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THE SECOND REPORT ON OLEOPHOBIC MONOLAYERS

TEMPERATURE EFFECTS AND ENERGIES OF ADSORPTION

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ABSTRACT

Experimental methods are described for observing the effect of temperature on oleophobic films adsorbed from solution. It was found that a critical temperature (T_w) existed above which the oleophobic property disappeared. The concentration of the solute (W) was found to be proportional to e^{-U/RT_w} where T_w is in degrees Kelvin. The temperature effects are reported for a number of homologous acids, amines, amides, and alcohols dissolved in either cetane or dicyclohexyl.

A quantitative kinetic treatment of the observed effects in terms of adsorption-desorption equilibria is given, and this is shown to lead to the observed relation of T_w, W, and U where U is the energy of adsorption. The relation of U to the nature of the polar group, the aliphatic chain length (N), and the solvent are discussed. The observed values of U are shown to be in good agreement with those reported for acids from data on the effect of temperature on the stick-slip boundary friction transition.

In the pure molten state these aliphatic compounds (from values of N = 6 to 8 to N = 26) were found to deposit monolayers on platinum which were also oleophobic. This happened at all temperatures above the melting point until a critical temperature τ was reached. An accurately linear relation between τ and N was found for each homologous series provided very pure compounds were used.

The relation of U to the heat of crystallization (Q) and to the chain length (N) are discussed and it is concluded that U, like Q, consists largely of the energy of cohesion due to van der Waal's forces between adjacent methylene groups of the hydrocarbon chains. Estimates are given of the adhesional energy between polar groups and the platinum foil. Calculations based on dipole moment data show that the adhesional energy consists primarily of the electrical interaction between the polar group and the metal surface.

The relation of these observations and conclusions to fundamental aspects of adsorption from solution, corrosion inhibition, and wear prevention are discussed.

PROBLEM STATUS

This is an interim report on this problem; work is continuing.

INTRODUCTION

An early investigation by us led to the discovery of the adsorption on solids of oleophobic monolayers. This was first described in NRL Report P-2206, Nov. 1943, and later in the Journal of Colloid Science (1). The properties of these films have been more fully investigated with respect to the nature of the forces involved between the adsorbed molecules and the adsorbing surface. The results obtained with platinum surfaces are presented here as the second of a series of investigations of these " ideal " monolayers.

THE SECOND REPORT ON OLEOPHOBIC MONOLAYERS TEMPERATURE EFFECTS AND ENERGIES OF ADSORPTION

Effect of Temperature on Films from Dilute Solutions

It was found, in the course of our earlier experiments (1), that increasing the temperature of solutions of long-chain polar compounds in non-polar solvents caused a decrease in the ability of the polar compounds to adsorb on solid surfaces as oleophobic monolayers. The effect of temperature changes on oleophobic properties was conveniently studied by using a simple apparatus named a "dip cell" (Fig. 1). Satisfactory cells were made from pyrex in sizes of 5, 10 and 25 ml. total capacity, the smallest size being used for the study of rare chemicals. The temperature of the liquid was measured with a thermometer inserted into the cell through a ground glass joint so arranged that the bulb was entirely immersed in the liquid which half filled the well of the cell. A rectangular dipper of platinum foil was spot welded to the end of a long, rigid platinum wire which projected beyond the ground glass joint, thus permitting the dipper to be lowered in and out of the solution by the manipulation of the free end of the wire. The cell was heated inside an electrically controlled oven which was equipped with a window and an internal light source to facilitate observation of the condition of the dipper and with an opening in the top of the oven through which the free end of the platinum wire and the thermometer stem projected. At intervals, while the temperature of the solution was being slowly increased, the dipper was raised out of the solution to observe whether the dipper surface was repellant to the liquid. If the liquid rolled off, leaving a dry surface, it indicated that the foil was covered with an adsorbed film which was oleophobic to the solution at the temperature of observation. The dipper was lowered back into the solution and the temperature was further increased until time for the next observation. This was repeated until a critical temperature (T_W) was reached at which the dipper remained completely wetted by the solution when withdrawn from the solution.

Interesting results were obtained from solutions of polar materials dissolved in hexadecane and in dicyclohexyl. The solutes were the pure preparations already discussed in Part I. The hexadecane was prepared from a commercial product by stirring it for some time in contact with concentrated sulphuric acid, separating the acid and washing the oil with an aqueous solution of sodium hydroxide. The fluid was then dried and freed from adsorbable impurities by repeated percolation through adsorption columns packed with layers of alumina and silica gel. The resulting material was divided into two batches called cetane A and cetane B; these hydrocarbon fluids consisted primarily of *n*-hexadecane and melted at 17.3°C. and 17.6°C., respectively. The dicyclohexyl was an Eastman product having a melting point of 3.6°C. A drop of each liquid did not spread on the clean surface of water maintained either at pH 3 or at pH 11, indicating high purity as far as hydrophilic adsorbable impurities were concerned.

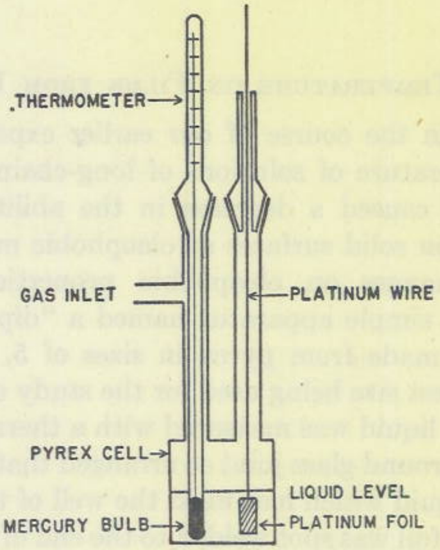

FIG. 1. "Dip cell" for observing effect of temperature on oleophobic films.

At or above a critical temperature T_W the oleophobic property of each solution always disappeared; *i.e.*, the platinum dipper was wetted permanently by the solution. It was found that T_W varied with the nature and concentration of the solute and also with the nature of the solvent. It could be reproduced with an uncertainty of less than ±1°C. and was reversible with temperature unless decomposition, oxidation, or other chemical changes occurred in the solute or solvent, or unless precipitation of the solute upon the dipper occurred during the preparation or cooling of the system. Increasing the weight percent concentration (W) of the solute always caused T_W to increase, and the initial value of

$\partial T_W/\partial W$ was the larger for the compounds which in (1) were shown by dilution experiments to be the more adsorbable on platinum. These compounds also had the longer average lifetimes of adsorption at the oil-water interface (2). The results obtained with some pure alcohols, acids, amines and amides dissolved in cetane and dicyclohexyl are summarized in Tables I and II, respectively.

A comparison of the effect on T_W of changing W for a series of straight-chain polar compounds derived from *n*-octadecane is given in Fig. 2 for solutions in cetane A. The existence of a saturation effect is evidenced by the nearly horizontal asymptotic maximum of each of these curves. The asymptotic value of T_W is smallest for the least adsorbable compounds and greatest for the most adsorbable. This agrees with the conclusions already reached from a comparison of the relative values of the initial slopes of the T_W *vs.* W curves. It will be noted that the highly adsorbable amide still shows curvature at the relatively high concentration of 2.0%. In Fig. 3 will be found data on the effect of varying the chain length of

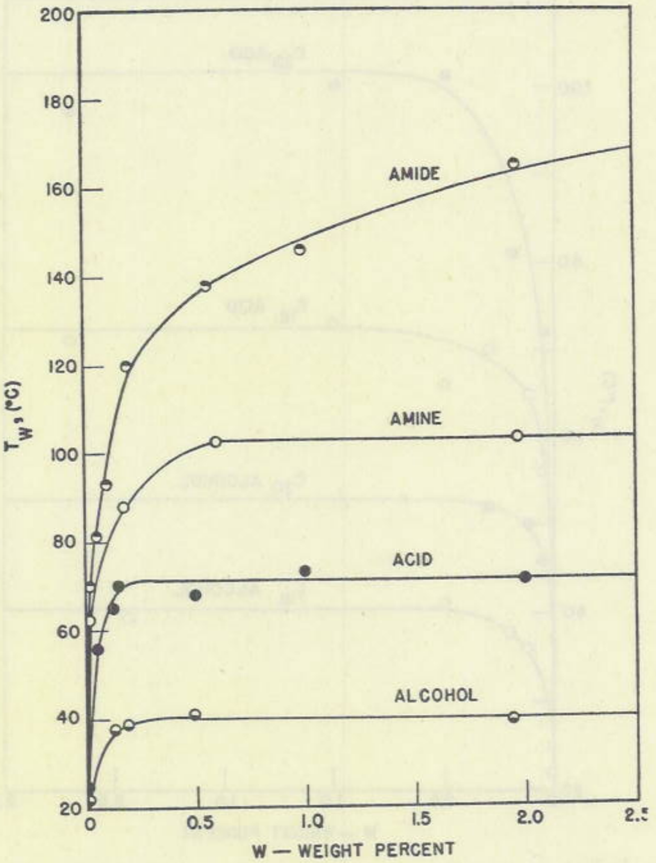

FIG. 2. Effect of concentration and polar group on 18-carbon compounds dissolved in cetane-A.

