

Adsorption and Contact Angle Studies

I. Water on Smooth Carbon, Linear Polyethylene, and Stearic Acid-Coated Copper

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Ellipsometrically determined adsorption isotherms are reported for water on two types of pyrolytic carbon, on polyethylene, and on stearic acid-coated copper, for relative pressures up to close to the saturation pressure, P^0 , and for various temperatures. Contact angle data for bulk water on the same solids are included; advancing angles of 60° – 90° were found. The adsorbed film thickness reaches 40–80 Å in the first two systems, but only a few angstroms in the second two; correspondingly, the surface pressures of P^0 , π^0 , are large in the first two cases and small in the second two. Large contact angle thus does not necessarily imply low π^0 . The data are fitted to a previously published potential-distortion model, which allows adsorption and contact angle behavior to be related.

INTRODUCTION

It has been pointed out that, if a liquid rests on a solid surface with a finite angle of contact, then the adsorption isotherm for the vapor of that liquid must show a limiting adsorbed film thickness, x^0 , as the vapor pressure P approaches the saturation vapor pressure, P^0 (1). There should be metastable and unstable regions as the isotherm goes through a maximum and a minimum region relative to the P^0 line, with x finally approaching infinity. This shape has been called type VI (2); it is analogous to P – V isotherms calculated from the van der Waals equation and, like such isotherms, allows for two-phase equilibrium. In our case the two phases are bulk liquid and adsorbed film. Application of the Gibbs adsorption equation shows that the integral around the maximum–minimum region, ΔI , gives the equilibrium spreading coefficient, S_{LSV}

$$\Delta I = S_{LSV} = \gamma_{SV}^0 - \gamma_L - \gamma_{SL} \quad [1]$$

and hence the contact angle (2–4),

$$\cos\theta = \frac{S_{LSV}}{\gamma_L} + 1. \quad [2]$$

Detailed knowledge of the adsorption isotherm thus implies knowledge of contact angle and spreading coefficient. Also, just as P^0 is central to the thermodynamics of liquid–vapor equilibria, so may π^0 be very important to the thermodynamics of adsorbed film–bulk liquid equilibria. Unfortunately, it is difficult and probably impossible to trace the isotherm experimentally through the maximum–minimum region, and usual isotherm is limited to $P \leq P^0$. An interest in our laboratory has been to develop an isotherm model which will allow extrapolation from the usual to the metastable region and thus yield values of ΔI (2, 3). The level of success hoped for at this stage is comparable to that whereby P^0 may be estimated from fitting the van der Waals equation to gas nonideality data. We believe that any model must recognize that film of thickness x^0 cannot be identical in nature to bulk liquid and,

further, that such a film, if thick, can be in equilibrium with pressure P^0 only by virtue of a balance between the attractive adsorption potential and some form of unfavorable structural distortion relative to bulk liquid.

An adsorption isotherm for a contact-angle-forming system is thus useful in several potentially important ways. It provides information on the propagation of attractive forces and of structural distortions. It allows the testing of semiempirical equations of state, through verification of the calculated contact angle. It gives π^0 and, if temperature dependence is obtained, various other thermodynamic quantities.

Unfortunately, the usual isotherm obtained for a powdered solid is not very useful since it cannot be followed to near P^0 without encountering serious interparticle condensation effects (5). The corollary contact angle measurement must be made on a flat sample of the solid, whose surface must be assumed to be the same as that of the powdered material.

A model which we have proposed gives the isotherm

$$kT \ln (P^0/P) = \epsilon_0 e^{-ax} + g/x^3 - \beta e^{-\alpha x}. \quad [3]$$

The long range form of the dispersion term, g/x^3 , is needed only at large x , and no serious error in the evaluation of ΔI is introduced if the term is neglected, so that

$$kT \ln (P^0/P) \simeq \epsilon_0 e^{-ax} - \beta e^{-\alpha x}, \quad [4]$$

whence (6)

$$S_{LSV} = (1/V) \epsilon_0 e^{-ax^0} (1/a - 1/\alpha) \quad [5]$$

and

$$\pi^0 = (1 - \cos\theta)\gamma_L + (1/V)(\epsilon^0/a - \beta/\alpha). \quad [6]$$

Testing of the above equations has been only very qualitative because of the lack of appropriate data (2, 6).

The present investigation was undertaken to provide data of the type needed—namely, adsorption isotherms on flat surfaces, accompanied by contact angle measurements using the same surface. The solids were chosen to cover a range of relatively common types and

the adsorbate, water, because of its ubiquitous importance. We felt that the ellipsometric method, used by Derjaguin and Zorin (1), provided the best general technique for adsorption measurements. There are limitations to the ellipsometric method, of course. It applies to specularly reflecting flat and smooth surfaces. One may, however, measure film thicknesses ranging from 1 to 1000 Å to within a fraction of an angstrom. Thus even submonolayer films may be observed, although the method is better suited to the multilayer region. Wade (7) has made successful gravimetric adsorption measurements on sets of thin sheets of adsorbent. Not all solids can be put in sheet forms, however, and there is a residual worry about condensation near P^0 at points of sheet-sheet contact and at reentrant angles in the suspension system.

