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## Nonionic Hydrophilic Surfaces: Adsorption and Interactions\*

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An overview is given of recent studies of nonionic, hydrophilic surfaces formed by the adsorption of surfactants or surface active polymers. Hydrophobic surfaces can be easily hydrophilized by the adsorption of nonionic surfactants or block copolymers containing hydrophobic chain segments; the cooperative interaction between the hydrocarbon moieties contributes more to the free energy of adsorption than the interaction with the hydrophobic surface.

Hydrophilic layers are also readily formed on hydrophilic surfaces provided specific interaction between the hydrophilic end groups and the surface creates a sufficiently hydrophobic surface so that a second layer can be formed through cooperative interaction. The temperature dependence of the interaction forces between layers of surfactants can be closely correlated with their phase equilibria with water.

In order to prevent protein adsorption the surface should be neither charged nor hydrophobic; it is shown that, accordingly, protein adsorption is extremely low on polyethylene oxide-covered surfaces.

### INTRODUCTION

The preparation, properties and interactions of neutral hydrophilic surfaces are of considerable scientific and practical interest. Well established applications involve, for instance, the use of monoglycerides and neutral lipids as stabilizers in food emulsions, stabilization of dispersions by means of oligoethyleneoxide-based surfactants and hydrophilization of hydrophobic surfaces. Recently the potential utilization of hydrophilic, nonionic surfaces in applications where »compatibility« with biological fluids or tissues is required has been emphasized. In this context, surfaces covered by poly- or oligoethyleneoxide have been rather extensively studied, due to the low tendency of almost any particle or dissolved molecule (e.g., soil, proteins, cells<sup>1</sup> to adsorb on such surfaces from aqueous solution. More generally, it is recognized that

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the preparation of »biocompatible« surfaces should be based on a better understanding of the interactions between surfaces that mimic those of cells or cell membranes that is presently available.

With this background, we have for some years been investigating the adsorption and the interactions of adsorbed layers of nonionic surfactants and low molecular weight polymers. The methods involved include determinations of adsorption isotherms by »classical« methods, ellipsometry, ESCA and direct measurements of forces between surfaces. In this paper we summarize some of the information obtained from this work. We discuss the forces that are involved in the adsorption process and the interaction between the nonionic hydrophilic surfaces formed by the adsorption, with emphasis on the interactions between nonionic surfactant layers adsorbed onto bare mica or hydrophobic substrate surfaces. Finally, the hydrophilic properties of surfaces prepared by adsorption of polyethylene oxide are illustrated by some studies of protein adsorption.

#### EXPERIMENTAL

For details on the experimental procedures, the reader is referred to the original papers cited below.

##### *Adsorption Isotherms*

Adsorption isotherms of the nonionic surfactants on latex were determined by the »serum replacement« method as described in ref.<sup>2,3</sup> Concentrations were analyzed by UV spectrometry. Protein adsorption was measured with a Rudolph research null ellipsometer (Autg El III). This instrument uses a 632.8 nm He-Ne laser light source and the angle of incidence of the light beam to the surface is 70°. The relative phase change ( $\Delta$ ) and amplitude change ( $\tan \Psi$ ) were measured with an accuracy of  $\pm 0.05$  and  $\pm 0.01^0$ , respectively. The refractive index,  $n_i$  and the thickness,  $d_i$  of the substrate polymer films was obtained by use of Drude's equations.<sup>4</sup> From these quantities the adsorbed amount was calculated using the formula given by Cuypers et al.<sup>5</sup> The amount of proteins adsorbed on the polymer-coated surfaces was calculated from the refractive index,  $n_p$ , and the thickness  $d_p$  of the protein layer using the equations developed by de Feijter et. al.<sup>6</sup>

##### *Preparation of Surfaces*

Hydrophobed mica surfaces were prepared by depositing dimethyldioctadecyl-ammonium (DDOA) ions by the Langmuir-Blodgett technique.<sup>7,8</sup> In several of the surface forces measurements, the surfaces were prepared by direct adsorption from solution, as indicated in the description of the results.

PVC, carboxylated PVC (Aldrich) and PMA (Fluka) surfaces for the ellipsometric studies were prepared by spin-coating onto silica wafers with a 2 nm thick SiO<sub>2</sub> overlayer.

The modification of surfaces by stable *polyethylene oxide layers* presents particular problems due to the low tendency of PEO to adsorb directly from aqueous solution. Several methods have been developed.<sup>9-12</sup> They involve surface oxidation or surface activation by hydrogen abstraction followed by derivatization reactions. On markedly nonpolar surfaces, such as polyvinylidene fluoride, hydroxyl groups can be introduced by treatment in glow discharge-activated water plasma, followed by attachment of trichlorotriazine. In a final reaction step, PEO is covalently attached to the triazine layer.<sup>9</sup> Another possibility is photocuring of acrylated PEO also containing a cross-linking agent such as hexanediol diacrylate.<sup>10</sup>

However, the surfaces reported on here were prepared using another method. First, a branched and modified polyethylene imine (Polymin SN, BASF) was adsorbed from an 1% aqueous solution (pH 9) onto carboxylated PVC (adsorption

time 60 min). After rinsing, an aqueous solution containing 1% aldehyde-terminal PEO (Aldrich,  $M_w = 1900$  g/mol in 0.15 M  $K_2SO_4$  at pH 6 was allowed to react with the surface at 60 °C. The reaction between aldehyde and imine results in the formation of a Schiff's base which is then converted to a secondary amine by adding  $NaCNBH_3$ .<sup>11,12</sup>

