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Surface Dilational Properties of Adsorbed Monolayers of Aqueous Sodium Dodecyl Sulfate Solutions

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The surface pressure relaxation of a freshly formed surface and the surface area creep at a constant surface pressure have been studied for aqueous surface of sodium dodecyl sulfate solutions. It was found that the area stress after the formation of a fresh surface undergoes relaxation according to the generalized Maxwell model, and that the surface area viscosity is not constant during the process but increases with the surface area. The concept of two-dimensional open system rheology was introduced and the observed phenomena were discussed. A surface equation of state applicable under such dynamic conditions has been derived.

Numerous studies[1-3] have been carried out on the adsorption kinetics of surface-active solute from aqueous solutions onto their surfaces in connection with the variation of surface tension with time. For such studies, it is necessary to change the measured surface tension (pressure) data into the amount of solute absorbed at each moment. However, there is no non-equilibrium surface equation of state that can be applied during the course of adsorption.

The rheological properties of the surface containing adsorbed surfactants have often been the cause of the stability of dispersion.[4] Four independent surface rheological paramenters are taken into consideration, surface shear viscosity and elasticity, and surface dilational (or area) viscosity and elasticity. The surface area modulus, the reciprocal of surface compressibility, is zero at equilibrium for the adsorbed surface, when the equilibrium surface tension of surfactant solution is constant, independent of the area at a constant temperature. The surface viscosity and elasticity contribute to foam drainge *via* surface transport phenomena.[5] The surface area viscosity seems to influence the damping of ripples a great deal.[6] As regards the measurement of the surface area viscosity, only a few reports have appeared for surfactant solutions.[7]

The expansion or contraction of the surface in equilibrium produces an area strain, and the corresponding stress changes the surface pressure (or tension) from the equilibrium value. Under the action of surface area viscosity, the surface pressure usually returns to its equilibrium value. This seems to be due to the relaxation of area stress. The change of surface tension after the formation of a fresh surface is a special case.

The process of the change of surface area under a constant surface pressure differing from the equilibrium value corresponds to the creep of the area strain under a constant stress, and under the action of the surface area viscosity. In the present paper, the relaxation and creep processes for the aqueous surface containing adsorbed film in contact with bulk of the solution were studied. Aqueous sodium dodecyl sulfate solutions were chosen for this purpose.

Experimental

Sodium dodecyl sulfate (SDS) was prepared by the reaction of pure dodecanol with chlorosulfonic acid in ether followed by neutralization with sodium hydroxide. The product was purified twice by addition of active charcoal to its hot saturated ethanol solution followed by recrystallization from the cold solution.[8] The product was sufficiently pure, showing no minima in the surface tension *vs.* concentration curve.

The surface pressure against pure water was measured within an error of ±0.02 dyn/cm by the Wilhelmy method using a vertical glass plate, peripheral length 4.790 cm.[9] The glass plate was cleaned by immersing it in concentrated aqueous alkaline–alcohol solution overnight, dipping in a hot chromic acid mixture for *ca.* 1 hr, and rinsing with water.

The stock solution of SDS was prepared and subjected to aging for *ca.* 17 hr before each measurement, since the variation of surface tension with time is considered to depend upon age. The water used for dissolving SDS was freshly distilled and boiled for *ca.* 1 hr to remove dissolved gas, which otherwise formed bubbles on the paraffin-coated walls during the course of measurement.

A Langmuir type trough of $60 \times 15 \times 1$ cm size coated with paraffin was used. Water from a thermostat was circulated beneath the trough, and the solution was maintained at 30 ±0.3 °C. The trough and the tensiometer, contained in a closed chamber of air thermostat at 30±1 °C, were protected from atmospheric contaminations. For measurements under a constant area, glass barriers coated with paraffin were used to clean and to provide a specified surface area. For measurements under a constant surface pressure, one of the barriers was driven by a motor to change the surface area continuously.

Reproducible surface pressure could be obtained after allowing the solution to stand in the trough for 1 hr and then sweeping its surface at least 10 times with three barriers. The error of the surface pressure measurement due to the fall of water level produced by the surface evaporation during the course of measurement was confirmed to be negligible as compared with the overall error.

