Interactions between Two Surfaces with Adsorbed Nonionic Surfactants in Aqueous Electrolyte and in a Free Polymer Solution

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The force as a function of the surface separation, D, between two mica surfaces bearing adsorbed layers of nonionic surfactant Triton X-405 was measured in 0.1 M KNO_3. The force commenced at $D \simeq 30$ nm and was monotonically repulsive at all surface separations $D < 30$ nm. The surfaces were subsequently immersed in poly(ethylene oxide) (PEO) solutions (mol wt $\sim$ 40,000) at concentrations of up to 1% PEO. No attraction between the surfaces was observed (as might be expected from depletion layer forces); rather, the behavior suggests that the nonionic surfactant is largely replaced on the mica surface by the higher-molecular-weight PEO from solution. © 1987 Academic Press, Inc.

I. INTRODUCTION

Polymer molecules adsorbed at the solid–liquid interface are widely used to stabilize colloidal dispersions; the adsorbed layers generally provide a "bumper" that prevents strong mutual adhesion in the van der Waals minimum between the colloidal particles (1). The polymer molecules to be used need contain surprisingly few monomeric units to be effective stabilizers, provided they are firmly attached to the particle surface; this condition is met by block and comb co-polymers and by nonionic surfactants where one of the polymeric (or oligomeric) moieties adsorbs strongly to the substrate surface. Alternately, polymers may be chemically grafted onto the particles (1).

Until recently few direct measurements of the so-called "steric" forces between surfaces bearing adsorbed polymer layers have been reported. One of the first was that of Homola and Robertson (2), who used a compression cell technique to measure the force as a function of distance between polystyrene latex particles bearing adsorbed layers of various poly(ethylene oxide)-based nonionic surfactants. A more direct and sensitive technique which measures forces between two atomically smooth mica surfaces, originally developed by Tabor and Winterton (3) and considerably extended by Israelachvili and co-workers (4–6), has been used by us over the past few years to study steric interactions (both repulsive and attractive), in a wide range of polymeric systems.

In this paper we describe the interactions across an aqueous medium between adsorbed layers of a nonionic polyethoxy surfactant. In particular we investigate the effect on the surface–surface forces of adding *free polymer* to the solution, with a view to observing attractive depletion layer forces (7, 8). Such forces may be expected to occur between two nonpolymer-adsorbing surfaces immersed in a polymer solution when the gap between them becomes depleted of polymer relative to the bulk solution. Thus in the present study the adsorbed surfactant is intended to make the mica surfaces nonadsorbing for polymeric poly-

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(ethylene oxide), PEO, which on addition to the aqueous medium should then result in depletion layer attraction (8).

In section II the technique and procedure are briefly outlined. In section III we describe the surface forces, following addition of the surfactant to the aqueous electrolyte, and the effect of adding free PEO to the system. Our conclusions are presented in the final section.

II. METHOD AND MATERIALS

The force $F(D)$ between molecularly smooth, curved mica surfaces of radius R was measured as a function of the closest distance D between the mica sheets, using the crossed cylinder technique, which has been described by us in recent publications (9–11). In the current experiments a fused silica bath (volume 25 ml) enclosed the mica surfaces. The experimental method is capable of measuring (i) D to ± 0.3 nm and $F(D)$ to ± 50 nN in the range 0–500 nm, (ii) the mean refractive index $n(D)$ of the medium separating the surfaces, and (iii) the mean radius of curvature R (~ 1 cm) of the mica surfaces at the region of closest approach.

All the water used in the experiments was deionized and doubly distilled from an all-silica glass apparatus. The potassium nitrate was BDH analytical-grade material and used as received. The surfactant used was Triton X-405 [octylphenoxy(ethylene glycol)$_N$] supplied by the Rohm and Haas Chemical Company and has the following structure,

$$CH_3(CH_2)_7C_6H_4O(CH_2CH_2O)_NCH_2CH_2OH,$$

where $N \simeq 40$. (Note, though, that the polydispersity of the ethylene glycol chain in nonionic surfactants is high.)

The Triton X-405 was purified by drying, dissolving in toluene, and filtering through filter paper. The filtrate was then precipitated with hexane filtered in a Büchner funnel and the residue was washed with hexane. The residue was dried in a dessicator and stored at -10°C before use.