### ESCA (XPS) Analysis

Chemical analysis of surfactant or polymer coated surfaces were carried out with a Leybold-Heraeus LH 200 X-ray photoelectron spectrometer equipped with an Al ( $K\alpha$ ) X-ray source and a hemispherical analyzer. Multiple scans were used to improve the signal-to-noise ratio when studying weak signals. Peak areas were calculated by numerical integration. The adsorbed amount was quantified from the peak intensities using the known number of exchangeable potassium ions on a newly cleaved mica surface as an internal standard.<sup>13</sup>

### Surface Force Measurements

The forces acting between two surfaces were measured as a function of surface separation using a surface force apparatus of the type developed by Israelachvili.<sup>14</sup> The substrate surfaces in this apparatus are two mica sheets (silvered on the backside) that are glued onto optically polished, half-cylindrical silica disks. By mounting the surfaces (in many cases after appropriate chemical modification) so that their axes cross, an experimentally suitable geometry is obtained. The force between the crossed cylinder,  $F_c(D)$ , is related to the energy of interaction per unit area between two flat surfaces,  $G_f(D)$ , according to<sup>15</sup>

$$F_c(D) / R = 2\pi G_f(D) \quad (1)$$

where  $R$  is the local mean radius of curvature and the surface separation  $D \ll R$ .  $D$  is determined to  $\pm 0.2$  nm using multiple-beam interferometry. The surface separation is changed by varying the potential across a piezoelectric crystal connected to one of the surface. The other surface is supported by a weak double leaf spring. Interferometric measurement of the spring deflection enables the force to be determined with a detection limit of 0.1  $\mu$ N.

TABLE I

Molecular area at plateau level (A), free energies of adsorption ( $\Delta\mu^0$ ) and free energies of micellization ( $\Delta\mu_{mic}^0$ ) for nonylphenol polyethyleneoxide surfactants (NP—EO<sub>n</sub>) on different latexes.

Surfactant	A nm <sup>2</sup> /molecule				$\Delta\mu^0$ kJ/mol			$\Delta\mu_{mic}^0$ kJ/mol
	PMMA	PS	PVC	Air	PMMA	PS	PVC	
NP—EO <sub>10</sub>	0.58	0.54	0.60	0.57	—38.6	—38.2	—39.4	—33.8
NP—EO <sub>20</sub>	1.31	1.06	1.19	0.81	—37.3	—37.0	—37.5	—31.9
NP—EO <sub>50</sub>	2.70	2.00	2.44	1.28	—34.3	—34.7	—35.3	—30.0

## RESULTS AND DISCUSSION

### Adsorption of Surfactants on Hydrophobic Surfaces

Figure 1 shows adsorption isotherms for homologous nonionic surfactants on polystyrene and polymethylmetacrylate latexes<sup>2,16</sup>. The molecular areas at the plateau levels and the free energies of adsorption of the surfactants on different surfaces are compared in Table 1. We note the following features:

1) The areas per molecule are except for the shortest EO chain, much larger than at the air/liquid interface. They increase strongly with increasing length of the EO chain.

2) The molecular areas are consistently larger on the more polar latexes, but the differences in the free energies of adsorption are hardly significant.

The immediate conclusion is that on these relatively hydrophobic surfaces, nonspecific factors such as the solution properties of the surfactant must be a much more important driving force for adsorption than specific interactions between the latex surface and the surfactant. An obvious model is that the surfactants adsorb with a strong preference for an orientation with the hydrocarbon moiety towards the surface and the polar part, which generally prefers to be surrounded by a medium with high dielectric constant, turned towards the aqueous phase. Starting from this notion a simple model for the adsorption equilibrium has been developed<sup>16,17</sup>. It is assumed that the surfactant is made up of  $r$  segments, (hydrocarbon or EO), each with the size of a water mole-

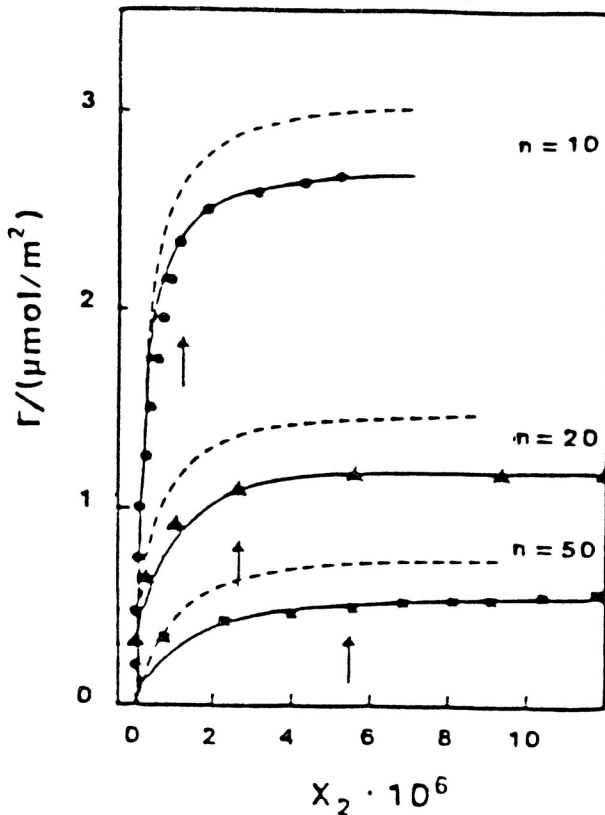


Figure 1. Adsorption isotherms for nonylphenol polyethyleneoxide surfactants (NP—EO<sub>n</sub>,  $n = 10, 20, 50$ ) on PMMA and PS latex<sup>16</sup>. The arrows indicate the critical micelle concentrations. The dashed lines are the isotherms for PS<sup>2</sup>. The drawn lines are calculated from eq. (2). Reproduced with permission from *J. Colloid Interface Sci.*