alcohols or acids dissolved in cetane A, while in Fig. 4 is the effect for homologous primary amines in dicyclohexyl. Evidently, the longer the chain length (or the smaller the solubility in the solvent) the greater is the initial value of $\partial T_W/\partial W$ and the higher the horizontal asymptotic value of T_W. In Fig. 5 are the results for octadecyl alcohol and stearic acid dissolved in dicyclohexyl and in cetane A. Evidently the observed differences arise from the fact that these compounds are less soluble in the dicyclohexyl than in the cetane A and hence adsorb from the former more readily. This is seen on comparing the results for octadecyl alcohol. The alcohol adsorbs more readily from the dicyclohexyl since the initial rapid increase of T_W with W is greater in that solvent and the curve attains its maximum value at a temperature 60°C. higher. The same qualitative results and the same 60° difference in the maxima are found on comparing the results for the C_{18} acid in the same two solvents. Similarly, the horizontal asymptote for C_{18} amine in cetane A occurs at a temperature of 103°C. while in dicyclohexyl it occurs at 160° (compare item 9 of Table I with item 7 of Table II).

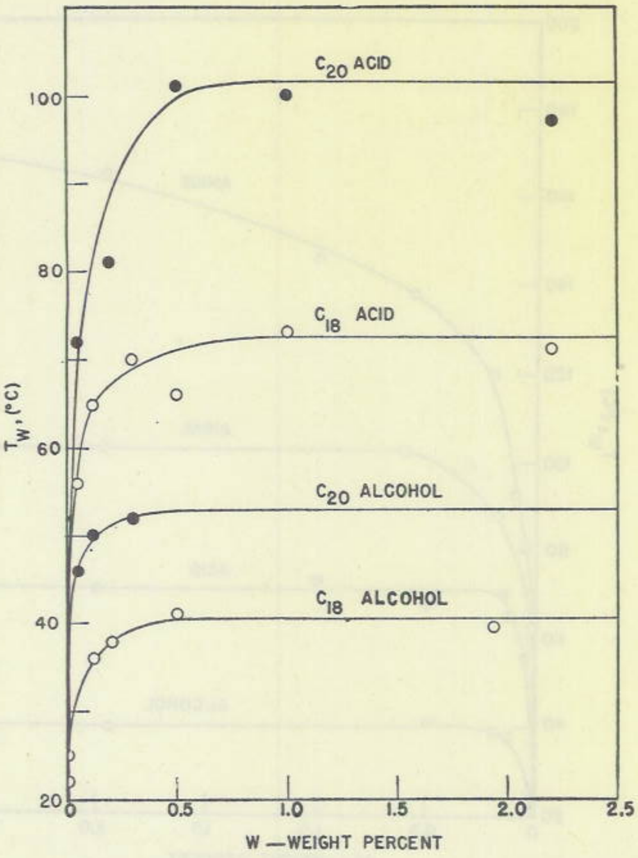

FIG. 3. Effect of chain length of acids and alcohols dissolved in cetane-A.

THEORETICAL DEVELOPMENT

An evident interpretation of the wetting of the oleophobic film at the temperature T_W is that it is caused by the desorption of some of the polar molecules and the resulting formation of holes in the film. The increased thermal agitation of the hydrocarbon chains of the adsorbed molecules with rise in temperature will act to nullify the cohesive forces between the adjacent molecules, while the polar groups adhering to the surface of the metal will also vibrate and try to leave the surface. Both thermal phenomena will act together to cause an increase in the rate of desorption of the molecules. When the factors causing desorption become dominant, the adsorbed film at dynamic equilibrium will not be packed closely enough to prevent the liquid from penetrating the film and wetting will result.

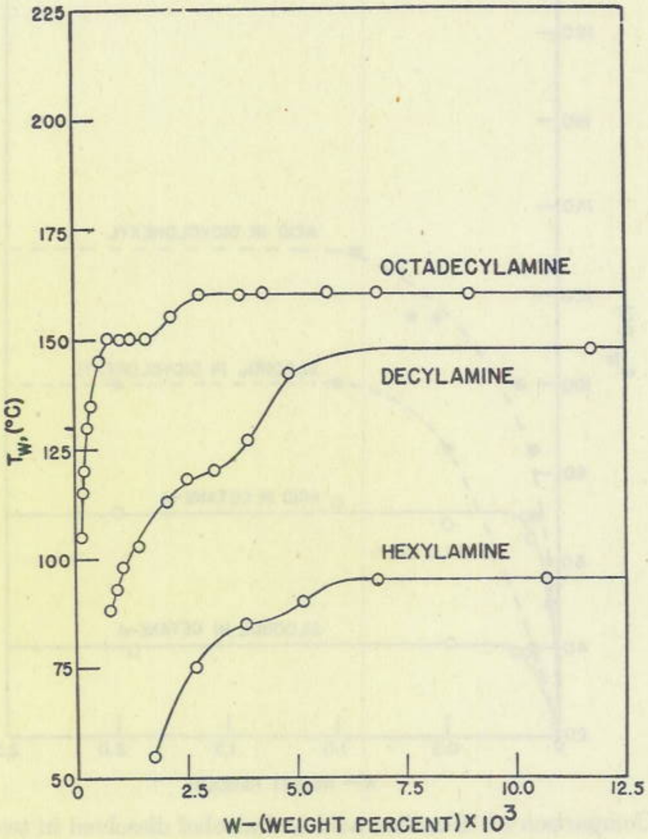

FIG. 4. Effect of chain length of amines dissolved in dicyclohexyl.

Increasing the concentration of the polar molecules increases the probability of adsorption from solution and makes the equilibrium monolayer more closely packed, Hence, wetting will not occur unless the temperature (T) is increased sufficiently to overcome the effect of the increase in molal concentration (C).

It is possible to express these ideas in a quantitative form by using the generalized Boltzmann relation of classical statistical mechanics. If the concentrations at thermal equilibrium of the molecules in two regions or states A and S having *a priori* probabilities P_A and P_S are n_A and n_S, and if the change in the potential energy per mole in going from state A to state S is U, then

$$n_A/n_S = P_A/P_S \exp{(U/RT)}, \tag{i}$$

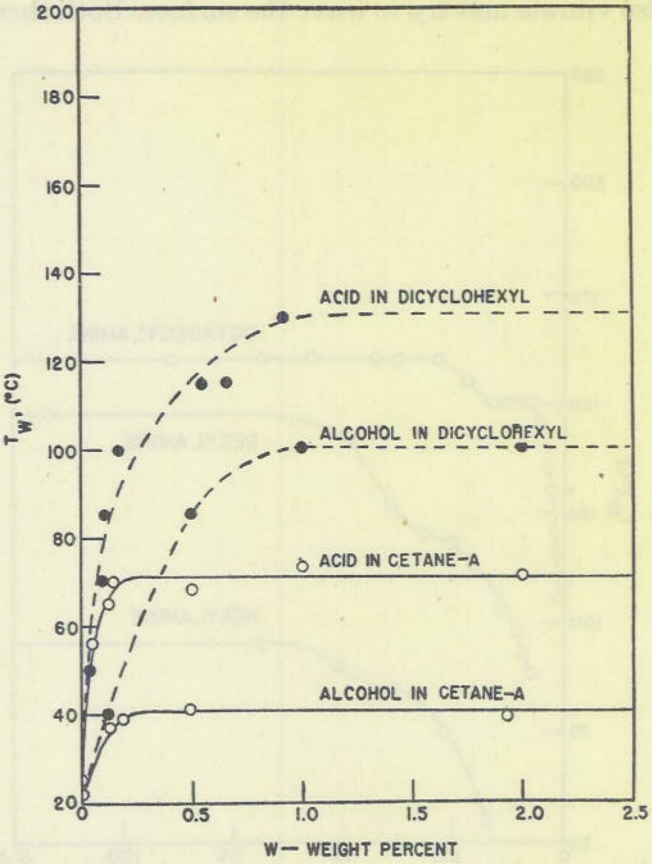

FIG. 5. Comparison of 18-carbon acid and alcohol dissolved in two solvents.

