

Adsorption of Dimer, Trimer, Stearic, Oleic, Linoleic, Nonanoic and Azelaic Acids on Ferric Oxide

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ABSTRACT

The adsorption isotherms of solutions of dimer, trimer, stearic, oleic, linoleic, nonanoic and azelaic acids in organic solvents, (mostly hexane) have been determined on an alpha ferric oxide with a surface area (B.E.T. N_2 adsorption) of 99 m^2 ($99 \times 10^{20} \text{ A}^2$) per gram. They all showed limiting adsorption as grams adsorbed per gram of iron oxide beyond a concentration of about $1 \text{ g}/100 \text{ cc}$, analogous to the Langmuir type monolayer isotherm. Areas per molecule were calculated and compared with areas of close-packed models in positions parallel to and perpendicular to the surface. The calculated areas corresponded more closely to the flat or parallel positions. Heats of adsorption were determined and were in the range of 27-71 kcal/eq, suggesting chemisorption of the COOH group at the surface. The value of dimer acid suggests that both COOH groups are chemisorbed. Models show that the parallel position permits both COOH groups to touch the surface. The perpendicular position generally does not permit both COOH groups to touch the surface. Dimer acid showed a value (71 kcal/eq) higher than the monobasic acids (44-55 kcal/eq), possibly due to interaction of the ring structure (partly aromatic) with the surface. Azelaic acid from an 80-20 *t*-butanol-hexane solvent showed a lower value of 27 kcal/eq, possibly due to adsorption of a hydrogen-bonded alcohol-acid moiety as such.

INTRODUCTION

The area occupied by fatty acids, especially stearic acid, as monomolecular films on water has been studied many times since the original classical work of Langmuir (1) who reported a cross sectional area of 22 A^2 for stearic acid with the molecular chain perpendicular to the water surface and with the polar COOH group oriented toward the water surface. A recent study (2) showed values of 19.0, 20.3, 23.1 and 24.7 A^2 for stearic acid on water (0.1 NHCl) corresponding to different points on the pressure area isotherms. These were related to the structures of different crystalline forms of stearic acid.

The adsorption of gases onto solids has been extensively studied and has resulted in the B.E.T. (3) method of estimating the specific area of finely divided solids, based on determining the amount of an inert gas (frequently nitrogen) necessary to form a monomolecular film on the surface. Ross (4) considers that "this method has been experimentally shown to be sufficiently accurate for most practical purposes and has successfully met an urgent requirement for a rapid estimate of particle size" (surface).

In spite of the assumptions involved in the B.E.T. theory, this is the most commonly used method of estimating surface area in relation to adsorption phenomena of organic substances onto surfaces.

The adsorption of a solute from its solution onto a solid surface is much more complex. The solute and solvent compete for adsorption on the surface. With a polar molecule, such as a fatty acid, and a polar surface, such as

an oxide, in a relatively nonpolar solvent, the competition of the solvent should be minimal and the analogy to a gas adsorption on a solid should be valid with the concentration of solute analogous to the pressure of a gas in gas adsorption.

Kipling and Wright (5) studied the adsorption of stearic acid on silica, alumina and titanium dioxide from cyclohexane. From the limiting values of adsorption (monomolecular film shown by the plateau of the adsorption curves) and the area of the oxides determined by B.E.T. adsorption, they calculated the areas occupied by stearic acid on these oxides. On SiO_2 , the adsorption corresponded to an area of 114 A^2 indicating an orientation parallel to the surface, while on TiO_2 and on Al_2O_3 , the adsorption corresponded to 20.5 A^2 , representing a perpendicular orientation. Russell and Cochran (6) had previously shown that stearic acid is adsorbed onto alumina from benzene solution as a monolayer corresponding to an area of 17 A^2 or perpendicular orientation.

Smith and Fuzek (7) reported on the adsorption of C_{10} , C_{12} , C_{16} , C_{19} and C_{22} saturated fatty acids on Raney Nickel and on Adams Platinum Catalyst (reduced platinum oxide) from benzene. The adsorption of all of these saturated straight chain acids on Raney Ni corresponded well with a cross sectional area of 20.5 A^2 (perpendicular) compared to the determined B.E.T. area. Their data showed that the adsorption equilibrium was quite rapid, occurring in less than 10 min, and suggested that it was chemisorption rather than physical adsorption.

Harkins and Gaus (8) studied the adsorption of oleic acid onto TiO_2 from benzene and found that a cross sectional area of 20 A for oleic acid agreed well with the surface area estimated by a microscopic method, assuming a spherical shape of the TiO_2 .