Results and Discussion

Relaxation Process under a Constant Area Strain. Figure 1 shows the variation of surface pressure π with time t after the formation of fresh surface for aqueous SDS solutions of varying concentrations under a constant area *ca.* 400 cm^2, and pH *ca.* 6. Since the surface pressure did not attain a constant value except for a very dilute solution (1×10^{-4} mol/l), the equilibrium surface pressure π_e was obtained by extrapolating plot π *vs.* $1/t$ to $1/t=0$.[10]

From a rheological point of view, the process shown in

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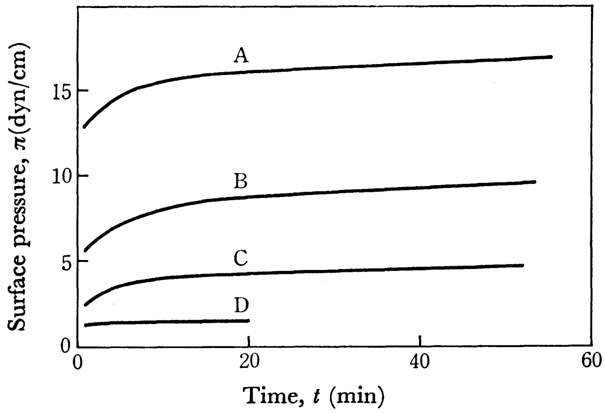

Fig. 1. Surface pressure *vs.* time plot for aqueous SDS solutions at 30 °C. Surface area: 400 cm^2.
Concn of SDS: A,2.02; B, 1.05; C, 0.52; D, 0.10×10^{-3} mol/l.

Fig. 1 is regarded as one in which the stress

$$\Delta\pi = \pi_e - \pi \tag{1}$$

produced by a constant area strain undergoes relaxation according to the generalized Maxwell model as given by

$$\Delta\pi = \sum_i^n K_i e^{-t/\tau_i}, \tag{2}$$

where K_i and τ_i are constants. At $t=0$, Eqs. (1) and (2) give

$$\sum_i^n K_i = \pi_e \tag{3}$$

since $\pi=0$ at $t=0$.

As regards the τ_i and K_i values, the largest value, τ_1, with the corresponding K_1 value can be determined from the linear part of the plot log $\delta\pi$ *vs.* t for sufficiently large value of t, and the next largest value, τ_2, with the corresponding K_2 value can be obtained from the linear part of the plot log $(\delta\pi - K_1 e^{-t/\tau_1})$ *vs.* t. Figure 2 shows such a plot. The values obtained (Table 1) express the curves in Fig. 1 within ±0.05 dyn/cm. It is the shorter relaxation time τ_2 which should be compared with thin film relaxation times of the order of minutes, measured by Razouk and Mysels[11] for the aqueous SDS solutions.

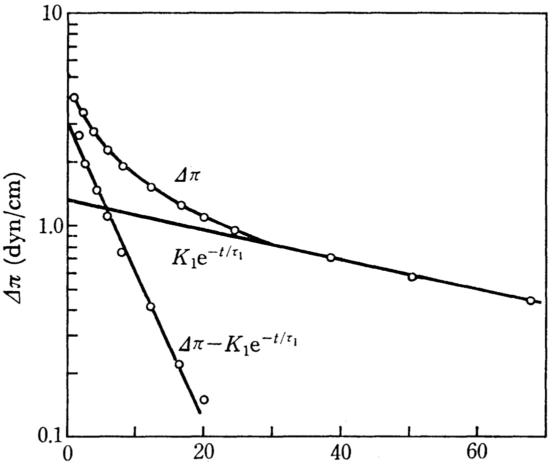

Fig. 2. $\Delta\pi$, K_1e^{-t/τ_1}, and $\Delta\pi - K_1e^{-t/\tau_1}$ *vs.* t plot.
Concn of SDS: 2.02×10^{-3} mol/l.
Surface area: 400 cm^2.

TABLE 1. RELAXATION TIMES (τ_1, τ_2) AND INITIAL STRESSES (K_1, K_2) FOR THE FRESHLY FORMED SURFACES OF AQUEOUS SDS SOLUTIONS AND THEIR EQUILIBRIUM SURFACE PRESSURES (π_e) AT 30 °C

	Concn (mol/l) $\times10^{-3}$	π_e (dyn/cm)	τ_1 (min)	τ_2 (min)	K_1 (dyn/cm)	K_2 (dyn/cm)
A	2.02	17.20	63	6.1	1.31	3.10
B	1.05	10.40	39	4.5	2.31	2.65
C	0.52	5.45	82	3.4	1.67	1.78

In all the cases, K_1+K_2 is not equal to the equilibrium surface pressure π_e. This means that the value of surface pressure (Fig. 1) extrapolated to $t=0$ is not zero and suggests the existence of at least one more relaxation element something like "semi-dynamic surface tension" postulated by Bouteric and Berthier[12] and Ross.[13] The presence of two relaxation elements has been reported,[14] when the relaxation was measured after expanding the lamellae of bovine hemoglobin solution.

