Surface forces measurements on a cationic polymer in the presence of an anionic surfactant

K.P. Ananthapadmanabhan, G.-Z. Mao, E.D. Goddard and M. Tirrell

*Union Carbide Chemicals and Plastics Company Inc., Old Saw Mill River Road, Tarrytown, NY 10591, USA

bDepartment of Chemical Engineering and Materials Science and The Center for Interfacial Engineering, University of Minnesota, 421 Washington Ave., SE. Minneapolis, MN 55455, USA

(Received 6 February 1991; accepted 10 June 1991)

Abstract

Surface forces measurements have been made between adsorbed layers on mica of a cationic polymer (Polymer JR-400) in distilled water, both in the absence and in the presence of the anionic surfactant sodium dodecylsulfate. In the absence of surfactant, the polymer was bound to the oppositely charged mica surface and exhibited hysteresis force curves which were monotonically repulsive up to a compression of 10^-8 N m^-1. In the presence of surfactant hysteresis was also observed but while the compressing force curves were monotonically repulsive, the separating force curves showed a significant attraction between the layers. This suggests that bound surfactant may be inducing hydrophobic interactions between the adsorbed layers.

INTRODUCTION

Adsorption of polymers and surfactants is a widely used method of modifying surfaces to impart desired chemical and physical properties. Combination of polymers and surfactants frequently occurs in technological formulations [1,2] either purposefully to manipulate product properties via the polymer–surfactant interactions or coincidentally when both serve important, though largely independent, functions in the product. Many coatings, especially, though not exclusively, those with associative thickeners [3] fall into the former category, whereas many cosmetics and cleansers are in the latter [4]. In general, flocculation–dispersion characteristics of colloidal dispersions and the

1In honor of Dr. Hans Lyklema’s 60th Birthday.

2Present address: Unilever Research, 45 River Road, Edgewater, NJ 07020, USA.
wettability of surfaces are often controlled by adsorbed polymer and surfactant films. Adsorbed films also play an essential role, inter alia, in lubrication, drag reduction and adhesion. In all of these, and related, applications, the nature of the adsorbed layers and the interactions between them determines the system’s behavior.

In multicomponent formulations, such as those under consideration here, it is important to understand the polymer–surfactant interactions, whether they are intentional or not. Polymers and surfactants can form complexes with one another, the structures of which are partially understood [5]. For this reason adsorbed films in media containing both kinds of components may have a very different structure from, for example, adsorbed polymer films without surfactant. It is well known that surfactants can influence strongly the adsorbed amounts of polymers under certain circumstances [6,7]. Little direct information is available on the structure, i.e. the physical extension and configuration of the adsorbed molecules, of such adsorbed layers. Some information of this sort is available on polymer–surfactant complexes in solution. Polymer-bound surfactant can influence the solubility of the complex, as when a water-soluble polyelectrolyte binds a surfactant of the opposite charge, thereby incorporating hydrophobicity into the complex [8]. Surfactant complexation can expand the chain configuration, as in the case where a neutral polymer binds charged micelles, and in so doing introduces electrostatic repulsions among the binding sites [9].

This paper presents preliminary results in an attempt to gain related information on molecules in adsorbed films. The surface forces apparatus was used to study a cationically modified cellulosic polymer, both in the absence and in the presence of the anionic surfactant sodium dodecylsulfate. In this way, information is obtained not only on the configuration of the adsorbed layer under various circumstances, but also on the forces between two such adsorbed layers. This latter sort of information pertains to situations such as lubrication, colloidal dispersions and adhesion where two modified surfaces may be in close proximity.

EXPERIMENTAL

Materials

The cationic cellulosic polymer used, namely UCARE® Polymer JR-400, a product of Union Carbide Chemicals and Plastics Company, is an N,N,N-trimethylammonium chloride-substituted hydroxyethyl cellulose with a molecular weight of approximately 500 000. Sodium
dodecylsulfate (SDS) of purity > 99% was used as received from the EM Corporation. All experiments were conducted in distilled, deionized water with an ionic strength below $10^{-4}$ M. All solutions were filtered through a 0.22 μm Millipore filter before injection into the surface forces apparatus.

**Methods**

The forces between two mica sheets bearing the adsorbed layers were measured using the basic method developed by Israelachvili et al. [10]. The specific procedures employed in this method at the University of Minnesota, along with a recent summary of prior work on polymers, is available in the review article of Patel and Tirrell [11]. The surface forces apparatus enables the measurement of interaction forces between two surfaces or adsorbed layers over a range of separations from several hundred nanometers down to molecular contact between the mica substrate surfaces. Separations ($D$) can be measured with a precision of better than 0.5 nm and forces ($F$) are measured to a precision of $10^{-1}$ μN. Data are represented in plots of $F/R$ versus $D$, where $R$ is the measured mean radius of curvature of the mica surfaces in the region where they are interacting. The quantity $F/R$ is equal to $2\pi$ times the energy per unit area of interaction between the surfaces [12].

Mica surfaces were prepared in the standard manner and mounted in the apparatus. Air contact and water contact between the bare mica surfaces was verified to be free of contamination before proceeding with the experiment. With uncontaminated surfaces, a polymer solution was introduced into the apparatus bringing the concentration of Polymer JR-400 to 0.05% by weight. Adsorption on the mica surfaces was allowed to proceed for at least 12 h. To study surfactant effects on the interactions curve, the polymer solution was drained and replaced with a submicellar SDS solution (0.05% by weight). Control experiments with distilled water showed that polymer desorption was not induced on the time scale of these experiments by exposing the adsorbed polymer layer to a polymer-free aqueous medium. All curves presented are either composites, or quantitatively representative, of data obtained from several independent experiments. No systematic study has yet been made of the possibly interesting effects of rates of compression and expansion.