Kipling and Wright (5) suggested that the greater electronegativity of silicon, compared to aluminum and titanium, might be related to the parallel orientation on silicon dioxide and the perpendicular orientation on aluminum and titanium oxides. Pauling's (9) electronegativity value for silicon is 1.8, for aluminum, 1.5 and for titanium, 1.5. For iron (Fe^{3+}), it is 1.9.

Dimer acid has been shown to inhibit rusting of iron surfaces when added to gasoline, naphthas and fuel oils (10,11).

A recent study (12) has been made on the adsorption of polymeric dimer acid derivatives and of fatty acid derivatives onto alumina and ferric oxide in relation to their corrosion-inhibiting properties.

This paper presents a study of the adsorption onto a ferric oxide of dimer acid, trimer acid and some fatty acids by adsorption isotherms and by measurement of heats of adsorption. Knowledge of the nature of adsorption might help to interpret the corrosion inhibition properties of dimer acid and its derivatives. The solvent was hexane, except for trimer acid (hexane-*t*-butanol, 90/10), stearic acid (cyclohexane) and azelaic acid (*t*-butanol-hexane, 80/20).

EXPERIMENTAL PROCEDURES

Materials

Dimer acid was a clay-catalyzed dimer of a linoleic acid rich mixture of fatty acids. It was hydrogenated and

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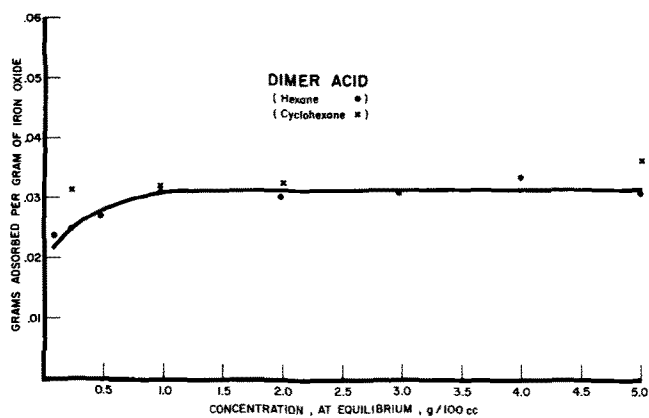


FIG. 1.

fractionally distilled in high vacuum to remove monomer and trimer (dimer, 99.5%; trimer, 0% by gas liquid chromatography (GLC); IV, 9.6; ϵ_{271} , 78).

Trimer acid was prepared from a high vacuum-distilled trimer methyl ester by conventional saponification (trimer, 93%; dimer, 6.5%; monomer, 0.5% by GLC; acid number, 192; saponification number, 198; IV, 16.2).

Stearic acid was C_{18} 94.5, C_{12} 0.3, C_{14} 0.2, C_{16} 4.0, $C_{18}^1 = 0.2$ and C_{20} 0.7.

Oleic acid was $C_{18}^1 = 93.9$, C_{16} 3.3, $C_{16}^1 = 0.2$, C_{17} 0.2, C_{18} 1.3 and $C_8^2 = 0.9$.

Linoleic acid was $C_{18}^2 = 97.0$, C_{16} 0.2, $C_{16}^1 = 0.1$, $C_{18}^1 = 2.6$ and $C_{18}^3 = 0.1$.

Nonanoic acid was C_9 97.5, C_8 1.9 and C_{10} 0.6.

Azelaic acid had a single peak by GLC.

Ferric oxide was prepared from a pure yellow iron oxide hydrate, $Fe_2O_3 \cdot H_2O$ (Pfizer Pure Yellow Oxide YLO 1788, 18.6 meters²/g) by heating at 300 C under vacuum (0.1 mm.) for 3 hr. Surface areas of two different preparations of the dried ferric oxide were 97.8 and 100.4 meters²/g by B.E.T. method (performed by American Instrument Company on their Adsorptomat). Both the hydrated form and the dried oxide showed x-ray spacings in good agreement with literature for the alpha form of the hydrate and the alpha form of the anhydrous Fe_2O_3 (13).

Adsorption was determined at room temperature, 25 C, by adding the Fe_2O_3 to a solution of the acid, usually at 1 g Fe_2O_3 per 100 cc of solution, shaking in a stoppered centrifuge tube in a mechanical shaker for 3 hr, centrifuging and titrating an aliquot of the clear supernatant solution with alcoholic KOH (phenolphthalein indicator) with a magnetic stirrer. A control sample of untreated solution of acid was then titrated and the difference in titration was used to calculate the amount of acid adsorbed. The adsorption was quite rapid, since a subsequent time study showed that dimer acid gave the same adsorption values within experimental error, at 5, 10, 15, 20, 60, 120 and 180 min.

