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NRL Report 6020

A Study of Autophobic Liquids on Platinum by the Contact Potential Method

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February 13, 1964

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ABSTRACT

Several nonspreading liquids were investigated on a platinum surface using contact potential and contact angle measurements to determine whether or not their nonspreading behavior was caused by "autophobicity," i.e., the property of a liquid being unable to spread upon its own adsorbed monolayer. The liquids studied were n-octanol, n-octanoic acid, tri-p-cresyl phosphite, mixed meta- and para-isomers of tricresyl phosphate, methylene iodide, and three chlorinated biphenyls. Each liquid was shown to be autophobic by the contact potential difference and contact angle data for adsorbed monolayers on platinum. Contact potential differences for the phosphate and phosphite were the same, indicating that the two types of molecules have different mechanisms of surface interaction with the metal surface. It was also found that raising the relative humidity affects the autophobic contact angle of liquid n-octanoic acid, n-octanol, and methylene iodide, but the effect is opposite in sign for the methylene iodide. This result sheds considerable light on the effect of water adsorption on the adsorptive properties of halogen derivatives of the hydrocarbons.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem CO2-10
Subproject RR 001-01-43-4751

Manuscript submitted October 28, 1963.

A STUDY OF AUTOPHOBIC LIQUIDS ON PLATINUM BY THE CONTACT POTENTIAL METHOD

INTRODUCTION

In previous studies of wetting (1) it has been shown that several classes of pure liquids, including the branched and unbranched aliphatic acids and alcohols, are nonspreading on such high-energy surfaces as platinum, α-alumina, and fused silica because they absorb unaltered to form low-energy surfaces upon which the bulk liquid will not spread; that is, the critical surface tension γ_c of the resulting coated surface is less than the surface tension γ_{LV} of the liquid. Liquids of this type were termed "autophobic" by Hare and Zisman (1). The nonspreading liquids reported later (2) included certain phosphate esters, chlorinated aromatic hydrocarbons, and ethers. The nonspreading properties of these liquids were not conclusively explained but were believed to arise from the same cause. In addition to nonspreading on high-energy surfaces due to autophobicity, nonspreading can be produced in all pure liquids investigated to date by the addition of an appropriate polar compound which preferentially adsorbs to form a suitable low-energy surface (3-11).

It is conceivable, however, that the above conditions need not be the only ones sufficient for the occurrence of nonspreading on high-energy surfaces. Harkins and Feldman (12) defined the initial spreading coefficient (S) as

$$S = W_a - W_c$$

where W_a and W_c are the work of adhesion and cohesion for a given liquid. For spreading to occur spontaneously S must be positive; hence, if $W_c > W_a$, nonspreading will result. It was the purpose of this investigation to examine a number of types of nonspreading liquids, including the phosphate esters and chlorinated aromatic liquids reported earlier (2), to determine whether each is autophobic or whether it does not lay down a low-energy adsorbed film and so is nonspreading simply because the spreading coefficient is negative. Obviously, if such a liquid exists, a drop of the liquid could be rolled over a smooth clean solid surface without leaving an adsorbed film behind. Similar studies were also made on n-octanol and n-octanoic acid, whose autophobic character had been firmly established earlier (1).

Because of their sensitivity to the presence of an adsorbed monolayer, both contact potential and contact angle measurements were made after passage of a liquid drop over a polished, clean, metal surface to determine whether the liquid had left behind a film adsorbed on the solid substrate. If the pure liquid was capable of exhibiting a finite contact angle without the formation of an adsorbed low-energy surface film, obviously there would be no contact potential difference ΔV before and after rolling the drop of liquid over the clean metal surface. On the other hand, if the liquid contained an oleophobic solute, after passage of the liquid drop, the contact potential difference and also the contact angle θ exhibited by a sessile drop of methylene iodide would be that expected of the metal substrate coated by a monolayer of that solute. If the liquid was autophobic, θ for that liquid on the monolayer-coated metal would be the same as the value manifested by the same liquid on the bare metal, and the contact potential difference would correspond to that caused by an adsorbed monolayer of the autophobic liquid.

