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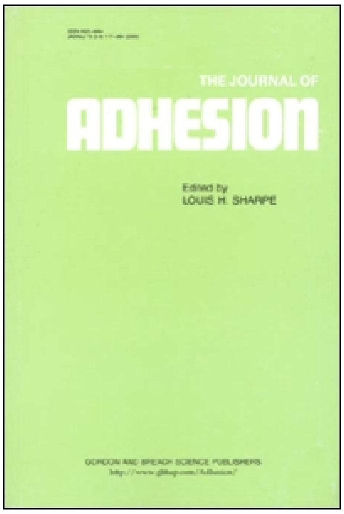

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F. Van Voorst Vader[a]; H. Dekker[a]
[a] Unilever Research, Vlaardingen, The Netherlands

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The Influence of Surfactants on the Adhesion between Solids

F. VAN VOORST VADER and H. DEKKER

Unilever Research, Vlaardingen, The Netherlands

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The force of adhesion between crossed carbon filaments submerged in an aqueous buffer solution has been measured. The decrease of this force, observed on addition of surfactants (cetyltrimethyl ammonium bromide or decylsulphonic acid) to the solution, is in agreement with that predicted by the thermodynamic theory of adhesion (B. V. Deryagin, *Koll. Z.* **69**, 155 (1934)). A relation between the force of adhesion between the filaments and their wetting properties was derived and is supported by the experiments. It is concluded that adhesion in the above systems can be described by thermodynamics.

INTRODUCTION

The effect of solutes on the adhesion between solids submerged in their solution has been the subject of a number of investigations that were primarily intended to explain the role of surfactants in the removal of solid soil from textiles. It was noted by early investigators[1] that plots of soil removal versus surfactant concentration resembled plots of surfactant adsorption versus concentration, but no explanation of this analogy has been given.

In 1934, a thermodynamic theory of adhesion was put forward by Deryagin,[2] who related the force of adhesion of bodies satisfying certain geometrical requirements to the change in free energy involved in removing two plane parallel unit surfaces from their distance at contact to infinity. It will be shown in the present paper that this principle can be developed to a theory relating adhesion between immersed solids to the composition of the medium.

In order to connect such a theory with experiments, the conditions must be found under which removal of solids from each other can be described by a thermodynamic formalism. All adhesional forces between solids rapidly decrease with increasing distance so that removal by a certain force becomes a self-accelerating process. When the velocity of this process becomes so large that the system can no longer adapt itself immediately to the novel situation—for instance as regards adsorption and charge distribution—non-equilibrium states are created that prohibit a thermodynamic treatment.[3] This problem can be avoided by means of the following artifice:

When a system is transferred isothermally from a state I, involving a certain free energy, to a state II having a different free energy, the required work W is least when the transfer is performed reversibly.[4] Thus, when the process consists in bringing two bodies that attract each other with a force $K(h)$ from a distance h_{I} to a distance h_{II}, against this force of attraction,

$$W = -\int_{\mathrm{I\,rev}}^{\mathrm{II}} K dh < -\int_{\mathrm{I\,irr}}^{\mathrm{II}} K dh \tag{1}$$

where the indices "rev" and "irr" indicate a reversible and an irreversible process respectively. Be h_{I} the distance at contact and h_{II} a very large distance, and assume that K decreases sharply with distance, so that $K(h_{\mathrm{II}}) \simeq 0$, then differentiation of Eq. (1) yields

$$K_{\mathrm{I\,rev}} < K_{\mathrm{I\,irr}} \tag{2}$$

It follows that when the contacting bodies are subjected to a force of removal that increases so slowly that any surface parameter assumes continuously the equilibrium value corresponding to the novel situation, the actual force at which removal is observed will approximate the value required for a reversible process. Therefore, the thermodynamic theory of detergency to be developed below will be verified by experiments that satisfy this condition.

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THEORY

Consider a heterogeneous system containing i components of which n_i moles are present at a thermodynamic potential μ_i. Its volume, V, the external pressure, as well as its temperature T are constant. It contains a medium 3 and two bodies 1 and 2 with rectangular cross section of area A, that exert a force on each other over a slit of width h. An external negative force K is applied to the bodies in order to compensate for this interaction. K is taken positive in the sense of decreasing slit width. The surfaces of 1 and 2 bounding the slit are smooth, parallel and perpendicular to K. We further assume that the interaction is only noticeable at narrow slit widths, so that $h_p \ll A^{\frac{1}{2}}$, and that K is proportional to A. Boundary effects at the slit rim are neglected. Changes in the free energy F of the system are given by

$$dF = -K dh + \Sigma \mu_i \, dn_i \tag{3}$$

Thus, the force exerted by the bodies on each other equals

$$K = -(dF/dh)(T, V, A, n_i \text{ constant}) \tag{4}$$

On introducing the parameters $k = K/A$, and $f(h) = F(h)/A(T, V, A, n_i$ constant), the change in free energy per unit area of contact interface, caused by increasing the width of the slit between the bodies from a value h_0 to a large value h_∞, can be written as

$$f(h_\infty) - f(h_0) = -\int_{h_0}^{\infty} k\, dh \tag{5}$$

Two recent papers[5, 6] have developed the thermodynamical relations governing adhesion on the basis of Eqs. (3)–(5).