Heats of adsorption were determined in a calorimeter which consisted of a dewar flask immersed in a constant temperature water bath at 25 C in a constant temperature room. The dewar flask was equipped with a sealed teflon cover, a sealed mechanical stirrer, an electrical heating element, a thermistor and a device for holding the glass ampule containing the ferric oxide. The thermistor was connected to a recording potentiometer. A glass rod extended into the ampule through a sleeve. A sharp tap of the glass rod caused the thin concave bottom of the vial to break clean from the wall and allowed the iron oxide to mix with the solution of acid.

In a typical run, 100 cc of fatty acid solution was placed in the dewar flask, 1 g of ferric oxide was weighed and placed in the glass ampule, in the dry box, and the

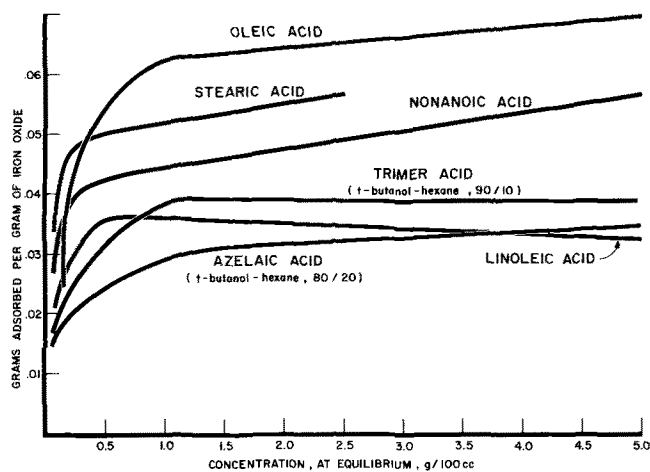


FIG. 2.

calorimeter was assembled and brought to thermal equilibrium by minor adjustment of the external constant temperature bath. Equilibrium was shown by a horizontal trace on the recording potentiometer. The ampule was then broken by a tap on the glass rod. Adsorption was quite rapid, as shown by a rapid rise on the recording, and leveled off to an essentially horizontal trace. Most of the rise occurred within 1 min and leveled off within 3-4 min. (Timed adsorption also showed equilibrium within 5 min or less.) Immediately after each run the calorimeter was calibrated by passing a known electric current at a known voltage for measured time with the equilibrated mixture present. The caloric equivalent per millimeter of scale was thus determined and used to calculate the calories equivalent to the rise observed due to adsorption. Reproducibility of heats of adsorption was about 5% with a scale rise of 40-50 mm (5-6 calories, approximately 0.2 C). Since the adsorption isotherms showed saturation of adsorbant at 2% or less concentration of acid, heats of adsorption were run at this concentration. In the oleic series, heats of adsorption were also run at 3%, 4% and 5% concentrations and were identical to the value at 2% concentration within experimental error.

Results of the adsorption isotherms are shown in Figures 1 and 2 and the saturation values and the heats of adsorption are shown in Table I.

The estimated areas of the molecules based on models were made by constructing them with Framework Molecular Models (Prentice-Hall). These models are designed to give the interatomic bonding distances to scale (1 in./Å) and also to give the Van der Waal radii of atoms which measures the effective size of the atoms in the nonbonded direction, in the sense of the nearest approach of molecules in crystalline form or in low energy collisions. This Van der Waal radius of hydrogen is 1.2 Å and, in fatty acid structures, results in an essentially circular cross section of the molecule when the carbon atoms are arranged in the usual zig zag arrangement assumed in crystalline and close-packed adsorbed films.

The stearic acid model can be represented by a comparatively simple rod-like structure. When perpendicular to the surface, its area was estimated from models to be 20 Å². The molecular area occupied by stearic acid in an orientation parallel to the surface was estimated to be 110 Å² from models. An area of 114 Å² has been reported for stearic acid (parallel) on certain carbon surfaces (14) and a value of 114 Å² was found to agree well with the parallel monolayer adsorption of stearic acid onto silica surfaces (5).

The molecule of oleic acid can be thought of as a rod which is slightly bent in the middle because of the *cis*

double bond between C₉ and C₁₀. In the perpendicular position, they can fit together to give an area (25 A²) only slightly greater than stearic acid. If there were no fitting together, the area would be about 43 A². In the parallel position, with fitting together, the area of oleic acid is 130 A or, without fitting, 235 A².

