Influence of Detergent Builders on Surface Properties of Sodium Dodecyl Sulfate Solutions Under Dynamic and Static Conditions

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The effects of various detergent builders on surface properties of sodium dodecyl sulfate (SDS) solutions have been investigated by measuring the equilibrium surface tension and hysteresis curves of surface pressure vs surface area under dynamic conditions. While the adsorbed layer of SDS under static conditions is in the liquid-expanded state, a two-dimensional phase transition of the adsorbed layer from liquid-expanded to condensed-film can be observed on compression at higher rates beyond the saturated adsorption. For the SDS solution containing excess NaCl (1×10^{-1} M), the adsorbed layer of SDS is already in the condensed state under static condition due to a depression in the dissociation of SDS.

It has been found that some polyelectrolytes, as well as conventional ionic builders, contribute to increasing the surface excess concentration of SDS together with promoting micelle formation and also to stabilizing the adsorbed layer of SDS. On the other hand, poly(vinyl alcohol) (PVA) as a nonionic polymer is adsorbed at the air-water interface in preference to SDS. In this case, the hysteresis of the dynamic surface behavior of the mixed solution can be attributed to the structural change of the adsorbed layer of PVA rather than SDS, which is different from the other ionic builders.

KEY WORDS: Detergent builders, hypertension curves, ionic builders, polyelectrolytes, sodium dodecyl sulfate, surface tension.

Aqueous surfactant solutions exhibit interesting dynamic surface properties such as surface elasticity and viscosity (1-6), which seem to be associated with detergency processes. Furthermore, the interaction between surfactants and detergent builders is of fundamental importance in any study of detergency, since this interaction is presumed to influence the states of adsorbed layers and adsorption-desorption processes of the surfactants. Lucassen et al. (5) investigated the adsorption-desorption kinetics of the mixed solutions of polylysine and sodium dodecyl sulfate (SDS) at the air-water interface by measuring the surface dilational modulus.

The aim of this paper is to obtain fundamental data for the interaction between surfactants and detergent builders at the air-water interface under static and dynamic conditions.

In the first step, the two-dimensional states of the adsorbed layer of SDS solution with and without NaCl under dynamic conditions have been examined by measuring the surface pressure-area curves at various rates of compression and expansion. In the next we have dealt with the influence of detergent builders of various types, such as neutral salts, chelating agents, polyelectrolytes and nonionic polymers on the adsorbed layer of SDS solutions under static and dynamic conditions. The behavior of the adsorbed layer at the air-water interface studied by measuring the equilibrium surface tensions and the hysteresis curves of surface pressure deviation vs surface area.

EXPERIMENTAL PROCEDURES

Materials. A sample of sodium dodecyl sulfate (SDS; Nippon Rikagaku Yakuhin Co., Ltd., Japan) was used without any further purification. Detergent builders used are shown in Table 1.

Methods. The techniques for measuring dynamic surface properties were as follows: The apparatus used was a KSV surface film balance (Type 2200) consisting of a Teflon trough (45 cm × 15 cm × 0.5 cm) and a platinum plate suspended from the beam of an electro-micro-balance. The system could be thermostated by circulating water beneath the trough. The trough was placed in a closed chamber to maintain clean conditions. The surface area of aqueous solution was continuously compressed and expanded by a Teflon barrier, which was attached to a variable- speed motor drive. Rates of compression or expansion were varied in the range of 15-180 cm²/min (38.6 and 3.8 min/cycle). Changes of the force acting on the plate with the compression-expansion of the surface area were analyzed and recorded by a computer system. Sensitivity of the apparatus was 0.01 mN/m. The measurement of surface pressure vs surface area was started after the equilibrium surface pressure was attained. For the aqueous SDS solution of 1×10^{-3} M used in most experiments, it took at least 2 hr until the rate of surface tension lowering became less than 0.01 mN/m/min. At this stage, it was assumed that the equilibrium was reached approximately.