EXPERIMENT

Apparatus

The ellipsometer used was a Rudolph Model 436/200, sensitive to 0.01° . The polarizer and quarter-wave plate were placed ahead of reflection from the sample. A mercury light source giving the 546.1-nm line was used, and the reflected intensity was measured by means of a photomultiplier tube whose output was read on a recording voltmeter.

Adsorption took place in an environmental chamber, triple walled and made of brass and stainless steel. Ports allowed entrance and exit of the light beam; either 50° or 70° angle of incidence to the sample could be used. The windows were of fused silica, 1-in. diameter and 0.5 in. thick, and were of low birefringency. The entrance and exit beams were always normal to the windows. The chamber could be displaced in any direction, and the sample holder could be tilted, so that the light beam could be focused in the sample. The flat sample of adsorbent was fastened to the backing plate of the holder by means of gallium solder. This procedure avoided any reentrant angles at which condensation might occur near the region of measurement. A thermistor mounted on the

backing plate allowed determination of the sample temperature.

When in use, the space between the outer and middle walls of the environmental chamber was evacuated so that the outer windows would be insulated and would not film over or frost during low temperature runs. Thermostatted water was circulated through the space between the middle and inner walls, and also through a hollow portion of the mount holding the backing plate. The inner chamber was connected, through a Pyrex vacuum line system, to an MKS baratron pressure transducer and to a bulb holding liquid adsorbate and thermostatted to one or another chosen temperature, T' , below the temperature, T , of the sample mount. Standard vapor pressure tables then gave P/P^0 from $(T - T')/T$; as a check, however, the absolute pressure, P , in the environmental chamber was measured separately by means of the baratron. The thermostats maintaining T and T' were controlled to 0.01°C . Low temperatures were achieved by cooling coils through which fluid from a back-up Lauda K120 ultrakryostat was circulated. The difference $(T - T')$ was determined essentially directly, being linearly related to the difference between the resistance of the thermistor at the sample mount and the resistance of the thermistor in the middle of the bulb holding the bulk liquid adsorbate. It might be noted that for water 0.01°C control of the two temperatures corresponds to control of P/P^0 to about 5×10^{-4} , in the range 0° – 25°C . In practice, P/P^0 was varied by varying T' at constant T . Generally, T' was first increased, to give increasing P/P^0 , and then decreased,

to follow the desorption. Ten minutes usually sufficed for equilibrium.

Ellispometric Method

The procedure followed for the use of the ellipsometer was that given by McCrackin and co-workers (8); a computer program due to McCrackin (9) was used for the calculations.

Ellispometry involves the measurements of the effect of reflection on the state of polarization of light. The measurements can be interpreted to yield the optical constants of the reflecting material and, when this last is a film-covered surface, the thickness of the film. The changes in the state of polarization of light upon reflection are represented by the changes in the amplitude and phase difference for beams polarized in the plane of incidence and perpendicular to it. The reflection coefficients for these two polarizations in the case of clean surface are given by the Fresnel coefficients as

$$r_{12}^P = \frac{n_2 \cos \phi_1 - n_1 \cos \phi_2}{n_2 \cos \phi_1 + n_1 \cos \phi_2} \quad [7]$$

and

$$r_{12}^S = \frac{n_1 \cos \phi_1 - n_2 \cos \phi_2}{n_1 \cos \phi_1 + n_2 \cos \phi_2}, \quad [8]$$

where ϕ_1 and ϕ_2 are shown in Fig. 1a, and n denotes index of refraction. Superscripts P and S denote parallel and perpendicular, respectively.

When a film is placed on the substrate, the reflection coefficients become

$$R^P = \frac{r_{12}^P + r_{23}^P \exp D}{1 + r_{12}^P r_{23}^P \exp D} \quad [9]$$

and

$$R^S = \frac{r_{12}^S + r_{23}^S \exp D}{1 + r_{12}^S r_{23}^S \exp D}, \quad [10]$$

where $D = -4\pi i n_2 \cos(\phi_2 x/\lambda)$, n_2 is now the index of refraction of the film, λ is the wavelength of light used, and x , the film thickness, is as shown in Fig. 1b.