Two poly(ethylene oxide) samples were used. For the low-polymer-concentration experiments a Toyo Soda fraction employed in our previous experiments (10, 11) was used. This polymer had a weight average molecular weight of 40,000 and $M_w/M_n = 1.03$. For the high-polymer-concentration experiments a poly(ethylene oxide) obtained from the Hoechst Chemical Company was used. This polymer had a weight average molecular weight of 38,000 and a M_w/M_n of 1.4.

All solutions were filtered through 0.2-μm Millipore GS-grade filters prior to introduction into the apparatus.

III. RESULTS AND DISCUSSION

Prior to the introduction of surfactant or polymer to any experiment, the force profile $F(D)$ between the mica surfaces immersed in 0.1 M KNO_3 was measured, typically 1 h after the addition of electrolyte. Figure 1 shows such an interaction–distance profile, plotted as $[F(D)/R]$ vs D, where R is the mean radius of curvature of the mica sheets ($R \simeq 1$ cm); this "normalizes" results from different experiments with respect to R and (in the Derjaguin approximation) gives the interaction energy per unit area between flat plates a distance D apart, obeying the same force–distance law (within a factor 2π). The profile of Fig. 1 is very similar to those profiles reported in earlier studies for the same system (4, 10), where it was interpreted in terms of an electrostatic double-layer repulsion at $D < 10$ nm (see inset to Fig. 1 on log-linear scale) and a weak secondary minimum at 20 nm $\gtrsim D \gtrsim$ 10 nm. Very recently, however, it has been clearly demonstrated by C. Toprakcioglu and ourselves (12) that the repulsion at $D < 10$ nm experienced between mica sheets in 0.1 M KNO_3 that had been filtered through Millipore filters is in fact due to the adsorption onto the mica of trace amounts of surfactant (mainly Triton X-100) leached out from the filter. Toprakcioglu *et al.* showed that the force profile obtained when using extractable-free filters or no filters at all is monotonically attractive at

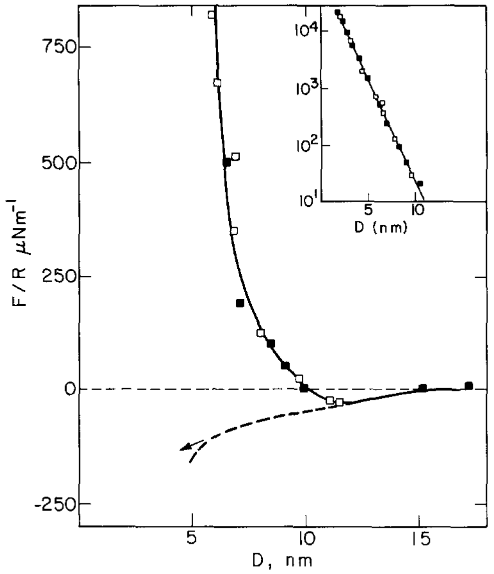

FIG. 1. Force–distance profile between curved mica surfaces at a closest distance D apart immersed in an aqueous 0.1 M KNO_3 solution which was filtered through GS-grade Millipore filters which contained Triton X-100 as a wetting agent. The data are presented (in the Derjaguin approximation, see text) as (F/R) vs D, where R ($\simeq$1 cm) is the mean radius of curvature of the mica surfaces. The broken line is the corresponding interaction–distance profile for the case where TF-grade Millipore or no filter at all was used, from the work of Toprakcioglu *et al.* (12). The inset shows the data on a log-linear plot. (■) In compression (surfaces approaching). (□) In decompression (surfaces moving apart).

$D < 20$ nm, with a strong ultimate repulsion (probably due to hydration forces) at $D < 2$ nm. These results are shown as a broken line in Fig. 1. The important feature to note at this stage is that the effect of the trace amount of the adsorbed Triton X-100 is only significant at $D < 10$ nm.

i. Surface Forces with Adsorbed X-405 Surfactant

The surfaces were moved far apart (to $D \simeq 3$ mm), Triton X-405 was introduced to a final concentration c, and the surfaces were allowed to incubate for 10 ± 2 h. Figures 2 and 3 show force–distance profiles determined following this incubation at concentrations c = 10 and 100 ppm (w/w), respectively. Within the scatter, the curves are the same, suggesting that the limiting adsorbance is reached already at the lower incubation concentration.