The influence of a salt (NaCl) and detergent builders on the dynamic surface properties of SDS solution was investigated by measuring the hysteresis curves for surface pressure vs surface area. Since the equilibrium surface tension of SDS solution was changed by the additions of a salt and detergent builders, surface pressure deviation was used instead of surface pressure against pure water surface. Surface pressure deviation ($\Delta \pi$) is given by

$$\Delta \pi = \pi - \pi_e = \gamma_e - \gamma$$

where π_e and γ_e are the surface pressure and the surface tension at equilibrium, respectively; π and γ are the surface pressure and the surface tension during compression or expansion of the surface, respectively.

TABLE 1

The Materials as Detergent Builder

Abbreviation[a]	Builder[b]	Material
1. NS	Sulfate	Reagent[c]
2. STPP	Tripolyphosphate	Reagent[c]
3. NTA	Nitrilotriacetate	Reagent[c]
4. CA	Citrate	Reagent[c]
5. PM	Hydrolyzed maleic anhydride-cyclopenten copolymer	The reaction product between Na hydrolyzed maleic anhydride and cyclopentene (Mw 6.3×10^3)[d]
6. DM	Hydrolyzed maleic anhydride-diisobutylene copolymer	The reaction product between Na hydrolyzed maleic anhydride and diisobutylene ($\overline{M}w$ 1.9×10^4)[d]
7. PVA	Poly(vinyl alcohol)	Gosenol GL-03 (Nihon Gosei Kagaku Co., Japan) Degree of saponification: 87.4% Degree of polymerization: 350

[a]The abbreviation is assigned to all Figures in this paper.
[b]All builders except PVA are sodium salts.
[c]The reagent is the product of Kanto Chemical Co., Inc., Japan
[d]These materials were kindly supplied by Hitachi Chemical Co., Ltd., Japan

Equilibrium surface tensions were measured by means of the Wilhelmy plate technique using a Shimadzu-ST1 electronic microbalance (Shimadzu Scientific Instruments, Kyoto, Japan). All experiments were carried out at 20°C.

RESULTS AND DISCUSSION

States of the adsorbed layer of SDS under dynamic conditions. Figure 1 shows surface pressure-area curves for the adsorbed layer of a SDS solution of 1×10^{-3} M at various rates of compression and expansion. The relation between surface pressure and surface area is hysteretic, and the shape and degree of the hysteresis curves vary with the rate of area change. Reasons for these hystereses seem to be as follows: In the first compression step, the surface pressure is enhanced since the surfactant molecules present in the adsorbed surface layer are crowded together and the surface concentration is increased. Simultaneously, a part of the surfactant molecules is described from the surface and diffuses into bulk solution; in the subsequent expansion step, as a result of partial desorption the decrease in surface pressure at each surface area is observed.

A speed-up of the compression-expansion results in an increase in the surface pressure and a decrease in hysteresis of the area, indicating that the amount of molecules desorbed from the surface becomes less. At higher compression-expansion rates, the effect of desorption and/or relaxation processes becomes less and less important, and the surface behavior becomes that of an "insoluble" monolayer. As shown in Figure 1, at rates above 45 cm²/min, the compression curves exhibit a behavior similar to the phase transformation from liquid-expanded film to condensed film for insoluble monolayers. At the lower rate, however, this transformation is not apparent. It is considered that since the desorption of SDS molecules from the surface can
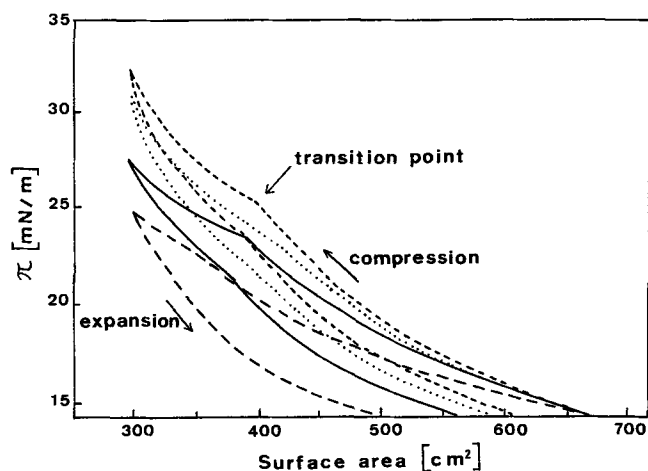