MATERIALS AND EXPERIMENTAL PROCEDURES USED

The following liquids were used in this investigation: n-octanol, n-octanoic acid, and tri-p-cresyl phosphite (Eastman Kodak Company); methylene iodide and mixed meta and para isomers of tricresyl phosphate (Fisher Chemical Company); and the chlorinated biphenyls-Aroclors 1242, 1248, and 1254 (Monsanto Chemical Company). With the exception of the phosphorus-containing compounds, each of these liquids, immediately before use, was percolated repeatedly through an adsorption column of silica gel and activated alumina to remove polar impurities. The phosphorus-containing liquids were percolated through Florisil only.

A pure platinum disc, 3/8 inch in diameter, was used as the solid substrate for observing the spreading behavior of each of the liquids studied. Before each experiment it was polished on a wet Buehler Selvyt cloth with levigated alumina having an average particle size of 0.3 micron; it was then rinsed in hot concentrated C.P. nitric acid, rinsed in flowing, grease-free distilled water, heated briefly to red heat over a Bunsen flame, and finally cooled in clean air at 50% R.H.

A monolayer of each liquid was adsorbed on the platinum substrate by the repeated wiping technique described by Levine and Zisman (13) and also by the retraction method (14) both from the melt and solution. The criterion used for concluding that only a monolayer remained on the substrate was that the results of contact angle and contact potential measurements were the same, within experimental error, for both techniques of monolayer preparation. In addition, when using the wiping technique, a valuable indication that a monolayer has been formed was that further vigorous wiping with clean filter paper caused no further changes in either the contact angle or the contact potential difference.

Solvents for preparing solutions used in the retraction process were nitromethane or methylene iodide, each of which had been freshly percolated through an adsorption column of activated alumina and silica gel. Properties of the monolayers retracted from solutions in these two solvents were identical.

Contact potential differences were measured between the platinum electrode, before and after coating it with the film being studied, and an aged reference electrode consisting of Ra-226 foil with a thin gold overlayer. Bewig's modification of the ionization method of measuring the contact potential difference was used because it allowed automatic recording (15). All results reported here were reproducible within ±0.015 volt or less.

The value of θ is the slowly advancing contact angle obtained by gradually increasing the volume of a sessile drop of a pure liquid resting on the horizontal surface of the solid at 20° to 25°C. Contact angles were measured with a goniometer telescope and were reproducible to within ±2 degrees.

All contact potential difference and contact angle results presented here are averages of at least six results obtained on monolayers prepared by both wiping and retraction techniques, and were performed at 20° to 25°C and 50% R.H. unless otherwise stated.

RESULTS AND DISCUSSION

Autophobic Behavior of the Phosphate and Phosphite Esters

The sample of mixed meta and para isomers of tricresyl phosphate exhibited a contact angle of 6 degrees on the bare platinum substrate. After adsorbing a monolayer of

this liquid on the platinum by the wiping method or by retracting a monolayer from a 1% by weight solution in methylene iodide, the tricresyl phosphate exhibited the same 6-degree contact angle on that monolayer. On the same film-coated surfaces, sessile drops of water and methylene iodide exhibited contact angles of 62 and 25 degrees, respectively (Table 1). The measured contact potential difference for such a monolayer of tricresyl phosphate on platinum was 0.620 volt (Table 2).

Table 1
Contact Angle (θ) for Various Liquids on Platinum and on Tricresyl Phosphate and Tricresyl Phosphite Monolayers Adsorbed on Platinum*

Solid Surface Studied	Contact Angle (θ) of Test Liquid (degrees)			
	Tricresyl Phosphate	Tri-p-cresyl Phosphite	Methylene Iodide	Water
Bare Platinum	6	5	11	Spread
Tricresyl Phosphate Monolayer	6	-	25	62
Tri-p-cresyl Phosphite Monolayer	-	5	21	62

*20°-25°C; 50% R.H.