The quantities measured by the instrument are Δ , the phase difference as given by the

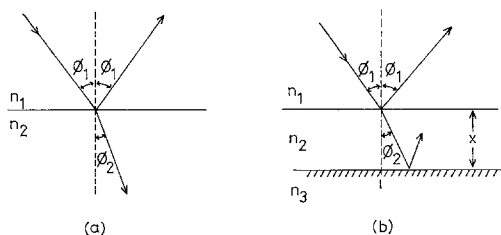


FIG. 1. (a) Reflection at a phase boundary. (b) Reflection through a film.

polarizer reading, and ψ , the azimuth, given by the analyzer reading. These give

$$R^P/R^S = \tan\psi e^{i\Delta}. \quad [11]$$

Several numerical methods are available for determining x through Eq. [11]. For example, if n_2 and n_3 are known, graphs of Δ and ψ may be computed for various values of x .

Alternatively, it has been observed that the linear relationships

$$\Delta = \bar{\Delta} - \alpha x \quad [12]$$

and

$$\psi = \bar{\psi} + \beta x \quad [13]$$

are approximately valid for a certain range of film thickness. Here, $\bar{\Delta}$ and $\bar{\psi}$ refer to the clean surface and Δ and ψ , to the surface covered with film; α and β are constants dependent upon the angle of incidence, the wavelength of the light used, and the indices of refraction of the film and the substrate. These relationships were first given by Drude for homogenous nonabsorbing films and were then shown to apply in the submonolayer coverage region and for absorbing films (10). In particular Eqs. [12] and [13] were observed to apply to the systems reported here, for water films up to about 100 Å in thickness. We computed tables of Δ and ψ values using Eq. [11], for various film thicknesses, and found Eqs. [12] and [13] to hold.

In the general case neither the index of refraction nor the film thickness is known, and Eq. [11] cannot be solved in closed form. A numerical method for the calculation of these two quantities from the ellipsometer readings is included in the computer program mentioned above. The method is based on calculation of the thickness of the film using a series of assumed refractive indexes and then choosing that value of n_2 which minimizes the imaginary part of the complex film thickness. We found only negligible deviations of n_2 from the value for bulk water, a typical result being 1.334 vs 1.333, and $\kappa = 0$, where κ is the coefficient of the imaginary portion of the index of refraction. Having verified that this situation applied to all of the systems studied, we proceeded to

use the bulk index of refraction of water for the temperature dependence studies.

Contact Angle Measurements

Unless otherwise specified, the measurements were made by means of the captive bubble method, using the thermostatted cell and goniometer telemicroscope previously described (11). In all cases, there was hysteresis in that receding angles were considerably less than the advancing ones; the latter are the ones reported unless otherwise specified. Also, there was a tendency for contact angles to decrease with time of soaking of the sample in the captive bubble apparatus. For this reason, angles were sometimes measured on a sessile drop of liquid, delivered to the sample surface in the same thermostatted chamber that was used for the captive bubble measurements. These were always measured as advancing angles. Our angle measurements were generally reproducible to $\pm 2^\circ$.

The surface tension of the water used was occasionally checked (by means of a tensiometer) to be sure of surface purity. It was thus determined that the soaking effects referred to above were not accompanied by changes in the water surface tension.

Materials

Two samples of pyrolytic high-density isotropic carbon were used, supplied by Gulf Electronic Systems (San Diego, CA). The first sample, designated as carbon I, was a silicon alloy with 11% Si by weight, present as SiC (lot No. 15C2). The sample was in the shape of a disk 1 cm in diameter and 1 mm thick. The second sample, carbon II, was of pure isotropic carbon of density 1.91 g cm⁻³ (lot No. 450B-21), and consisted of a disk 2 cm in diameter and 1 mm thick. Both had been polished with 0.25-μm diamond abrasive. For further details on the properties and structure of these pyrolytic carbons see Ref. (12). The samples were cleaned with toluene and acetone, and then degassed for 10–15 hr at room temperature prior to use.

Linear polyethylene of density 0.95 g cm^{-3} was obtained from Beckman Instruments Inc. (Bel-Art products). The samples were in the form of sheets 7 mm thick and were prepared for use as follows. An 18×10 -mm slip was cleaned with ethanol and boiling water. It was then air dried and polished. This last was accomplished by placing the sample between two flat glass plates and then heating from both sides by means of hot plates to 177°C . The slip was squeezed by pressing on the plates slowly, until the thickness was reduced to 3 mm. The temperature was kept at 177°C for 30 min, and the sandwich allowed to cool slowly down to room temperature. The sample was washed with boiling water and then degassed for 20 hr at room temperature.

Stearic Acid on Copper

A $30 \times 20 \times 3$ -mm slip of commercial copper was polished with garnet finishing paper and then cleaned by washing with toluene, acetone, and then water. The slide was immersed vertically in a 500-ml beaker filled with distilled water. Two drops of a saturated benzene solution of stearic acid (reagent grade) were placed on the water surface and the solvent allowed to evaporate. The copper slide was then slowly raised through the interface and allowed to dry in air and later, in the environmental cell, under vacuum.