On a first approach of the surfaces following incubation no interaction was measurable from large D down to $D \sim 30$ nm (see insets to Figs. 2 and 3 showing $F(D)$ on an expanded linear scale) when a monotonically increasing repulsion was observed down to $D \sim 5$ nm. The weak attraction at 10 nm $< D <$ 20 nm observed prior to addition of the X-405 had disappeared. It is appropriate to comment on two other features of the force–distance profiles with the adsorbed surfactant. First, the profiles were reproducible and reversible at all (experimentally accessible) rates of compression and decompression of the surfaces. This is in some contrast to the case of adsorbed PEO in the same medium, for example, when a clear relaxation effect of the polymer was noted (for times <15 min) and $F(D)$ was generally lower for a given D on rapid decompression of the surfaces relative to its equilibrium value. We shall return to this point later. Second, replacing the Triton X-405 solution by pure 0.1 M KNO_3 electrolyte, so that an approximately 5000-fold dilution of the original incubation concentration was achieved, resulted in no subsequent change within error in the force profile, even after overnight incubation with the surfaces far apart. This strongly suggests a quasi-irreversible adsorption of the surfactant over the times of our experiments.

The repulsive forces between the mica plates as the adsorbed surfactant layers overlap are probably due to osmotic interactions between the opposing oligo-ethoxy moieties. We might expect that as the surfaces approach, the mean concentration of ethoxy segments in the overlap region will increase and result in an increasing repulsion in the "good solvent" conditions of our experiments. The onset of interaction between the surfactant layers is typically at ~30-nm separation. Triton X-405 has an average of 40 ethoxy monomer units

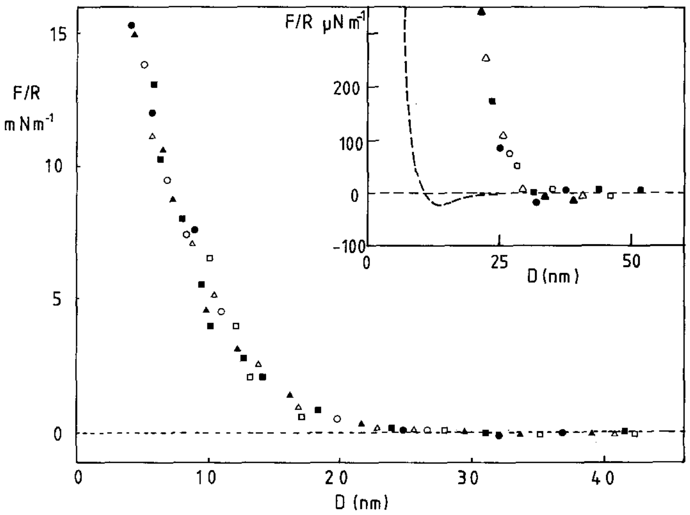

FIG. 2. Force–distance profile between curved mica surfaces (radius of curvature R) following addition of Triton X-405 to the 0.1 M KNO_3 medium to a 10 ppm (w/w) concentration and at 10± 2 h incubation. (■) First compression. (□) First decompression immediately following (■). (▲) First compression in a different experiment. (△) First decompression immediately following (▲). (●) Compression after replacement of Triton X-405 solution by pure 0.1 M KNO_3 and after overnight standing. (○) Decompression following (●). Inset: symbols as above but on an expanded scale. Broken line taken from data of Fig. 1.

per molecule so that this moiety has a fully extended chain length of some 12–13 nm and random coil dimensions of ~3 nm. It is of interest that the interaction between the two adsorbed layers is slightly greater than twice the mean extended chain length; this could be