TABLE II

Contributions to free energies of adsorption of nonionic surfactants on a polystyrene latex, assuming  $q = 4$  (from ref. (16))

Surfactant	Contact adsorption $\frac{qa_0}{kT}(\gamma_1 - \gamma_2)$	Interaction difference $\tau(\chi - \chi_s)$
NP—EO <sub>10</sub>	1.6	5 ± 2
NP—EO <sub>20</sub>	1.6	7
NP—EO <sub>30</sub>	1.6	6

cule.  $q$  of the hydrocarbon segments are in direct contact with the surface. The Flory-Huggins expression is used to calculate the chemical potentials in the aqueous and surface phases. The following expression for the adsorption isotherm is obtained:

$$\ln \frac{(1 - \bar{\Phi}_s)^v}{\bar{\Phi}_s} = \ln \bar{\Phi} + \frac{qa_0}{kT}(\gamma_1 - \gamma_2) + \tau\chi - \tau\chi_s(1 - 2\bar{\Phi}_s) \quad (2)$$

where  $\bar{\Phi}$  and  $\bar{\Phi}_s$  are the volume fractions of surfactant in the solution and the surface phases and  $\chi$  and  $\chi_s$  are the average surfactant-water interactions parameters in these phases.  $\gamma$  and  $\gamma_2$  are the water/surface and hydrocarbon/surface interfacial tensions. Thus, the quantity  $(a_0/kT)(\gamma_1 - \gamma_2) = \Delta E$  depends on the surface polarity and represents the free-energy gain per segment when a surface/water contact is replaced by a surface/hydrocarbon contact. The two last terms in eq (2) represent the change in the average surfactant/water interaction energy when the surfactant is transferred from solution into the surface phase. Table II compares the different contributions to the total free energy of adsorption on polystyrene latex. On PS,  $\Delta E \approx 0.4$ , on PMMA,  $\Delta E \approx 0$ .

Thus, unless the hydrocarbon chain is oriented so that a large number of segments are in direct contact with the surface, the change in surfactant/water interactions is the main driving force for adsorption, i.e. the same type of force that drives the surfactant self-assembly into micelles (and other aggregates) also is the main driving force for adsorption on hydrophobic surfaces. This view is strengthened by the direct correlation between the free energies of adsorption and the free energies of micellization for the surfactants, calculated from

$$\Delta\mu_{\text{mic}}^0 = RT \ln x_{\text{cmc}} \quad (3)$$

where  $x_{\text{cmc}}$  is the critical micelle concentration. Values of  $\Delta\mu_{\text{mic}}^0$  are given in Table I. We also note that the curves in Figure 1. were calculated from eq (2) with  $q = 4$ , which is much less than the total length of the chain. It can be concluded that hydrophobic surfaces may relatively easily be rendered hydrophilic by adsorption of relatively short-chain nonionic surfactants that will form stable monolayers containing relatively large amounts of

water at concentrations below the c.m.c. This conclusion is varified by surface force measurements (see below). Specific interactions (due to the occurrence of groups) with the surface play a relatively minor role.