Table 2
Contact Potential Differences Resulting from Monolayers Adsorbed on Platinum*

Adsorbed Compound	Contact Potential Difference ΔV (volts)	Calculated Apparent Perpendicular Moment μ_p (debyes)
Tricresyl Phosphate	0.620	1.65
Tri-p-cresyl Phosphite	0.619	1.65
Aroclor 1242	0.110	0.34
Aroclor 1248	0.053	0.18
Aroclor 1254	-0.020	-0.07
n-Octanol	0.140	-
n-Octanoic Acid	0.120	-
Methylene Iodide	0.120	0.11

*20°-25°C; 50% R.H.

Tricresyl phosphate presumably adsorbs with the highly polar phosphate group nearest the metal surface. Inspection of a Stuart-Briegleb ball model of this compound indicates that the planar aromatic ring portions of the adsorbed molecule may orient at right

angles to the solid surface. Fox, Hare, and Zisman (9) have reported water contact angles of from 92 to 95 degrees on the solid surfaces covered with benzene rings when the planar ring was oriented perpendicular to the solid surface, and contact angles of from 55 to 58 degrees when the planar ring was tilted slightly from the vertical. They also reported a contact angle of 37 degrees for methylene iodide on a surface composed of benzene ring edges and faces. The contact angles obtained here are consistent with their results if we assume the benzene rings are nearly at right angles to the adsorbing solid surface.

The fact that θ for a drop of tricresyl phosphate was the same on bare platinum and on platinum coated with a tricresyl phosphate monolayer proves that it is an autophobic liquid. The cross-sectional area for the adsorbed tricresyl phosphate molecule was taken to be $100A^2$ because (a) inspection of the ball model indicates the projected area to be about $115A^2$, and (b) Ries (16) obtained a molecular area of $95.0A^2$ for a condensed monolayer of tri-p-cresyl phosphate adsorbed on water. Using this value and the fact that ΔV was equal to 0.620 volt, the apparent perpendicular component μ_p of the dipole moment of the adsorbed molecule was computed from the Helmholtz equation

$$\Delta V = 4\pi n \mu_p$$

where n is the number of adsorbed molecules per unit area. In this case $\mu_p = 1.65$ debyes. Although no gaseous or dilute solution dipole moment data are available for this compound, it is a reasonable approximation to assume that the contribution of the methyl substituent on each benzene ring can be neglected and to compare this value with the dipole moment of 2.81 debyes obtained for triphenyl phosphate in benzene at 25°C (17). One is left with the same situation reported recently by Bewig and Zisman (18) that the dipole moment of the molecule adsorbed on platinum as computed from contact potential data is much less than that measured in the gaseous state or in dilute solution by other methods. The probable causes are the neglect of the dipole induced by the proximity of the adsorbed molecules to the metal surface and to each other as well as the effect of any adjacent dipoles of adsorbed water present under the conditions of these experiments.

Table 1 also summarizes the results of measurements of θ for tri-p-cresyl phosphite on bare platinum and for several liquids on platinum which had been coated previously with an adsorbed monolayer of tri-p-cresyl phosphite by both the wiping method and by retraction from a 1% by wt. solution in methylene iodide. A sessile drop of tri-p-cresyl phosphite exhibited a 5-degree contact angle both on bare platinum and on platinum coated with the phosphite monolayer. Therefore, tri-p-cresyl phosphite is also an autophobic liquid. On the surface coated with the phosphite monolayer, θ for water and methylene iodide were 62 and 21 degrees, respectively. Thus the water contact angle is the same and the methylene iodide contact angle is 4 degrees lower than on the tricresyl phosphate monolayer. The near equality of the contact angles on the phosphate and phosphite monolayers is entirely consistent with our expectation that their outermost structures would be the same.