FIG. 1. Dependence of surface pressure-surface area hysteresis curves for 1×10^{-3} M SDS on the rates of compression and expansion: — —, 15; ——, 45 ...., 90; and - - -, 180 cm²/min. Equilibrium surface pressure (π_e) of 1×10^{-3} M SDS was 14.4 mN/m.

not follow at the higher compression rates, change in the state of adsorbed layer can be observed on super-compression beyond the saturated adsorption at static condition.

The change in state of the adsorbed layer of SDS was investigated in detail from estimation of surface areas per molecule. Figure 2 shows the results of surface tension as functions of SDS concentration for salt-free solutions and that containing 1×10^{-1} M NaCl. In these curves, the minimum value of surface tension is observed at the critical micelle concentration (CMC), which implies that our sample of SDS contains some impurities, such as dodecanol. The surface excess concentration (Γ) and the surface area per
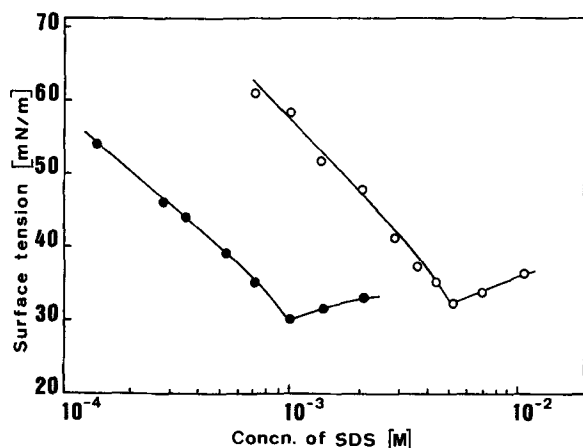
FIG. 2. Surface tension vs concentration of SDS solution: O, salt-free; and ●, containing 1×10^{-1} M NaCl.

TABLE 2

Surface Excess Concentration (Γ) and Surface Area (A) per Molecule of SDS Estimated from the Results of Figure 2 Using Gibbs' Equation with a Factor of n = 2

SDS concentration (10^{-3} M)	1	5.2 (CMC)
Γ (10^{-10} mole/cm²)	2.22	3.85
A (Å²/molecule)	74.7	43.2

molecule (A) of SDS for salt-free solution were estimated using Gibbs' equation with a factor of n = 2. The obtained values at CMC (5.2 $\times$ 10^{-3} M) and 1 $\times$ 10^{-3} M are given in Table 2. Many investigators (7–12) have reported the surface areas per molecule of SDS at saturated adsorption which ranged from 40–52 Å². The value of 43.2 Å² per molecule at CMC obtained in this work falls into this range. One of the reasons for scattering values is presumably ascribed to a difference in purity of samples.