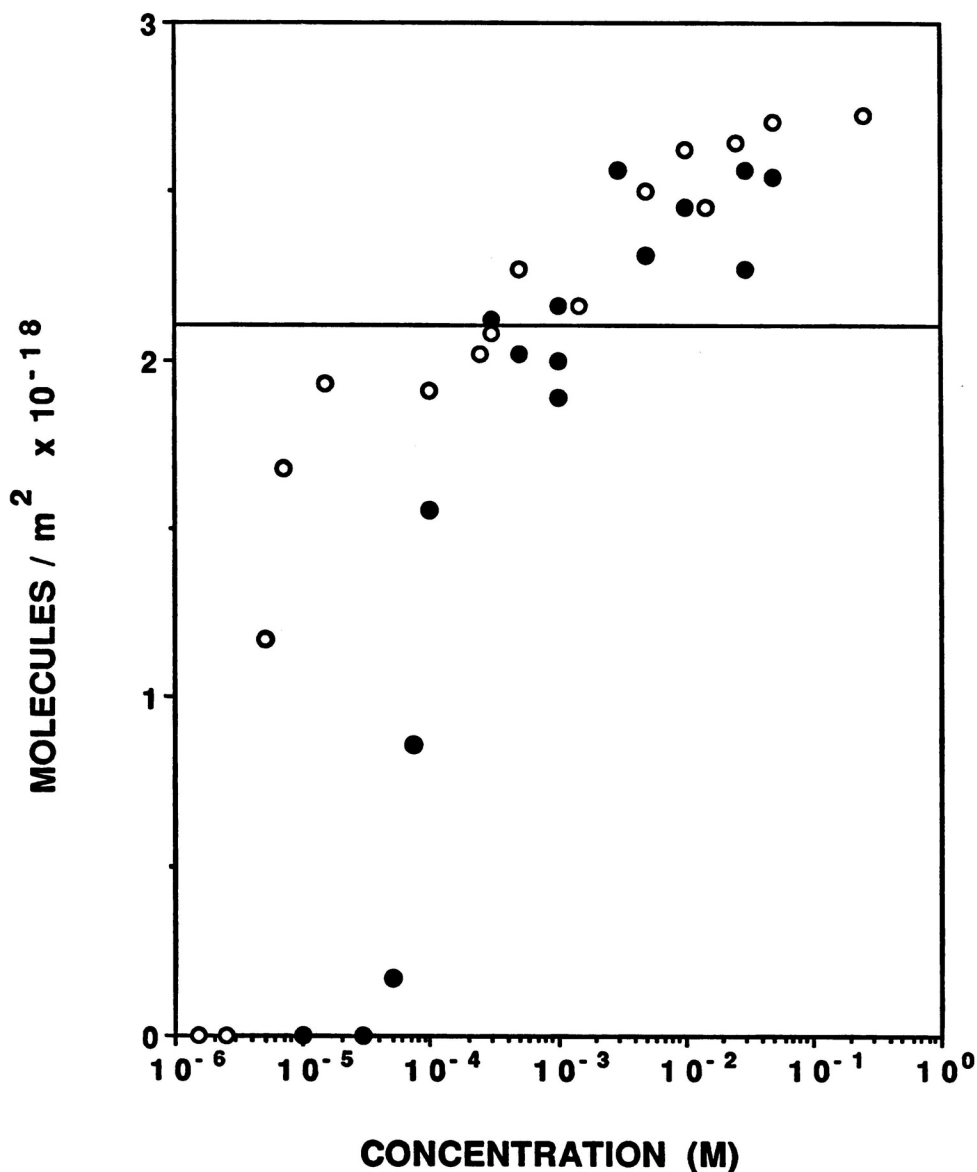


Figure 2. Adsorption of dodecylammonium ions (open circles) and octylammonium ions (filled circles) on the muscovite mica basal plane as a function of the bulk surfactant concentration. The horizontal solid line corresponds to the number density of negative charges on mica ( $2.1 \cdot 10^{-18} \text{ m}^{-2}$ ).

*Adsorption of Surfactants on Hydrophilic Surfaces*

The adsorption behaviour of surfactants on hydrophilic surfaces is considerably more complex. The adsorption strength and the preferential orientation of the molecules in the adsorbed layer depends on the surface composition as well as on the type of surfactant.

If the surfactant end group and the surface are oppositely charged, electrostatically driven adsorption will take place at extremely low concentrations at low ionic strength. As an illustration of this effect the adsorption of alkylammonium ions onto negatively charged mica, as determined by ESCA analysis of the adsorbed amount, is shown in Figure 2.

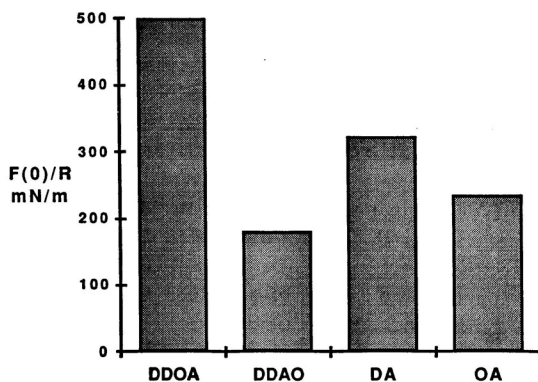


Figure 3. Adhesion between mica surfaces with adsorbed monolayers of surfactants. The figure shows the force (normalized by the radius of the hemicylindrical mica surfaces) required to separate the surfaces from contact in aqueous solution of the surfactants. The surfaces with dimethyldodecylammonium ions (DDOA) were prepared by Langmuir-Blodgett deposition. The other surfaces (dimethyldodecylamine oxide, DDAO, dodecylamine, DA, octylamine, OA) were prepared by equilibration with aqueous solution. The force varies with surfactant concentration and the values given in the figure are taken at the surfactant concentrations giving the maximum force.

It is notable that a strongly cooperative adsorption occurs at a well-defined concentration which is much lower for the dodecylammonium ions than for the octylammonium ions. The isotherms begin to flatten out at a level which is somewhat higher than the molecular density corresponding to the number of negative sites on the mica.

The strong interaction between the polar end group of the surfactant and the surface implies that the surfactants may be adsorbed although a considerable part of the hydrocarbon moieties remain exposed to the aqueous solution. However, the creation of a hydrocarbon/water interface is expected to be energetically highly unfavourable and we have found that cooperative adsorption of the type indicated in Figure 2 hardly ever leads to the creation of a surface that could be characterized as fully hydrophobic. This is illustrated in Figure 3. The figure shows the maximum force (normalized by the radius of the cylindrical surfaces) required to separate two mica surfaces covered by surfactant layers from contact in aqueous solution. The force between two insoluble monolayers immersed in pure water (deposited on mica

by the Langmuir-Blodgett technique) is 500 mN/m, while the forces between layers adsorbed from solution are only 40—60% of this value. A stronger affinity between the polar group and the surface and a longer hydrocarbon chain appears to lead to higher adhesion, but nevertheless it is clear that the layers are far from pure hydrocarbon surfaces.

The comparatively low interfacial tension for surfaces coated by a surfactant »monolayer« can be explained in two ways. On the one hand, a tightly packed monolayer with some molecules intercalated in the layer with the polar headgroup towards the solution may be formed. On the other hand, a loosely packed second layer may form on top of a monolayer in which all end groups are oriented towards the surface. Experimentally it is difficult to distinguish these two situations from each other. Most likely, the real situation lies somewhere between these two extremes, with both some chain interpenetration and some freedom of translation of those molecules that turn their polar groups outwards. Once a more or less hydrophobic monolayer has formed, a second outer layer readily adsorbs due to the same type of driving forces that characterize typical hydrophobic surfaces. This renders the surfaces completely hydrophilic.

The adsorption of cationic surfactants on negatively charged surfaces has been rather extensively studied. Detailed studies of the adsorption of nonionic surfactants on hydrophilic surfaces are less numerous. In most cases, the adsorption strength is expected to be low unless specific interactions between the surface and the polar end group occur.

The adsorption of pentaethyleneoxide dodecyl ether,  $C_{12}EO_5$  onto mica has been investigated by Rutland and Cristenson<sup>18</sup>. They found that no well-defined layers were formed and that an immeasurably small force was needed in order to squeeze out the surfactants from between the surfaces. The presence of the surfactant was deduced from a decrease in the surface charge density and, at high concentrations ( $300 \times \text{cmc}$ ), an increased viscosity.

