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Investigation of Fatty Acid Monolayers on Metals by Contact Potential Measurements

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ABSTRACT

Each of the homologous series of pure *n*-fatty acids from formic to hexacosanoic has been studied as a condensed monomolecular layer adsorbed on Pt and NiO substrates. Both the stearic and nonadecanoic acids were also studied on various polished metal surfaces including Fe, Cr, Cu, Au, W, Mo, Ag, Nb, Al, Cd, Mg, Sn, Pb, Be, Zn, and Ni. The change in contact potential difference (ΔV) between the metal and an aged reference electrode was measured in air at 23°C and 50% R.H. Surface packing in each monolayer was characterized by the methylene iodide contact angle (θ). Systematic and reproducible values of ΔV and θ were found for each member of the homologous series. An asymptotic maximum occurred in the ΔV vs *N* curves when *N*, the number of carbon atoms per adsorbed molecule, was 14 or more for Pt and NiO substrates. Alternation of ΔV occurred for odd and even values of *N* on NiO and the baser metals but not on Pt and Au. Values of θ for stearic acid varied with the nature of the metal substrate, and the results were in reasonable accord with the lattice spacing of the substrate atoms. Values of ΔV for stearic acid monolayers varied from a maximum of 0.365 volt on W to -0.095 volt on Pb, and it was concluded that the perpendicular component of the dipole moment of the adsorbed acid molecule was a function of the specific interaction of metal substrate and the acid carboxylic group. Stearic acid desorbed readily from Pt but not from NiO, and it was concluded that chemisorption had occurred on the NiO.

PROBLEM STATUS

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

AUTHORIZATION

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INVESTIGATION OF FATTY ACID MONOLAYERS ON METALS BY CONTACT POTENTIAL MEASUREMENTS

INTRODUCTION

Results have been reported recently on contact potential studies of the monolayer adsorption of the homologous family of primary fatty amines (1). The same methods were used to advance our knowledge of the properties of a number of autophobic liquids on platinum (2), and Bewig and Zisman (3) have succeeded with similar techniques in demonstrating the induced polarization of *n*-alkanes, benzene, toluene, and carbon tetrachloride when adsorbed upon a variety of metals. In each of these studies the contact potential difference and the methylene iodide contact angle were found to be informative about the packing, orientation, and polarization of the molecules comprising the adsorbed monolayer.

This report presents the changes in the contact potential difference (ΔV) resulting from the adsorption of a monolayer of each of the homologous series of *n*-fatty acids, from formic (C_1) to hexacosanoic (C_{26}), on clean polished platinum and nickel(ous) oxide. It also reports results obtained upon adsorption of stearic and nonadecanoic acids on many other metal substrates.

EXPERIMENTAL PROCEDURES AND MATERIALS

Measurements of ΔV were made using the modified ionization method described by Bewig (4). The reference electrode, procured from the United States Radium Corporation, consisted of a 6-mm-square radium-226 foil sandwiched between a silver base plate and a thin gold overlayer. The electrode had an activity of 5 microcuries.

Measurements of the slowly advancing contact angle (θ) exhibited by a sessile drop of pure methylene iodide were made on each of the monolayers studied to indicate the closeness and reproducibility of molecular packing. Contact angles were reproducible within ± 1 degree. All measurements were made in air at 23°C and 50% relative humidity.

Each of the monolayers studied was prepared as an adsorbed condensed film on the metal specimen by the retraction method from the melt and/or from nitromethane solution (5).

The formic through valeric acids used were "White Label Grade" products of Eastman Organic Chemicals, while the remainder were procured from Lachat Chemicals Company. The acids caproic through stearic were stated by the manufacturer to be of 99.5% purity, and the nonadecanoic through hexacosanoic acids to be of 99.0% purity. Melting points of those acids which were solid at room temperature were measured and all melted within 1° to 2°C of the best literature values. The liquid acids were percolated through a long, narrow adsorption column of silica gel and activated alumina just before use to remove any traces of polar impurities.