As indicated in Table 2, the adsorbed monolayer of tri-p-cresyl phosphite caused nearly the same contact potential difference as tricresyl phosphate, although both compounds occupy essentially the same surface area per adsorbed molecule. This surprising result leads to the same apparent perpendicular component of the dipole moment, 1.65 debyes, which may be compared with the dipole moment of 2.02 debyes (in benzene solution at 25°C) for the analogous triphenyl phosphite (17). One might expect a greater contact potential difference and apparent dipole moment from the phosphate than the phosphite since the dipole moments from measurements on the dielectric constants of gases or dilute solutions are larger for the phosphates that have been studied than those of the analogous phosphites. However, it is very probable that the unpaired electrons of the phosphite phosphorus atom are able to react or associate with oxygen atoms already

adsorbed on the platinum surface. This would result in a molecular species identical with the phosphate, thereby resulting in the same apparent dipole moments.

Autophobic Behavior of the Chlorinated Biphenyls

Aroclors 1242, 1248, and 1254 are commercial mixed chlorinated biphenyls which, as stated by the manufacturer, have on the average three, four, and five chlorine atoms per molecule, respectively. However, in each liquid there are present molecules containing more or less chlorine. From inspection of Stuart-Briegleb molecular models and from the fact that chlorine substitution in biphenyl (19) proceeds in the order para, para', ortho, ortho', it can be seen that the two phenyl groups will not be coplanar.

Table 3 summarizes the values of θ observed for each of the Aroclors on bare platinum and its own adsorbed monolayer prepared by the wiping technique and by retraction from methylene iodide solution. Contact angles of drops of methylene iodide and water on these monolayers are also given. It can be concluded from these results that the Aroclor liquids are autophobic since each exhibits the same contact angle on bare platinum coated with the respective Aroclor monolayer.

Table 3
Contact Angle (θ) for Various Liquids on Platinum and on Aroclor Monolayers Adsorbed on Platinum*

Aroclor Compound Studied	Average Number of Chlorine Atoms	Contact Angle (θ) for (degrees)			
		Liquid Drop of Aroclor on Bare Pt	Liquid Drop of Aroclor on Its Own Monolayer	Methylene Iodide on Aroclor Monolayer	Water on Aroclor Monolayer
Aroclor 1242	3	10	11	24	68
Aroclor 1248	4	10	12	15	67
Aroclor 1254	5	20	21	9	69

*20°-25°C; 50% R.H.

Nearly identical water contact angles of from 67 to 69 degrees were observed on each of the Aroclor films, but the methylene iodide contact angles decreased from 24 to 15 to 9 degrees on monolayers of Aroclors 1242, 1248, and 1254, respectively. The planes of the phenyl groups of an adsorbed Aroclor molecule would lie in varying degrees of tilt with respect to the monolayer/air interface as chlorination progresses. The same argument used with tricresyl phosphate can be employed here, i.e., that the contact angles of water and methylene iodide on an Aroclor monolayer should be somewhere between those found on adsorbed benzene rings when oriented perpendicular to the surface or tilted slightly from the vertical. These extremes, for water, are 55 and 95 degrees; the methylene iodide contact angle is 37 degrees for benzene rings tilted slightly from the vertical orientation (9). The fact that chlorine atoms are present at the monolayer/air interface probably has little significance as far as contact angles are concerned since the number of chlorine atoms is small compared to the number of aromatic groups and the critical surface tension of wetting γ_c of a partially chlorinated surface, such as polyvinyl chloride, is nearly the same as that for a surface of benzene rings oriented perpendicular to the surface (14).

Although a methylene iodide contact angle of 24 degrees is reasonable for Aroclor 1242, it is difficult to understand why θ decreases with the others. It is possible that as chlorination progresses, close packing becomes more difficult and hence, methylene iodide exhibits a lower value of θ. That the lower methylene iodide contact angles were not caused by their solution of the monolayer was shown by using a sessile drop of methylene iodide containing a small amount of the Aroclor in question. Sessile drops of these solutions exhibited the same values of θ as did drops of pure methylene iodide.

