Attractive Forces Between Uncharged Hydrophobic Surfaces: Direct Measurements in Aqueous Solution

Abstract. *Long, double-chained alkylammonium acetate surfactants are soluble in water and, under suitable conditions, adsorb onto sheets of muscovite mica, forming an electrically neutral, hydrophobic surface. Attractive forces measured between such surfaces are 10 to 100 times stronger than expected from van der Waals theory over distances* D *up to about 10 nanometers. The forces decay exponentially [with a force proportional to* $\exp(-D/1.4)$*] instead of following the power-law behavior of continuum theory. The results of these and earlier experiments indicate that the strength of these attractive forces depends critically on the degree of hydrophobicity of the surface and is due to the long-range influence of the surface on the structure of water. In addition, for very hydrophobic surfaces, the cavitation effects on pulling the surfaces apart are described.*

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Although hydrophobic processes are thought to play a key role in biological self-assembly (*1*), much of what is known about water at hydrophobic interfaces has been deduced from the solubility of rare gases and small hydrocarbon molecules (*2*), from micellization (*3*), and from theoretical studies (*4*). It has been generally held that the range of any hydrophobic driving force for aggregation of small molecules is of the order of the correlation length for hydrogen bond ordering in bulk water—that is one or at most a few water molecules (*2*). Apart from its central importance in biology, the hydrophobic force is crucial to a wide range of phenomena, such as mineral flotation, wetting, coagulation, and many processes that involve surfactant aggregation, such as detergency.

We now report direct measurements of the forces between electrically neutral, planar hydrophobic surfaces in aqueous solution. Such forces reflect interactions due to surface-induced water structure, and they are long ranged, with an exponential decay length of about 1.4 nm. Over 0 to 8 nm the forces are 10 to 100 times stronger than the van der Waals forces that would operate in the absence of any surface-induced order in water. This situation is in direct contrast with that observed for hydrophilic bilayers, in which the decay length of (repulsive) hydration forces is at most 0.3 nm (*5*). That the hydrophobic interaction on contact is strong is evident from observed free energies of dimerization of surfactants and from the high free energy (approximately 50 mJ/m^2) of the oil-water interface. Our results support inferences from earlier work on partially hydrophobic, charged surfaces (*6*) and indicate that the magnitude of the attractive interaction is a function of the degree of hydrophobicity of the surface.

An earlier study of attractive forces between adsorbed monolayers of cetyltrimethylammonium bromide (CTAB) first suggested that the hydrophobic interaction between planar interfaces was long ranged and decayed exponentially with distance. But in that case the surfaces were charged and not strongly hydrophobic, with a relatively low monolayer-water interfacial energy (γ_{Sl}) of 9 mJ/m^2 and an advancing contact angle (θ) of 65°. In the present study we avoided this situation by working with electrically neutral and considerably more hydrophobic surfaces ($\theta = 95°$) formed by equilibrium adsorption of a monolayer of a double-chained quaternary ammonium salt on mica. The particular salt used, dihexadecyldimethylammonium acetate [DHDAA, $(C_{16}H_{33})_2(CH_3)_2N^+CH_3COO^-$], belongs to a class of recently investigated double-chained surfactants that spontaneously form vesicles (*7*) as opposed to the insoluble liquid crystals formed by their halide counterparts.

A surfactant monolayer was adsorbed onto the basal planes of thin sheets of muscovite mica immersed in a 2.5 × 10^{-5} *M* DHDAA solution. The mica support sheets were glued to silica disks in a crossed-cylinder geometry and set up in an Israelachvili force-measuring apparatus (*8*). Fringes of equal chromatic order produced from white light passing through the sheets were used to measure surface separations to an accuracy of ±0.2 nm. One of the mica sheets was attached to a variable double-leaf spring with a wide range of spring stiffness (*6*). Under purely attractive forces the mica surfaces jumped together once the slope of the force-distance curve equaled or slightly exceeded the spring constant (*8*). When the separations were plotted as a function of spring stiffness, this slope, and hence the attractive force law, could be determined.