**RESULTS AND DISCUSSION**

Figure 1 shows the data on the adsorbed layers of Polymer JR-400, along with data for the interaction in polymer-free distilled water. The
Fig. 1. Data on force vs distance for three successive approaches of two mica surfaces with an adsorbed layer of cationic polymer. The order of the approaches was (a), (b), (c). Curve (d) is the measured interaction arising from electrical double layer effects in polymer-free distilled water.

force profiles for the polymer layer lack the long-range tail found between bare mica surfaces in distilled water owing to the partial neutralization of the negative charge on the surface of mica by the cationic polymer [13]. At a shorter range there is enhanced repulsion with the polymer due to steric effects. Adsorption on the mica surface in water may be a good model system for the adsorption of Polymer JR-400 on other negatively charged surfaces. On first compression, a long range (≈500 Å) repulsion is observed. On further compression along this first approach curve a steep, barrier-type repulsion of 10⁴ μN m⁻¹ at a separation of about 40 Å is observed. Separating the two surfaces from this point leads to a different hysteresis profile of forces that fall much more steeply with increasing distance than the first approach curve. Subsequent approaches at the same contact position resulted in almost the same compression trajectory. Relaxation of the compressed profile did not occur within hours. Preliminary data indicated that compression to force levels significantly higher than 10⁴ μN m⁻¹ could produce some adhesion on separation but this requires further measurements to be definitive.

These results are qualitatively similar to data published by Luckham
and Klein [14], and Dix et al. [15], on surface forces between adsorbed layers of polylysine, a cationic polypeptide, on mica in water. They demonstrated strong hysteresis between approach and separation. They showed that the profile of the separating force curve depended upon how much the layer had been compressed. The explanation that was developed [14], which we believe also applies to the present data, asserts that on compression more cationic segments which reach the surface during the initial adsorption process are forced into contact with the negatively charged mica surface. Strong binding ensues that is not readily reversed on decompression. Figure 2 shows a schematic diagram of this irreversible compression hypothesis. Future work on the present system to study the possible sensitivity of the separating force curves to the degree of compression is planned. We note that in our work, as well as in that on polylysine, the initial, uncompressed adsorbed state may not be an equilibrium state since the strong ionic binding may trap the segments in configurations that are difficult to relax.

Figure 3 shows the force profiles in the presence of SDS. The first approach curve is similar though more gradual in its long-range shape to that without SDS, with a detectable onset of repulsion at about 500 Å. The shorter range, steep repulsion is at larger separation than without SDS, possibly owing to additional repulsion, and or looser binding to the surface, of the polymer bearing bound anionic surfactant molecules. Subsequent compressions are different from the first compression in a manner very similar to the data of Fig. 1 without SDS.

The principal difference arising from the presence of surfactant is seen in the separating force curves from a compression of less than $10^4 \mu N m^{-1}$. Strong attraction occurs ($\approx 1000 \mu N m^{-1}$), with the minimum at a separation of about 200 Å. The mechanism of this attraction remains to be discovered but is clearly related to the presence of surfactant in the solution. One possibility is illustrated schematically in Fig. 4, where polymer-bound surfactant molecules are hypothesized to give rise to hydrophobic interactions between the two layers. Bridging, possibly aided by looser binding to the surface induced by surfactant, is an additional potential source of attraction.

CONCLUSIONS

These preliminary data do not prove any physical mechanism for the force profiles which we have observed. Rather they demonstrate clearly via direct mechanical probing that the configuration of a macromolecule in an adsorbed layer is different in the presence, from what it is in the absence, of a surfactant molecule that is anticipated to interact with the polymer. Furthermore, the interaction between two
such adsorbed layers is qualitatively different (attractive rather than purely repulsive) when surfactant is added. This is the principal point of this paper.  
This work raises interesting questions and demonstrates the feasibility of several intriguing lines of investigation. Questions that can be studied further by the methods used here include effects of temperature and ionic strength on the force profiles. These factors will affect
Fig. 3. Data on force vs distance for (a) approach and (b) separation for two adsorbed layers of cationic polymer in the presence of 0.05 wt.% SDS. Negative values of force are attractive forces. Curve (c) is identical to curve (a) of Fig. 1.

As Surfaces are Pushed Close to Each Other:

(a) Hydrophobic Interaction
(b) Bridging

Fig. 4. Schematic diagram of hypothetical mechanisms for the induction of attractive forces between adsorbed layers of cationic polymer by the binding of surfactant to the polymer.
the strength of ionic and hydrophobic bonding in this system. Varying
the sign and degree of charge on the polymer and the surfactant are
other possibilities that should be examined to ascertain the pattern
and the generality of these phenomena.

ACKNOWLEDGMENT

This work was done while K.P.A. was an Industrial Research Fellow
of Union Carbide Chemicals and Plastics Company at the Center for
Interfacial Engineering at the University of Minnesota, an NSF-
supported Engineering Research Center (NSF-CDR-8721551).

REFERENCES

1 I.D. Robb, in E.H. Lucassen-Reynders (Ed.), Anionic Surfactant-Physical Chemis-
try of Surfactant Action, Marcel Dekker, NY, 1981.
7 J.E. Glass (Ed.), Polymers in Aqueous Media: Performance through Association,
12 B.V. Derjaguin, Kolloidn. Zh., 69 (1934) 155.