This surface is not entirely defined since

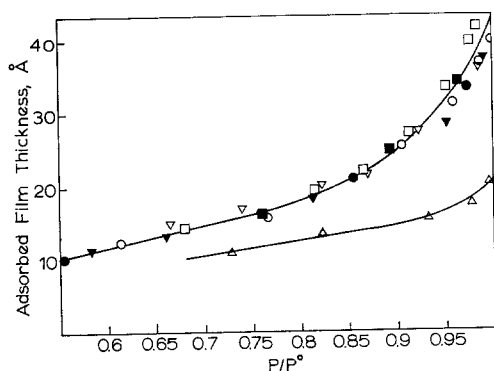


FIG. 2. Adsorption of water vapor on pyrolytic carbon-silicon. Δ 21.5°C , \circ 16.5°C , \square 9.5°C , ∇ 5.5°C . Shaded symbols denote desorption points.

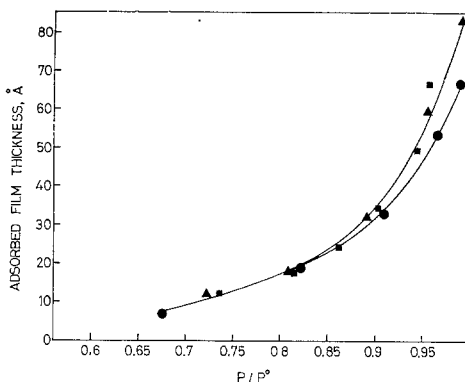


FIG. 3. Adsorption of water vapor on pyrolytic carbon. Δ 21.5°C , \bullet 16.5°C , \blacksquare 9.8°C .

constant film pressure was not maintained during withdrawal and since no special precautions were taken to be sure of a surface chemical level of purity of the stearic acid. The copper, of course, had the inevitable surface corrosion layer. We were primarily interested, however, in having a surface of this general type, and in relating adsorption and contact angle data to each other rather than separately to literature values for variously prepared films.

RESULTS

The Water-Carbon System

The complex index of refraction, $n(1 - i\kappa)$, of carbon I was found to be $n = 1.632$ and $\kappa = 0.492$. For the water films, the constants α and β of Eqs. [12] and [13] were found to be 0.06 and 0.004, respectively, for 50° angle of incidence. Similar results were found for carbon II, $n = 1.85$, $\kappa = 0.44$, $\alpha = 0.06$, and $\beta = 0.004$. With these surfaces the practical reproducibility was $\pm 0.01^\circ$ for the analyzer readings and $\pm 0.02^\circ$ for the polarizer readings, with the consequence that the adsorbed film thickness could be determined to $\pm 0.7 \text{ \AA}$.

The two adsorption isotherms are shown in Figs. 2 and 3; there was no hysteresis—desorption points retraced the adsorption ones. After completion of an adsorption-desorption run, the carbons were degassed at room temperature for 10–15 hr, and a new run started at the

same or some different value of T . Reruns at the same T reproduced the original isotherms well.

As may be seen from the figures (and confirmed by isosteric heat plots), the heat of adsorption was within experimental error, $0.1 \text{ kcal mole}^{-1}$, of that for condensation of bulk water, $10.6 \text{ kcal mole}^{-1}$, for film thicknesses ranging from 15 to 40 \AA for carbon I and from 20 to 70 \AA for carbon II, for temperatures in the range $9.5\text{--}21.5^\circ\text{C}$. The values of x^0 were about 42 and 80 \AA for carbons I and II, respectively. The isotherm for carbon I at 5.5°C is quite different from those at the higher temperatures, giving an x value of only 20 \AA ; we suspect that a phase change has occurred in the adsorbed film.

The advancing contact angles for water on carbon I were 70° at 50°C and 74° at 1°C ; $d\theta/dT$ was thus -0.08 , although the uncertainties in the angle measurements make this value approximate. For carbon II, we find 63° at 53°C and 65° at 1°C and $d\theta/dT = -0.04$. Receding angles were around 30° .

The contact angle decreased slowly on soaking the sample but could be returned to the original value if the carbon disk were redried under vacuum. We report the values as measured initially; these agreed well with those obtained by the sessile drop method.

Contact angle values were observed qualitatively at various temperatures intermediate between 50 and 1°C ; there was no indication of any special behavior on passing through the region from 9°C downward. Thus the distinct alteration in the nature of the adsorption isotherm was not noticeably reflected in the contact angle behavior.