The "active" electrode was always an exceptionally pure metal; the materials studied were platinum, gold, chromium, cadmium, copper, silver, beryllium, and lead, indicated to be of 99.999% purity by the supplier, and nickel, magnesium, aluminum, iron, tin, niobium, molybdenum, zinc, and tungsten, which were reported 99.9% pure or better.

Each metal studied as the active electrode was a flat disk prepared by abrasion under flowing water using a graded series of carborundum metallurgical papers to a final grit size of 600-C. Next, the metal specimen was given a mirror finish on a polishing wheel covered with a Buehler Selvyt cloth using levigated alumina having an average particle size of 0.3 micron. Finally, the polished surface was scrubbed on a clean Selvyt cloth under flowing distilled water and dried in an air atmosphere from which organic contamination had been removed.

The nickel oxide surface used was prepared by heating inductively a freshly polished sample of pure nickel for three minutes at about 650°C in clean air.

EXPERIMENTAL RESULTS AND DISCUSSION

The contact potential change (ΔV) caused by the adsorption of a condensed monolayer of fatty acid is the result of the fact that each molecule in the monolayer contains a permanent and oriented electrostatic dipole. To this system the Helmholtz relation

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

may be applied. Here n is the number of molecules adsorbed per unit area and μ_p is the average perpendicular component of all dipole moments resulting from the adsorption process. The quantity μ_p includes the effects due directly to the electrostatic dipole moment of the adsorbate molecule, the effects due to any redistribution of charge in the vicinity of the surface of the substrate, the reorientation of any adsorbed atmospheric gases present, and lateral polarization arising from neighboring dipoles (6-8). It is thus clear that μ_p bears no simple relation to the dipole moment of the molecule as determined in the gaseous state, although it is probably approximately proportional.

Adsorption of Fatty Acids on Platinum

Figure 1 includes a plot of ΔV vs N , the number of carbon atoms per molecule, for the homologous series of n -fatty acids adsorbed on platinum. The rectangular markers in the graph indicate the spread of the individual and independent measurements and the circles represent the arithmetical average. In general, the average deviation of any measurement from the curve is about ± 0.015 volt. The curve passes through a 0.160 volt minimum for $N = 3$ (propionic acid) and then rises to an asymptotic maximum of 0.355 volt for $N \geq 14$, i.e., for myristic acid and higher homologues. Any changes in ΔV , from one member of the series to another, must reflect differences in molecular packing and dipole orientation, since the dipole moments of the fatty acids are virtually the same for each member of the series (9).

A plot of the cosine of the methylene iodide contact angle (θ) vs N (Fig. 2) has an analogous asymptotic minimum for $N \geq 14$. The constancy of θ in this region is good evidence of constant molecular packing in these monolayers. Since there is no variation in ΔV for the higher homologues, one must conclude that the packing as well as orientation of adsorbed molecules is the same in all acid monolayers having $N \geq 14$. The simplest interpretation is that when a fatty acid molecule has a paraffin chain of sufficient length, intermolecular cohesive forces between adjacent molecules become large enough to hold the monolayer in a closely packed array. Similar behavior of the primary fatty amines adsorbed on platinum has been reported by Bewig and Zisman (1). Levine and Zisman also came to the same conclusion from their studies of the friction and wetting properties of retracted monolayers of the fatty acids adsorbed on glass (10,11). In each of these investigations methylene iodide contact angles of from 68 to 71 degrees were reported on monolayers of the higher homologues. It has been shown (5,10,11) that methylene iodide contact angles of from 68 to 71 degrees are characteristic of a surface