On the basis of these data (Table 2), and assuming that SDS molecules would be scarcely desorbed from the surface by compression at higher rates such as 180 cm²/min, the surface pressures were replotted as a function of area per molecule, as shown in Figure 3. Since the surface of 1 $\times$ 10^{-3} M SDS solution before compression should be in the adsorption equilibrium (but not saturated), the area per molecule is taken to be 74.7 Å² from Table 2. Thus, the area per molecule at the transition point was obtained as 44.3 Å². This agreed well with the value of 43.4 Å² per molecule estimated at the saturated adsorption in our experiments. Therefore, it can be deduced that the transition point of the surface layer under dynamic condition corresponds to the saturated adsorption under equilibrium condition. Adsorbed layers of ionic surfactants (such as SDS) are considered to be in the liquid-expanded states due to electrical repulsion among the ionic head groups. On compression at higher rates beyond the saturated adsorption, the two-dimensional phase transition of the adsorbed layer from the liquid-expanded film to the condensed film can occur. In Figure 3, the values of two-dimensional compressibility [−(dA/dπ)/A] are also
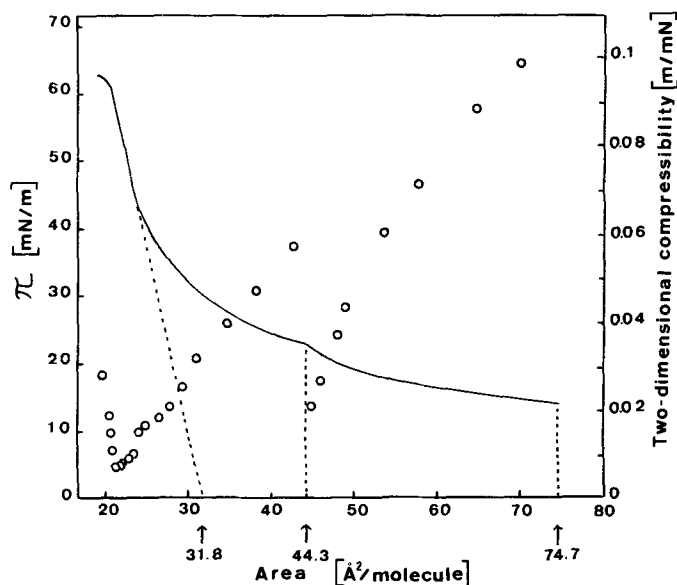

FIG. 3. Surface pressure-area curve (—) and two-dimensional compressibility (O) for 1 $\times$ 10^{-3} M SDS. Compression rate was 180 cm²/min.

given. Two-dimensional compressibilities reported for insoluble monolayers were 0.08–0.02 m/mN in the liquid-expanded state and 0.01–0.004 m/mN in the liquid-condensed state (13). Since the compressibility obtained for the adsorbed layer of SDS in the high pressure region under forced compression is 0.005 m/mN, it is reasonable to consider it to be in the liquid-condensed state. From extrapolation of the curve in the high pressure region giving the minimum two-dimensional compressibility to zero pressure (Fig. 3), we have obtained a value of 31.8 Å² corresponding to a limiting area per molecule of SDS in the condensed state. From these considerations, it has been found that the closely packed state of SDS molecules at the air-water interface can be realized under compulsory compression.

The limiting area per molecule of long-chain fatty acids is known to be approximately 20 Å². The difference between this value and the value of 31.8 Å² observed for SDS is presumably due to the size of sulfate head group, which is larger than the carboxyl group, and also the electrical repulsive force among the ionized sulfate groups.

Influence of an added salt on the adsorbed layer of SDS. The influence of NaCl added to SDS solution on the dynamic surface properties was investigated. The surface pressure deviation-surface area curves of mixed solutions of SDS and NaCl at compression-expansion rate of 45 cm²/min are shown in Figure 4. The concentrations of NaCl were 1.359 $\times$ 10^{-2} and 1 $\times$ 10^{-1} M.

The equilibrium surface tensions (γ_e) of SDS solution without and with added NaCl were 58.5 mN/m (NaCl, 0), 45.4 mN/m(NaCl, 1.359 $\times$ 10^{-2} M), and 32.4 mN/m(NaCl, 1 $\times$ 10^{-1} M), respectively.

