactant molecules on the surface, Γ, and only upon the monodispersed concentration of surfactant molecules in the bulk solution, *C*, respectively, it may be concluded that the measured relaxation processes are the desorption process of the surfactant molecules in excess in the surface due to a negative area strain in the case of compression, and the adsorption process of the surfactant molecules to supply the lack in the surface due to a positive area strain in the case of dilation. Thus, the characteristics of the adsorbed film as an open system appear specifically in the relaxation time against the area strain.

The surface dilational viscosity, η_d^A, and the surface compressional viscosity, η_c^A, which were estimated from ε^A and either τ_d or τ_c according to Eq. 3, are plotted against the bulk concentration, *C*, in Fig. 7. η_c^A increases with *C* and has a constant value in the saturated adsorption region. On the other hand, η_d^A increases with *C* in the dilute region, but decreases in the saturated adsorption region up to the CMC. As a consequence, there appears a maximum in η_d^A around the concentration at which the surface becomes saturated. An adsorbed film, and thus some dispersions stabilized by such a film may be expected to become most stable against the surface-area changes around such a concentration. When a periodical area strain is given to a surface by repeating the dilation and compression in turn, an equal area viscosity has often been assumed for both processes symmetrically.[10] Such an assumption is not consistent with the present results.

If both the adsorption and desorption processes of

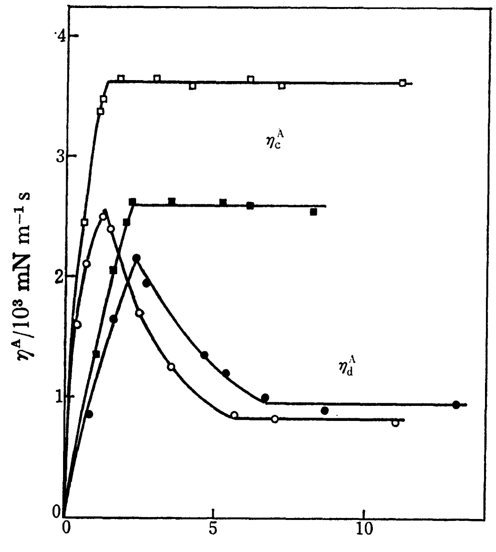

Fig. 7. Surface-area viscosity *vs.* bulk concn plots. Marks are the same as in Fig. 4.
η_d^A: Surface dilational viscosity, η_c^A: surface compressional viscosity.

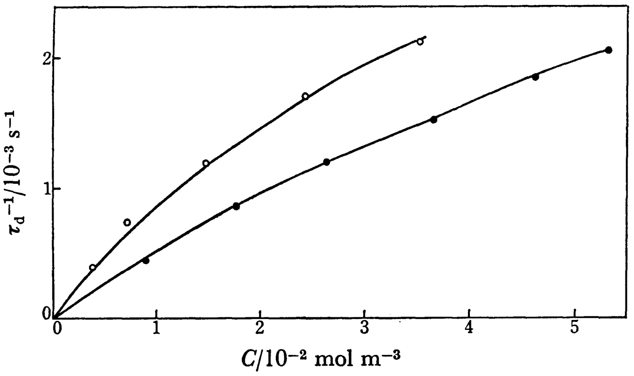

Fig. 8. Reciprocal of relaxation time when dilated *vs.* monodispersed concn plots.
○: n=5, ●: n=7.

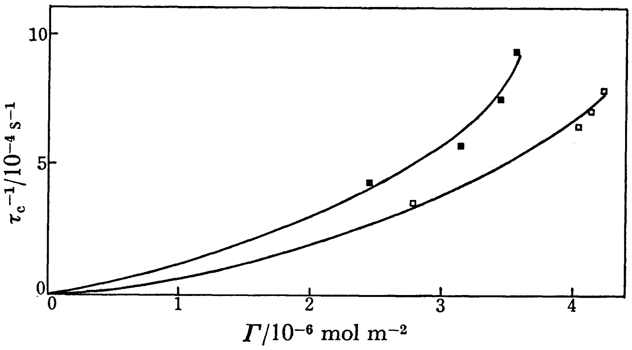

Fig. 9. Reciprocal of relaxation time when compressed *vs.* adsorption amount in the surface plots.
□: n=5, ■: n=7.

TABLE 1. RATE CONSTANTS FOR THE ADSORPTION, k_d, AND DESORPTION, k_c, OF $C_{12}H_{25}(OC_2H_4)_nOH$ AT 303 K

n	$k_d \times 10^2$	$k_c \times 10^{-7}$
5	3.5	4.2
7	2.0	6.5

surfactant molecules are represented by a single relaxation process, as in the present results, the activated adsorption mechanism[11] would be more fitting than the diffusion-controlled mechanism,[12] which has been assumed by most authors since Ward and Tordai,[13] because the former mechanism needs a single exponential term with respect to time, while the latter needs plural such terms, according to Sutherland.[14] The reciprocal of the relaxation time would correspond to the rate for the process. When the reciprocal of τ_d is plotted against the bulk concentration below the CMC, curves are obtained for n=5 and 7, as is shown in Fig. 8. These curves may be approximated by

$$1/\tau_d = k_d \cdot C^{0.8}, \qquad (4)$$

by expressing both axes with the logarithmic scale and by drawing two straight lines for n=5 and 7 parallel to each other; here k_d may be regarded as the rate constant for the adsorption process. On the other hand, if the reciprocal of τ_c is plotted against the amount of adsorption of the surfactant molecules, Γ, evaluated by applying the Gibbs adsorption equation to the curves in Fig. 4, then the curves shown in Fig. 9 are obtained for n=5 and 7. The curves may be approximated by

$$1/\tau_c = k_c \cdot \Gamma^2, \qquad (5)$$

by treating them similarly to the relation between τ_d and C, where k_c is the rate constant for the desorption process. As is shown in Table 1, the degree of polymerization of poly(oxyethylene) chain, n, has a reverse effect on k_d and k_c. This reveals that the rate-determinig steps can be different for the adsorption and desorption processes.

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