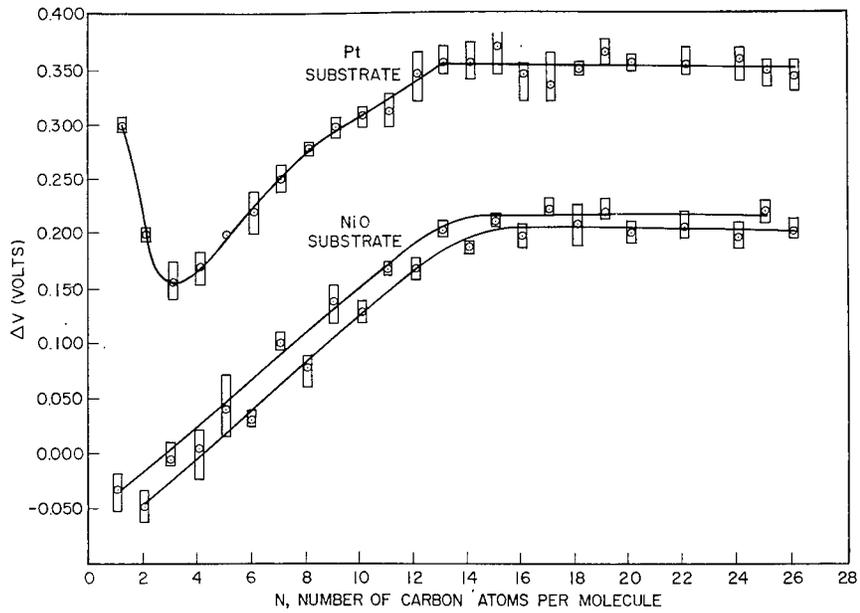


Fig. 1 - Contact potential difference data for the homologous series of fatty acids adsorbed on Pt and NiO

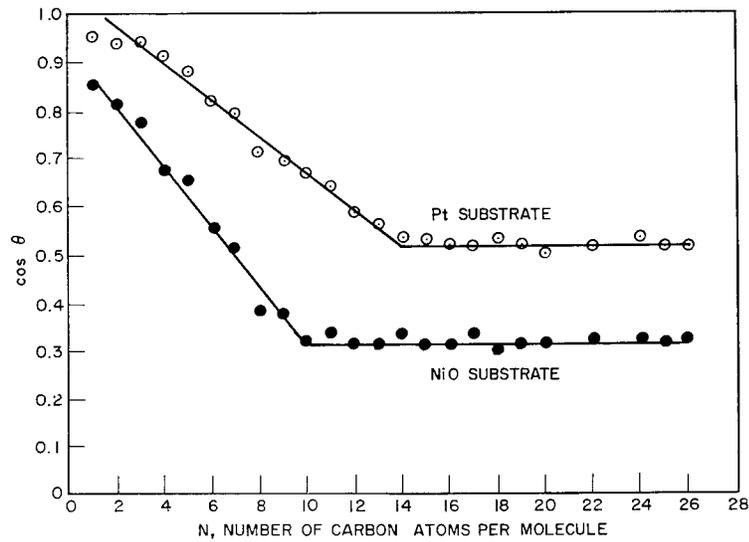


Fig. 2 - Methylene iodide contact angle data for the homologous series of fatty acids adsorbed on Pt and NiO

comprised of close-packed methyl terminal groups. But it should be noted that in the present study the maximum value of θ obtained on monolayers of the fatty acids adsorbed on platinum was 58 degrees. From this result it can be concluded that the fatty acid molecules adsorbed on platinum are either not as closely packed as on glass or are oriented at a rather large angle from the vertical, thereby exposing methylene groups of the hydrocarbon chain to the surface. The former conclusion is preferred because electron diffraction studies of Brockway and Karle (12) have established that stearic acid molecules are oriented nearly perpendicularly to the surface of platinum.

As N decreases below 14, the progressive decrease in ΔV and the increase in $\cos \theta$ are indicative of decreased lateral attraction between the adsorbed molecules which allows looser molecular packing and increased tilting of the molecular axis away from the vertical.