It is extremely difficult to perform meaningful measurements on the force of adhesion between two macroscopic, plane bodies, because this force decreases very rapidly with their average distance at contact. This distance is determined by the magnitude of local asperities and faults of these surfaces, which are difficult to control. Several solutions to this problem have been described.[7, 8] In the present paper, the crossed filament method proposed by Tomlinson[9] will be used. In this method, the surface area over which interaction occurs between the bodies can be taken so small that interference from irregularities can be avoided.

The theory of Deryagin indicates how the total force of interaction between two circular filaments is related to the change in free energy per unit area, $f(h_\infty) - f(h_0)$, defined in Eq. (5). The physical basis of this relation is discussed in the appendix. In the present case,

$$-K_t = \frac{2\pi r}{\sin \omega}|f(h_\infty) - f(h_0)| \tag{6}$$

where K_t represents the force of removal, r the filament radius and ω their crossing angle.

Eq. (6) will now be applied to predict the influence of the addition of detergent on the force of removal between two crossed carbon filaments that have been brought into contact while submerged in water. For this purpose it should be noted that the geometrical factor contained in the right-hand side of Eq. (6) is only valid for perfectly rigid bodies. In reality, mutual interaction will lead to deformation of the filaments on contact.

For the case of two spheres of radii r_1 and r_2, suffering only elastic deformation, it has been shown[8] that the force of removal equals

$$-K_t = \tfrac{3}{2}\pi\frac{r_1 r_2}{r_1 + r_2}[f(h_\infty) - f(h_0)] \tag{7}$$

while for the case of rigid spheres[2]

$$-K_t = 2\pi\frac{r_1 r_2}{r_1 + r_2}[f(h_\infty) - f(h_0)] \tag{8}$$

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Within the limits of the Hertzian approximation,[10] the contact between the elastic cylinders of radius r that cross perpendicularly, is equivalent to that of two spheres having an equal radius $2r$. It follows that

$$-K_t = \tfrac{3}{2}\pi r[f(h_\infty) - f(h_0)] \tag{9}$$

for the case of elastic fibres crossing at 90°.

The free energy of two surfaces of unit area at infinite distance equals twice the value of their superficial tension, σ_{sl},

$$f(h_\infty) = 2\sigma_{sl} \tag{10}$$

No such estimate as regards the value of $f(h_0)$ can be made. However, the value of h_0 at contact is about 5.10^{-10} m,[11, 12] i.e. small in comparison with the dimensions of surfactant molecules. It may therefore be expected that, after contact is established, surfactant adsorption in the contact area will be sterically impossible so that $f(h_0)$ will be independent of surfactant concentration.

The adsorption of the surfactants on carbon suspension was found to obey the Langmuir equation. Consequently, their influence on σ_{sl} can be described by Szyskowski's equation.[13]

$$\sigma_{sl} = \sigma_{sl}^0 - RT\Gamma^\infty \ln\left(1 + \frac{c}{a}\right) \tag{11}$$

where σ_{sl}^0 is the superficial tension in the absence of surfactant, R is the gas constant, T the absolute temperature, and Γ^∞ and a are parameters characterizing the solute.

On assuming that $f(h_0)$ is independent of surfactant concentration, combination of Eqs. (9), (10) and (11) leads to:

$$K_R^0 - K_R = 3\pi rRT\Gamma^\infty \ln\left(1 + \frac{c}{a}\right) \tag{12}$$

where $K_R = -K_t$, and $K_R^0 =$ the force of removal in the absence of surfactant. The left-hand side of Eq. (12) can be measured directly, while the various parameters on the right-hand side can be determined by independent measurements. Thus, Eq. (12) allows verification of the theory developed above.

Moreover, the force of adhesion can be related to the wetting energy of the carbon filament against the same surfactant solutions in which the adhesion experiments have been performed. The wetting energy K_w of the carbon filament equals

$$K_w = 2\pi r\sigma_{ol}\cos\theta = 2\pi r(\sigma_{os} - \sigma_{ls}) \tag{13}$$

where

o stands for an arbitrary reference fluid

s for the surface of the carbon filament

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l for the surfactant solution

θ for the contact angle across the aqueous phase.