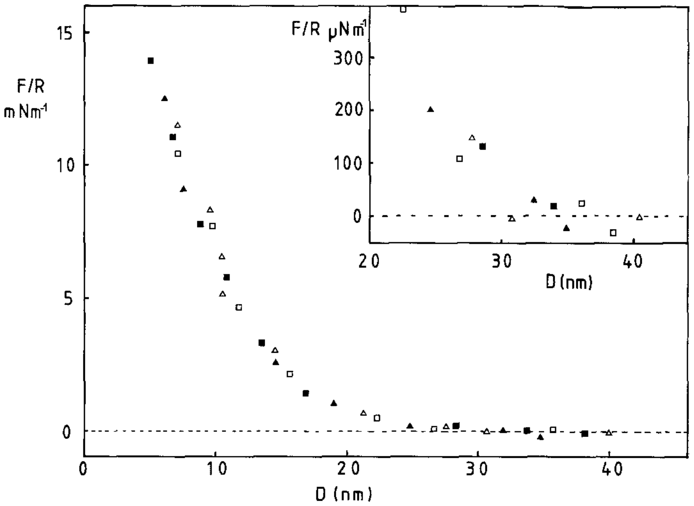

FIG. 3. Force–distance profile as in Fig. 2, but with Triton X-405 added to 100 ppm (w/w) concentration prior to incubation for 10 ± 2 h. (■) and (▲) Compression (two different experiments). (□) and (△) Immediate subsequent decompression (following (■) and (▲), respectively). Inset: symbols as above on an expanded scale.

due to a number of factors: if the surfactant molecules are adsorbed end-on (with the hydrophobic alkyl moieties anchoring the surfactant to the mica and the oligo-ethoxy tails extending freely from the surface (18)) then the effective adsorbed layer thickness may be determined by the longest tails (13) and, as a consequence of the polydispersity of N, be considerably larger than suggested by its mean value above.

It is also possible that micellization of the surfactant molecules has occurred and that we are dealing with either micelles—with the hydrophobic alkyl tails on the inside—adsorbed on the mica (though this is not a likely alternative in view of the fact that such micelles in solution rarely adsorb at interfaces) or an effective adsorbed "bilayer" consisting of a "sandwich" of the oligo-ethoxy moieties enclosing the hydrophobic alkyl chains. In both cases the effective thickness of the adsorbed layers would be greater; however, the quasi-irreversible nature of the force-distance profiles on extreme dilution of the surfactant solution argues against the micellization effects suggested above.

Finally, we note that the rapidly increasing force-distance trend of Figs. 2 and 3 is reasonably well described by an exponential force law

$$F(D) \propto e^{-D/\lambda} \qquad [1]$$

over three orders of magnitude in $F(D)$, as indicated in Fig. 4, where $\lambda \simeq 4$ nm.

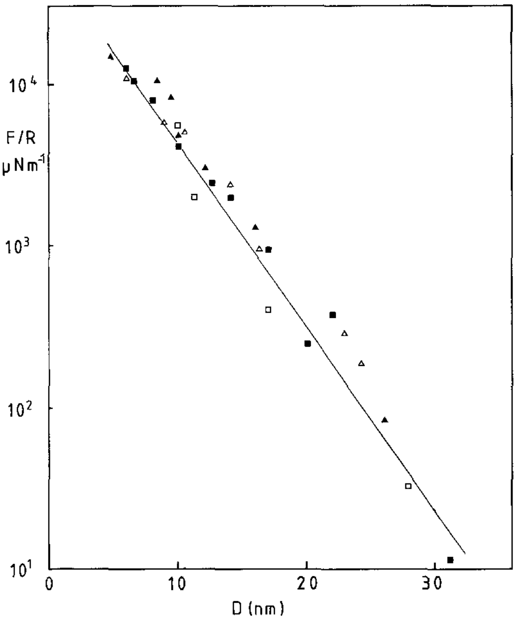

FIG. 4. Data of Fig. 2 on log-linear plot showing exponential region (solid line) $F(D) \propto e^{-D/\lambda}$, where $\lambda \simeq 4$ nm. Symbols same as for Fig. 2.

It is instructive to compare our results with those obtained by Homola and Robertson (2) using a compression cell technique. They measured the pressure between polystyrene latex particles in aqueous electrolyte with an adsorbed layer of a $C_{18}E_{40}$ surfactant (where C stands for (CH_2) and E for (CH_2-CH_2-O)), a molecule with a structure similar to Triton X-405. They found an onset of repulsive interaction between the particles at surface separations of 20–25 nm (evaluated somewhat indirectly), with a force law varying approximately exponentially with separation over about $1\frac{1}{2}$ orders of magnitude with a decay length close to λ (Eq. [1]). They also found that the range of interaction did not vary when the length of the alkyl moiety of their molecules was varied (at constant ethoxy length), suggesting that these molecules were anchored to the (hydrophobic) polystyrene surface via adsorption of the alkyl tail, with the oligo-ethoxy end (E_{40}) extending out into the liquid.