Specific interactions with the surface, on the other hand, can lead to the formation of layer structures much in the same way as for the electrostatically bound surfactants. Thus, weak adsorption of dimethyldodecylphosphine oxide (DDPO) on mica was observed by Herder<sup>19</sup>. It was also clearly demonstrated that well defined double layer structures form on each surface at high (0.01 M) DDPO concentrations. As another example, Table III shows the free energies of adsorption of the NP- $EO_n$  type of surfactants on kaolinite and polystyrene, calculated from the same model as used in Table I. These surfactants attach primarily to the silanol groups on the kaolinite, which occur only on one of the basal planes of the kaolinite structure. This explains the high areas per molecule observed. It is noteworthy that the free energies of adsorption on P'S and kaolinite are very similar. The reason obviously is that a thin layer of surfactant bound to the silanol groups renders the surface sufficiently hydrophobic so that a second layer can be formed with hydrophobic interaction between the hydrocarbon chains as the main driving force.

We conclude that relatively strongly bound hydrophilic layers of surfactants may be formed on hydrophilic surfaces provided there is some specific interaction that may initially bind the polar end groups to the surfaces so that conditions for the formation of a second layer with hydrophobic interaction as the main driving force are created.



TABLE III

Molecular areas and free energies of adsorption for nonylphenol polyethyleneoxide surfactants (NP—EO<sub>n</sub>) on polystyrene (PS) and kaolinite<sup>20</sup>.

Surfactant	A nm <sup>2</sup> /molecule	$\Delta\mu^\circ$ kJ/mol	
		PS	kaolinite
NP—EO <sub>10</sub>	1.0	—38.6	—38.4
NP—EO <sub>20</sub>	2.5	—37.3	—35.9
NP—EO <sub>50</sub>	13.4	—34.3	—40.4

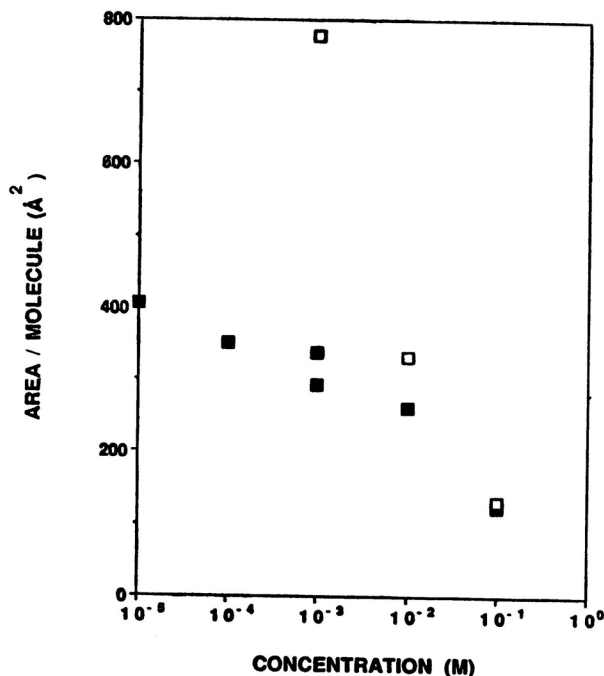


Figure 4. The adsorbed amount (given as area/molecule) of polyethylene oxide (open squares) and polyethyleneoxide with a terminal lysine group on the basal plane of muscovite mica. The molecular weight of the PEO in both cases is 1900 g/mol.

#### Adsorption of Nonionic Polymers

Most hydrophilic nonionic polymers, like all polymers, adsorb on most surfaces. The reason is that although the free energy of adsorption per segment may be small and the entropy of adsorption may be unfavourable the affinity to the surface is amplified by the large number of segments that may be in contact with the surface. However, when a high segment density of an adsorbed nonionic polymer is required it is preferable to modify the polymer by introducing an anchoring group. For instance, the attachment of a positi-