Contact potential differences caused by the adsorption of a monolayer of each of these liquids and the calculated perpendicular component of the apparent dipole moment are given in Table 2. The large decrease in the contact potential difference with increasing chlorination of the molecule can be explained in terms of the directed permanent dipole moment contributions of the individual C-Cl bonds. Assuming that chlorine substitution in biphenyl proceeds as indicated above and because they are so highly polarizable, as many of the chlorine atoms as possible will adhere to the metal substrate, the endview projections of the three Aroclors would be expected to appear as in Fig. 1. The arrows refer to the positive direction of the permanent C-Cl moment projected onto the plane of the paper, and "into" and "out" indicate whether the bond is directed at approximately 30 degrees into the plane of the paper or 30 degrees from it. Not shown in Fig. 1 are the C-Cl moments at the para positions of the molecule; they are directed normal to the plane of the paper and in opposite directions, thereby effectively cancelling one another.

Figure 1a is the endview projection of Aroclor 1242. The positive end of the C-Cl dipole pointing away from the metal substrate and whatever moments are induced in the molecule by the electric field of the metal give rise to the measured contact potential difference of 0.110 volt. In Aroclor 1248 (Fig. 1b), with the addition of the fourth Cl atom, two C-Cl dipoles are directed away from the metal substrate and in the plane of the paper, toward each other. Although one dipole is directed into the plane of the paper and the other away, they are located near the center of gravity of the molecule, and the fourth C-Cl dipole tends to reduce the molecule's net permanent moment. This causes the reduction of the contact potential difference, in this case, to 0.053 volt. In Aroclor 1254, the addition of the fifth C-Cl dipole to the molecule (Fig. 1c) causes a reverse in sign of the measured contact potential difference (-0.020 volt) because now there is an oriented dipole with its negative end directed away from the substrate.

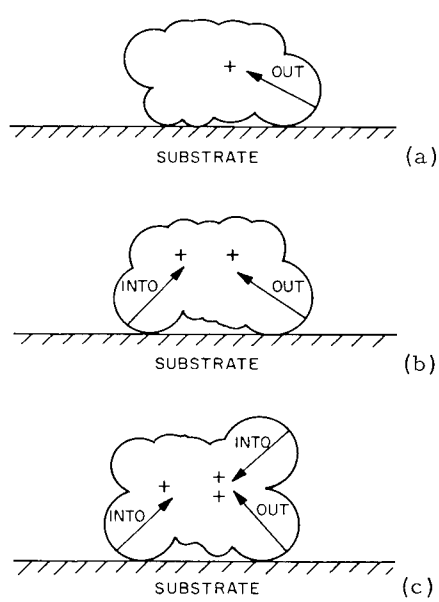

Fig. 1 - Endview projections of Aroclor molecules

Autophobic Behavior of n-Octanol and n-Octanoic Acid

The results obtained in studying the autophobic properties of liquid n-octanol and n-octanoic acid are similar and will be discussed together. Table 4 summarizes values of θ obtained for these liquids on bare platinum and on their own adsorbed monolayers, as well as the contact angles of methylene iodide and water on each monolayer. The monolayers were prepared by (a) the wiping method, (b) retraction from the melt, and (c) retraction from 0.1% by weight solution in nitromethane.

Table 4
Contact Angle (θ) for Various Liquids on Platinum and on Several Kinds of Monolayers Adsorbed on Platinum*

Solid Surface Studied	Contact Angle (θ) of Test Liquid (degrees)			
	n-Octanol	n-Octanoic Acid	Methylene Iodide	Water
Bare Platinum	35†	35†	11†	Spread
n-Octanol Monolayer	18	-	37	68
n-Octanoic Acid Monolayer	-	22	45	75
Methylene Iodide Monolayer	-	-	23	73

*20°-25°C; 50% R.H.
†Nonequilibrium value.