In the presence of 1.359 $\times$ 10^{-2} M NaCl the phase transition of the surface layer was observed, but with increased concentration of NaCl (1 $\times$ 10^{-1} M) it could
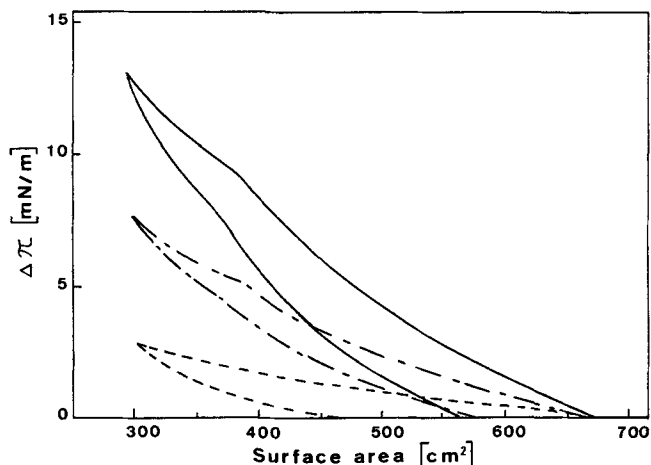
FIG. 4. Influence of NaCl added to 1 × 10⁻³ M SDS on the surface pressure deviation-surface area hysteresis curves. NaCl concentration: —, 0; — -, 1.359 × 10⁻² M; and — —, 1 × 10⁻¹ M.
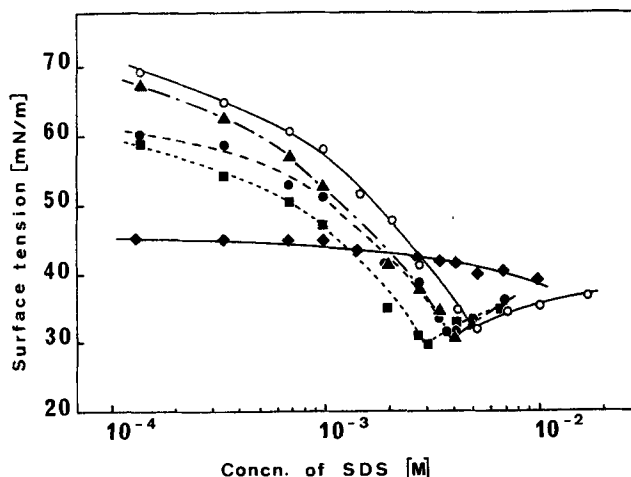

FIG. 5. Surface tension vs concentration curves for SDS in the presence of various detergent builders: ○, SDS alone; ■, STPP; ▲, PM; ●, DM; and ◆, PVA. Concentration of detergent builders was 1g/L. See Table 1 for abbreviations.

not be observed and the change in $\Delta \pi$ was rather small.

For the SDS solution containing 1 × 10⁻¹ M NaCl, the CMC and the surface area per SDS molecule at saturated adsorption were estimated to be 9.12 × 10⁻⁴ M and 33.7 Å², respectively, from the data shown in Figure 2 using Gibbs' equation with a factor of n = 1. These values are consistent with those reported in the literature (10, 12, 14).

The concentration of SDS solution (1 × 10⁻³ M) used in this study was near the CMC in the presence of 1 × 10⁻¹ M NaCl. Therefore, it is evident that the adsorption of SDS is nearly in saturation and the molecules of SDS are close-packed at the air-water interface, because 33.7 Å² is close to 31.8 Å² obtained for the limiting area per molecule in the condensed state. On compression, the adsorbed layer of SDS molecule may be squeezed out from the surface or collapsed to become the bulk phase, such as multilayer.

Since the excessive NaCl depresses the dissociation of SDS and reduces the electrical repulsive force among the hydration layers of SDS ions, the adsorbed layer of SDS is considered to be in the condensed state before compression. Moreover, the value of π_e was as high as 40.5 mN/m. Thus, the state of the adsorbed layer of SDS with excess NaCl under equilibrium condition seems to correspond to that in the high pressure region beyond the transition point under dynamic condition for the case of SDS alone (Fig. 3).

Influence of detergent builders on surface tension of SDS solution. The influence of addition of detergent builders on the curves of surface tension vs concentration of SDS solution is shown in Figure 5. Ionic builders led to a lowering of CMC of SDS. Nonionic PVA, however, exhibited a specific behavior; the surface tension merely decreased slowly with increasing SDS concentration without any break corresponding to the CMC.

Figure 6 shows the values of equilibrium surface tension with varying concentrations of detergent builders in the absence and presence of SDS at a constant concentration (1 × 10⁻³ M).