When two solute concentrations [1] and [2] are compared, the difference Δ_{12} in the wetting energies equals

$$\Delta_{12}K_w = 2\pi r(\Delta_{12}\sigma_{os} - \Delta_{12}\sigma_{ls}) \tag{14}$$

Likewise, from Eqs. (9) and (10):

$$\Delta_{12}K_R = 3\pi r\Delta_{12}\sigma_{ls} \tag{15}$$

On differentiation of Eqs. (14) and (15) with respect to ln c and application of Gibbs' adsorption law, we obtain:

$$\frac{dK_R}{dK_w} = \frac{3}{2}\frac{\Gamma_{ls}}{\Gamma_{os} - \Gamma_{ls}} \tag{16}$$

where Γ represents the surfactant adsorption at the relevant interface. The wetting properties of surfactant systems can be characterized by plotting the wetting energy ($\sigma_{ol}\cos\theta$) against the interfacial tension (σ_{ol}).^{14} The slope of such a plot is given by

$$\frac{d(\sigma_{ol}\cos\theta)}{d\sigma_{ol}} = \frac{\Gamma_{os} - \Gamma_{ls}}{\Gamma_{ol}} \tag{17}$$

On combining (16) and (17):

$$\frac{dK_w}{dK_R} = \frac{2}{3}\frac{\Gamma_{ol}}{\Gamma_{ls}}\frac{d(\sigma_{ol}\cos\theta)}{d\sigma_{ol}} \tag{18}$$

Eq. (18) shows that for a given system, plots of wetting energy against force of adhesion should show analogy to plots of wetting energy against interfacial tension. For instance, it appears that in many systems the slope of $\sigma_{ol}\cos\theta$ against σ_{ol} is independent of the surfactant concentration$^{14, 15}$; this suggests that in such cases a linear relationship will exist between the adsorptions at the various interfaces:

$$\alpha\Gamma_{os} = \beta\Gamma_{ls} = \gamma\Gamma_{ol} \tag{19}$$

where the coefficients α, β and γ are constants.

Insertion of Eq. (19) into Eqs. (16) and (17) indicates that, when the wetting energy is linearly related to the interfacial tension, a plot of the wetting energy against the force of adhesion will likewise be linear.

MATERIALS

The force of adhesion and the wetting energy were measured on carbon filaments from Kureka, type KGF 200. These appeared smooth at a magnification of 10,000 (electroscanning microscope) and had a circular cross section, $r = 5.5\ \mu$m. Dust particles were removed by translating a rotating filament across a second one under gentle rubbing.[12] In order to obtain homogeneous surface properties, it was then oxidized for 2 hours in 40% nitric acid at 90°C, washed with distilled water and dried.

Surfactant adsorption was measured in Sterling MT-FF suspensions that had also been oxidized with nitric acid. It was assumed that the surface properties of such particles were identical to those of the carbon filaments.

Decylsulphonic acid was obtained from sodium decylsulphonate prepared as described by Reed and Tartar[16] applying percolation through a Bio-Rad Ag50-WX-8-H^+ ion exchanger.

Cetylmethylammoniumbromide (CETAB) was Cetavlon from I.C.I.

MEASUREMENT OF FORCE OF REMOVAL OF CROSSED CARBON FILAMENTS

The measurements were performed in the apparatus shown in Figure 1. One filament is mounted on a quartz support suspended from the arm of an electric microbalance (type EMB-1 from Res. Ind. Inst. Cy London) by means of a thin gold wire ($r = 10^{-5}$ m). Weight changes are recorded with a sensitivity of 2×10^{-8} N. The second filament is mounted on a quartz

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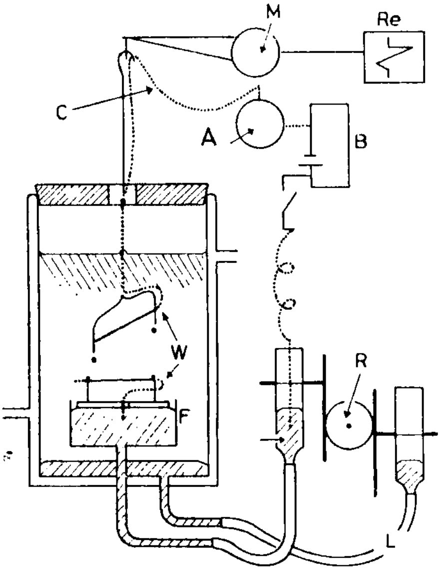

FIGURE 1 Apparatus for measuring force of adhesion: (A) microammeter, (B) battery, (C) electric circuit (gold wire, $\phi = 20\ \mu$m), (F) float, (L) levelling vessels, (M) microbalance, (R) rack- and pinion mechanism, (Re) recorder, (W) filaments.

support floating on a pool of mercury, the level of which can be varied by a levelling tube attached to an electrically driven rack-and-pinion mechanism. The average speed of displacement can be varied stepwise between 10^{-6} and 10^{-9} ms^{-1}. Thus, the floating filament can be raised to and lowered from the suspended filament. The crossing angle between the filaments can be read from a scale attached to the wall of the thermostatted vessel in which the filaments are placed. Changes in the liquid volume in the vessel caused by motion of the mercury below the float are compensated by a simultaneous change in volume of a second pool of mercury at the bottom of the vessel. However, with the thin suspension wires used in the present study, buoyancy effects are very small. On the other hand, wetting hysteresis of the suspension wire leads to large apparent weight changes of the suspended carbon filaments; good wetting of the suspension wire is therefore essential. Satisfactory results were obtained using gold wires that were first heated in air to a red glow and afterwards exposed for several hours to the solution in which the measurements were to be performed.