Equations (1) and (2) give

$$\pi = \sum_i^n K_i(1-e^{-t/\tau_i}). \tag{4}$$

The two longest relaxation times of τ_i were thus determined. The remaining shorter relaxation times can not be measured by the vertical plate technique. They might be detected by a more rapid measurement, such as the jet method.

Creep Process under a Constant Stress. The change of surface area A under a constant surface pressure was determined with time t for solutions whose area stress relaxation had been measured. The results are shown in Fig. 3. Measurements were made first by sweeping the surface with a paraffin-coated glass barrier to form a fresh surface and then with a motor-driven barrier to expand the surface in order to keep the surface pressure within 0.5 dyn/cm of the predetermined value of π_s. Surface area A thus obtained was plotted against time t.

Since the rate of area strain is expressed by $(1/A)$ $(\mathrm{d}A/\mathrm{d}t)$ and the stress by $\delta\pi=(\pi_e-\pi_s)$, the area viscosity η_A is defined by

$$\Delta\pi = \eta_A \frac{1}{A}\cdot\frac{\mathrm{d}A}{\mathrm{d}t}, \tag{5}$$

according to Boussinesq.[15] By integration under the assumption that $\delta\pi$ and η_A are constant, we have

$$\ln A - \ln A_i = \frac{\Delta\pi}{\eta_A}\cdot t, \tag{6}$$

where A_i is the value of A at $t=0$. Thus, log A should change linearly with t. However, this was not the case actually, the dependence of η_A on A or t being shown. Equation (5) combined with the $A(\mathrm{d}t/\mathrm{d}A)$ *vs.* A relation gives

$$\frac{\eta_A}{\Delta\pi} = \frac{rA}{1+qA} + s, \tag{7}$$

where q, r, and s are constants.

The fact that η_A increases with area is in line with the result of van Voorst Vader's experiments in which $(1/A)$