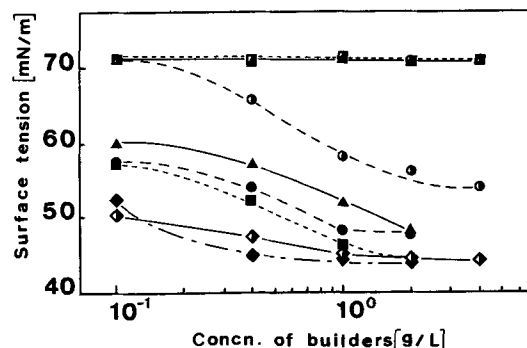FIG. 6. Surface tension vs concentration curves for detergent builders. In the absence of SDS: □, STPP; ▲, PM; ◑, DM; and ◆, PVA. In the presence of 1 × 10⁻³ M SDS: ■, STPP; ▲, PM; ●, DM; ◆, PVA. Surface tension of 1 × 10⁻¹ M SDS was 58.5 mN/m.

DM and PVA themselves exhibit a surface activity, showing the surface tension lowering with concentration, while it is not the case for STPP and PM.

All ionic builders lead to a lowering of surface tension of the SDS solution. Consequently, ionic builders contribute to increasing the surface excess concentration of SDS, as well as to promoting micelle formation. Although DM has a surface activity by itself, it behaves similarly to the other ionic builders in the mixed solution wtih SDS.

In the case of PVA alone, the surface tension lowering is significant even at lower concentrations, and the surface adsorption seems to be saturated approximately above 1g/L. The surface tensions with varying concentration of PVA in the presence of SDS (1 × 10⁻³ M) are almost same as those in the absence of SDS. Therefore, it is considered that PVA molecules are adsorbed on the air-water interface in preference to SDS molecules.
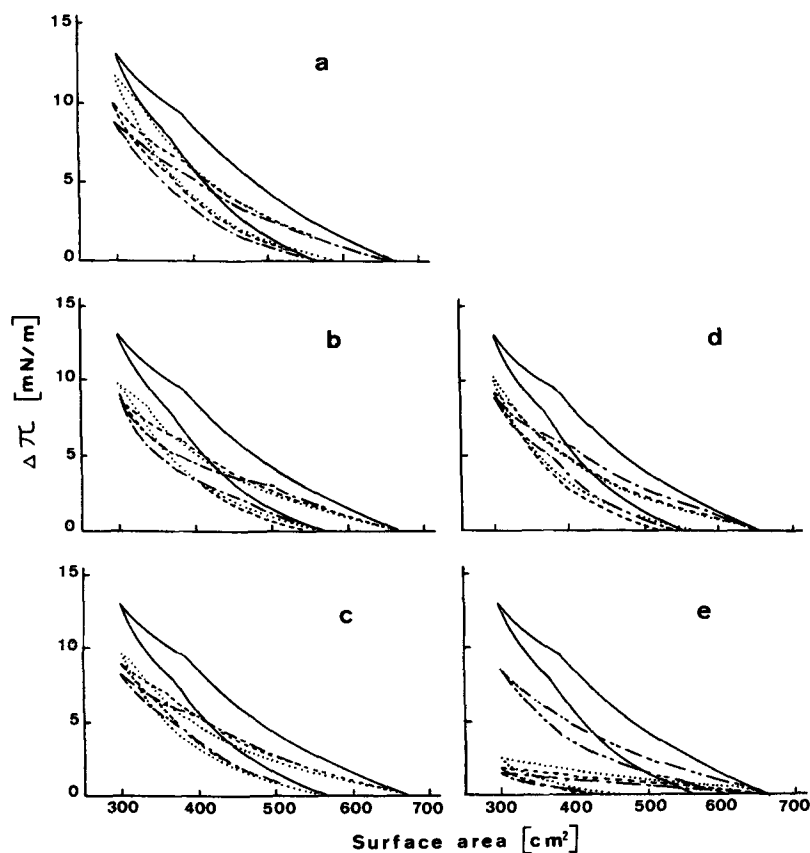
FIG. 7. Influence of detergent builders mixed with 1×10^{-3} M aqueous solution of SDS on surface pressure deviation vs surface area hysteresis curves: a, NS; b, STPP; c, PM; d, DM; and e, PVA. Concentration of detergent builders: ——, 0 — — — 0.001 g/L; ...., 0.1 g/L; - - -, 0.4 g/L; and — -, 1 g/L.