The minimum occurring in the ΔV curve at propionic acid and the increase from acetic to formic acid needs explanation. Obviously, at this point a different factor enters into the mechanism determining the value of ΔV other than the trend, as N decreases, toward looser molecular packing and increased molecular tilt. There is an interesting similarity in this region of Fig. 1 with the curves of Figs. 3 and 4 obtained by plotting the viscosities and surface tensions of the pure, liquid fatty acids as a function of the number of carbon atoms per molecule (13,14). A minimum also occurs in these curves at propionic acid. This minimum has been attributed to the greater association of the lower members of the homologous series (13). It is possible that the large values of ΔV obtained for formic and acetic acids are caused by the adsorption of an associated species, or because of differences in the water-displacing abilities of the lowest and higher members of the fatty acid family.

Adsorption of Fatty Acids on Nickel Oxide

Since the higher homologues of the fatty acids did not close pack when adsorbed on platinum, nickel oxide was chosen as a substrate on which close packing would occur. Electron diffraction patterns obtained from the oxidized nickel indicated that the surface oxide was NiO (15).

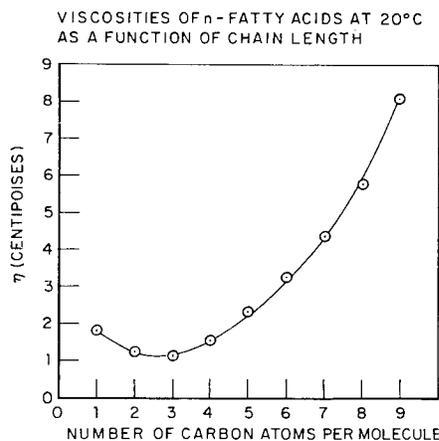


Fig. 3 - Viscosities of *n*-fatty acids as a function of chain length at 20°C

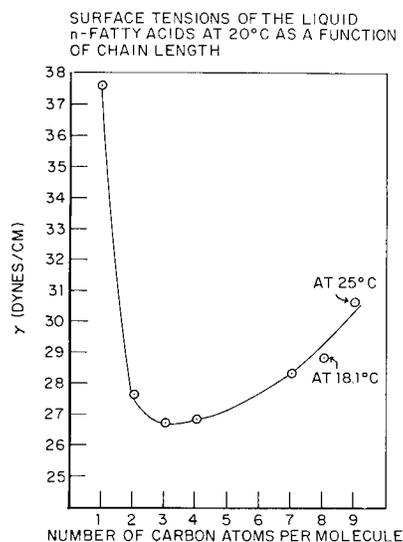


Fig. 4 - Surface tensions of the *n*-fatty acids as a function of chain length at 20°C

In Fig. 1 will also be found a plot of ΔV vs N for the series of fatty acids adsorbed on nickel oxide. Two curves may be drawn through the experimental points, one for odd values of N , and another, about 0.020 volt lower, for even values of N . Both curves have asymptotic maxima for $N \geq 14$. This alternation of ΔV between odd and even members of the series is reminiscent of the alternation found in melting points, specific heats, etc. of these acids. That the alternation of ΔV is not caused by differences in molecular packing in the monolayers is evidenced by the single curve fitting the contact angle data in Fig. 2; there is no indication of alternation whatsoever. No alternation of molecular dipole moments has been reported for these acids. Nevertheless, there existed the possibility that the odd and even members of the series adsorbed with the molecular axes at different angles of tilt from the vertical. However, electron diffraction patterns obtained from monolayers of stearic and nonadecanoic acids adsorbed on both NiO and copper showed there was no difference, over 1 or 2 degrees, in the tilt angle (15). Although a difference in tilt angle of 1 or 2 degrees could contribute to the observed alternation in ΔV , it is unlikely that it is the primary cause. The major contribution of the molecular dipole moment to ΔV is the vector sum, in a vertical direction, of the group moments at opposite ends of the molecule, viz., the carboxyl group and the terminal methyl group. The addition of one more carbon atom, in going from an odd to even numbered acid, for example, will result in the group moment of the terminal methyl group being directed in the opposite direction from which it had been with respect to the moment of the carboxyl group; however, as the vertical component of the dipole moment is the same in each case, this cannot be the cause of the observed alternation.