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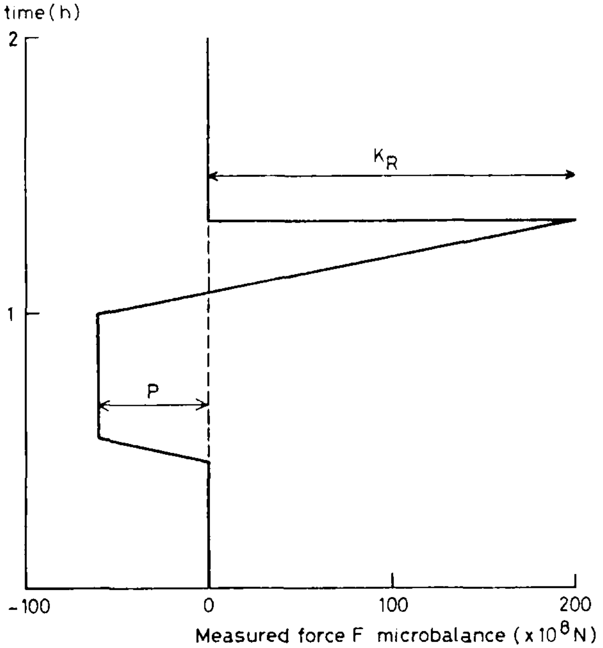

FIGURE 2 Record of measuring force of adhesion: (P) compressive force, (K_R) force of adhesion.

Both filaments are connected with an electric circuit by thin gold wires. An external potential of 50–100 mV was required to obtain electrical contact

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between the submerged filaments, even when these were pressed together with a force of 1–2 μN. After contact had been established, the contact resistance between the filaments was measured by comparison with a known resistor switched in parallel to the crossing filaments. Then, concentrated surfactant solution was added. This did not influence the value of the contact resistance. After waiting for 0.5 hour, the floating filament was lowered at a rate of 1.67×10^{-9} ms^{-1}; the force of removal can be calculated (Figure 2) from the recorded weight changes. During removal, the electric circuit was short-circuited. Further details about the apparatus and its operation have been presented elsewhere.[12]

TABLE I

Force of removal K_R for crossed carbon filaments in aqueous surfactant solutions at pH = 2.5; $\omega = 90°$, $T = 20°C$. R is the electrical contact resistance, $S(K_R)$ the standard deviation of the force for 5 measurements.

System	Surfactant concentration (mmol m^{-3})	K_R (10^{-8} N)	$S(K_R)$ (10^{-8} N)	R ($K\Omega$)
Decylsulphonic acid + H_2SO_4	—	69	2.7	12–49
	6.5	56	1.2	35–50
	33	47	3.6	13–15
	325	27	2.8	8–10
	1615	11	1.7†	8–10
Cetylmethylammoniumbromide (CETAB) + HCl	—	70	2.4	14–18
	25	64	3.9	12–17
	50	53	4.2	10–15
	100	44	3.5	9–15
	250	31	3.5	10–13
	400	18	1.9	9–11
	600	9	2.9	9–13

† 4 measurements.

Adhesion between carbon filaments in an aqueous solution is maximum at the zero point of charge[17] which, for the present samples, is at pH 2.5. Therefore the accuracy of the measurements will be optimal at this pH. In measurements in decylsulphonic acid the pH of each solution was adjusted to 2.5 by means of sulfuric acid; in measurements in CETAB solutions, the pH was adjusted to 2.5 with HCl. In all cases, the surfactant ion concentration remained small in comparison with the total electrolyte concentration. Before use, all solutions were filtered through a millipore filter in order to remove dust. The results of the measurements are collected in Table I.

DETERMINATION OF SURFACTANT ADSORPTION ON OXIDIZED CARBON BLACK

Weighed amounts of oxidized Stirling MT were ultrasonically suspended into aliquots surfactant solution at pH 2.5. After shaking for 24 hours, the carbon black was filtered off through a millipore filter. The equilibrium concentrations *c* of decylsulphonic acid were determined by titration with CETAB solution; CETAB concentrations were determined by titration with pure sodium tetradecylsulphonate.

In order to evaluate the adsorption Γ from the observed decrease in surfactant content Δm per g carbon, the specific surface area *S* of the carbon sample was determined by means of two independent methods. Evaluation of electron micrographs gave a specific surface area of 16.7 m^2/g. Conductometric titration of the aqueous carbon suspension with potassium laurate[18] gave the somewhat lower value of 13.3 m^2/g.