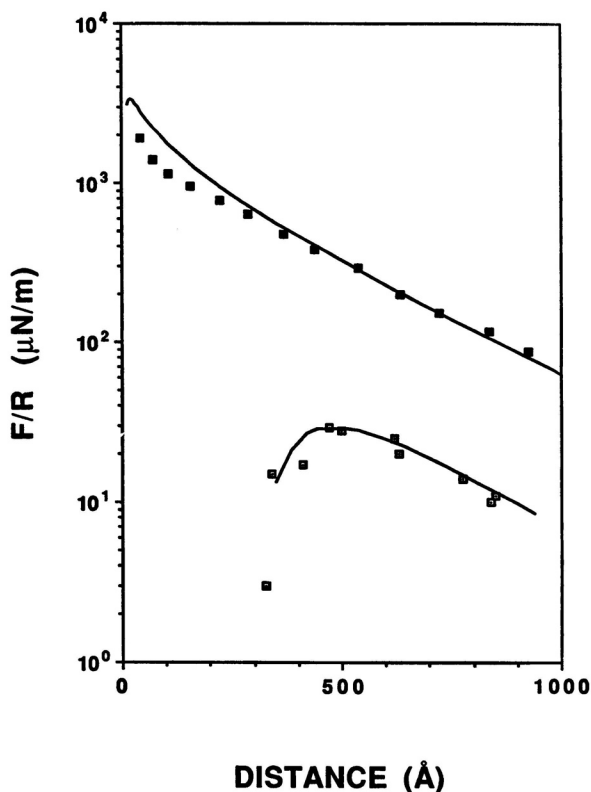


Figure 5. Force normalized by the radius as a function of surface separation in a 0.1 mM KBr solution. Filled squares: forces measured between mica coated with a 1:12 mixture of docosane dioic acid and eicosylamine (the surface contains a 1:1 mixture of  $-\text{COOH}$  and  $-\text{CH}_3$  groups). Corresponding solid line: Expected DLVO interaction for surfaces with constant charge density (area/charge  $31 \text{ nm}^2$ , Debye length  $27.5 \text{ nm}$ ). Open squares: Forces between mica coated with a monolayer of dimethyldioctadecyl ammonium ions (the surface contains  $-\text{CH}_3$  and  $-\text{CH}_2-$  groups). Corresponding solid line: calculated interaction assuming constant surface charge (area/charge  $195 \text{ nm}^2$ , Debye length  $31.0 \text{ nm}$ ) and the presence of a long-range attraction given by the empirical equation  $F/R = 2000 (\mu\text{Nm}^{-1}) \exp(-D/10.5 \text{ nm})$  in addition to the van der Waals interaction. A non-retarded Hamaker constant equal to  $2.2 \cdot 10^{-20} \text{ J}$  was used in all calculations. The surfaces were prepared by the Langmuir-Blodgett technique. Note the logarithmic force scale.

vely charged terminal group strongly enhances the adsorption of polyethylene oxide chains on negatively charged surfaces, such as mica<sup>21</sup> (Figure 4). Adsorption of polyethylene oxide to hydrophobic surfaces can be strongly enhanced by the copolymerization of polypropylene blocks or addition of terminal hydrocarbon chains, the latter method being much more effective<sup>22</sup>. The adsorption behaviour of another type of highly water-soluble nonionic polymer, ethyl(hydroxyethyl) cellulose (EHEC) has been extensively studied by Malmsten and Lindman<sup>23</sup>. They found that adsorption was much stronger to hydrophobic than to hydrophilic surface. The adsorbed amount increases

as the temperature increases towards the lower critical solution temperature. Evidently, hydrophobic interaction between the polymer and the surface is the driving force for adsorption.

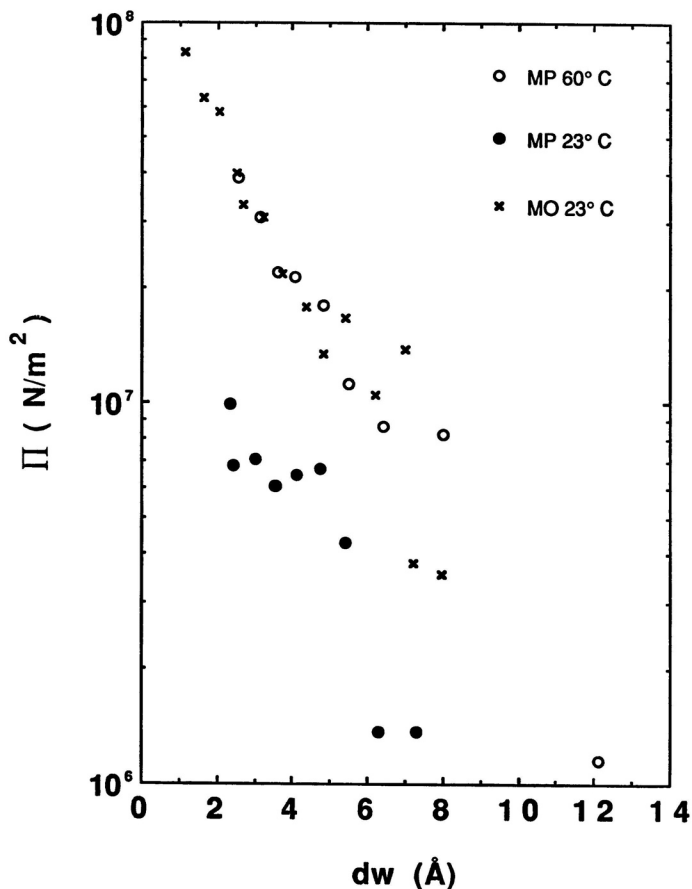


Figure 6. Repulsive osmotic pressure in the lamellar (open circles) and gel (closed circles) phases of monopalmitin (MP) and in the lamellar phase (crosses) of monoolein (MO) as a function of bilayer separation. Note the logarithmic pressure scale. The force was measured according to the method developed by Parsegian et al.<sup>31</sup>.

### Adsorption of Proteins

The »surface« exposed by proteins is very heterogeneous and consists of positive and negative sites, hydrophobic groups and polar groups that may participate in acid-base interactions or hydrogen bonds. Hence it is not surprising that all proteins, except small compact ones adsorb on almost any surface. The basic idea when creating surfaces which prevent protein adsorption from aqueous solution is to reduce all possible attractive interactions between the surface and the protein (or to create a surface that under all circumstances binds to