The DHDAA was prepared by eluting dihexadecyldimethylammonium bromide dissolved in methanol on ion-exchange resin (Fisher REXYN 201) in acetate form. The solution was evaporated, and the resulting surfactant was recrystallized twice from cold ether.

Mica surfaces that had been equilibrated with 2.5 × $10^{-5}M$ DHDAA gave an advancing contact angle of 95°, so the surfaces were almost completely hydrophobic. The contact angle measurements showed hysteresis after several hours. Comparison of contact distances between mica surfaces in water before and after surfactant adsorption showed that the monolayers have a thickness of 1.5 ± 0.1 nm, which means the surfactant head group area is about 66 Å^2. No double layer forces were measurable at large distances, so the surfaces appeared to be completely neutralized by adsorption. At lower or higher concentrations, the surfactant formed an incomplete charged monolayer or a charged bilayer, respectively. The surfaces then interacted by means of the long-range, electrostatic double-layer forces that have been well described by theory. The solid-liquid interfacial energy γ_{Sl} was deduced from measurements of the pull-off forces F_A, which gave $\gamma_{\mathrm{Sl}} = 28$ or 36 erg/cm^2, depending on which of two extreme theoretical limits was applicable (*9*). Since it is impossible to achieve higher interfacial energies with solid hydrocarbon–water interfaces, our surfaces were indeed hydrophobic.

The slope of the attractive force (scaled with the mean radius of the supporting cylinders *R*) as a function of the surface-to-surface separation of the monolayers [$d(F_H/R)/dD$] is plotted against *D* in Fig. 1. In the same figure are the earlier results obtained for partially hydrophobic CTAB monolayers and the theoretical predictions of van der Waals theory as calculated from Lifshitz theory. The theoretical curve ignores retardation and is calculated with a Hamaker constant mica and hydrocarbon separated by water. For both monolayers the slopes (and hence *F*/*R*) decay exponentially with distance unlike the decay predicted by van der Waals theory in which the slope varies as $1/D^3$. Since, from the Derjaguin approximation (*8*), the interaction energy *E* per unit area between parallel flat surfaces is given by

$E = F/2\pi R$, the interaction energy as a function of separation can be calculated from the results in Fig. 1. The interaction for the DHDAA monolayer has the form

$$E = -0.056 \exp(-D/1.4)\ \mathrm{J/m^2} \quad (1)$$

in which D is measured in nanometers. By comparison the weaker interaction measured between adsorbed CTAB monolayers is

$$E = -0.018 \exp(-D/1.0)\ \mathrm{J/m^2} \quad (2)$$

In Fig. 2 the interaction energy measured for the DHDAA monolayer is compared with the maximum possible van der Waals energy. The observed attraction is between 10 and 100 times stronger than that expected at separations less than about 10 nm and is apparently due to the hydrophobic interaction between the monolayer surfaces. The forces appear to merge with the continuum theory limit at about 15 nm. These results suggest that there is no universal hydrophobic force and that the strength and range of the force depend on the nature of the surfaces, although exponential decay may be a general feature of the phenomenon. Water structure apparently decays rapidly in the vicinity of small hydrophobic molecules, whereas at a planar hydrophobic interface the induced hydrogen bonding extends farther and gives rise to attractive forces over a large distance.

We also studied the phenomenon of cavitation (*10*). With an almost rigid spring to pull the surfaces from adhesive contact, the surfaces came to an equilibrium separation of about 100 nm with a bridging bubble about 20 nm in width. From the known geometry of the surfaces and the assumed contact angle of 95°, we estimated the Laplace pressure drop across the bubble surface was about 1 bar. This pressure difference suggested that the bubble contained water vapor only, which was supported by the observation that on separating the surfaces to about 1 μm the bridging bubble ruptured with no bubbles remaining on the mica surfaces. If the cavitation region contained air at atmospheric pressure rather than water vapor, air bubbles would have remained attached to the separated mica surfaces.