Plots of Δm versus *c* for the adsorption of decylsulphonic acid and of CETAB on carbon at pH 2.5 are presented in Figure 3. The values for the

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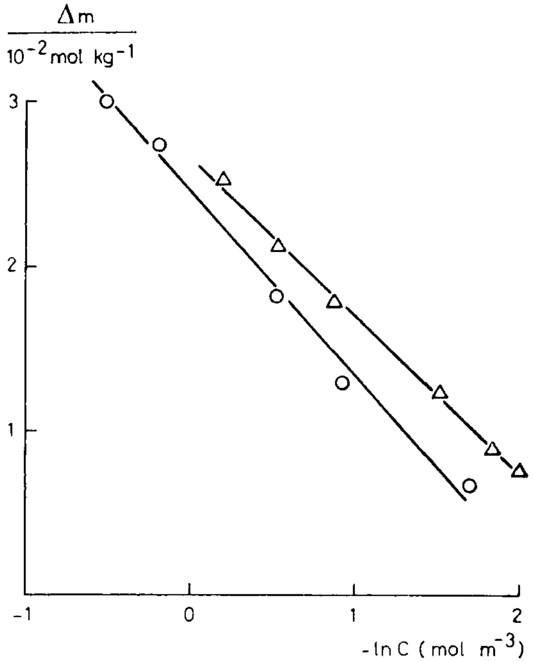

FIGURE 3 Amount of aqueous surfactant adsorbed on oxidized Sterling MT-FF; pH = 2.5.

○ decylsulphonic acid in sulphuric acid.

△ CETAB in hydrochloric acid.

parameters Γ^{∞} and a were evaluated from these graphs by means of Equation (18):

$$\frac{c}{\Gamma} = \frac{c}{\Gamma^{\infty}} + \frac{a}{\Gamma^{\infty}} \tag{18}$$

The results are collected in Table II.

TABLE II

Values of Szyszkowski parameters obtained from adsorption of decylsulfonic acid + H_2SO_4 and of CETAB + HCl on oxidized Sterling MT–FF; pH = 2.5

Surfactant	Surface area (m^2/g carbon black)	$\Gamma^{\infty}/10^{-6}$ mol m^{-2}	$a/10^{-2}$ mol m^{-3}
Decylsulphonic acid	16.7	1.81	16.2
	13.3	2.29	16.0
CETAB	16.7	1.56	5.1
	13.3	1.93	4.35

WETTING ENERGY OF CARBON FILAMENTS

In order to make a valid comparison between forces of removal and wetting energy it is necessary to perform both measurements at solid interfaces having identical properties. Because the surface properties of carbon vary widely, a direct method has been developed to measure the work of adhesion at the carbon filaments used in our adhesion experiments. A small gold sphere is

TABLE III

Wetting energies K_W of carbon filaments for the surfactant solution/reference fluid interface, at 20°C, pH = 2.5; $S(K_W)$ = standard deviation of 4 measurements

Reference fluid	Surfactant	Concentration (mol. m^{-3})	$K_w/$ 10^{-8} N	$S(K_w)/$ 10^{-8} N	$\sigma_{ol}/$ 10^{-3} N m^{-1}	$\sigma_{ol} \cos\theta$ 10^{-3} N m^{-1}
Argon	Decyl-sulphonic acid	—	171	2.0	72.8	49.5
		0.0068	152.5	5.2	72.1	44.2
		0.033	137	4.3	71.7	39.7
		0.325	121.5	3.5	70.5	35.2
Iso-pentane		—	167	3.4	49.2	48.4
		0.033	135	2.8	44.8	39.2
		0.325	113	2.6	39.6	32.7
		1.615	92	4.2	28.6	26.6
Cyclohexane	CETAB	—	148	3.3	50.5	42.9
		0.05	110	2.5	32.8	31.9
		0.10	93	2.8	28.6	27.0
		0.25	65	2.0	20.7	18.6
		0.50	24	1.5	14.7	7.0

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suspended from a thin gold filament ($\phi = 2 \times 10^{-5}$) attached to the arm of a microbalance. An oxidized carbon filament of about 1 cm length is glued in a vertical position in a small hole ($\phi = 2 \times 10^{-4}$ m) drilled in the lower side of the gold sphere.

Gold sphere and carbon filament are submerged in the reference fluid so that the lower tip of the carbon filament is about 10^{-3} m above the interface with the aqueous surfactant solution; the weight at the balance arm is recorded. The level of the interface is slowly raised so that it is pierced by the carbon filament. After equilibrium is re-established, the weight at the balance arm is recorded again. The difference between the two weighings equals the wetting energy K_w as defined in Eq. (13).