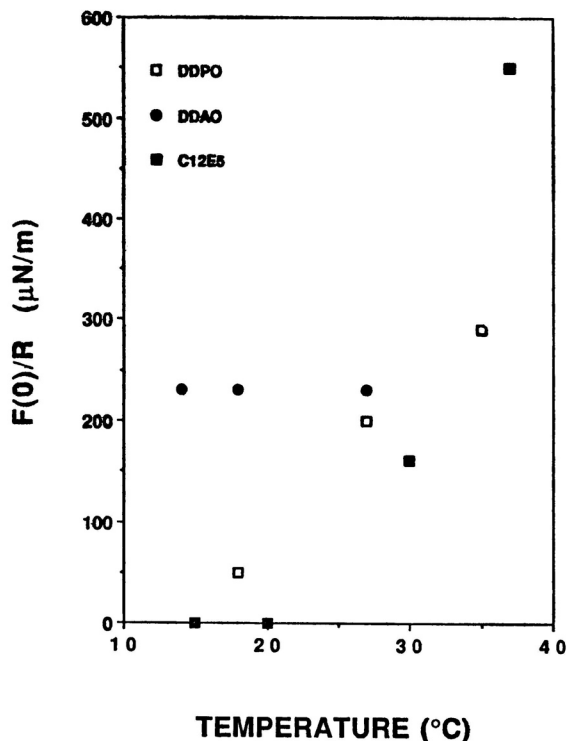


Figure 7. Temperature dependence of the adhesion between mica surfaces covered by surfactant layers. The mica was first hydrophobed by Langmuir-Blodgett deposition of a layer of dimethyldioctadecyl ammonium ions and then equilibrated with appropriate surfactant solutions. The points represent the minima observed in the force versus distance curves at constant surfactant concentration. Open squares: dodecyldimethyl phosphine oxide (DDPO); filled circles: dodecyldimethylamine oxide (DDAO); open squares: penta(oxyethylene)dodecyl ether ( $C_{12}EO_5$ ).

water more strongly than to the protein). Therefore, in order to prevent adsorption, positive and negative surface charges should be removed without the formation of hydrophobic domains. Furthermore, it is beneficial to reduce the van der Waals' attraction between the surface and the protein as much as possible. This is achieved if the surface layer contains a large amount of water. A third important aspect is the flexibility of the substrate polymer. In some cases, protein adsorption is reduced because it would impose additional constraints on the polymer segment mobility, i. e. a reduction in the configurational entropy.

From these considerations it is clear that surfaces coated with nonionic, strongly hydrophilic polymers (e.g. PEO or EHEC) have the potential to prohibit protein adsorption (and denaturation). The most efficient polymer layer in this respect should not be so tightly packed that the water content and the polymer chain flexibility are substantially reduced.

*Interactions Between Layers of Nonionic Surfactants*

An important question is: how thick a layer is needed to obtain a low protein adsorption. It is clear that a water-rich layer of at least 5 nm is needed to reduce the van der Waals' attraction and create a flexible surface layer. However, as has been shown by the surface forces technique<sup>14</sup>, much thinner layers are sufficient for reducing hydrophobic interactions. It turns out that the long-range interaction that has been observed between hydrocarbon surfaces<sup>24</sup> is removed already at partial coverage by polar groups<sup>25</sup> (Figure 5). However, a more or less full coverage is required to completely remove the strong attraction observed between hydrophobic surfaces in contact. When the hydrophobic surface is completely covered by a nonionic surfactant a repulsive hydration force predominates at small separations. This has been observed for all surfactants studied.

For example, the hydration force between dimethyldodecylamine oxide (DDAO) layers oriented with the polar end groups towards the solution extends about 2 nm from the surfactant/water interface<sup>26</sup>. A weak attractive minimum is observed at larger separations. Neither the hydration force nor the depth of the attractive minimum show any clear temperature dependence.

The temperature dependence of the short-range forces between adsorbed layers of  $C_{12}EO_5$  is different<sup>27</sup>. In this case the range of the repulsive hydration force decreases with increasing temperature. As with the DDAO layers, a weak attractive minimum occurs at larger distances; this minimum deepens with

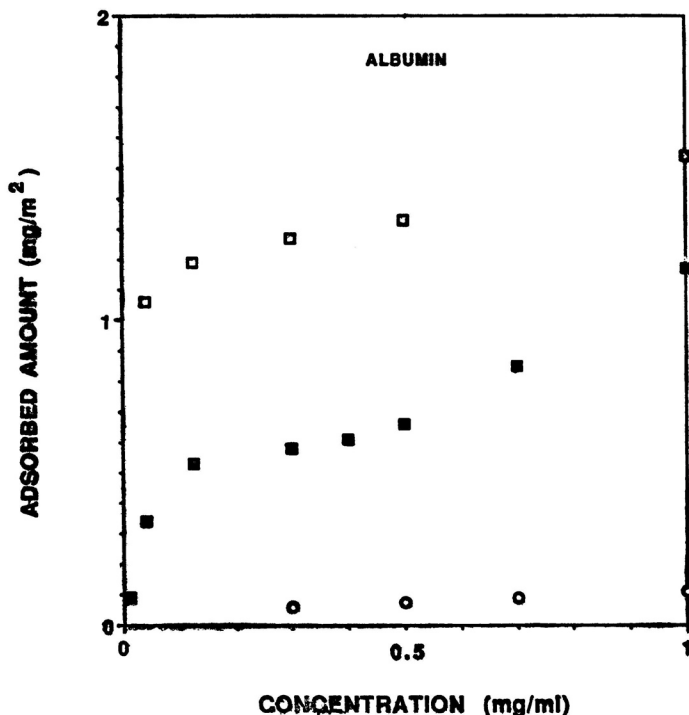


Figure 8.