Cavitation is expected to occur with strongly hydrophobic surfaces when the contact angle with water is greater than 90°, since in that case the solution-surface interface has a higher energy than the vapor-surface interface. Under those circumstances, the nucleation of a vapor bubble and formation of a three-phase contact region is energetically favorable. In comparison, no evidence of nucleation was observed for the CTAB monolayer, where the contact angle was less than 90°. Also, because of the high energy of the DHDAA surface, even in dilute solutions, a second layer of surfactant adsorbed during a period of 8 hours to several days depending on thermal fluctuations.

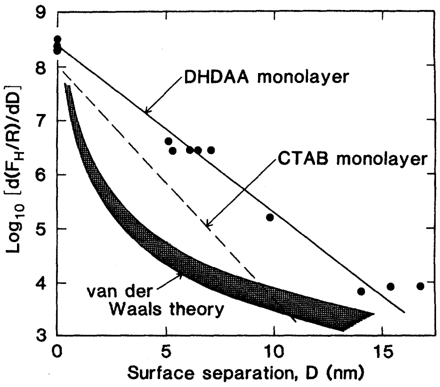

Fig. 1. The slope of the attractive force between DHDAA and CTAB monolayers as a function of surface separation, *D*, plotted against *D*. The slopes decay exponentially with separation. The calculated nonretarded van der Waals forces for hydrocarbon and mica surfaces separated by water ($F/R = -A/6D^2$, where $A = 0.8 \times 10^{-20}$ to 2.2×10^{-20} J) (shaded area) are different from those forces observed.

Why the monolayer-water interfacial energy varies so much depending on surfactant (CTAB or DHDAA) and why it is less than that of an oil-water interface is an unresolved issue. It may be that in each case the monolayer contains a significant fraction of surfactant molecules with head-groups facing away from the mica surface when immersed in surfactant solution. The less pronounced differences between $-CH_3$ and $-CH_2-$ groups at the interface could not account for the differences. In any event we conclude that the hydrophobic interaction between planar surfaces is long ranged and that the strength and range depend on the surface. In different geometries or between small hydrophobic molecules, the range will be smaller, which reflects the enhanced cooperative ordering of water adjoining a large interface. Cavitation is expected for very hydrophobic surfaces with contact angles greater than 90° but not for those with angles less than 90°. These results suggest that the term "hydrophobic" is appropriate for any surface not completely wetted by water.

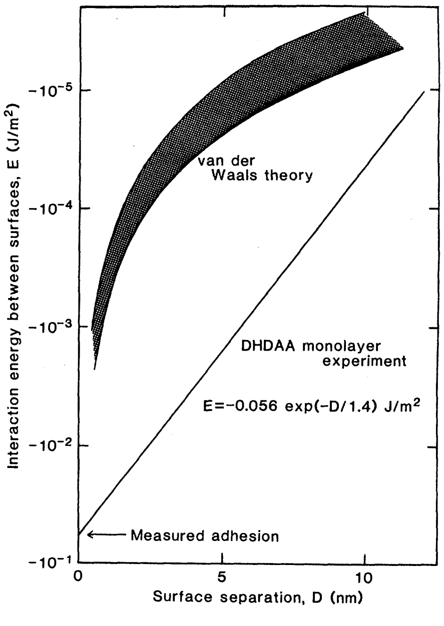

Fig. 2. The interaction energy *(E)* per unit area between flat surfaces plotted as a function of surface separation. This interaction is compared with the calculated van der Waals energies (shaded curve). At separations between 1 and 8 nm the attractive energies are 10 to 100 times greater than those expected. Theoretical and experimental values appear to converge at separations of about 15 nm.

Our results suggest that there is available to biological systems a hierarchy of attractive forces that operate between hydrophobic moieties. These forces depend upon the dimensions and geometry of the surfaces, and they are much stronger, longer ranged, and more variable than classical colloid science previously indicated. The selection by macromolecules of a particular functional configuration from the multitude of states with similar free energies must in part be driven by these forces.

References and Notes

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11. D.F.E. and P.M.M. were supported by NIH grant GM 34341. We thank J. E. Brady for preparation and supply of surfactants.

11 February 1985; accepted 12 June 1985