Both the acid and the alcohol exhibited an initial contact angle of 35 degrees on bare flamed platinum under ambient room conditions (20° to 25°C at 50% R.H.), whereas Hare and Zisman (1) reported an angle of 42 degrees under the same conditions. This initial 35-degree contact angle is a nonequilibrium condition and, in both cases, the angle decreased to about 20 degrees in the course of two hours. The contact angles of methylene iodide and water on the adsorbed n-octanol monolayer were 37 and 68 degrees, respectively. Since Levine and Zisman (13) obtained methylene iodide contact angles of 56 and 57 degrees on close-packed monolayers of n-octanol and n-octanoic acid adsorbed on soda-lime glass, the 37-degree contact angle obtained here probably indicates that the n-octanol molecules were unable to adsorb as closely together on flamed platinum. Similar results were observed with n-octanoic acid monolayers upon which sessile drops of methylene iodide and water exhibited contact angles of 45 and 75 degrees, respectively. Because of the higher contact angles obtained on the n-octanoic acid monolayers, it can be concluded that the adsorbed n-octanoic acid molecules are packed more closely than the n-octanol molecules on flamed platinum, but not as closely as on soda-lime glass.

Although n-octanol and n-octanoic acid each exhibited an initial contact angle of 35 degrees on bare flamed platinum, neither liquid gave this contact angle on its own adsorbed monolayer when measured at 20° to 25°C at 50% R.H. Instead the contact angles observed were 18 and 22 degrees respectively, which agree well with the equilibrium value of 20 degrees obtained for these liquids on bare flamed platinum. It is probable that the lower contact angles (ca. 20 degrees) are a result of a mixed film of water molecules, which are certainly present, and either alcohol or acid molecules. It is well known that an adsorbed monolayer has a high permeability to water unless it is close-packed and has very high intermolecular cohesion. Neither of these conditions are satisfied by the short chain alcohol and acid studied here.

The 35-degree contact angle observed initially on flamed platinum is probably a result of relatively smaller amounts of water present initially on the platinum surface. If the flamed platinum is allowed to stand for as long as one hour in room atmosphere before adding the test drop of acid or alcohol, the 35-degree contact angle no longer manifests itself and angles of 18 and 22 degrees are observed. These results indicate that n-octanol and n-octanoic acid are autophobic when equilibrium with adsorbed water is complete and the autophobic contact angles, under these conditions, are 18 and 22 degrees, respectively.

An interesting result, which further shows the effect and importance of the amount of adsorbed water present, is obtained when n-octanol is studied on flamed platinum in an atmosphere maintained at less than 10% R.H. Under these conditions a 35-degree contact angle is observed for the alcohol on both the bare metal and on its own adsorbed monolayer. In this case n-octanol behaves as an autophobic liquid with an autophobic contact angle of 35 degrees. These contact angles are also much more stable than those measured at 50% R.H. as no changes were observed until after four hours. At the same time a marked change in the methylene iodide contact angle resulted. In air at less than 10% R.H. methylene iodide gave a 28-degree contact angle on the n-octanol monolayer. At 50% R.H., this angle was 37 degrees. This is to be expected when one considers that the octanol monolayer under study contains some water molecules. Since methylene iodide is nonspreading on water, it is reasonable to expect the methylene iodide contact angle to increase as the amount of included water increases.

The contact potential difference resulting from the adsorption of monolayers of n-octanol and n-octanoic acid were 0.140 and 0.120 volt, respectively (Table 2). (Interestingly, these same values were obtained when measured in air at less than 10% R.H.) The perpendicular component of the apparent dipole moment of each compound was not calculated because each monolayer was definitely not close-packed and it was not possible to determine reliably the value for the number of molecules occupying a unit area of surface and the inclination of the dipole axis from the vertical.