The diameters of both the carbon filament and the gold suspension wire are sufficiently small to allow buoyancy corrections to be neglected. Results of

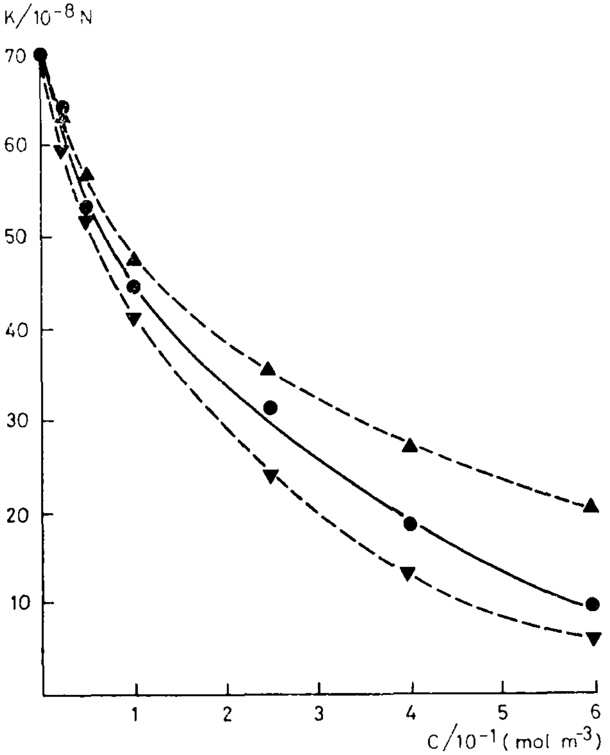

FIGURE 4 Force of adhesion vs concentration of CETAB in hydrochloric acid; pH = 2.5.

● experimental.
▲ calculated for specific surface area Sterling MT–FF = 16.7 m^2/g.
▼ ditto for 13.3 m^2/g.

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such measurements are collected in Table III. Measurements clearly indicating a zero contact angle have been omitted, because Eq. (13) then becomes invalid. This was checked by comparing the value of $K_w/2\pi r$ with surface or interfacial tension measurements performed by means of the Wilhelmy plate method.

DISCUSSION

In Figures 4 and 5 the experimental data from Table I are compared with the force of removal predicted by Eq. (12) on inserting the values of Γ^∞ and a given in Table II. The uncertainty of the true surface area of the carbon

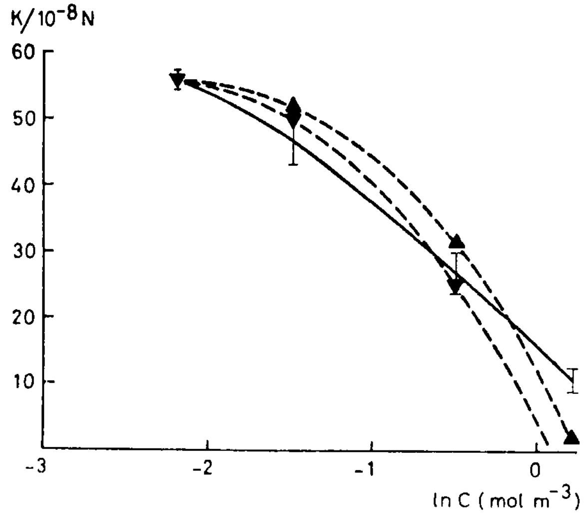

FIGURE 5 Force of adhesion vs concentration of decylsulphonic acid in sulphuric acid; pH = 2.5.
I experimental.
▲ calculated for specific surface area Sterling MT-FF = 16.7 m²/g.
▼ ditto for 13.3 m²/g.

suspension used in the adsorption measurements is reflected by the two theoretical curves shown in these figures. Within the limits set by this uncertainty, good agreement between theory and experiment is obtained in the case of CETAB. The large decrease in adhesive force caused by adding a small amount of decylsulphonic acid (c = 6.5 m moles m^{-3}) cannot be accounted for by the present theory. We suspect that it is due to the presence of a slight positive charge on the filaments under the measurement conditions chosen. Then, exposure of the filaments to the anionic solution may lead to

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chemisorption of a certain amount of sulphonic acid, which should decrease K_R^0 (cf. Eq. (12)). When the decylsulphonic acid concentration is further increased, the subsequent decreases in adhesion will be caused by physical adsorption of the surfactant; these are indeed of the order of magnitude predicted by Eq. (12).