The maximum methylene iodide contact angle obtained on retracted monolayers of the fatty acids adsorbed on NiO was 71 degrees, which is identical with the results for fatty acids on glass (9) and for fatty amines on platinum (1). Therefore, on NiO the long-chain fatty acids formed monolayers having close-packed methyl groups outermost. Contact angles of 71 degrees were also obtained with methylene iodide on monolayers of capric through tridecanoic acids adsorbed on this same substrate; hence, a close-packed monolayer was formed with these compounds even though the hydrocarbon chain was not of sufficient length to cause such close packing through the action of intermolecular cohesive forces alone. For reasons that will be discussed below, it is concluded that a reaction between the fatty acid monolayer and the NiO substrate had contributed to cause the observed close packing. In other words, the monolayers of acids having $N \geq 10$ were held in a close-packed array because of the combined effects of a chemical bond between the acid and the substrate and the forces of intermolecular attraction.

The shorter chain fatty acids adsorbed on NiO caused smaller values of ΔV and θ . Decreasing values of θ indicate looser molecular packing; this result, coupled with the possibility that the molecules below $N = 10$ can develop larger angles of tilt from the vertical, will explain the decrease in ΔV with decreasing chain length. The ΔV vs N graphs of the fatty acids adsorbed on NiO are essentially rectilinear between formic and lauric acids, and there was no such minimum as that observed with the platinum substrate. This result is evidence of a different mechanism of adsorption on NiO than on Pt.

It will be noted that ΔV for formic, acetic, and propionic acids when adsorbed on NiO was negative. These values should be considered only as being less positive than the values given by the longer chain homologues. The reversal in sign in going to lower values of N is caused by the contact potential of the adsorbed monolayer becoming negative with respect to the reference electrode.

Desorption of Stearic Acid from Platinum and Nickel Oxide

In seeking to determine, at least qualitatively, whether or not the fatty acids were adsorbed more firmly, or differently, on nickel oxide than on platinum, an attempt was made to desorb a stearic acid monolayer from Pt and NiO by using two different

techniques. One involved raising the temperature of the substrate to a degree sufficient to cause desorption, and the other the extraction of the monolayer with an appropriate pure solvent. Measurements of ΔV and θ before and after treatment of the surface were used to indicate the extent of desorption of the monolayer.

Condensed monolayers of stearic acid were adsorbed on both polished platinum and on nickel oxide and, after ΔV and θ had been measured, each specimen was either heated or was exposed to solvent extraction using pure diethyl ether in a Soxhlet extractor. (Diethyl ether was chosen because stearic acid is soluble in ether but nickel stearate is not.) After each specimen was treated and was allowed to equilibrate in clean air at 23°C, measurements were again made of ΔV and θ . The solvent extraction treatment was repeated until no further changes in ΔV or θ were observed. It was also necessary to heat the solvent-extracted specimen to 100°C to remove any adsorbed diethyl ether since recent work (3) had shown that such a monolayer might remain after the solvent treatment even if the stearic acid monolayer had been removed. A temperature of 100°C was not sufficient to remove any stearic acid from Pt or NiO. Equilibrium values of ΔV and θ for stearic acid monolayers, before and after desorption experiments, are given in Table 1.

Table 1
Results of Desorption Experiments on Stearic Acid Monolayers
(23°C; 50% R.H.)