In addition, it has been reported that ionic surfactants interact with nonionic polymers, probably by "hydrophobic bonding", and that the resulting polymer-surfactant "complexes" behave as polyelectrolytes (15-18). Tadros (18) investigated the interaction of sodium dodecyl benzene sulfonate with PVA (12% acetate groups, $\overline{M}\upsilon$ = 42000) using surface tension and other measurements. According to his results, at higher polymer concentrations (> 0.1%, w/v), where all surfactant ions are "adsorbed" on the PVA chains, surface tension γ decreased only slightly with increasing surfactant concentration without any break in the γ-log C curve (without CMC). Our results resemble those of Tadros. Thus, it is apparent that the equilibrium surface properties of mixed solution of PVA and SDS are dominated mainly by the adsorbed layer of PVA, either with or without SDS.

Dynamic surface properties for mixed solutions of detergent builders and SDS. The effects of the addition of detergent builders on the hysteresis curve for surface pressure deviation vs surface area of the aqueous SDS solution are shown in Figure 7. In these measurements, the rates of compression and expansion were kept at 45 cm²/min. The very similar hysteresis curves (Fig. 7, a-d) were obtained by the addition of all build-

ers except for PVA (Fig. 7e). In these curves, the two-dimensional phase transition of adsorbed layers from liquid expanded to condensed states was observed to be similar to the case of SDS alone, but the extent of hysteresis and the change in $\Delta\pi$ were small as compared with those in the case of SDS alone that was discussed previously (Fig. 1). Moreover, the increase in the concentration of STPP led to a shift of the phase transition point to the larger area and the lower surface pressure deviation (Fig. 7b). Taking the similarity to the phase transformation of insoluble monolayers (19) into account, the adsorbed layer of SDS seems to become more condensed by the addition of STPP. Similar phenomena were also observed by the addition of PM and DM. Consequently, these polyelectrolytes (as well as STPP) are available for stabilization of the adsorbed layer of SDS. Thus, it has been found that ionic builders, irrespective of simple or polymeric molecules, exert similar effects on the dynamic surface properties of the adsorbed layer of SDS. By the addition of PVA, however, the phase transformation of the adsorbed layer was not observed, and the change in $\Delta\pi$ was significantly small at concentrations above 0.1 g/L.
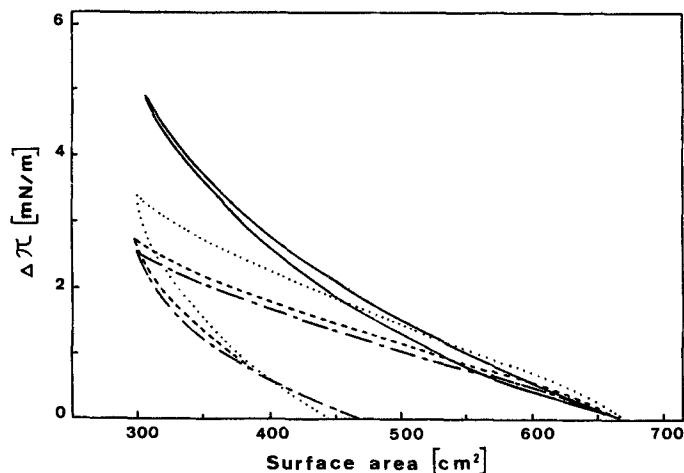
Figure 8 shows the hysteresis curves of surface

FIG. 8. Surface pressure deviation vs surface area hysteresis curves for PVA solutions: ——, 0.001 g/L; ...., 0.1 g/L; - - -, 0.4 g/L; — -, 1 g/L.

FIG. 9. Surface pressure deviation vs surface area hysteresis curve.

pressure deviation versus surface area for the solutions of PVA alone. At a concentration of 0.001 g/L PVA, the hysteresis is very small, which indicates that the molecules are scarcely desorbed from the surface by compression. On the other hand, hysteresis is markedly observed at the concentrations of PVA higher than 0.1 g/L, where the adsorption of PVA is almost in saturation from the results of equilibrium surface tension (Fig. 6) and the PVA molecules would be closely packed at the air-water interface. On compression, the adsorbed layer of PVA seems to be squeezed out from the surface, forming a multilayer or has a conformational change, such as looping. In this case, it takes a long time to recover the adsorbed state before compression, and this time lag causes the large hysteresis.