Linoleic acid, with two *cis* double bonds, is like a rod bent near the middle more severely than the oleic model. In the perpendicular position with best fitting, the area is the same as oleic acid, 25 A². Without fitting, the area is 54 A². In the parallel position, with fitting, the models showed an area of 143 A² or 246 A² without fitting.

Dimer acid is a mixture of isomeric C₃₆ dibasic acids made by polymerizing unsaturated C₁₈ monobasic fatty acids such as linoleic acid by heat or heat with catalysts, such as certain clays (15).

The sample of dimer acid used as starting material was made by polymerizing natural linoleic rich fatty acids with a clay catalyst. The structure of clay catalyzed nonconjugated linoleic acid dimer has been shown to contain monocyclic, bicyclic and tricyclic structures (16).

The monocyclic catalytic dimer was shown to be partially a benzene structure with saturated and unsaturated side chains. Its formation was suggested as a result of conversion by the catalyst of the nonconjugated linoleate to a conjugated form which dimerized by a Diels-Alder addition with another nonconjugated or conjugated monomer. It was proposed that the resulting substituted cyclohexane structure was converted by action of the catalyst to the benzene structure by hydrogen transfer from the ring to dimer side chains or monomers.

The bicyclic structure was proposed to result from a mechanism similar to that previously suggested for noncatalytic thermal dimerization of normal linoleate (17). According to this mechanism, radicals are thermally generated by a bimolecular hydrogen transfer from C₁₁ with conjugated resonance forms with free radicals at C₉ and C₁₃. These radicals couple to give noncyclic dehydrotype dimer with conjugated double bonds which then cyclize rapidly by an intramolecular Diels-Alder addition to give a bicyclic structure with a cyclohexane ring and a second fused ring of 4, 5 or 6 carbons.

Another mechanism proposed for thermal dimerization of normal linoleate (18) involves intermolecular addition of a linoleate free radical (at C₉ or C₁₃ from the conjugated resonance form of a dehydrolinoleate radical) to a double bond of another linoleate (rather than coupling of two free radicals), followed by intramolecular free radical addition to give monocyclic and bicyclic dimers with cyclopentane rings. This intramolecular radical addition could give a 4, 5, 6 or 7 membered ring, depending on which carbon of the double bonds the radical adds itself to.

Models of the various monocyclic and bicyclic structures, both aromatic and nonaromatic, were made with the hydrocarbon and the carboxy-terminated hydrocarbon chain substituents arranged in the zig zag carbon arrangement as in stearic acid, with the chains in the plane of the central ring structure and with arrangement of the chain to the ring to give minimal hydrogen repulsion due to hydrogen overlap in the region of the ring. The resulting structures were something like a four-legged spider with thick legs of different lengths.

Areas in the parallel position were estimated by measuring the area of a rectangle which enclosed the projection of the model onto a plane surface with the plane of the model parallel to the plane of the surface. This was considered the area without fitting or close packing.

The areas with fitting or close packing were estimated by measuring the area of a projection of the molecule onto the plane, or by subtracting the unoccupied areas from the rectangular area determined without fitting. The areas with

TABLE I

Adsorption of Fatty Acids Onto Ferric Oxide

Acid	Grams absorbed per gram Fe ₂ O ₃ at saturation	Mmoles/g Fe ₂ O ₃	Calculated area from adsorption, A ²	Area, models ^a		Ratio of areas, calculated-model		Heat of adsorption, kcal/eq.
				Parallel, A ²	Perpendicular, A ²	Parallel	Perpendicular	
Dimer	0.0304	0.0543	302	230-320	60-120	1.3-0.94	5.0-2.5	71
Trimer ^b	0.0392	0.0466	350	---	---	---	---	52
Stearic ^c	0.054	0.190	87	120	20	0.73	4.3	55
Oleic	0.062	0.220	75	130	25	0.67	3.0	44
Linoleic	0.035	0.125	131	143	25	0.92	5.7	47
Nonanoic	0.044	0.278	59	66	20	0.89	2.9	53
Azelaic ^d	0.032	0.171	96	70	20	1.37	4.8	27

^aAreas estimated from models with best fitting (see text).

^bSolvent was hexane-*t*-butanol (90:10). All others from hexane, except as noted.

^cSolvent was cyclohexane.