where R is the gas constant/gram mole or 1.986 cal./°C./mole. State A is selected to be that of adsorption of the solute molecules as a monolayer on the surface of the platinum foil, while state S is that of uniform distribution of the adsorbable molecues in the solution in adsorption equilibrium with the surface. The number of moles of adsorbed solute molecules per unit area (n_A) can be written $n_A = r\nu$ where r approaches unity, as the adsorbed monolayer approaches the condition of closest packing, ν obviously representing the number of adsorbed molecules in a closest packed film, and evidently $n_S = C$. Now P_A and P_S are the probabilities that the polar molecules are adsorbed or in solution, respectively, an

U is evidently the energy required to remove a mole of the adsorbed film to a condition of uniform distribution in the solution. Relation (i) can now be written

$$r\nu = C\left(\frac{P_A}{P_S}\right)\text{exp.}\,(U/RT). \tag{ii}$$

This is true whatever the precise mechanism involved in the adsorption and desorption equilibrium. Now P_A and P_S concern the probability of being adsorbed or in solution, respectively, due to all mechanisms other than those involving the thermal movement of the molecules over the potential barrier U. It should be a reasonably good first approximation to assume that

$$P_A = \alpha p\,(1 - r), \tag{iii}$$

where p is the osmotic pressure of the solute and α is a constant of the materials of the system. If there are strong mutual forces between adsorbed molecules this may not be correct, especially when r approaches unity. If the solution is dilute

$$p = CRT. \tag{iv}$$

It is also assumed that the desorption of molecules merely involves the development by a sufficient number of molecules of kinetic energy in excess of the barrier value (*i.e.*, solvent reactions with the adsorbed molecules are neglected). Hence,

$$P_S = K\,C, \tag{v}$$

where K is assumed independent of the temperature. Applying relations (iii), (iv) and (v) to (ii) there results:

$$(r/1 - r)\,\nu = \frac{\alpha CRT}{K}\,\text{exp.}\,(U/RT). \tag{vi}$$

At constant temperature relation (vi) becomes the familiar adsorption isotherm.

The experimental results in Part I indicate that films are oleophobic only when r is equal to or greater than some constant f which is itself not much less than unity; that is, wetting occurs only when r is less than f.

In order to keep the film oleophobic as the temperature is raised, it is necessary to increase the probability of adsorption from solution by increasing C so that the following relation holds:

$$C = (f/1 - f)K/\alpha R\cdot\text{exp.}\,(-U/RT). \tag{vii}$$

Assuming f like α and K is constant (or is nearly so), relation (vii) is to a good approximation equivalent to

$$C = A\ \text{exp.}\,(-U/RT). \tag{viii}$$

TABLE I

Effect of Concentration of Cetane Solution on Temperature of Wetting

Solute	M.Pt.	Cetane type	Conc. W	Temperature of wetting T_W		$\frac{1}{°K} \times 10^3$	Heat of adsorption	Figure
	°C.		*Per cent by wt.*	*°C.*	*°K.*		*cal./g. mole*	
1. *n*-Hexacosanol	79–80	A	0.093	50	323	3.10	*	
			0.506	52	325	3.08		
			1.08	56	329	3.04		
			1.90	56	329	3.04		
			2.31	51	324	3.09		
2. *n*-Eicosanol	64–5	A	0.044	25	298	3.35	*	3
			0.054	46	319	3.13		
			0.125	50	323	3.10		
			0.300	52	325	3.08		
			0.728	60	333	3.00		
			1.32	67	340	2.94		
3. *n*-Octadecanol	55.5	A	0.129	37	310	3.23	*	2, 3 & 5
			0.188	39	312	3.21		
			0.485	41	314	3.18		
			1.94	39.5	312.5	3.20		
			30.8	78	351	2.85		
4. *n*-Octadecanol (purified)	58.0	A	0.132	46	319	3.14	10,700 to 11,200	9
			0.247	48	321	3.12		
			0.271	57	330	3.03		
			0.387	57	330	3.03		
			0.585	64	337	2.96		
			0.813	83	356	2.81		
			0.990	68	341	2.93		
			1.24	80	353	2.83		
5. *n*-Hexacosanoic acid		A	0.050	63	336	2.98	*	
			0.100	71	344	2.91		
			0.498	78	351	2.85		
			1.00	75	348	2.87		
			2.00	75	348	2.87		
			3.01	83	356	2.81		
6. *n*-Eicosanoic acid	74.35	A	0.049	72	345	2.90	*	3
			0.100	81	354	2.82		
			0.50	101	374	2.67		
			1.00	100	373	2.68		
			2.00	97	370	2.70		
			3.10	104	377	2.65		

* Early runs. Too much scatter for good determination of U.

TABLE I (*Continued*)

Solute	M.Pt.	Cetane type	Conc. W	Temperature of wetting T_W		$\frac{1}{°K} \times 10^3$	Heat of adsorption	Figure
	°C.		*Per cent by wt.*	*°C.*	*°K.*		*cal./g. mole*	
7. *n*-Eicosanoic acid	74.35	A	0.0016	29	302	3.13	10,100	
			0.00194	32	305	3.28		
			0.00375	45	318	3.18		
			0.00599	60	333	3.00		
			0.00756	64	337	2.97		
			0.0102	68	341	2.94		
			0.0124	74	347	2.88		
			0.0253	73	346	2.89		
8. *n*-Octadecanoic acid	69.8	A	0.0001	25	298	3.35	*	2, 3 & 5
			0.05	56	329	3.04		
			0.126	65	338	2.96		
			0.299	70	343	2.92		
			0.500	68	341	2.93		
			1.00	73	346	2.89		
			2.01	71	344	2.91		
			3.00	73	346	2.89		
9. *n*-Octadecylamine bicarbonate	80	A	0.00005	25	298	3.35	12,400	2
			0.020	62.5	315.5	3.17		
			0.1836	88	361	2.77		
			0.497	103	376	2.66		
			1.97	103	376	2.66		
			2.07	104	377	2.65		
10. *n*-Octadecylamine bicarbonate	80	B	0.00082	65	338	2.96	14,200	6 C
			0.0024	80	353	2.83		
			0.0039	90	363	2.76		
			0.0055	97	370	2.70		
			0.0117	113	386	2.59		
			0.0234	111	384	2.60		
			0.0504	111	384	2.60		
			0.0775	112	385	2.59		
			0.130	113	386	2.59		
			0.252	110	383	2.61		
			1.3	115	388	2.58		
			6.2	130	403	2.48		
11. *n*-Octadecylamide	108–109	A	0.020	70	343	2.92	14,300	2 & 8
			0.050	81	354	2.82		
			0.100	93	366	2.73		
			0.200	120	393	2.54		
			0.463	138	411	2.43		
			0.987	146	419	2.39		
			1.97	165	438	2.28		
			3.08	171	444	2.25		

Several other derivations of (vii) can be made and each leads to the same exponential function of temperature multiplied by a weaker function of T such as T, $T^{\frac{1}{2}}$ or $1/T$. As in the classic studies of Richardson, Dushman and Langmuir on the effect of temperature on thermionic emission and on the evaporation rates of liquids, all these relations will lead to identical values of U over a considerable range of temperatures. From this theoretical argument it is evident that C should be an exponential function of T at low concentrations.

ENERGY OF ADSORPTION

From (viii) the more convenient relation (ix) is derived:

$$2.30 \log_{10} C = \text{Const.} - 1/T \, (U/R). \tag{ix}$$

Thus a plot of log C against $1/T$ should result in a straight line whose slope, multiplied by 4.57, equals the energy of adsorption U in calories/gram mole. The same value of U results if log W is used instead of log C. In the 4th column of Tables I and II are given the temperatures of wetting in degrees Kelvin, while in the 5th column are the reciprocals of those values. The data of the second and fifth columns were graphed on semilogarithmic paper, and a straight line relation was found. Generally, only small deviations from the straight line resulted. From the slope of this line and relation (ix) the value of U given in the 6th column was calculated.