From the optical method it is possible to evaluate the mean refractive index $n(D)$ of the medium between the mica surfaces as well as the surface separation D. Measurements of $n(D)$ were taken before and after addition of Triton X-405 and the results are presented in Fig. 5. Also shown in Fig. 5 are the $n(D)$ results following replacement of the surfactant solution by pure electrolyte (open symbols). Prior to adding surfactant, $n(D)$ is essentially independent of D and close to the value of 1.338 expected for 0.1 mole dm^{-3} KNO_3 solution (this gives the most direct indication that the

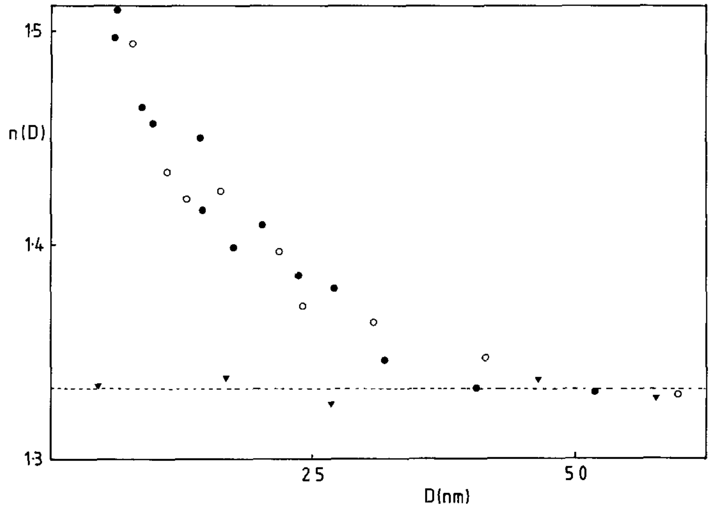

FIG. 5. Refractive index profile $n(D)$ of medium separating curved mica sheets at point of closest approach (separation D). (▼) In aqueous 0.1 M KNO_3 filtered through a GS Millipore filter prior to addition of surfactant X-405. (●) Following addition of Triton X-405 to a 10 ppm (w/w) concentration and standing for 10 ± 2 h. (○) After incubation (10 ± 2 h) in Triton X-405, subsequent *replacement* of the Triton solution by pure aqueous 0.1 M KNO_3 and overnight standing. The broken line is the refractive index of pure aqueous 0.1 M KNO_3. The refractive index of pure Triton X-405 (determined by an Abbé refractometer) is 1.49.

adsorbance of surfactant leached from the Millipore filter—which is responsible for the short-range repulsion at $D < 10$ nm shown in Fig. 1—is very small). Following 10 h of incubation in the Triton X-405, the mean refractive index $n(D)$ increases from the value for bulk electrolyte at large D to a value close to that of bulk X-405 (n(Triton X-405) = 1.49) at $D \simeq 4$ nm (the distance of closest approach in our experiments, see also Fig. 5).

The $n(D)$ profile was reproducible and reversible (within the scatter) on both compression and decompression of the surfaces and was essentially unchanged following extreme dilution of the surfactant solution by pure 0.1 M KNO_3 solution as previously described (open circles on Fig. 5). This again supports the concept of irreversible adsorption of the surfactant under the conditions of our experiments, as suggested by the force–distance measurements of Figs. 2 and 3.

It is possible from the $n(D)$ data to evaluate the amount Γ of Triton X-405 adsorbed per unit area; one finds $\Gamma = 2\text{–}3$ mg m^{-2}, a value similar to the adsorbance of nonionic surfactants onto various surfaces (2, 14, 15). If we assume that the X-405 is anchored to the substrate via flat adsorbance onto the mica of the hydrophobic alkyl moiety, with the oligoethoxy tails extending into the solution, we may also estimate the maximum amount per unit area $\Gamma_{\max}$ of the surfactant that could adsorb in a monolayer. Taking the surface area of the hydrophobic part, $(CH_3(CH_2)_7C_6H_4)$ as ca. 0.5 nm^2, we estimate $\Gamma_{\max} \simeq 7$ mg m^{-2}. This suggests that in the present experiments some 30–40% of the mica is covered with adsorbed surfactant (corresponding to an area of ca. 1.2 nm^2 per surfactant molecule).