As regards the proposed relations between the force of adhesion and wetting properties, Figure 6 shows that for all systems investigated, the

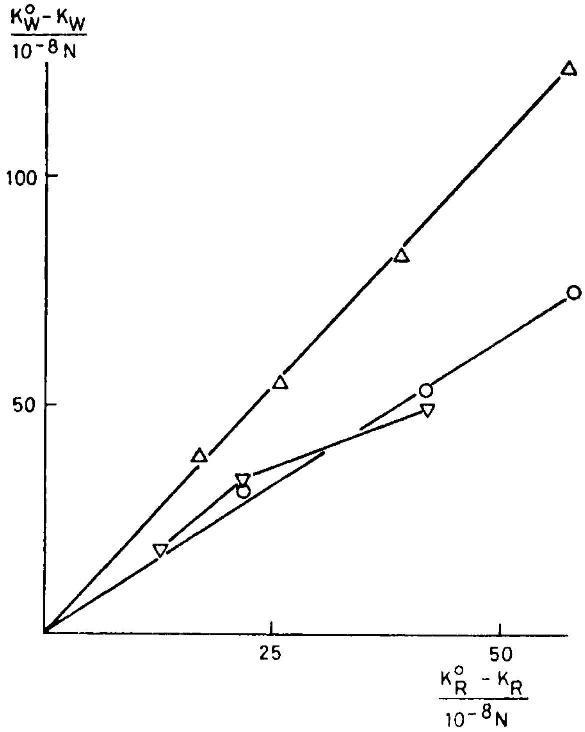

FIGURE 6 Changes in force of adhesion ΔK against changes in filament wetting energy ΔK_w.

▽ decylsulphonic acid, H_2SO_4/air.
○ decylsulphonic acid, H_2SO_4/isopentane.
△ CETAB, HCl/cyclohexane.

difference in wetting energy in the presence and absence of surfactant is nearly proportional to the corresponding difference in the force of adhesion. This supports the existence of a relation between these quantities as expected from our theory. However, Figure 7 shows that plots of the wetting energy against interfacial tension all show some curvature, so that the expected

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correspondence between $\sigma \cos \theta - \sigma$ plots and $K_w - K_R$ plots is not well established by the present experiments. Further measurements would be needed to settle this point.

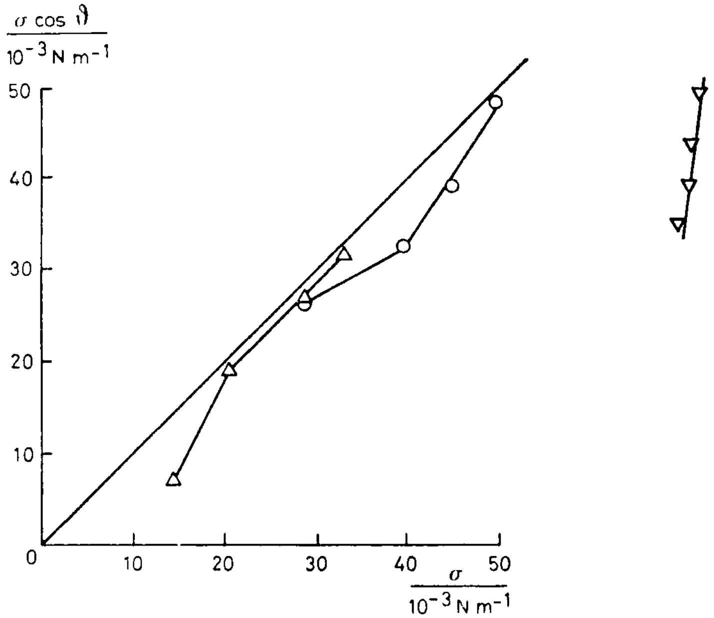

FIGURE 7 Wetting energy $\sigma \cos \theta$ against interfacial tension σ.
▽ decylsulphonic acid, H_2SO_4/air.
○ decylsulphonic acid, H_2SO_4/isopentane.
△ CETAB, HCl/cyclohexane.

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CONCLUSION

The experimental data appear to confirm the thermodynamic theory of adhesion as described above. In the present case, this agreement was realized experimentally by applying a very slowly increasing force of removal to a single contact between adhering bodies. Practical removal problems often consist in the removal of a large number of similar particles from a single substrate by application of a known and constant force during a prolonged time.[13] When the distribution of the adhesive free energies of these particles can be estimated, the above theory can predict how the fraction of particles removed will change with the solute composition. It must be emphasized that Eqs. (12) and (16), used in the interpretation of our experiments, are only valid when the free energy at contact, $f(h_0)$, is not affected by changes in solute concentration. Preliminary experiments indicate that this condition is not fulfilled when the solute molecules are commensurate with those of the solvent. While it is possible to describe such effects by assuming a solute adsorption in the contact area, such a quantity is not amenable to independent measurement, so that model considerations are required to predict the solute dependency of adhesion in such systems.