Fig. 6 gives the results for octadecylamine in dicyclohexyl and in cetane B. Equally good linear graphs having practically the same slopes but different limiting or asymptotic temperatures were obtained using these solvents. Nearly as good straight lines were also obtained with the acids (see Fig. 7) and with the amide (see Fig. 8). The results with the alcohols (see Fig. 9) were more erratic due to the much lower temperature at which the T_W *vs.* W curve attains its asymptotic maximum value. The same difficulty became increasingly evident in going to all lower molecular weight solutes. Thus, the curve for decylamine (Fig. 4) approached a maximum T_W value nearly 25°C. less than that of octadecylamine, while the maximum for hexylamine was 50°C. lower. In agreement with the theory advanced in section B the lower concentration region of the T_W *vs.* W curve was exponential. At the higher concentrations, T_W increased much more rapidly with W, so that even in a logarithmic plot the higher concentration region of each curve was practically a vertical line (see Figs. 6, 7, 9). The observed temperatures of wetting and the calculated energies of adsorption were the more reproducible the greater the care exercised in handling the platinum foil dippers. It was found advisable not to flame the foil oftener, longer or hotter than necessary because a physical change in the surface structure of the platinum foil

TABLE II

Effect of Concentration of Dicyclohexyl Solution on Temperature of Wetting

Solute	M.Pt.	Special atmosphere	Conc. W	Temperature of wetting T_W		$\frac{1}{°K} \times 10^3$	Heat of adsorption	Figure
	°C.		Per cent by wt.	°C.	°K.		cal./g.-mole	
1.								
n-Octadecanol	55.5		0.115	40	313	3.19	8,600	5 & 9
			0.500	85	358	2.79		
			1.00	100	373	2.68		
			2.00	100	373	2.68		
			2.99	100	373	2.68		
			4.02	105	382	2.62		
2.								
n-Octadecanol	58.0		0.112	34	307	3.26	10,000	9
			0.157	33	306	3.27		
			0.360	55	328	3.05		
			0.383	56	329	3.04		
			0.602	72	345	2.90		
			0.895	77	350	2.86		
			3.14	110	383	2.61		
3.								
n-Eicosanoic acid	74.35		0.010	67	340	2.94	12,700	7
			0.020	75	348	2.87		
			0.040	89	362	2.76		
			0.080	118	391	2.56		
			0.16	119	392	2.55		
			0.49	118	391	2.56		
			1.0	117	390	2.57		
			1.9	118	391	2.56		
			2.0	134	407	2.46		
4.								
n-Octadecanoic acid			0.0413	50	323	3.10	10,000	5 & 7
			0.15	80	353	2.83		
			0.176	100	373	2.68		
			0.553	115	388	2.58		
			0.915	130	403	2.48		
5.								
n-Dodecanoic acid	43.8		0.0416	26	299	3.34	2,800	7
			0.102	99	372	2.69		
			0.114	110–115	383–388	2.67–2.58		
			0.559	120	393	2.54		
			1.47	127	400	2.50		
			2.61	127	400	2.50		
6.								
pri-n-Octadecylamine	51.5–52.5	Helium & CO_2-free air	0.000380	135	408	2.45	14,800	6 B
			0.000622	145	418	2.39		
			0.000860	150	423	2.36		

TABLE II (*Continued*)

Solute	M.Pt.	Special atmosphere	Conc. W	Temperature of wetting T_W		$\frac{1}{°K}\times 10^3$	Heat of adsorption	Figure
	°C.		*Per cent by wt.*	°C.	°K.		*cal./g.-mole*	
			0.00132	150	423	2.36		
			0.00191	150	423	2.36		
			0.00291	150	423	2.36		
			0.00389	150	423	2.36		
			0.00553	150	423	2.36		
			0.00833	150	423	2.36		
7. *n*-Octadecylamine			0.0000372	90	363	2.75	14,800	4,6 A
bicarbonate	80		0.0000656	100	373	2.68		
			0.000101	105	378	2.65		
			0.000131	115	388	2.58		
			0.000177	120	393	2.54		
			0.000280	130	403	2.48		
			0.000350	135	408	2.45		
			0.000358	135	408	2.45		
			0.000550	145	418	2.39		
			0.000750	150	423	2.36		
			0.00102	150	423	2.36		
			0.00126	150	423	2.36		
			0.00162	150	423	2.36		
			0.00218	155	428	2.34		
			0.00281	160	433	2.31		
			0.00374	160	433	2.31		
			0.00427	160	433	2.31		
			0.00572	160	433	2.31		
			0.00685	160	433	2.31		
			0.00898	160	433	2.31		
8. *n*-Decylamine			0.000770	88	361	2.77	11,500	4
bicarbonate			0.000965	93	366	2.73		
			0.00108	98	371	2.69		
			0.00144	103	376	2.66		
			0.00208	113	386	2.59		
			0.00252	118	391	2.56		
			0.00316	120	393	2.54		
			0.00391	127	400	2.50		
			0.00485	142	415	2.41		
			0.117	147	420	2.38		
9. *n*-Hexylamine			0.00172	55	328	3.05	6,400	4
bicarbonate			0.00269	75	348	2.88		
			0.00341	90	363	2.75		
			0.00382	85	358	2.79		
			0.00511	90	363	2.75		
			0.00689	95	368	2.71		
			0.0107	95	368	2.71		

TABLE II (*Continued*)

Solute	M.Pt.	Special atmosphere	Conc. W	Temperature of wetting T_W		$\frac{1}{°K} \times 10^3$	Heat of adsorption	Figure
	°C.		*Per cent by wt.*	°C.	°K.		*cal./g.-mole*	
10. *n*-Octadecylamide			0.000480	100	373	2.68	13,100	
			0.000995	110	383	2.61		
			0.00172	120	393	2.54		
			0.00199	125	398	2.51		
			0.00236	130	403	2.48		
			0.00251	130	403	2.48		
			0.00355	135	408	2.45		
			0.00364	135	408	2.45		
			0.00381	135	408	2.45		
			0.00442	135	408	2.45		
			0.00580	135	408	2.45		

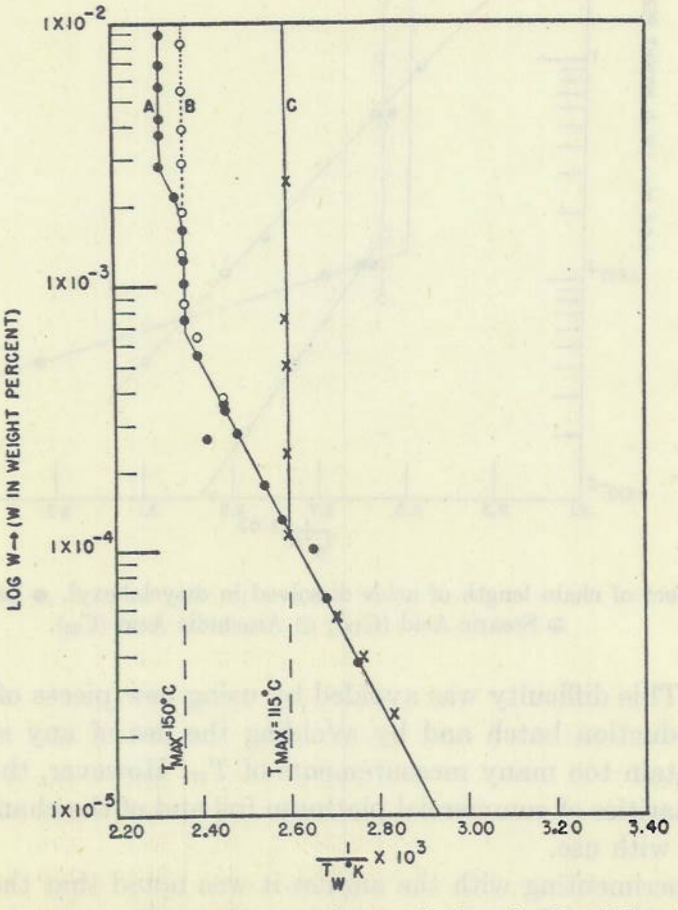

FIG. 6. Adsorption of octadecylamine from solutions in dicyclohexyl: ● Curve A, bicarbonate in atmosphere; ○ Curve B, amine in CO_2-free air; × Curve C, bicarbonate in atmosphere using cetane B.

developed gradually as the result of such treatment. This was evidenced by the appearance of a dull gray color in the foil which microscopic examination showed was associated with the formation of a network of fine cracks. The occurrence of this greying was unpredictable, the results varying with the sample of foil, the source, and the heat treatment. Variations in U and T_W were found to occur as this physical change developed. This difficulty was avoided by using new pieces of foil from the same production batch and by avoiding the use of any single piece of foil to obtain too many measurements of T_W. However, these variations are peculiarities of commercial platinum foil and of the changes in surface structure with use.