ii. Surface Forces following Addition of Polymer

The use of the mica technique to detect depletion layer attraction between nonadsorbing surfaces in a polymer solution was considered in detail in a previous publication (11). A polymer concentration on the order of 1–3% was determined as optimal; at much lower concentrations the sensitivity of the method would not be adequate to detect such forces, whereas at much higher concentrations the width of the depleted region between the surfaces, whose dimensions are those of the correlation length in the solution of overlapping polymer, becomes prohibitingly small. Thus, following adsorption of the Triton X-405 onto the mica and replacement of the surfactant solution by 0.1 *M* KNO_3, PEO of molecular weight 38,000 (see section II) was added to the experimental cell to a concentration of 1% (w/w). The surfaces were held well apart (~2 mm) and permitted to equilibrate in the PEO solution for periods of between 1 and 16 h (1 h is the characteristic period required for *thermal* equilibration of the cell following solution exchange or addition); *F*(*D*) and *n*(*D*) were then determined again.

Figure 6 shows the force–distance profiles between the mica sheets following 10 h of incubation in the Triton X-405 surfactant solution and an additional 16 h of incubation in the 1% PEO solution as described above. As the surfaces approach there is little interaction between them down to $D \simeq 45$ nm, when increasing repulsion commences. In particular, within the scatter of our data, there is no evidence of any *attraction* between the mica sheets prior to the onset of monotonic repulsion (see inset to Fig. 6). In addition to the increased *range* of repulsion compared with the profile following incubation in the X-405 surfactant solution (28–30 nm, see Fig. 4), the force–distance profiles of Fig. 6 exhibited a qualitatively different behavior when *F*(*D*) was examined at different *rates* of compression and decompression. On a first approach following incubation the data (Fig. 6) followed curve A to the point of closest approach C; subsequent behavior depended on the *rate* at which decompression took place. Rapid decompression from C (ca. 5 min for *D* going from 5 to 200 nm) followed curve B. On the other hand, slow decompression from C (ca. 1 h for *D* going from 5 to 100 nm) followed curve A again, as did all *compression* profiles irrespective of rate.

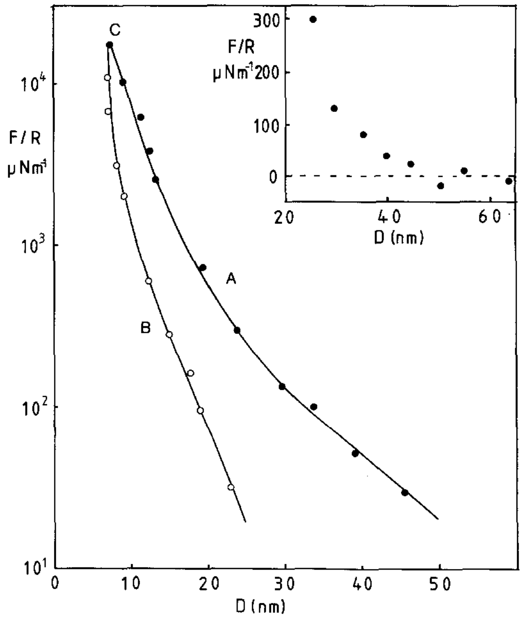

FIG. 6. Force–distance profiles between mica surfaces following 10 h incubation in Triton X-405 solution and an additional 16 h incubation in a 1% PEO solution. Curve A: First compression and subsequent "relaxed" compressions (see text). Curve B: Rapid decompression from point of closest approach C. Inset: data for a "relaxed" compression (as in curve A) on an expanded linear scale.

Similar profiles were obtained with different mica sheets and other incubation times from 1 to 16 h, suggesting that this is the limiting force law under these conditions. We also used a 10^{-4}-w/w PEO solution with the Toyo Soda polymer (mol. wt. = 40,000) employed in previous studies (10, 11). For incubation times of 16 ± 2 h, the resulting behavior was very similar to that shown in Fig. 6.