Surface Investigated	Contact Potential Difference, ΔV (volts)	CH ₂ I ₂ Contact Angle, θ (degrees)
Bare Pt	0.000	23
Stearic acid monolayer on Pt	0.355	58
Stearic acid monolayer on Pt after heating to 130°C	0.005	22
Stearic acid monolayer on Pt after 1 hr. ether extraction and heating to 100°C	-0.015	25
Bare NiO	0.000	Spread
Stearic acid monolayer on NiO	0.210	71
Stearic acid monolayer on NiO after heating to 150°C	0.180	61
Stearic acid monolayer on NiO after 4 hr. ether extraction and heating to 100°C	0.165	51

A monolayer of stearic acid on Pt caused ΔV to be 0.355 volt and θ to be 58 degrees. When the temperature of the Pt covered by stearic acid was raised, at the rate of about 1°C per minute, in clean air to 130°C and then cooled to room temperature, values of ΔV and θ each returned to the respective values obtained on bare Pt. However, it can be seen from the values of ΔV and θ in Table 1 that raising the temperature of the stearic acid coated NiO surface to 150°C (at the same heating rate) removed little of the monolayer. Similarly, a 1-hour ether extraction of a stearic acid monolayer on Pt, followed by subsequent heating to 100°C, removed all the monolayer, whereas a 4-hour ether

extraction and subsequent heating removed little of the monolayer from the NiO substrate. Thus it is clear that stearic acid is adsorbed on NiO much more strongly than on Pt, presumably by chemisorption on the former substrate and by physical adsorption on the latter.

Adsorption of Stearic and Nonadecanoic Acids on Various Metals

Condensed monolayers of stearic and nonadecanoic acids were also adsorbed on a variety of polished clean metals, and the resulting contact potential difference (ΔV) and the methylene iodide contact angle (θ) obtained on the monolayer were measured. These results will be found in Table 2. Values of ΔV for stearic acid monolayers varied between the extremes of 0.365 volt on tungsten and -0.095 volt on lead; nonadecanoic acid caused values of ΔV between 0.415 volt on tungsten and 0.130 volt on both cadmium and tin. With the exception of the values of ΔV caused by nonadecanoic acid on niobium and copper, there is the same progression from high to low values of ΔV for both stearic and nonadecanoic acid monolayers on the various metals. Nonadecanoic acid monolayers gave higher values of ΔV than did stearic acid monolayers on the same metal, except when adsorbed on gold and platinum; on these metals the same ΔV was obtained for each acid. This difference is not a result of differences in molecular packing in the monolayer because θ was the same for both monolayers on the same metal. These facts indicate that the alternation in ΔV between acids having an odd and even number of carbon atoms is observed on all but the noble metals. They also indicate that the phenomenon of alternating ΔV is dependent upon the ability of the monolayer to react with the substrate or otherwise adsorb more strongly than through physical adsorption alone.

Table 2
Contact Potential Difference and Methylene Iodide Contact Angle Data for
Monolayers of Stearic and Nonadecanoic Acids Adsorbed on Various Metals
(23°C; 50% R.H.)

Adsorbent Metal	Stearic Acid Monolayer		Nonadecanoic Acid Monolayer	
	ΔV (volts)	θ (degrees)	ΔV (volts)	θ (degrees)
Tungsten	0.365	59	0.415	59
Platinum	0.355	58	0.360	58
Molybdenum	0.350	65	0.380	64
Aluminum	0.300	68	-	-
Nickel	0.275	63	0.315	63
Chromium	0.260	61	0.305	62
Iron	0.240	71	-	-
Silver	0.235	61	-	-
Niobium	0.220	64	0.330	63
Gold	0.140	45	0.140	47
Cadmium	0.115	64	0.130	65
Tin	0.110	66	0.130	65
Copper	0.095	66	0.170	66
Magnesium	-0.070	68	-	-
Lead	-0.095	62	-	-
Beryllium	-	68	-	-
Zinc	-	68	-	-