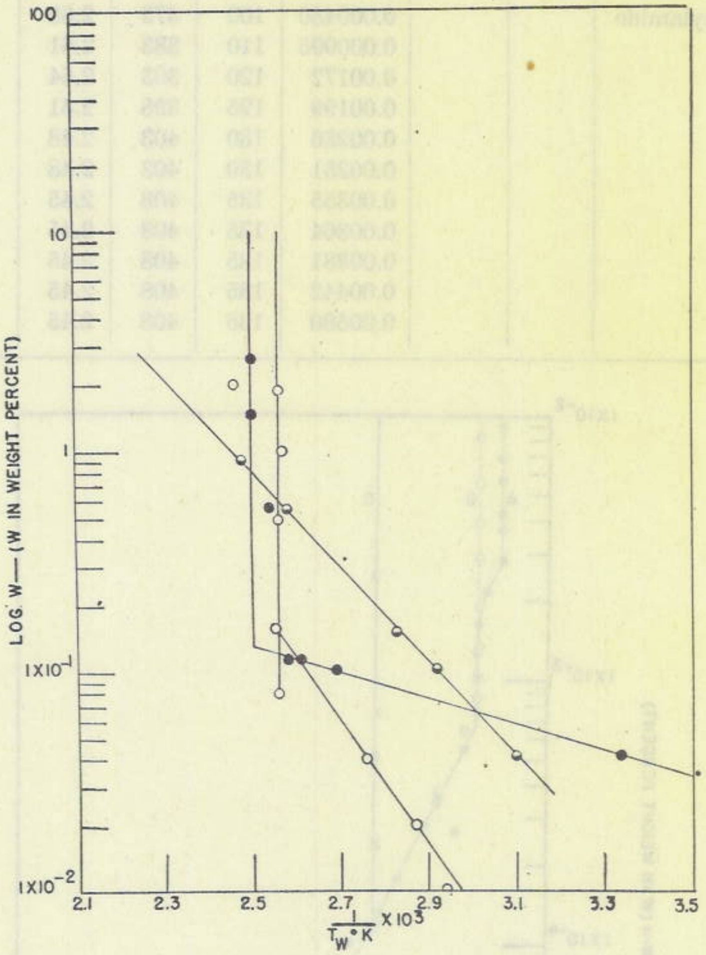

FIG. 7. Effect of chain length of acids dissolved in dicyclohexyl. ● Lauric Acid (C_{12}); ◒ Stearic Acid (C_{18}); ○ Arachidic Acid (C_{20}).

In experimenting with the amines it was noted that the vertical rise of the log W *vs.* $1/T$ curve contained an abrupt but reproducible bend or displacement of 10°C. (see curve A of Fig. 6). It was finally discovered that an impurity in the octadecylamine was the cause. The melting point of the amine used was around 80°C. and the reported value in Beilstein is 53°C. As the formation of an amine bicarbonate by reaction of the amine with CO_2 in the moist air was likely, some of the compound was heated for 30 minutes in a vacuum just above its melting point and, after the evolved CO_2 had been pumped off, the sample was cooled in CO_2-free air. The melting point was then 51.5–52.5°C. indicating good purity. While in CO_2-free air this amine was transferred to the dicyclohexyl and measurements of T_W were made. The resulting curve (see Curve B of Fig. 6) was identical with that obtained before the heat treatment and degassing except that the abrupt bend was absent. Hence U was the same for the amine and the amine bicarbonate and the presence of bicarbonate merely increased by 10°C. the maximum value of T_W attainable. A similar displacement of 25°C. was encountered in the experiments with decylamine in dicyclohexyl, and even the less detailed hexylamine curve showed evidence for a 10°C. displacement (see Fig. 4).

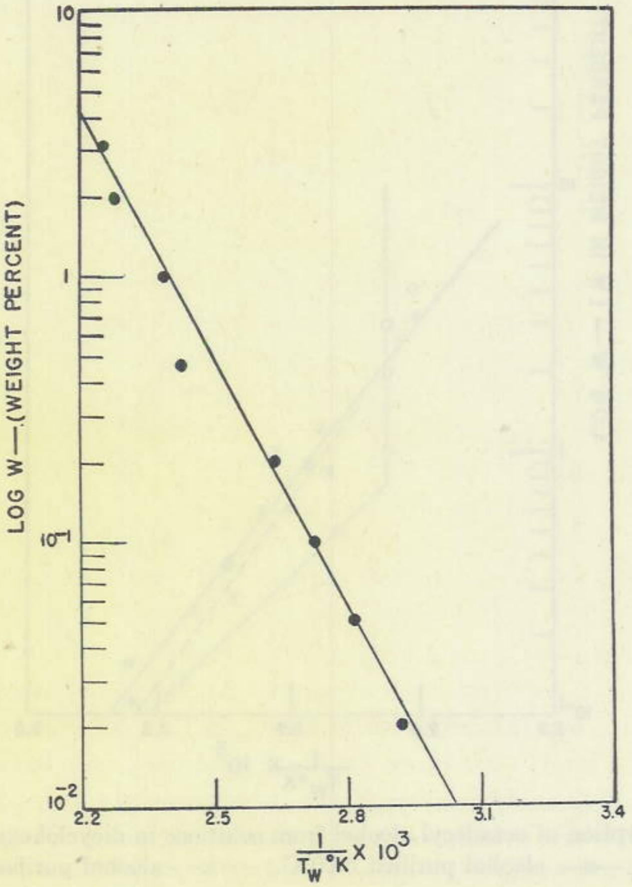

FIG. 8. Adsorption of octadecylamide dissolved in cetane A.

A comparison has been made in Table III of the values of U taken from Tables I and II. It will be noted that the value of U for films on platinum is, to a first approximation, independent of the solvent. Thus, the best value for octadecylamine in cetane is 14,200 cal./mole while in dicyclohexyl it is 14,800. Similarly, the adsorption energy of octadecyl amide is 14,300 in the former solvent and 13,100 in the latter. There is evidently some decrease in U with the number of carbon atoms per molecule, since with dicyclohexyl the values of U obtained are 14,800 cal./mole for the octadecylamine, 11,500 for the decylamine, and around 6,400 for the hexylamine. This indicates a rate of decrease for long-chain compounds of approximately 400 cal./mole per carbon atom. From the values of 12,700 obtained for eicosanoic acid, 10,000 for stearic acid, and 2,800 for lauric acid in dicyclohexyl, there appears to be a linear decrease in energy per carbon atom of approximately 1,200 cal./mole (see Fig. 11).

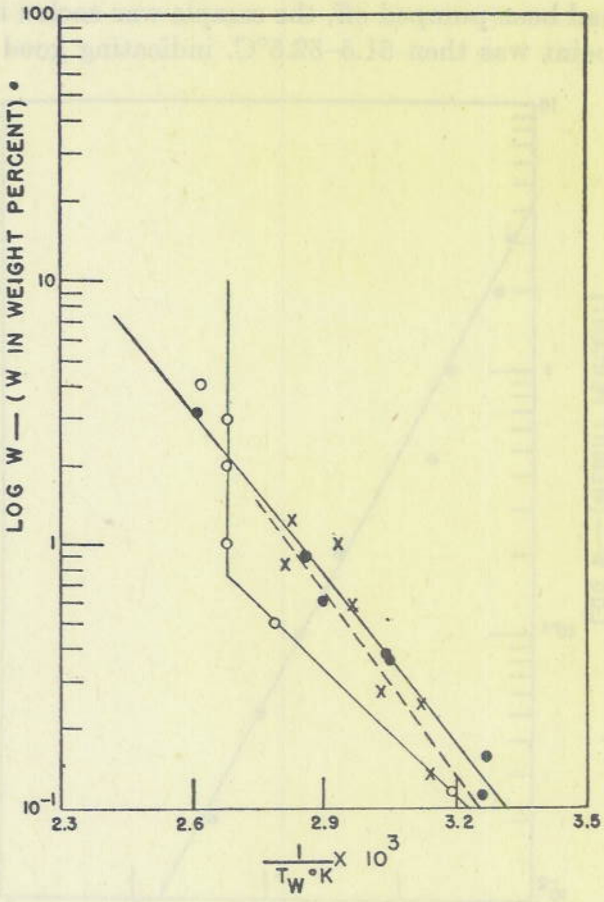

FIG. 9. Adsorption of octadecyl alcohol from solutions in dicyclohexyl;—○— alcohol m. pt. 55.5°C.; —●— alcohol purified 58.0°C.; – – x – – alcohol purified 58.0°C. and in cetane.

On comparing the results for the group of C_{18} compounds in the same solvent, dicyclohexyl, the values of U are 14,800 cal./mole for the amine, 13,100 for the amide, 10,000 for the acid and between 8,600 and 10,000 for the alcohol.