We also determined the mean refractive index profile *n*(*D*) of the medium separating the mica sheets following the incubation in the PEO solution. The profile is given in Fig. 7 (solid circles); it contrasts somewhat with the earlier *n*(*D*) profile between the mica sheets bearing adsorbed Triton X-405 alone (Fig. 5),

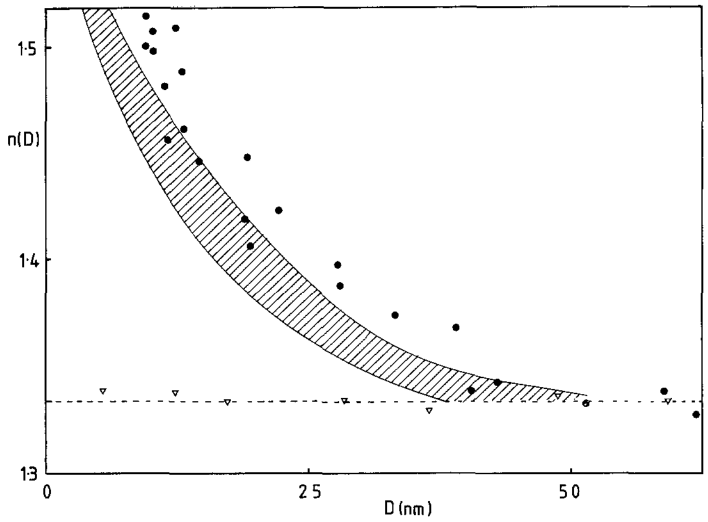

FIG. 7. Refractive index profile $n(D)$ between curved mica surfaces at closest distance D apart. (▽) In aqueous 0.1 M KNO_3 solution prior to addition of Triton X-405 surfactant. Broken line: refractive index of pure aqueous 0.1 M KNO_3. Shaded band: spread of $n(D)$ data following addition of Triton X-405 and incubation for 10 h (taken from Fig. 5). (●) $n(D)$ following replacement of Triton X-405 by a 1% PEO solution and incubation for 16 h.

shown as a shaded strip in Fig. 7, both in regard to the overall adsorbance ($\Gamma_{PEO} \simeq 3$–4 mg m^{-2} compared with 2–3 mg m^{-2} for Triton) and to the fact that it has "moved out" to a higher D value. The $n(D)$ profile of Fig. 7 was essentially identical on both compression and decompression.

The rate-dependent behavior of the force–distance law, Fig. 6, is thus somewhat different from that of the adsorbed Triton X-405 (Fig. 4), where—within the scatter—both compression and rapid decompression yielded the same $F(D)$ profile. More particularly, however, the kinetic behavior of Fig. 6, as well as the *range* of interaction, is reminiscent of force–distance profiles obtained in earlier studies where the interaction between mica surfaces which had been incubated in PEO solutions *alone* was investigated (10) (i.e., without previous immersion in a surfactant solution as in the present study). The kinetic behavior (that is, a lower $F(D)$ for a given D on rapid decompression) was attributed to the time required for surface relaxation of the highly compressed polymer. This similarity is brought out in Fig. 8, where the broken curves correspond to curves A and B of Fig. 6 of the present study; the experimental points in Fig. 8 are the compression (solid circles) and rapid decompression (empty circles) profiles from the previous study of interaction between PEO (Mol. wt. = 40,000, close to the present case) adsorbed onto mica in the same electrolyte (0.1 M aqueous KNO_3) as that in the current experiments. The force–distance profile for adsorbed layers of PEO immersed in *toluene,* not shown on Fig. 8, is qualitatively very similar. For comparison, the shaded strip on Fig. 8 is taken from Fig. 4 and corresponds to the $F(D)$ profile between the adsorbed surfactant layers.