In the mixed solutions of PVA and SDS, the hysteresis curves of surface pressure deviation vs surface area resemble that of PVA alone. Consequently, the surface properties of the mixed solution are considered to be governed predominantly by the adsorbed layer of PVA, although it may be accompanied by SDS molecules.

As shown in Figure 9, the "area" ABC bounded by the hysteresis curve has the dimensions of the work (6). This "area" can be taken as a measure of the irreversibility of the process, since it is equal to the work lost in the system through the compression and expansion. The "area" ABO is equal to the total work added to the system. The work loss factor given by ABC/ABO is associated with the degree of molecular desorption from the air-water interface and/or structural changes in the adsorbed layer and also the rate of recovery by expansion.

Figure 10 shows the work loss factor for the SDS solution mixed with detergent builders as a function of builder concentration. The addition of ionic builders has a tendency to stabilize the adsorbed layer of SDS, although there are some differences in the work loss factor among the ionic builders. This contribution is due to inhibition of the molecular desorption of SDS
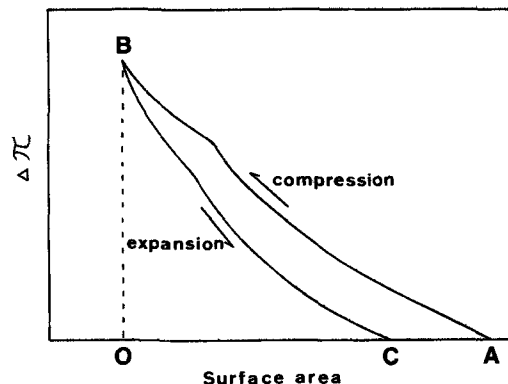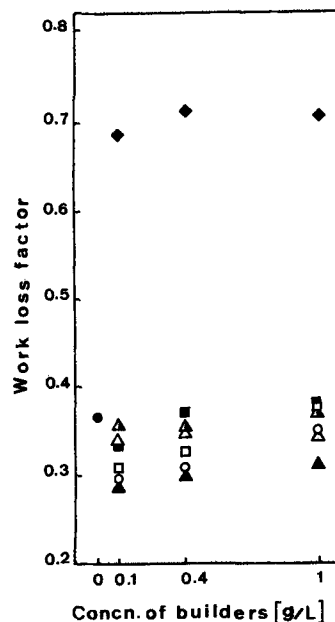

FIG. 10. Work loss factors for 1×10^{-3} M aqueous solution of SDS mixed with detergent builders as a function of builder concentration: ●, SDS alone; □ NS; △, STPP; ○, NTA; ▲, CA; △, PM;■, DM; and◆, PVA.

and promotion of the phase transformation from liquid expanded to condensed states of the adsorbed layer. PM and DM are found to exert similar effects with conventional builders. In contrast, the work loss factor for PVA is significantly greater than those for the other builders. In this case, the hysteresis of dynamic surface behavior can be ascribed to a less recoverable structural change of the adsorbed layer of PVA rather than SDS, which comprises the conformational change such as looping and/or the formation of multilayers.

Thus, polyelectrolytes as well as conventional ionic builders contribute to the enhancement and stabilization of the surface adsorption of SDS, together with promotion of micelle formation. On the other hand, PVA as a nonionic polymer is strongly adsorbed at the

air-water interface, and the conformational change of the PVA adsorbed layer under dynamic conditions causes a stable structure with sufficient relaxation time for our usual experiments.

In a separate paper (20), the authors have found that PVA exhibits a remarkable effect of anti-deposition in the detergency processes as compared with conventional ionic builders because of its strong adsorption on both soils and fabrics, which seems to be associated with the characteristic surface behaviors of PVA obtained in this paper.

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