The Water-Polyethylene System

The refractive index parameters for polyethylene were found to be $n = 1.532$, $\kappa = 0$. This last value means that the material was not significantly light absorbing. The constants α and β of Eqs. [12] and [13] were calculated to be 0.057 and 0.0001 , respectively, for water films and 50° angle of incidence. Again, the

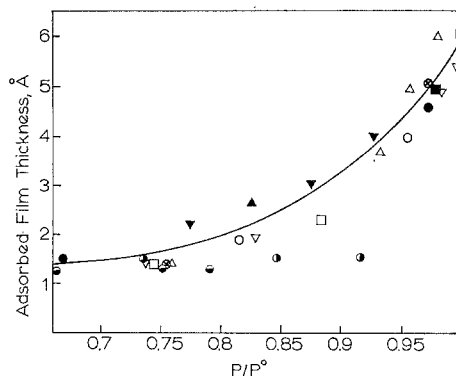


FIG. 4. Adsorption of water vapor on polyethylene: open circles, 21.5°C ; erect and inverted triangles, 16.5°C (two runs); circles with \times , 9.7°C ; vertically half-filled circles, -9°C ; horizontally half-filled circles, -24°C . Shaded symbols denote desorption points.

polarizer readings were reproducible to $\pm 0.01^\circ$, and the analyzer to $\pm 0.02^\circ$, corresponding to an uncertainty in film thickness of $\pm 0.5 \text{ \AA}$.

The set of isotherms obtained is shown in Fig. 4. There was no desorption hysteresis. Since x^0 is now only 6 \AA , the uncertainty in the film thickness values introduces some scatter in the points. The scatter does not appear to be systematic, however, and the isotherms are essentially temperature independent. The heat of adsorption in the range $5.5\text{--}21.5^\circ\text{C}$ is thus indistinguishable from that of condensation of bulk water.

Some additional measurements were made at -9 and at -24°C . In both cases icing occurred in the environmental chamber once P reached the ice vapor pressure, P^0 . The points therefore terminate at P^0/P^0 . These isotherms are very flat; x is about 1 \AA at $P/P^0 = 0.4$ and shows no perceptible increase up to P^0/P^0 . Again, we infer that a phase change has occurred in the adsorbed film.

The contact angle of water on the polyethylene was $88 \pm 2^\circ$ over the range $5^\circ\text{--}58^\circ\text{C}$, with measurements at a number of intermediate temperatures. Thus $d\theta/dT$ is zero within our experimental error. Our value is $6^\circ\text{--}7^\circ$ lower than those previously reported (13). It has been found (14) that there is no contact angle difference between untreated polyethylene and that molded against a glass

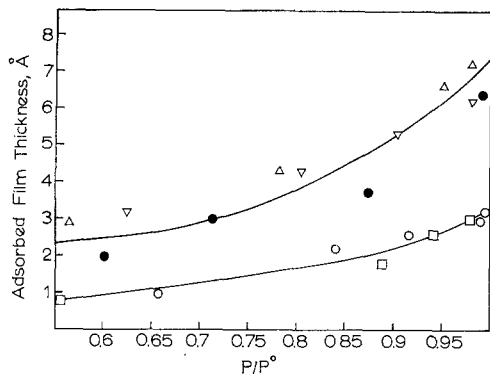


FIG. 5. Adsorption of water vapor on stearic acid-coated copper. Δ , ∇ 20.5°C (two runs), \bullet 16.0°C, \circ , \square 9.4°C (two runs).

surface, so our values are presumably not different because of the polishing procedure. We found some drift downward on soaking, although again we are reporting initial values. Hysteresis was present. Our receding angles were about 50°, again temperature independent.

The Water-Stearic Acid on Copper System

The refractive constants for the copper slide were $n = 0.9926$ and $\kappa = 2.4431$. Using values of $n = 1.52$ and $\kappa = 0$ for stearic acid (15), the thickness of the stearic acid film was calculated to be 22.7 Å. Reported values from electron microscopy are around 25 Å (16); it is possible that our film density was somewhat less than that for a close-packed condensed film.

The effective refraction parameters were calculated from the ellipsometer readings for the film-covered surface, and found to be $n = 0.9425$, $\kappa = 2.4605$. These values were used to calculate the constants α and β of Eqs. [12] and [13] for water films at 50° angle of incidence, giving 0.0485 and 0.002, respectively. These same constants were also calculated by a procedure allowing for the presence of multiple films (9). Here, the refraction parameters of the copper and of the stearic acid are used, along with the thickness of the stearic acid film (22.7 Å). Tables of Δ and ψ are then computed for various x values. The values of Δ , ψ , and x obeyed Eqs. [12] and

[13], to give the same α and β values that were found by the simple, first approach. We therefore believe that our x values are not appreciably in error because of the complexity of the interface involved in this system.