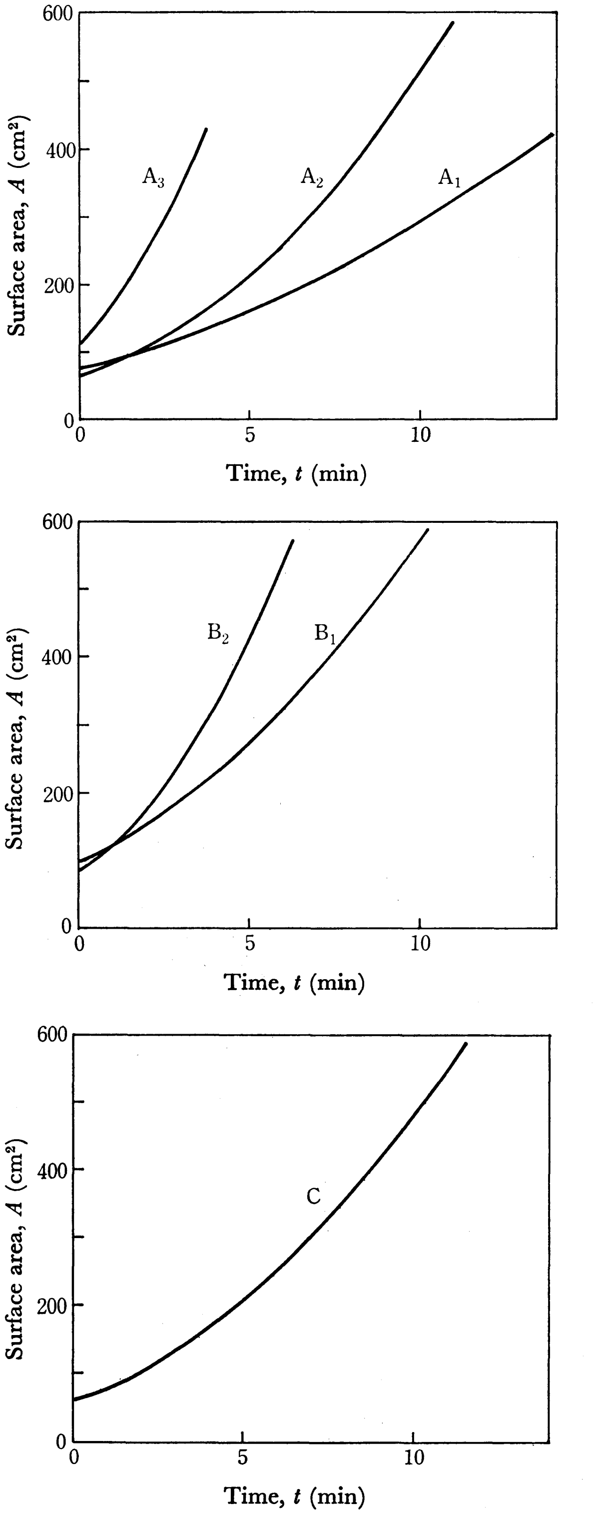

Fig. 3. Surface area *vs.* time plot under constant area stress.

	A$_1$	A$_2$	A$_3$	B$_1$	B$_2$	C
Concn of SDS ($\times 10^{-3}$ mol/l)	2.02	2.02	2.02	1.05	1.05	0.52
Area stress, $\Delta\pi$ (dyn/cm)	2.02	2.68	3.34	3.14	3.80	1.13

(dA/dt) is kept constant.[7] We see that the relation of $\delta\pi$ *vs.* $(1/A)(dA/dt)$ at a given A of the same solution (A$_1$, A$_2$, and A$_3$, or B$_1$ and B$_2$ in Fig. 6) gives a relation similar to the curve in the steady state obtained by van Voorst Vader *et al.*[7] The area viscosity obtained can be separated into two parts, if two Maxwell elements are considered. It would be reasonable to divide η_A into two portions in a ratio of $\tau_1 K_1$ and $\tau_2 K_2$, since

$$\eta_{Ai} = \tau_i \varepsilon_{Ai}, \tag{8}$$

in which ε_{Ai} is the area elastic modulus of the i'th element, to which K_i is proportional. Since K_1 and K_2 are of the same order of magnitude (Table 1), η_{A1} and η_{A2} would be roughly proportional to τ_1 and τ_2. If there are more relaxation elements as given by Eq. (2), area viscosity should be separated into more than two elements.

Rheology of Two-dimensional Open System. The system treated here differs essentially from the ordinary rheological system in that the number of molecules involved in the system changes in the former (open system), and remains constant in the latter (closed system). In the rheology of a two-dimensional system, the open system treatment is required when the area of liquid surface with its soluble adsorbed film changes. The above four rheological parameters are similarly defined for both open and closed systems, but the molecular behavior brought about by an area strain is quite different for the two systems. Thus, in the closed system, the stress relaxation after area strain is due to the change in the rearrangement, orientation, conformation and/or other chemical change of the molecules in the system, while in the open system the relaxation involves the transfer of the molecules into or out of the system, *i.e.*, the adsorption from or desorption into bulk of the solution, in addition to the above changes of the closed system. As a result, the area viscosity is much more significant in the mechanical behavior of the two-dimensional open system than the volume viscosity of the three-dimensional closed system.

The surface film flows and the adsorbed molecules in the surface generally rearrange themselves by the pressure gradient due to the compression or expansion of the surface. Since the surface shear viscosity is sufficiently below the order of magnitude of 10^{-4} surface poise for an adsorbed film of pure SDS,[16] the surface flow would rapidly follow the surface expansion in the creep experiment and the surface might be regarded to be uniform as a whole. The rate of orientation of adsorbed molecules on the water surface is also considered to be fairly rapid in a dilute solution of SDS, similar to that of water molecules on the surface, though the exact rate is not known.[17] The measured rheological properties might be governed mainly by the transfer of molecules from bulk of the solution to the surface.

In such a case, when the rate of adsorption is constant and the rate of desorption simply depends upon the surface pressure, the relaxation due to the process would be rather simple. On the other hand, when an unstirred diffusion layer of certain thickness exists just below the surface, several exponential terms should be taken into account in order to elucidate the relaxation mechanism, regardless of the presence of energy barrier at the surface, as Sutherland suggested.[18] The relation between relaxation and creep observed might be discussed as rheology of an open system.