These results show that, on immersing the (X-405) surfactant-covered mica sheets in the 1% PEO solution, the behavior (within experimental error) rapidly reverts to that observed between two mica sheets bearing adsorbed PEO alone. This strongly suggests that the PEO in solution has caused the surfactant molecules

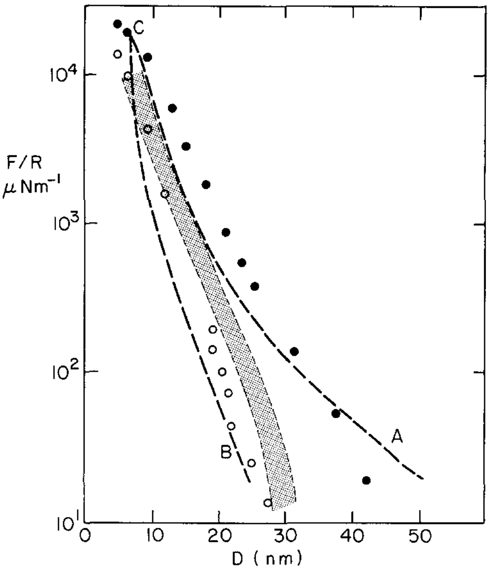

FIG. 8. Force–distance profiles between curved mica sheets (radius R). Shaded band corresponds to the spread of data following adsorption of Triton X-405, taken from Fig. 4, at all compression–decompression rates. Broken lines correspond to profiles following incubation of adsorbed Triton X-405 layer in 1% PEO solution. Curve A is the "relaxed" profile (see text) and curve B is the unrelaxed decompression profile following compression to point of closest approach C. (Data taken from Fig. 6.) The experimental points are taken from a force–distance profile between mica sheets that were incubated in a PEO (mol. wt.= 40,000) solution in aqueous 0.1 M KNO_3, *without* prior adsorption of Triton X-405, taken from Ref. (10). (●) "Relaxed" profile (corresponding to curve A). (○) "unrelaxed profile" on rapid decompression from point of closest approach, corresponding to curve B.

to desorb and has replaced them on the mica surface. There are also other possibilities: (i) trapping of free PEO molecules between the adsorbed surfactant layers, (ii) partial (rather than total) replacement of the X-405 on the mica surface by the PEO, or (iii) adsorption of PEO on the mica without desorption of the surfactant. The first of these seems unlikely as the amount of free PEO trapped in a 1% solution would be small and unlikely to lead to the substantive moving-out of the $n(D)$ profile shown in Fig. 7. (We recall in this context that very similar behavior was observed when a 10^{-4}-w/w PEO solution, of mol. wt. = 40,000 (Toyo Soda; see section II), was used rather than the 1% Hoechst PEO. At such a low concentration the amount of free PEO trapped would be very small indeed.) The second and third possibilities—that some surfactant remains on the surface—are more difficult to rule out entirely because any substantial replacement of Triton X-405 by PEO would also lead to the latter dominating the force profiles. Nonetheless, the qualitative as well as quantitative differences between the force and refractive index profiles prior and subsequent to immersion in the PEO solution, together with the close similarity of the resulting $F(D)$ behavior to that between adsorbed PEO alone, lead us to conclude that the surfactant molecules have been essentially replaced on the mica by the poly(ethylene oxide). It is especially suggestive that on rapid decompression following immersion in PEO solution (curve B, Fig. 8) the force $F(D)$ is sensibly *lower* than that with the adsorbed surfactant alone (shaded strip, Fig. 7) over a considerable D range. This behavior is difficult to reconcile with the presence of significant remaining amounts of Triton X-405 on the mica. Such exchange of the Triton X-405 by PEO would be consistent with previous observations (in different systems) where surface-adsorbed species do not desorb on *dilution* of solution, but can be adsorbed and replaced by polymer *added* to the solution (16, 17).

IV. SUMMARY AND CONCLUSIONS

The force–distance profiles between mica sheets immersed in a solution of a nonionic surfactant, Triton X-405, in 0.1 M aqueous KNO_3 are monotonically repulsive and suggest that the surfactant is anchored to the mica via adsorption of the alkyl moiety onto the surface, with the oligo-ethoxy tail extending into solution. Immersion of such surfactant-covered mica surfaces in a poly(ethylene oxide) solution does not lead to any depletion layer forces between the surfaces. Rather, the subsequent behavior is strongly reminiscent of that between two adsorbed PEO layers on mica in both aqueous and organic media and indicates that the surfactant has been substantially *replaced* on the mica surface by the PEO from solution.[3]

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[3] This is consistent with the findings of Ref. (2). In addition, in a separate experiment where Triton X-405 was allowed to adsorb onto freshly cleared mica, there was no indication of any hydrophobicity of the mica surface, as might be expected if alkyl groups were exposed at the Triton–water interface.