The isotherms are shown in Fig. 5. The x^0 value is about 7 Å in the range 16–20.5°C. As with the polyethylene system, the ± 0.5 -Å uncertainty in our x values introduces a large relative error, but it appears that there is little temperature dependence of the isotherms in this range of temperature. On dropping to 9.4°C, however, x^0 falls to 3.3 Å, and it again appears that a phase change has occurred. About this same thickness of water film was observed in some preliminary measurements using solid paraffin wax at 20°C.

The contact angle results indicate a somewhat more complex behavior than for the other systems. As shown in Fig. 6, the advancing angle rises slowly with temperature up to about 40°C, and then rises rapidly, levelling off at around 60°C. The curve was retraceable within experimental error on cooling, and the same results were obtained for two independently prepared stearic acid-coated copper surfaces. We suspect a change in state of the stearic acid film. Our apparatus, unfortunately, did not allow the obtaining of isotherms above about 25°C, or room temperature, so no comparative results are available.

DISCUSSION

The results may be viewed from several aspects. First, they may be compared to

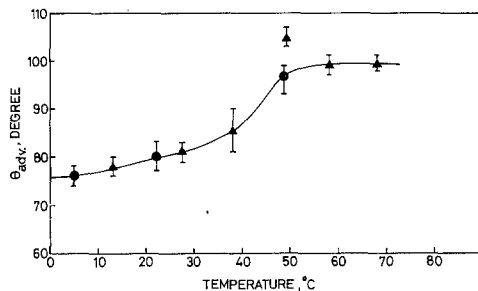


FIG. 6. Advancing contact angles for water on stearic acid-coated copper. \bullet Sample 1, \blacktriangle sample 2.

literature data. No isotherms have been reported for flat carbon surfaces, although data for water adsorption on various carbon blacks are available. Isotherms may be of the Brunauer type II in the relatively low P/P^0 region, followed by a strong rise above $P/P^0 = 0.5$. Wiig and Juhola (17) have attributed this last to capillary condensation, while Dubinin and co-workers (18) thought that the rise represented a delayed onset of second layer adsorption. While our carbons are different, and perhaps not therefore comparable, our isotherms show only a monotonic rise to a fairly large x^0 value. There is no indication of steps, for example. Our contact angles are somewhat lower than the 86° reported for water on graphite (19); no temperature dependence data seem to have been reported.

The situation is equally sparse for the other systems. Kiselev and co-workers (20) have reported some results for water adsorption of powdered polyethylene using a volumetric adsorption method. They find an amount adsorbed at $P/P^0 = 0.7$ corresponding to about 13 \AA film thickness. As mentioned in the preceding section, our contact angle values are a few degrees lower than literature values. No strict comparison should be made since the samples are undoubtedly not the same. No water adsorption data on stearic acid films are available, although contact angle measurements are. Yiannos (21) reports 104° for a monolayer deposited on copper-coated glass surface, which is distinctly higher than our value, but gives no temperature dependence data. No temperature dependence is reported for this case. The angle is dependent on the manner of preparation; we find one of 110° , for example, if the stearic acid is deposited from a benzene solution and the excess wiped off. Beischer's (22) work on the melting of stearic acid monolayers on mica suggested that they undergo a melting or loosening process below the 70°C melting point of the bulk acid. Recent work reported by Poling (23) provides indications that formation of copper-stearic acid salt (which should be high melting) does

not necessarily occur on copper, and that the free acid may be present in both ionized or un-ionized form. It seems entirely possible, then, that we observe a melting or expansion of the stearic acid film at around 50°C . Since θ rises, the effect must be to diminish $\gamma_{SV} - \gamma_{SL}$.

A second aspect of our results is the qualitative comparison afforded between adsorption and contact angle behavior. The contact angles are in the range from 60° to 90° , and a common assumption has been that in such cases little vapor adsorption occurs and that π^0 is small. This is the case, for example, in treatments based on the critical surface tension concept (24), and in those which attempt a summation of van der Waals forces across the liquid-solid interface (24). For example, the Girifalco and Good-Fowkes equation (25),

$$\cos\theta = -1 + 2(\gamma_S'\gamma_L')^{1/2}/\gamma_L, \quad [14]$$

where the primes denote effective surface tension, neglects π^0 . Since the minimum value for γ_L' is the dispersion only value, taken to be about 22 erg cm^{-2} , the maximum values for γ_S' range from 60 to 130 erg cm^{-2} . If π^0 is not small, the missing term on the right of Eq. [14], π^0/γ_L , seriously alters the inferences made in this type of approach.

Our isotherms may, of course, be integrated graphically. About the same results are obtained, however, if this is done analytically, as reported in Table I. The π^0 values range from over 140 for carbon I to about 14 for polyethylene; these are minimum values since the extrapolation to low P values neglects any contribution to π^0 from high-energy sites which adsorb strongly at low pressures. Use of $\pi^0 = 140 \text{ erg cm}^{-2}$ would, for example, raise the minimum value of γ_S' to about 620 erg cm^{-2} . Even a value of 14 erg cm^{-2} brings the minimum to around 90 erg cm^{-2} .