Since the adsorption of surfactant molecules is the principal cause common to both the relaxation of area stress and the creep of area strain observed as an open system, a certain relation might be expected to exist between these phenomena. Because of the lack of exact equation of state available for the adsorbed film under such dynamic conditions, surface pressure is first assumed to be proportional to the surface density of adsorbed SDS molecules, namely, an ideal gas type equation is assumed to hold:

$$\pi A = nkT, \tag{9}$$

where n is the total amount of adsorbed SDS, k the Boltzmann constant, and T absolute temperature. Thus at a given moment of surface area expansion, the relation between creep and relaxation is given by

$$A\left(\frac{\partial \pi}{\partial t}\right)_A = \pi\left(\frac{\partial A}{\partial t}\right)_\pi. \tag{10}$$

This is derived by differentiation of Eq. (9) with respect to time t keeping π or A constant. In order to examine the validity of Eq. (10), $(\partial A/\partial t)\pi$ and $(\partial \pi/\partial t)_A$ obtained by drawing tangents to the curves shown in Figs. 3 and 4, respectively, are used. However, both sides of Eq. (10) calculated differed from each other by about one order of magnitude. It was also found that Amagat's type of equation of state does not hold in the present case. We assume a surface equation of expanded film type

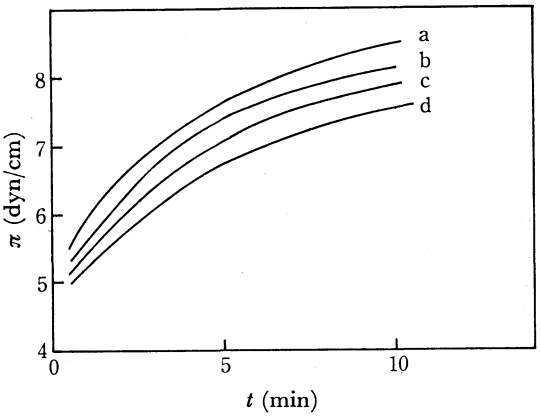

Fig. 4. Area effect on π *vs.* t curve for aqueous SDS solution.
Concn of SDS: 1.0×10^{-3} mol/l.
Surface area: a, 55; b, 100; c, 175; d, 250—400 cm².

$$(\pi+\pi_0)(A-A_0) = nkT, \tag{11}$$

where π_0 and A_0 are constants. A similar calculation gives the following equation:

$$(A-A_0)\left(\frac{\partial \pi}{\partial t}\right)_A = (\pi+\pi_0)\left(\frac{\partial A}{\partial t}\right)_\pi. \tag{12}$$

Neither Eq. (12) nor Eq. (11) holds, since π_0 found was not constant but increased in proportion to π. However, we found at least experimentally that the relation

$$A - A_0 = p\pi_s\left(\frac{\partial A}{\partial t}\right)_{\pi_s}\left(\frac{\partial t}{\partial \pi}\right)_A \tag{13}$$

holds as a whole with constants $A_0=25$ cm² and $p=0.13$ (Fig. 5) for the systems of B_1 and B_2 under a constant π_s. The original state of equation corresponding to Eq. (13) would then take the form

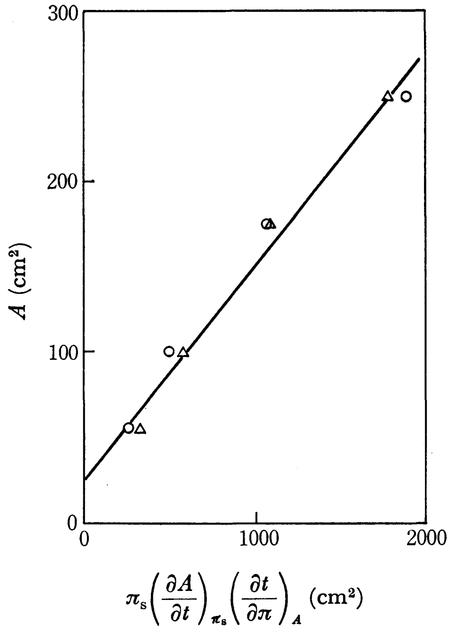

Fig. 5. A *vs.* $\pi_s\left(\frac{\partial A}{\partial t}\right)_{\pi_s}\left(\frac{\partial t}{\partial \pi}\right)_A$ plot.
○: B_1, △: B_2.

$$\pi(A-A_0)^p = \alpha n, \tag{14}$$

where α is a constant. We see that π decreases rapidly with increasing A in the region of small A with an asymptote at $A=A_0$ while the decrease is small in the region of large A as compared with π *vs.* A relation for ideal gas film. This suggests that the curve π *vs.* A shifts towards the region of larger area than that of ideal gas film, and that a large apparent repulsive force prevails. The ionic nature and steric factor are also considered to have certain relations.