It will be seen that there were also considerable variations among the metals in the values of θ ; the extremes were 71 degrees for iron and 45 degrees for gold. Such a range in θ indicates either a variation in the packing of the adsorbed acid molecules or in β , the angle of departure from the normal of the principal molecular axis. Since ΔV will be proportional to both the number of adsorbed molecules per unit area and to $\cos \beta$, ΔV should increase with decreasing β if no other factor is altered. Nevertheless, the variation in ΔV does not appear related to that in θ . The orientation of adsorbed retracted monolayers of the even members of the family of fatty acids has been studied with electron diffraction techniques by many able investigators (12,16-19) and all have agreed that the higher members (above 8 or 10 carbon atoms per molecule) are oriented on Pt, Fe, Ag, Zn, Cd, Cu, Ni, and Al within a few degrees of the vertical, i.e., $\beta = 0$ degrees. Hence, the variation in θ reported in Table 2 cannot be due to a variation in β and must be caused by variation in the surface density of packing of the acid molecules.

Any analysis of adsorption sites, whether on bare metal or metal oxide surfaces, must take into account the atomic dimensions of the outermost layer of metal atoms. The structure and orientation of a thin oxide film in its early stages of development, such as we have on the freshly polished metals studied here, is directly related to the structure and orientation of the underlying metal (20). As an approximate method of analysis, we ignored the effects of crystallinity of the substrate and the fact that the metals studied, besides being oxide coated, probably were covered with adsorbed atmospheric gases, and plotted θ for methylene iodide on the various metals coated with stearic acid against the covalent radius of the metal in question (Fig. 5) (21). It was necessary to use the metallic atomic radii, assuming a coordination number of 12, for the transition metals. It will be seen that the data fall on two curves; the lower curve involves only the transition metals and the upper curve the other metals, with the exception of the transition metals Nb and Mo. The points for Au and Fe do not fit the curve well. The upper curve reaches a maximum of $\theta = 68$ degrees at an atomic radius of 1.31A. If one assumes that the metallic atoms of the substrate are arranged in a hexagonal close-packed array and that a stearic acid molecule will always adsorb directly over one of the metal atoms when possible, it can be seen that because of the relatively large dimensions of the acid molecule with respect to the substrate atoms, the acid molecules will not completely close pack as long as the cross-sectional radius of the acid is less than twice the atomic radius of the substrate metal. Using this model for the adsorption process, it is an evident inference that the closest packing of adsorbed molecules will occur when the cross-sectional radius of the acid molecule is exactly twice the atomic radius. Assuming the cross-sectional area of stearic acid to be $21A^2$, the cross-sectional radius is 2.59A. The radius of substrate atom, then, which will create closest packing (and therefore the maximum contact angle) is 1.29A, which is almost exactly the value at which the maximum contact angle is reached in Fig. 5. This interesting observation indicates the possibility of selecting the dimensions of both metal adsorbent and adsorbate in such a way as to obtain the maximum contact angle.

All of the evidence presented has led to the conclusion that a condensed retracted monolayer of stearic acid, for example, adsorbs on a metal in a vertical orientation and with a surface packing density determined by the spacing of adsorption sites on the metal (or oxidized metal) surface. The spacings deduced from the distances between nearest neighbors in the surface of the metal are in reasonable accord with the minimum possible spacing between adsorbed stearic acid molecules. It should now be obvious that for a fair comparison of the values of the contact potential change (ΔV) due to the adsorption of the acids on the various metals of Table 2 it will be necessary to allow for the variation in the number of adsorbed molecules per unit area (n). We are attempting the measurement of n by using C-14 labeled stearic acid. It should then be possible to use n and ΔV from Table 2 with the Helmholtz equation to compute the value of μ_p , the average perpendicular component of the dipole moment per adsorbed stearic acid molecule. Any variation in μ_p would then reflect any differences in the adsorption mechanism between the acid group and the different metals and oxides. It should be apparent from