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APPENDIX

Calculation of the force of interaction between finite, non-planar bodies

Assume that the space between the opposing surfaces of two bodies can be approximately described as a series of slits of equal area whose widths ascend according to the series h_0, $h_0 + \Delta h$, $h_0 + 2\Delta h, \ldots h_0 + n\Delta h$, such that at $h_0 + n\Delta h$, just as at h_∞, the interaction between the bodies has become negligible. The total free energy of interaction of such an assembly equals

$$F_t(h_0) = \Delta A[f(h_0) + f(h_0 + \Delta h) + f(h_0 + 2\Delta h)] \ldots \qquad \text{(A1)}$$

When the minimum distance h_0 between the bodies is increased to a value $h_0 + \Delta h$, this free energy of interaction becomes:

$$F_t(h_0 + \Delta h) = \Delta A[f(h_0 + \Delta h) + f(h_0 + 2\Delta h) \ldots + f(h_\infty)] \qquad \text{(A2)}$$

The work necessary to perform this change in distance equals

$$-K_t \, . \, \Delta h = F_t(h_0 + \Delta h) - F_t(h_0) \qquad \text{(A3)}$$

where K_t represents the total force of interaction between the bodies. Combination of Eqs. (A1), (A2) and (A3) leads to

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$$-K_t = \frac{\Delta A}{\Delta h}[f(h_\infty) - f(h_0)] \tag{A4}$$

The geometrical condition that must be satisfied by the bodies in order to allow the above treatment is

$$\frac{\Delta A}{\Delta h} = g \tag{A5}$$

where g is a constant. Moreover, for $h < h_0$, $\Delta A = 0$, so that

$$A = g(h - h_0) \tag{A6}$$

where A represents the area projected on a plane perpendicular to h of those points of the surfaces of both bodies whose mutual distances d, when measured parallel to h, satisfy $h \geqslant d \geqslant h_0$.

In order that distortions of the interaction force by the boundaries of the slits may be neglected, the following inequality must be satisfied:

$$\frac{\Delta A}{(\Delta h_0)^2} \approx \frac{g}{h_0} \gg 1 \tag{A7}$$

The following examples of bodies satisfying Eq. (A6) will be given:

1. Wedge opposite half space.

The wedge can be approximated by a series of slabs, having as constant base area (Fig. 8)

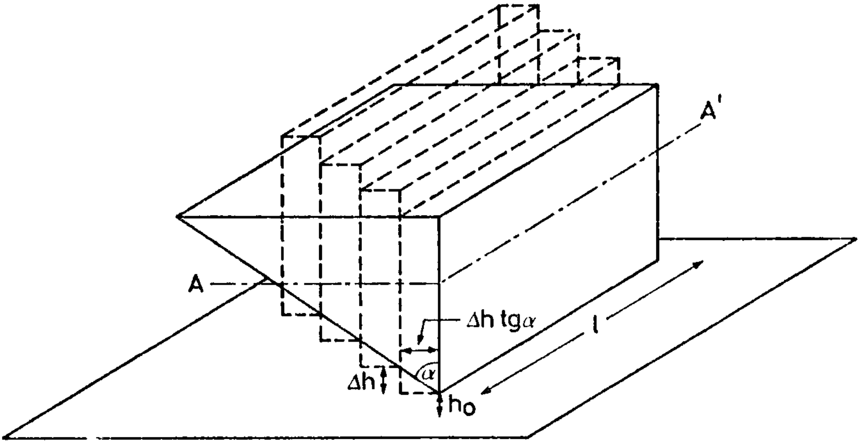

FIGURE 8 Model for wedge against half space. Broken lines: approximate model. Above line AA′, interaction between wedge material and that of the half space can be neglected. For other symbols see text.

$$\Delta A = \Delta h \, . \, l \, . \, tg\alpha \tag{A8}$$

where l represents the width of the wedge, and α its cutting angle. Consequently

$$g = \frac{\Delta A}{\Delta h} = l \cdot tg\alpha \tag{A9}$$

2. Helix with axis perpendicular to half space.

The helix can be approximated as a series of sectors like a winding stair case. Their base area equals

$$\Delta A = \tfrac{1}{2}R^2\Delta\phi = \frac{\pi R^2}{l}\Delta h \tag{A10}$$

R is the helix radius, $\Delta\phi$ the sector angle, l the speed of the helix.

$$g = \frac{\Delta A}{\Delta h} = \frac{\pi R^2}{l} \tag{A11}$$

3. Second order surfaces

The space between two bodies whose surfaces can be described analytically by second order equations—like spheres and cylinders—can be represented approximately by a series of concentric tubes, with axis parallel to h. Deryagin[2] derived the following equation for g:

$$g = 2\pi[(\rho_1^{-1}\rho_2^{-1} + \rho_3^{-1}\rho_4^{-1}) + (\rho_1^{-1}\rho_3^{-1} + \rho_2^{-1}\rho_4^{-1})\sin^2\omega + (\rho_1^{-1}\rho_4^{-1} + \rho_2^{-1}\rho_3^{-1})\cos^2\omega]^{-\frac{1}{2}} \tag{A12}$$

ρ_1, ρ_2, respectively ρ_3, ρ_4, are the principal radii of curvature of body 1, respectively of body 2, at their points of closest approach ($h = h_0$); ω is the angle between ρ_1 and ρ_3.

Substitution of $\rho_1 = \rho_3 = r$, $\rho_2 = \rho_4 = \infty$ into Eq. (A12), and application of Eqs. (A5) and (A4) leads to Eq. (6).

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