The values $(\partial \pi/\partial t)_A$ at sufficiently large A were calculated by means of Eq. (14) and compared with the observed values. According to Eq. (13), we have

$$\left(\frac{\partial \pi}{\partial t}\right)_A = p\pi_s\left(\frac{\partial A}{\partial t}\right)_{\pi_s}\Big/(A-A_0). \tag{15}$$

In order to obtain an empirical formula for $(\partial A/\partial t)\pi_s$, a trial and error method was attempted and the following relation was found to hold (Fig. 6):

$$A\left(\frac{\partial t}{\partial A}\right)_{\pi_s} = \frac{rA}{1+0.002A} + s. \tag{16}$$

The values of r and s are given in Table 2. Substituting $(\partial A/\partial t)\pi_s$ of Eq. (16) into Eq. (15), the value $(\partial \pi/\partial t)_A$ at infinite A is obtained as

$$\left(\frac{\partial \pi}{\partial t}\right)_{A_\infty} = p\pi_s q/r, \tag{17}$$

where $q=0.002$ cm⁻². The values $(\partial \pi/\partial t)_{A_\infty}$ calculated by means of Eq. (17) are given in Table 2 together with the observed values obtained at π_s from Fig. 1.

The values agree as a whole, although the disagreement is not small in some cases. The discrepancy might come from the nature of Eq. (14) for the open system under dynamic conditions, together with the fact that the states of the film in an immediate vicinity of the

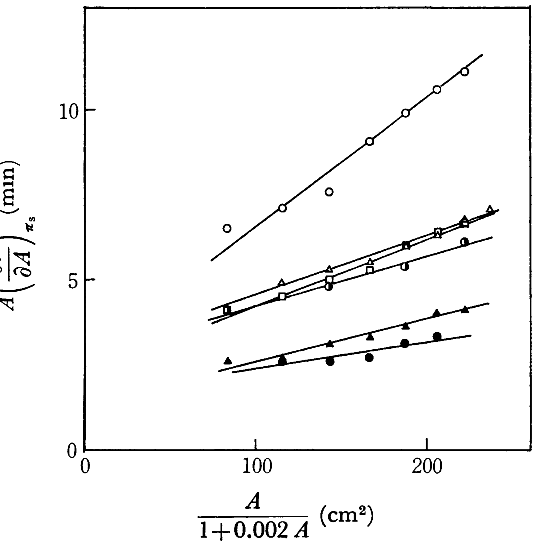

Fig. 6. $A\left(\frac{\partial t}{\partial A}\right)_{\pi_s}$ *vs.* $\frac{A}{1+0.002A}$ plot.
○: A_1, ◑: A_2, ●: A_3, △: B_1, ▲: B_2, □: C (see Fig. 3).

Table 2. Observed and calculated values of $(\partial\pi/\partial t)_{A\infty}$, and r and s in Eq. (16)

	Concn (mol/l) × 10^{-3}	π_s (dyn/cm)	$\left(\frac{\partial\pi}{\partial t}\right)_{A\infty}$ (dyn/cm·min) obsd	calcd	r (min/cm^2)	s (min)
A_1	2.02	15.18	0.17	0.11	0.038	2.8
A_2	2.02	14.56	0.28	0.24	0.016	2.6
A_3	2.02	14.06	0.36	0.35	0.011	1.1
B_1	1.05	7.26	0.17	0.094	0.020	2.4
B_2	1.05	6.60	0.28	0.13	0.014	1.2
C	0.52	4.32	0.013	0.048	0.023	1.8

barrier and rim of the trough differ from those in the main part of the film. It may be further inferred that A_0 in Eq. (14) when expressed per molecule seems to correspond to the co-area of Amagat's equation, but it may involve contribution of some other factors, which reduce the area effective for adsorption.

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