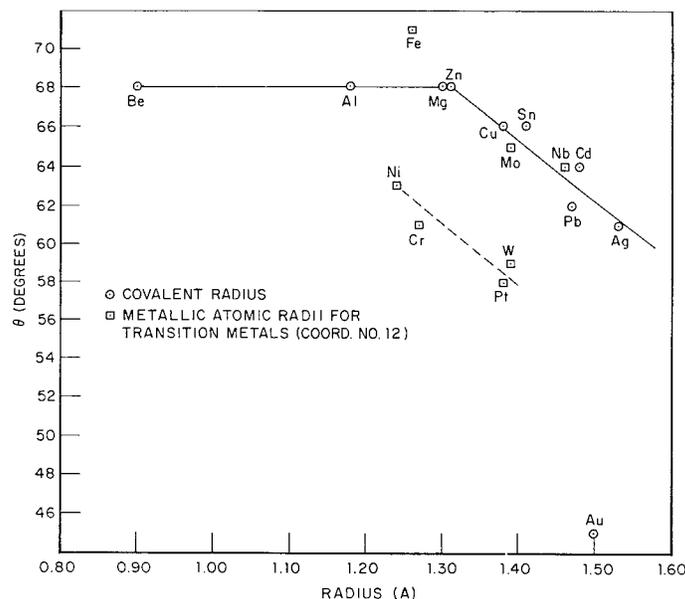


Fig. 5 - Methylene iodide contact angles (θ) on various metals with stearic acid monolayers vs covalent radius (r_o)

Table 2, because of the much larger range of values of ΔV than of θ , that stearic acid has an interaction with each metal which varies remarkably with the nature of the metal (or oxide).

Any chemical reaction of the carboxyl group of a fatty acid with the oxidized surface of a metal would be expected to change the original dipole moment of the molecule, and the extent of such a reaction may be different at higher temperatures. But adsorbed water on the metal could also participate in the mechanism, and excess water may be displaced by the adsorbing organic film; if so, then the value of μ_p would be altered because of contributions from dipole moments of water molecules. Apart from any chemical reaction occurring which would alter μ_p , there would be changes in the induced polarization of the adsorbed carboxyl group caused by the highly localized electrostatic fields of the various metals (3). Of course, it would be interesting to separate these three effects on ΔV , but further research is needed to do so.

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13. ABSTRACT		
<p>Each of the homologous series of pure n-fatty acids from formic to hexacosanoic has been studied as a condensed monomolecular layer adsorbed on Pt and NiO substrates. Both the stearic and nonadecanoic acids were also studied on various polished metal surfaces including Fe, Cr, Cu, Au, W, Mo, Ag, Nb, Al, Cd, Mg, Sn, Pb, Be, Zn, and Ni. The change in contact potential difference (ΔV) between the metal and an aged reference electrode was measured in air at 23°C and 50% R.H. Surface packing in each monolayer was characterized by the methylene iodide contact angle (θ). Systematic and reproducible values of ΔV and θ were found for each member of the homologous series. An asymptotic maximum occurred in the ΔV vs N curves when N, the number of carbon atoms per adsorbed molecule, was 14 or more for Pt and NiO substrates. Alternation of ΔV occurred for odd and even values of N on NiO and the baser metals but not on Pt and Au. Values of θ for stearic acid varied with the nature of the metal substrate, and the results were in reasonable accord with the lattice spacing of the substrate atoms. Values of ΔV for stearic acid monolayers varied from a maximum of 0.365 volt on W to -0.095 volt on Pb, and it was concluded that the perpendicular component of the dipole moment of the adsorbed acid molecule was a function of the specific interaction of metal substrate and the acid carboxylic group. Stearic acid desorbed readily from Pt but not from NiO, and it was concluded that chemisorption had occurred on the NiO.</p>		

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fatty acid monolayers Contact potentials Adsorption on metals and oxides Surface chemistry Contact angle Chemisorption Adsorbed monolayers						

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