We believe that our results establish (a) that π^0 is not always negligible in high-contact-angle systems, (b) that π^0 can vary considerably among systems having about the same contact angle, and (c) that therefore this term should be included in even first-order semiempirical

TABLE I
 PARAMETERS OF THE POTENTIAL-DISTORTION MODEL

Adsorbent	$t, ^\circ\text{C}$	ϵ_0'	β'	a°	α°	x^0	θ		π^0 erg cm^{-2}	(Work of adhesion) erg cm^{-2}	
							Calc.	Obs.		W	W_e
Carbon I	21.5	1.03	0.13	0.067	0.015	39.8	72	72	142	236	94
	16.5	1.03	0.13	0.067	0.015	39.8	71	73	139	246	107
	9.5	0.876	0.15	0.053	0.014	45.2	74	73	130	224	94
	5.5	4.34	3.0	0.077	0.058	19.4	76	74	113	205	92
Carbon II	21.5	0.50	0.179	0.0216	0.0105	98	63	64	124	229	105
	16.5	0.558	0.25	0.023	0.013	80.3	63	64	106	213	107
	9.8	0.50	0.179	0.0216	0.0105	98	61	65	119	229	110
Polyethylene	21.5	0.643	0.041	0.463	0.0074	6.0	89	88	14.4	88	72
	16.5	0.643	0.041	0.463	0.0074	6.0	88	88	14.2	90	76
	9.7	0.643	0.041	0.463	0.0074	6.0	85	88	13.8	94	80
	5.5	0.643	0.041	0.463	0.0074	6.0	84	88	13.7	96	82
Stearic acid	20.5	2.1	0.035	0.541	0.0076	7.7	79	80	48.5	135	86
	16.0	2.1	0.035	0.541	0.0076	7.7	78	78	47.7	136	88
	9.4	1.75	0.042	1.12	0.009	3.3	78	78	17.9	108	90

treatments of contact angle and spreading phenomena.

Another comment has to do with the generally accepted practice of using advancing contact angles. We observe no hysteresis in adsorption and are disturbed by its presence in contact angle behavior, which suggests that the latter is not an equilibrium phenomenon. Modelistic treatments of contact angle hysteresis suggest that it is the receding angle that is the more suspect (26); it may be low because of patches of liquid, that is, of wetted surface, being left behind. We do observe a tendency in all four systems for both angles, but especially the receding angle, to diminish on soaking when using the captive bubble method. The sessile drop method, even when carried out under saturated vapor pressure conditions, generally gave our initial captive bubble advancing angle. However, because of the soaking effect, we have doubts as to whether initial advancing angles are the ones which properly relate to adsorption behavior. We have used them in deference to general practice and in the absence of definite convictions otherwise.

Finally, the sudden drop in x^0 suggests that a definite structural change occurs between 9.5° and 5.5°C in the case of carbon I, between 5.5° and -9°C in the case of ethylene, and between 16° and 9.4°C in the case of the stearic acid system. It seems unlikely, especially in the first case, that this change occurs in the solid, and we conclude that the adsorbed water film undergoes some kind of freezing process. There is no simple correlation between the temperature ranges and the types of systems, and we suppose that the interplay of factors involved is a complex one.

Potential-Distortion Model

It was of interest to us to determine to what extent the potential-distortion model, in the form of Eq. [4], would serve to treat our data. The equation can be fitted to the adsorption isotherms, the various parameters being summarized in Table I, where ϵ_0' and β' are in units of kT , and a° and α° , in \AA^{-1} . Various sets of values of the four parameters will fit the adsorption data, although the range of each is limited. We have used sets which give θ values

close to those observed. The model is thus consistent with, but is not established by, the data.

There are certain indications in the variations shown by the four parameters. The ϵ_0' values are all around unity and show no trend relative to the π^0 or π^0 values; the range between carbon I and carbon II is about that between polyethylene and the stearic acid film. The β' values, however, are about threefold higher for the first two systems relative to the second two, which indicates that the carbon surfaces generate a greater distortion in the film relative to the bulk water structure than do polyethylene or stearic acid. The a values for the carbon surfaces are about tenfold smaller than those for the other two, meaning that the attractive potential decays much more slowly in the first instances. The α values are again about the same for all systems, so that the relaxation of structural distortion is not very sensitive to the nature of the adsorbent. It thus appears that the two pairs of surfaces differ mainly in rate of relaxation of the attractive potential and in the absolute magnitude of the distortion potential.