The work of Smyth and Rogers on the dimerization of carboxylic acids in nonpolar solvents is well known (4) and it might be inferred that it is the dimer molecule which adsorbs on the platinum foil in these experiments; in fact, Frewing (5) concluded from his study of the stick-slip phenomena for oil solutions of the fatty acids that the acids adsorbed on steel as dimers. But in our earlier work on oleophobic films (1) it was concluded that the adsorbed molecules were vertically oriented monomers which were nearly close packed. The later electron diffraction studies by Brockway and Karle (3) have demonstrated the essential correctness of those conclusions. If only dimer molecules were adsorbed, it is difficult to understand how the observed orientation of monomers could have occurred. It is much more likely that in the dilute solutions used in these

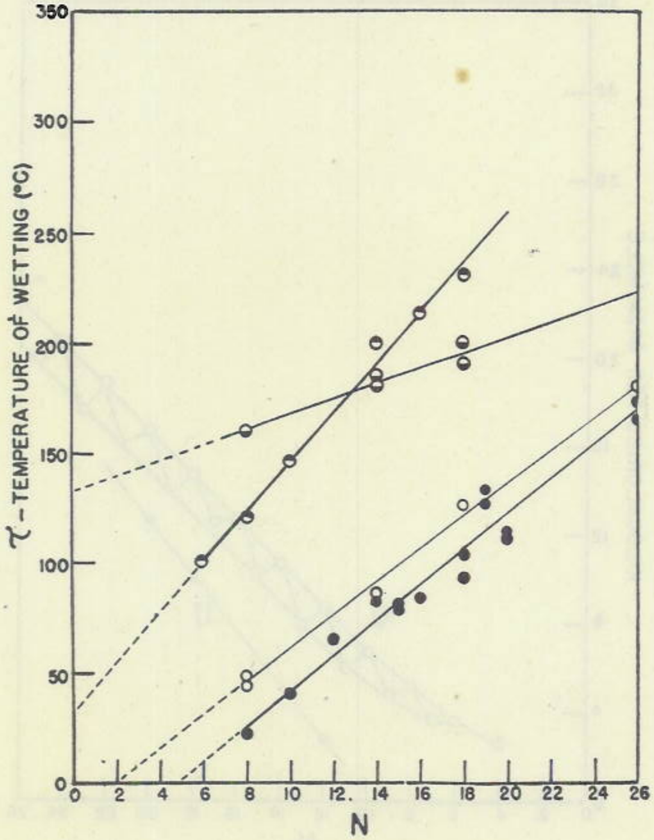

FIG. 10. Temperature of wetting τ of oleophobic films from molten pure compounds.

● Acids ◓ Amines
○ Alcohols ◒ Amides

experiments the acid molecules were present as both monomers and dimers and the adsorption equilibrium observed was between the monomers in solution and those attached to the adsorbing surface. Hence, U is believed to be the energy of adsorption of the monomeric acid. For the same reason it is believed that the value of U obtained for each of the other polar solutes discussed here is the adsorption energy of the unassociated molecule.

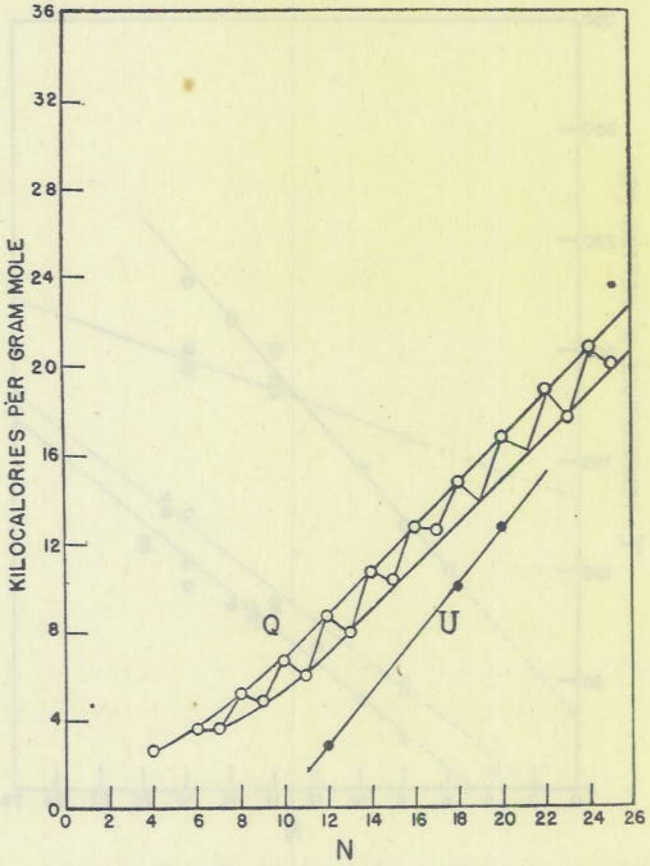

Fig. 11. Energy of adsorption and heat of crystallization of acids. Note: Q from data of Garner, King *et al.*; U from solutions in dicyclohexyl.

The more recent dielectric constant studies of Le Fevre and Vine (6) and of Pohl, Hobbs and Gross (7) on solutions of carboxylic acids in nonpolar solvents have shown that equilibrium mixtures of monomers and dimers must exist, the proportion of monomers increasing with the dilution. The results of the latter showed that at a molal concentration of 10^{-3} almost half of the solute molecules were monomers. It is to be expected that the proportion of monomers to dimers will also increase with the temperature, and a statistical treatment having that result has been given by Rushbrooke (8). These dielectric studies lend support to

TABLE III

Comparison of Melting Points, T_{max}, U and τ for Solutes Studied

Compound	M.Pt.	Approximate T_{max}[a]		U in cal./g.-mole		τ Pure, molten
		in cetane	in dicyclo-heyxl	in cetane	in dicyclo-hexyl	
	°C.	°C.	°C.			°C.
C_{26} Alcohol	79–80	56				180
C_{20} Alcohol	64–65	67				
C_{18} Alcohol	55.5	41	105		8,600	125
	58.0	80	110	10,700–11,200	10,000	
C_{26} Acid		80				165,175
C_{20} Acid	74.4	101	120		12,700	110,113
		75		10,100		
C_{18} Acid	69.8	73	130		10,000	92,103
C_{12} Acid	43.8		127		2,800	65
C_{18} Amine	51.5–52.5		150		14,800	
C_{18} Amine·HCO_3	80	105,115	165	12,400–14,200	14,800	230
C_{10} Amine·HCO_3			147		11,500	145
C_6 Amine·HCO_3			95		6,400	100
C_{18} Amide	108–109	>170	135	14,300	13,100	190,200

[a] T_{max} = Approximate asymptotic value of T_W *vs.* W curve from measurements on dilute solutions.

our conclusion that under the conditions of our adsorption experiments enough monomers were present to have been responsible for the adsorbed films observed.

APPARENT SATURATION EFFECTS IN DILUTE SOLUTIONS

As an aid to interpreting the phenomenon at high concentrations (as in Fig. 3), the asymptotic maximum values of the T_W *vs.* W curves (denoted here as T_{max}) have been compared with the melting points of the solutes. For a given solute T_{max} bears an inverse relationship to the solubility. Although T_{max} may be smaller, equal to, or larger than the melting point of the solute when dissolved in cetane, it is always larger than the melting point when dissolved in dicyclohexyl. For a series of polar compounds of the same chain length, the values of T_{max} in a given solvent increase with the energy of adsorption U.

Several possible explanations for this asymptotic behavior can be suggested: (1) The adsorbed monolayer may become liquid due to increased thermal agitation at the temperature T_{max}; (2) Although the solubility of the solute rises with temperature, it is not a significant factor until micelle formation begins at temperature T_{max}. Thereafter, increasing the concentration cannot increase the probability of adsorption and there results a constant value of T_W; (3) Although the solubility increases with temperature, it does not increase rapidly enough, and the observed T_W *vs.* W curve is merely the effect of increased thermal agitation causing desorption. However, at a high enough temperature, T_{max}, solubility effects become so important that the increased probability of adsorption due to a rise in concentration is compensated by the increased rate of desorption due to the effect of temperature on the solubility.

Theory (1) is not acceptable since it does not provide an explanation for the observed large differences in T_{max} with solvent nor does it account for the persistence of oleophobic behavior at and above the same T_{max} when the concentration of the solution is greatly increased. Explanations (2) and (3) are both consistent with the theoretical treatment advanced in section B in which it was postulated that solvent effects were unimportant in the low concentration region. They are also consistent with the observed marked increase of T_{max} in going to a poorer solvent. The nearly vertical rise in the log W *vs.* $1/T_W$ graphs of Figs. 6, 7 and 9 is also understandable if a rapid increase in the solvent action occurs at the temperature T_{max}.