*Fig. 8 to be continued*

Fig. 8 continued

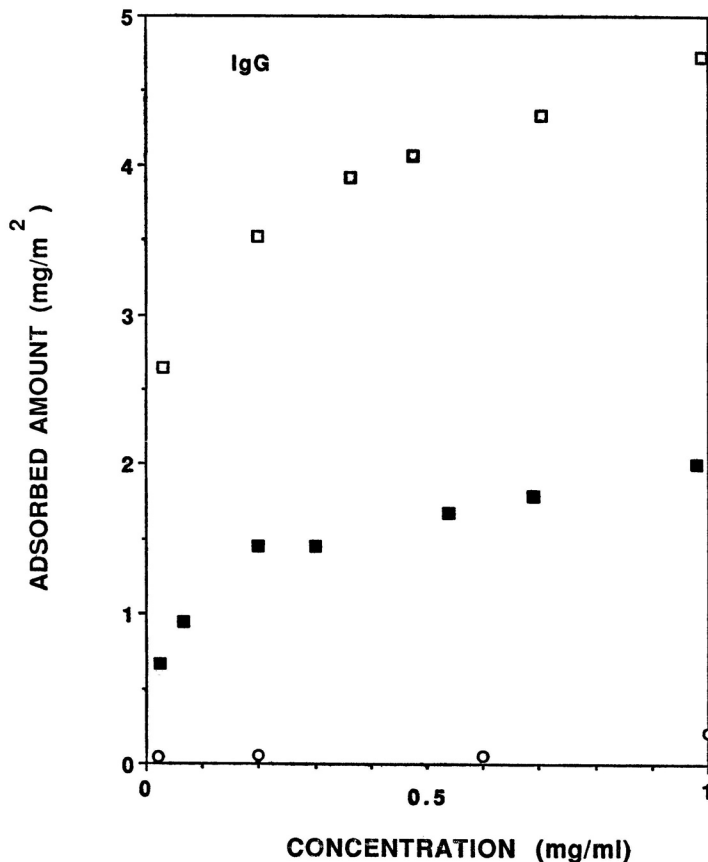


Figure 8. Adsorption of bovine serum albumin (fig a) and IgG (fig b) on different polymer surfaces, as determined by ellipsometry. The surfaces are: PVC (open squares), a metacrylic acid/metacrylate copolymer (filled squares) and polyethylene oxide (open circles). The surfaces were prepared by spin coating or grafting (see text).

increasing temperature. A qualitatively similar behaviour has been observed for dimethyldodecyl phosphine oxide<sup>19</sup>. Kjellander<sup>8</sup> has explained this behaviour in terms of the hydration of the polar group. For ethylene oxide, Karlström<sup>29</sup> has put forward an alternative molecular interpretation based on temperature-induced conformational changes.

The temperature dependence of the hydration forces between monoglyceride layers is quite different. The range of the repulsion increases and the depth of the attractive minimum decreases as the temperature increases<sup>30</sup>. We have suggested that this is caused by a transformation of intralayer hydrogen bonds to hydrogen bonds between the surfactant and water, resulting in an increased thermal motion of the adsorbed layer. This idea is supported by the fact that the hydration repulsion is stronger, and the attraction

weaker between monoolein layers in the fluid state than between monopalmitin layers in the frozen state (Figure 6).

The differences in the temperature dependence of the short-range forces are fully consistent with the phase behaviour of the corresponding surfactant/water mixtures. In particular, the temperature dependence of the adhesive minimum for  $C_{12}EO_5$  correlates with the occurrence of a lower critical solution temperature for the water/surfactant solution. The temperature dependence of the adhesion force for the different nonionic surfaces is illustrated in Figure 7.

#### *Adsorption of Proteins on PEO-Covered Surfaces*

We have shown that a number of different types of completely hydrophilic, neutral surfaces can be prepared by adsorption of surfactant or polymers on either hydrophobic or hydrophilic surface. In almost all cases, hydrophobic interaction is a major driving force for the formation of stable layers. The adsorption and interactions of proteins on these different layers is an exciting field of research where much remains to be done. To illustrate some effects, we compare in Figure 8 the adsorption of bovine serum albumin and IgG on PVC (hydrophobic), PMA (negative) and PEO (neutral hydrophilic) surfaces. Adsorption is an order of magnitude lower on PEO than on the other surfaces. This illustrates that if both hydrophobic and electrostatic interactions are removed, protein adsorption can be substantially reduced and, indeed, surface modification with PEO may be a possible way of prohibiting protein adsorption.

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## SAŽETAK

### Neionske hidrofilne površine: adsorpcija i interakcije

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U radu su prikazana novija istraživanja u formiranju neionskih hidrofilnih površina i interakcija biogenih molekula (proteina) s takvim površinama. Neionske hidrofilne površine pokazuju minimalni adsorpcijski afinitet za biogene molekule, posebno proteine, što je izuzetno važno za sprečavanje denaturacije proteina.

Formiranje površinskog neionskog hidrofilnog sloja može se postići adsorpcijom površinskih aktivnih molekula ili iona (na pr. dodecylamonium ion) odnosno polimera (na pr. polietilenoksid) bilo na hidrofobnu površinu (na pr. polivinilklorid ili polistiren) ili na hidrofilnu površinu (na pr. tinjac).

Smatra se da je za proces adsorpcije površinsko-aktivne tvari na hidrofobnoj površini bitna međusobna interakcija hidrofobnih segmenata dok je kod adsorpcije površinskoaktivne tvari na hidrofilnoj površini bitna specifična interakcija funkcionalnih skupina s površinom pri čemu se formira čvrsti primarni sloj. Adsorpcija sekundarnog sloja površinsko-aktivne tvari zbog jake hidrofobne interakcije s primarnim slojem dovodi do potpuno hidrofilne površine.

Direktnim načinom (metodom Israelachvili) mjerena je sila između dvije predhodno modificirane površine u ovisnosti o njihovoj međusobnoj udaljenosti s granicom detekcije od 0,1  $\mu\text{N}$ . Podaci pokazuju da su sile dugog dometa jako reducirane kod površina potpuno prekrivenih neionskom površinsko-aktivnom tvari dok kod malih udaljenosti i između površina dominiraju odbojne sile hidratacije. Temperaturna ovisnost sila kratkog dometa u uskoj je vezi s faznom ravnotežom između površinsko-aktivne tvari i vode.

Rezultati adsorpcije proteina (albumin govedeg seruma i imunoglobulin G) pokazuju da je na neionskoj hidrofilnoj površini (polietilenoksid) količina adsorbiranog proteina približno deseterostruko manja nego u slučaju hidrofobne površine (polivinilklorid) ili negativno nabijene površine (metakrilna kiselina/metakrilat).