The large difference in a values for the two pairs of surfaces suggest that the relaxation mechanism may be different. It is possible, for example, that polarization effects are more important for the carbon surfaces since these must have unsaturated or broken surface bonds, while dispersion interactions are more important for the two hydrocarbon-type surfaces. It would be consistent with this interpretation that the magnitude of the distortion effect, given by β' , is larger for the carbon surfaces than for the hydrocarbon ones since a broken bond surface should have more structuring influence than a molecularly saturated one. From an algebraic point of view the small a values for the carbon surfaces are primarily responsible for the large π^0 and π^0 values, while the near constancy of α has the effect of implying little variation in θ .

In the case of carbon I, the "frozen" film at 5.5°C shows larger values for all of the parameters, the increase being especially marked in

β' . By contrast, in the case of the film on stearic acid at 9.4°C, only the a parameter shows a major change. This comparison suggests that it would be unwise to assume that the structural change involved is the same for all systems.

In the case of the polyethylene and stearic acid surfaces, the isotherms range from about one-half to about two statistical monolayers in thickness, and there is a question as to the state of such films. The ellipsometric data, unfortunately, do not distinguish between "gas-like" and "liquidlike" water since the refractive properties of water vapor and of liquid water are virtually the same, as reflected in nearly identical molar refractions. The observation that the index of refraction of the film is close to that of bulk water thus does not actually enable us to affirm that the structure of the adsorbed film is liquidlike. It is, however, tempting to conclude from the reasonable success of the model, but especially from the near-zero (relative to bulk water) isosteric heats of adsorption, that adsorption has indeed occurred in liquidlike patches. By the term patch, we mean areas of two-dimensional condensed film for which lateral interactions would make a major contribution to the heat of adsorption to give it a value close to that of condensation of the adsorbate [see Ref. (27)].

If we add the experimental $d\theta/dT$ values for the carbon systems, the temperature-dependent extension of the model (6) leads to a prediction of T_c , the temperature at which θ should go to zero. The extension also allows calculation of the heat adsorption as a function of x ,

$$\Delta H^0 = -\epsilon_0 e^{-\alpha x} + \beta_0 e^{-\alpha x}, \quad [15]$$

where $\beta = \beta_0(1 - T/T_c)$. Some representative values are given in Table II; ΔH^0 is the enthalpy of adsorption taking bulk liquid adsorbate as the reference state. The ΔH^0 values are small, consistent with the experimental observation that the enthalpy of adsorption is close to that of condensation. Included in the table are calculated values for the heat of immersion, q_i , around 20°C. There is, unfor-

TABLE II

TEMPERATURE-DEPENDENT QUANTITIES^a

Adsorbent	<i>t</i> , °C	<i>T_c</i> , °K	ΔS^0 ^b cal mole ⁻¹	q_i^0 erg cm ⁻²	ΔH^0 ^b cal mole ⁻¹
Carbon I	21.5	621	+0.16	-8.4	-13.4
	16.5	612	+0.16	-10.9	-13.2
	9.5	634	+0.17	-5.1	-23.6
Carbon II	21.5	933	+0.11	-42.0	-31.4
	16.5	1010	+0.13	-42.3	-15.6
	9.8	962	+0.11	-45.4	-33.0

^a See Ref. (6). Calculated using $d\gamma_L/dT = -0.16$ erg cm⁻² °K⁻¹ and $\gamma_L V = 1366.7 - 2.735T$ (°C), and experimental $d\theta/dT$ values.

^b Calculated for $x = 25$ Å for carbon I and $x = 35$ Å for carbon II.

^c For surface with film at π^0 ; the sign convention is that heat is involved in immersion if q_i is negative.

tunately, no available experimental check on these values.

The large T_c values indicate that, according to the model, the temperature at which θ should go to zero is hypothetical, being above the bulk critical temperature. Alternatively, T_c is related to ΔS^0 , the entropy of the adsorbed phase relative to bulk liquid (6),

$$\Delta S^0 = (\beta_0/T_c)e^{-\alpha x}. \quad [16]$$

Thus at $x = 0$, ΔS^0 is 0.23 cal deg⁻¹ mole⁻¹ for carbon I at 21.5°C, and diminishes to 0.13 cal deg⁻¹ mole⁻¹ at x^0 . The distortion entropy is thus small in magnitude compared to say, the entropy of freezing of water, and is of the opposite sign.

The adsorption and contact angle data allow calculation of the ordinary and equilibrium works of adhesion, W and W_e , where $W = \gamma_s + \gamma_L - \gamma_{SL} = W_e + \pi^0$. These values are included in Table II.

Use of the value of $d\pi^0/dT$ for the carbon allows calculation of the corresponding energies of adhesion, E and E_e . We hope to determine shear adhesion strengths of ice to these various surfaces to observe whether they correlate with one or another of these four types of thermodynamic adhesion quantities.

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