ADSORBED FILMS FROM MOLTEN POLAR COMPOUNDS

A small pyrex dip cell permitting manipulation with from 1 to 2 ml. of solution was used to study the formation of oleophobic films on platinum from a melt of each of the pure polar solutes described in sections A through D. The temperature at which the film commenced to be wetted by the molten liquid is denoted as τ. In such experiments it was found absolutely essential to use polar compounds of high purity. In many instances a small percentage impurity which had caused a melting point change of a few degrees caused changes in τ of 10°–60°C. The values of τ obtained are given in Table IV and are graphed in Fig. 10 as a function of the number (N) of carbon atoms per molecule. The result is a series of straight lines which (except for the amides) tend to converge close to 0°K. Where compounds gave graphic points which deviated greatly from the straight line, they were found to be less pure and subsequent careful purification always resulted in a good fit leaving no doubt of the essential correctness of the linear relationship between τ and N. It is noteworthy that the graph for the alcohols lies between that for the acids and that for the amines.

Oleophobic films on platinum could always be prepared from those melted polar compounds which had been found to adsorb as oleophobic films from solutions in nonpolar solvents. But these films could not be prepared from such pure liquid compounds as oleic acid, oleyl alcohol, stearolic acid and linoleic acid. After oleophobic films have been formed from the melted polar compounds, the contact angles with drops of hexadecane and water were observed at 25°C. Typical results were as follows:

	Against cetane	Against water
Octadecyl Acid...........	27°	80°
Octadecyl Alcohol.........	30°	84°
Octadecyl Amide.........	27–30°	88°
Octadecyl Amine.........	31–35°	88°
Decyl Amine.............	30°	high, but drops rapidly

These angles are of the same magnitude as those reported in Part I, Sections (d) and (g), for oleophobic films formed from dilute solutions. The results of Table IV qualify the earlier statement in Section (d) of Part I that oleophobic films on platinum could not be prepared from solutions of amines, acids and alcohols having values of N less than 8 for the first two series and less than 10 for the third. If the pure melted solute is used, the lowest homologues giving oleophobic films are hexylamine, octanoic acid and octyl alcohol. It was not possible to prepare films from pure butylamine, even at low temperatures.

TABLE IV

Effect of Chain Length on Temperature of Wetting τ (°C.) of Films Adsorbed from Molten Pure Normal Aliphatic Compounds

Number of carbon atoms	Acids	Alcohols	Amines	Amides
4				
6			100	
8	22	44,48	120	160
10	40		145	
12	65			
14	82	85	200	180,185
15	78,80			
16	83		215	
18	92,103	125	230	190,200
19	123,125			
20	110,113			
26	165,175	180		

To facilitate comparison, the pertinent values of τ from Fig. 10 have been inserted in the last column of Table III. It will be seen that τ is sometimes approximately equal to the largest value of $T_{\max}$ found from the studies of dilute solutions, but more often it is larger; for the long-chain compounds τ is much greater than $T_{\max}$. It appears that only when a poor solvent is used does $T_{\max}$ approach the value of τ. The larger values of τ are understandable, for the liquid polar compound is then in equilibrium with the adsorbed monolayers. Whenever an adsorbed molecule is released by the surface it is replaced rapidly by a like molecule. Here it is difficult to understand how wetting can occur unless: (a) a temperature is reached at which the liquid compound begins to wet the close-packed adsorbed film of like molecules; (b) a temperature is reached at which the probability of desorption or "evaporation" from the surface becomes so great that an oriented film becomes very improbable. The most plausible interpretation is that given in (b).

The preceding conclusion leads to an interesting calculation based on the hypothesis that condition (b) occurs when the probability of desorption due to thermal effects becomes sufficiently large. The probability of desorption is assumed as in Section B to be proportional to Exp $(-U/RT)$; this is equivalent to the requirement that U/RT shall be small. Hence, at temperature τ it is assumed that

$$\frac{U}{R\tau} \leqq b^2, \tag{x}$$

where b^2 is not large. Since our earlier experimental results (1) and later electron diffraction measurements (3) have shown these adsorbed films are monomolecular and closely packed, it is reasonable to assume that the molar energy of adsorption U should consist of a term U_o due to attraction of the polar group for the adsorbing surface and a term U_c due to the cohesive forces between adjacent methylene groups of the hydrocarbon chains. If the number of carbon atoms (N) per molecule is large enough, and if the polar groups aren't so large as to prevent close enough approach of the methylene group, then $U_c = Nu$, where u is the energy of cohesion per methylene group. Hence,

$$U = U_o + Nu. \tag{xi}$$

The condition (x) for wetting of the film from the melted oleophobic polar compound can now be written

$$\frac{U_o + Nu}{R\tau} \leqq b^2 \tag{xii}$$

or

$$\tau \geqq \frac{U_o}{b^2R} + N\frac{u}{b^2R}. \tag{xiii}$$

Relation (xiii) predicts a straight line relation between τ and N with a positive slope just as was found in Fig. 10. Evidently from (xiii) the constant u can be computed from

$$u = b^2R\frac{\partial\tau}{\partial N}. \tag{xiv}$$

The observed values of $\frac{\partial \tau}{\partial N}$ from Fig. 10 were inserted in (xiv) and values were found for u/b^2. The best values of U given in Table III for the C_{18} compounds were inserted in relation (x) as were the corresponding values of τ of Table IV. The resulting calculated values for b^2 were then applied to the above values of u/b^2 to calculate u. When these values of U, u and N were inserted in relation (xii) U_o could be computed. In Table V are listed U, τ, b^2, u and U_o for the four types of compounds

TABLE V

Summary of Calculated Data on Cohesional and Polar Energies of Adsorption

Type compound	U	τ	b^2 from x	u from xiv	U_o from xi	u from xvii
	cal./mole	°K.		*cal./mole*	*cal./mole*	*cal./mole*
C_{18} Alcohol	10,000	393	12.8	188	6,600	
C_{18} Acid	10,000	378	13.3	212	6,200	1,200
C_{18} Amine	14,500	508	14.4	336	8,400	400
C_{18} Amide	13,700	468	14.7	103	11,900	

studied. It is noteworthy that the four calculated values of b^2 vary less than 15%.

RELATION OF U TO HEAT OF CRYSTALLIZATION

From Table III the energy of adsorption (U) increases with the number of carbon atoms (N). A linear relation of U and N could be expected for large values of N from relation (xi) provided the polar group is not too large. In Fig. 11 the results for acids have been graphed and do lie on a straight line. Turning to the condition of aliphatic acids when in the 3-dimensional crystal state, it is known that the molecules cohere in plane layers due to the weak forces between adjacent aliphatic chains and the layers adhere in pairs by hydrogen bonding between the carboxyl groups. If Q_p is the molal energy of the crystal due to the hydrogen bonding (or to dimerization), Q_c the molal energy of the cohesional forces between the adjacent chains in the same layer, and Q_{me} the molal energy due to end-to-end cohesion occurring in alternate layers between the methyl terminal groups of the acid molecules, then the total molal energy of crystallization Q is

$$Q = Q_p + Q_{me} + Q_c. \qquad \text{(xv)}$$

If N is large and the polar group does not prevent close packing, then it is reasonable to assume that $Q_c = Nq$, where q is the cohesional energy per methylene group. Hence,

$$Q = (Q_p + Q_{me}) + Nq. \qquad \text{(xvi)}$$

On recalling the earlier similar relation (xi) between U and Nu, an evident and reasonable approximation is that $q = u$. This need not be exactly true, since the unit of the crystal of acid is the dimer and when it melts little dissociation occurs, while the unit of the adsorbed film is the monomer. Hence conditions of packing are not identical. The error in the energy by making the approximation $q = u$ becomes smaller as N increases. Differentiation of (xi) and (xvi) then gives the result that if N is large:

$$\left(\frac{\partial U}{\partial N}\right)_{N\text{ large}} = \left(\frac{\partial Q}{\partial N}\right)_{N\text{ large}} \qquad \text{(xvii)}$$

Garner and his coworkers have published accurate data on the molal heats of crystallization of the fatty acids (15, 16, 17, 18); their results have been plotted in Fig. 11 also. It will be noted that U is always less than Q but at large values of N both graphs have become straight lines which should meet at values of N of approximately 30. This is a check on relations (xvi) and (xvii). From Fig. 11 it is found that $q = 1000$ cal./mole of methylene groups for the series of even numbered acids, while U is 1200 cal./mole of methylene groups. These values have been inserted in Table V for comparison with those computed from relation (xiv). The value of $\frac{\partial U}{\partial N}$ for amines for large N computed from the data of Table III is 400 cal./mole of methylene groups, and this value has been added to the last column of Table V. The agreement of the two values of u is good in this case.