Autophobic Behavior of Methylene Iodide

The results obtained with methylene iodide are analogous to those obtained with n-octanol and n-octanoic acid. Methylene iodide exhibited an 11-degree contact angle on bare previously flamed platinum and, under ambient room conditions, a 23-degree contact angle on its own adsorbed monolayer. Water gave a 73-degree contact angle on methylene iodide monolayers (Table 4) which were prepared both by the wiping technique and by retraction from the melt.

The 11-degree contact angle of methylene iodide on bare flamed platinum was also a nonequilibrium condition and was found to increase gradually, approaching a value of 23 degrees after three hours. When the experiment was repeated in air at less than 10% R.H., methylene iodide exhibited an 11-degree contact angle both on the bare metal substrate and on its own adsorbed monolayer.

These results indicate again the importance of adsorbed water included in a monolayer. In air at 50% R.H., methylene iodide behaves as an autophobic liquid, after equilibration with water is complete, and exhibits an autophobic contact angle of 23 degrees. In air of less than 10% R.H., the effect of water is not immediately so pronounced and methylene iodide behaves as an autophobic liquid with an autophobic contact angle of 11 degrees. It would seem likely that this contact angle, given enough time, would also finally equilibrate at 23 degrees; however, no changes were observed over a course of four hours.

The differences in spreading behavior of methylene iodide on flamed platinum under varying conditions of relative humidity is remarkable and suggestive. It is well known that the liquid alkyl halides, as well as methylene iodide, are nonspreading on water or have negative spreading coefficients (12). From the results it appears possible that the n-alkyl halides could be made to spread over a noble metal surface and adsorb as more or less close-packed monolayers by eliminating the presence of water on the metal surface.

The measured contact potential difference resulting from the adsorption of a monolayer of methylene iodide was 0.120 volt (Table 1) and reduction of the relative humidity to less than 10% caused no change in this value. From measurement of the Stuart-Briegleb molecular model of this molecule, one obtains a projected rectangular molecular area of about $36A^2$. Assuming closest molecular packing in the adsorbed film, the apparent perpendicular moment calculated from the Helmholtz relationship is 0.11 debye. This value is considerably less than the reported dipole moments of this molecule measured in solution. These vary from 2.12 debyes (in benzene at 25°C) (Ref. 20) to 1.1 debyes (in benzene at 25°C) (Ref. 21). However, it is again probable that our calculated moment is low as a result of the proximity of the metal surface and the neighboring methylene iodide atoms, and the effect of included water molecules.

CONCLUSIONS

A number of pure liquids which are nonspreading on high-energy surfaces were investigated on platinum using contact angle and contact potential difference measurements to determine whether or not they are properly classed as autophobic liquids.

Because each of the liquids studied formed monolayers on a flamed platinum surface, as evidenced by contact angle and contact potential difference measurements, and because each of the liquids exhibited the same contact angle on bare platinum and on its own adsorbed monolayer, it is concluded that all are autophobic liquids.

Where possible, the apparent perpendicular component of the dipole moment of the adsorbed liquid was calculated from the observed contact potential difference using the Helmholtz relationship. These values were compared with literature values of dipole moments of these, or similar, compounds measured in solution. The results of this investigation are in agreement with earlier work done at this Laboratory (18) in that the apparent moment calculated from contact potential difference data is, in all cases investigated, considerably less than the dipole moment determined by conventional methods. This is probably a result of induced moments caused by the proximity of the adsorbed molecules to the metal surface and to each other as well as the effect of adsorbed water molecules.

No differences in results were discernible between the methods of monolayer preparation used. This fact indicates that no solvent molecules were trapped in the monolayers and did not contribute to the measured values of contact potentials or contact angles.

The rather remarkable adsorptive behavior of n-octanol, n-octanoic acid, and methylene iodide under conditions of varying relative humidity indicate that it may be possible to adsorb close-packed monolayers of the n-alkyl halides on metal substrates by eliminating the presence of adsorbed water.

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