Discussion

From the theoretical interpretation given the T_W *vs.* W curve, the values of $T_{\max}$, τ, U and U_o would be expected to vary with the nature of the adsorbing surface, τ and U being higher when the polar group is able to react with the atoms of the adsorbing surface. An interesting calculation can be made using the values of U_o listed in Table V in conjunction with dipole moment data to obtain approximate values for the distance between the center of the dipole and the surface of the metal on which the polar material is adsorbed. A simple treatment for the interaction of a rigid dipole with a conducting and polarizable surface can be made by assuming that the only forces involved are those of attraction between the dipole and its mirror image, as was done by Lorenz and Lande (19, 20) using the formula

$$U_o = \frac{\mu^2}{4r^3}(6.06 \times 10^{23}),$$

where μ, r and 6.06×10^{23} are the dipole moment, the distance of the midpoint of the dipole to the surface and Avogadro's number, respectively. Maximum possible distances of 1.2 A for the alcohols and 0.9 A for the amines were obtained where the dipoles were assumed to be normal to the surface. A more plausible approach in the case of the alcohols oriented with their long hydrocarbon axes normal to the surface is made by assuming that the dipole is not codirectional with the molecular axis. A deviation of up to 65° from normal can be calculated using the tetrahedral carbon angle and 105° for the C—O—H angle together with the moments associated with the O—C and O—H bonds. The resulting smaller normal component of the moment leads to the shorter calculated distance of 0.7 A for the alcohols. Measurements on ball models showed that the midpoint of the dipole lies between 1.1 and 1.9 A for the alcohol and 1.1 and 1.6 A for the amines. The agreement is as good as can be expected from the simple assumptions made.

The results of similar experiments with adsorbing materials other than platinum will be presented in Part III. These methods and results appear to be of value in the study of adsorption from solution and of adsorbed monolayers. Some of the conclusions obtained here are also closely related to basic phenomena involved in the wear-preventive action of mild boundary lubricants as well as to the rust-inhibitive property imparted to oils by aliphatic polar additives. A theoretical discussion and the results of experiments on the latter will soon be presented elsewhere. The connection with the early studies of wear-prevention is obvious, for many of the polar compounds described here were among those most carefully investigated by Sir William Hardy in his classic experiments on the static coefficient of friction of lubricated surfaces (9). An authoritative review of the subject of boundary lubrication has recently been given by Bowden and Tabor (10).

We have demonstrated the existence of an adsorption equilibrium between the polar molecules adsorbed by the metal and dissolved in the oil, and of the rapid decrease at higher temperatures in the number of adsorbed molecules per unit area. Although the temperature of wetting, (T_W) increases considerably with the concentration of additive used, in present day practice polar additives are rarely used in excess of a few per cent by weight. Therefore, the temperature of wetting to be expected from such a range of concentrations of additives in hexadecane will be around the apparent asymptotic values ($T_{\max}$) indicated earlier. These values are from 40°–100°C. for the alcohols, 70°–130°C. for the acids, 100°–150°C. for the amines, and 140°–170°C. or more for the amides. Of course, these temperature ranges will vary if solvents other than cetane or dicyclohexyl are used; they may also vary considerably where a chemical reaction with the adsorbing metal takes place. However, the relative order of these values is, in all likelihood, the relative order of the chemical activity of these compounds when adsorbed from any of the petroleum oils used in practice. The aliphatic amines are not particularly stable in contact with iron or steel above 60°C., and the metals used in practice would eventually react at temperatures above 100°C. with the additives discussed here with the exception of the alcohols. Hence, it appears unlikely that additives will be found which will remain adsorbed from oil solutions at high temperatures but which will not react chemically with the usual bearing metals. When boundary lubricants are employed it is desired that the load-carrying capacity be improved over the entire range of operating temperatures. Temperatures of from 50° to 100°C. in bearings and up to 150–200°C in internal combustion engine cylinders can be expected. The preceding conclusions make it evident that improvements in boundary lubrication manifested in tests with lubricants and bearings or engines at ordinary temperatures can be expected to be lost at the higher operating temperatures unless it is permissible to use wear-preventive additives capable of chemically reacting to some extent with the metals in contact with the oil. It would also appear that the more unreactive the bearing metal used, the lower the load-carrying capacity which can be imparted to it by an oil containing a boundary lubricant. This suggests that bearings made of unreactive metals like gold and platinum will be unsatisfactory for reasons other than the high cost of the metal.

In the past seven years Tabor (11), Hughes and Whittingham (12), Frewing (13) and Bowden, Gregory and Tabor (14) have used the Bowden "stick-slip" apparatus for numerous boundary friction and lubrication studies of the effect of temperature on pure compounds such as aliphatic hydrocarbons, acids, alcohols, esters and soaps. A transition from smooth sliding to "stick-slip" occurred at or above a temperature (T_S) which was characteristic of the metals, the polar compound, and the concentration. They concluded that the transition effect was due to the disorientation or desorption of the polar molecules above a critical value which depended upon the nature of the metal surface, the chain length, and the active end group of the polar compound.

Frewing (5) studied the value of T_S for mild steel on steel with solutions in white mineral oil and found that the concentration of solute was an exponential function of the temperature for each solute studied. By assuming that (1) desorption occurred at higher temperatures, (2) "stick-slip" occurred when the film density dropped below a critical value, and (3) the Van't Hoff isochore could be applied to the adsorption equilibrium constant, he derived a relation equivalent to our relation (viii). This was applied to a large number of careful measurements of T_S as a function of W, and from these he was able to calculate U for a series of aliphatic compounds. At present, a good comparison of our results with Frewing's (5) is difficult since our observations relate to platinum surfaces with dicyclohexyl or cetane as the solvent while his concerned mild steel and solutions in a white mineral oil. The effects of temperature on solubility are involved in our observation of T_W, but in observations of T_S the shearing stress caused by the motion of the slides may be important in determining the temperature of the film transition observed.

Despite these differences, Frewing's work and ours agree in that the concentration and reciprocal of the absolute temperature involved in the transition have an accurate linear relation; however, the almost vertical rise in log W at temperature $T_{\max}$ was not encountered by Frewing. Another interesting difference is the much larger solute concentrations needed by Frewing to observe the change in T_S with concentration: for example, his data on stearic acid involved concentrations in white oil varying from 0.1% to almost 3% while ours involved concentrations in cetane or in dicyclohexyl of from 0.01% to 0.5%. These differences may be partly due to a greater solubility of the acid in the white mineral oil and to the need in Frewing's work for closer packing of the adsorbed molecules in order to prevent metal-to-metal contact and subsequent stick-slip. Frewing's values of U for capric, myristic, and stearic acids were 12.5, 13.0 and 13.0 Kcal./mole while for α-bromostearic, α-iodostearic, and α-hydroxystearic acid they were 10.0, 10.0 and 13.5 Kcal./mole. Our values for stearic and arachidic acids of 10.0 and 12.7 are in as good agreement as could be expected, considering these differences in metals and methods.

It is not theoretically necessary that our temperature of wetting (T_W) and the stick-slip transition temperature (T_S) should be equal even when identical concentration of solute and the same metals are used. It appears from a comparison of our work with that of Bowden, Gregory and Tabor (15) that it is essential to have closer packing in an adsorbed monolayer to prevent stick-slip than to prevent wetting. Therefore, with a given concentration (W) of solute, a film which will just give an oleophobic effect will already be giving stick-slip. Hence, the stick-slip effect will have occurred at a lower temperature, *i.e.*, $T_S < T_W$. Since a shearing stress on the adsorbed films causes the stick-slip transition, it is possible for the film to collapse under the action of the slider when it would still be oleophobic. It may not always be necessary to desorb molecules of the film to get stick-slip. All that is needed is sufficient loss in shear strength through softening or reorientation of the film; hence, it is again evident that $T_S < T_W$.

As a practical matter, it is very unlikely that films of these compounds adsorbed from solution in oils will be any more closely packed than those discussed here. Films on metals made by melting the pure polar compound or by using concentrations in oils of from 5 to 50% of solute will be the exception rather than the rule. Hence, the adsorption effects reported here should be typical of those to be encountered in working with the usual ranges of solutions in oils of these classes of polar additives. It is evidently essential to obtain more information on how the adsorptivity of oleophobic films varies with the nature of the adsorbing material.

Since the molal energy of adsorption (U) for long chain compounds has been shown here to contain an appreciable contribution from the energy of cohesion between hydrocarbon chains ($U_c = Nu$), it is evident that any branched chain molecules having the same polar groups will have lower values of U and will be even less adsorptive. Therefore, their ability to resist the desorptive effect of increased temperature and, hence, their usefulness as wear-preventives will be even more limited.

RECOMMENDATIONS

The conclusions reached make advisible similar measurements of the energy of adsorption of various types of polar molecules when adsorbed on surfaces of other polished metals. Exploratory work is under way on copper, iron, stainless steel, zinc, tin, aluminum, and nickel. This will be supplemented by electron diffraction analyses of the surfaces of the metals in order to identify the true adsorbing surfaces which more often are some oxide of the metals.

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