^dSolvent was *t*-butanol-hexane (80:20).

fitting, 230 A² to 320 A², were about one half of the areas without fitting, 460 A² to 590 A². With all parallel arrangements, both carboxyl groups were in contact with the surface.

In the arrangement with the plane of the dimer molecule perpendicular to the surface, areas ranged from 60 to 120 A² without fitting. Fitting was not possible with many models and, where possible, usually resulted in an area only 10-20% less than with fitting. Without about one half of the models, only one carboxyl group could contact the surface in the perpendicular arrangement.

Models of trimer were not attempted, since its structure is much less clear.

DISCUSSION

The adsorption isotherms all showed a fairly close approximation to the Langmuir type of monomolecular adsorption isotherm or the type I isotherm of Brunauer (19). Stearic acid, nonanoic acid and, to a lesser extent, oleic acid, showed a slight upward slope of the plateau. This is often interpreted as indication of a secondary adsorption onto the first monolayer. Azelaic acid was absorbed from a *t*-butanol-hexane (80:20) mixture, which has limited solubility in hexane, which probably accounts for the slower approach to saturation. Dimer acid from cyclohexane showed the same saturation value as from hexane, but showed saturation at a lower concentration than from hexane. Trimer acid was from hexane-*t*-butanol (90:10) due to limited solubility in hexane.

The areas calculated for the various molecules, as shown in Table I, were obtained by dividing the B.E.T. area of the iron oxide (99 X 10²⁰ A²/g) by the number of molecules of adsorbate (mmoles X 10⁻³ X 6.02 X 10²³) per gram of iron oxide at saturation (2% solution) as determined by the adsorption isotherm.

The areas are in fairly close agreement with those estimated for flat or horizontal arrangements rather than perpendicular. The ratio of area calculated from adsorption to the areas estimated from models in the horizontal position ranges from 0.67 to 1.3, while the ratio of calculated areas to areas estimated from models in the vertical position ranges from 2.9 to 5.7. The horizontal position would have been predicted by Kipling and Wright's consideration of electronegativity of metals (as oxides) in relation to fatty acid adsorption (5).

The heats of adsorption were of a magnitude which is generally considered to represent chemisorption rather than physical adsorption. Physical adsorption (when molecules are held by Van der Waal's forces of attraction) generally give heats of adsorption of less than 10 kcal/mole. Chemical adsorption or chemisorption which occurs when bonds to the surface result from an exchange or a sharing of electrons, usually gives values above 20 kcal/mole (20). The higher value for kcal/eq with dimer acid is somewhat surprising and might be due to some sort of interaction of the ring structures (partly aromatic) with the adsorbing surface.

The low value for azelaic acid is anomalous if both carboxyls are chemisorbed, since the adsorption data indicate a parallel orientation which should allow both of the carboxylic acid groups to contact the surface. However, the solvent used with azelaic acid was quite different (80% *t*-butanol-toluene), and the ratio of calculated to model area for parallel orientation was 1.37, compared to values slightly less than one for the monobasic acids. If the azelaic acid, in the presence of the high concentration of alcohol, existed as a hydrogen-bonded alcohol-acid moiety and was adsorbed to some extent as such, without breaking the hydrogen bonds, the lower heat of adsorption of azelaic acid would be largely explainable. Further studies with non-hydrogen bonding solvents would be interesting but limited by the low solubility of azelaic acid in nonpolar solvents.

Since carboxylic acids are largely hydrogen-bonded "dimers" in nonpolar solvents, the hydrogen bond energy would presumably have to be overcome to make a monomolecular chemisorbed film. Values for hydrogen bonding of the monobasic acids, acetic through butyric, have been reported as 16-17 kcal/eq (21). The heats of adsorption of nonhydrogen bonded carboxylic acids would presumably be 16-17 kcal/eq greater.

The interpretations of data are based on the following assumptions:

1. The area occupied by the fatty acids is the same as the area determined by B.E.T. surface measurements. If the area available to the fatty acids were less than the B.E.T. area, the calculated areas per molecule would be less than those reported.

2. The saturation level of adsorption represents a monomolecular layer of acid on the surface.

3. The heats of adsorption measured are due essentially to adsorption of the acid, not the solvent. If assumption No. 2 is correct, this assumption is reasonable.

4. The models represent a reasonable representation of the size and shape of the acid molecules, and fitting or close packing occurs. Lack of fitting or close packing would make the area based on models greater (cf. above).

These assumptions appear reasonable in view of the nature of the results and the nature of the adsorbants and adsorbates, and indicate that these fatty acids are adsorbed as monomolecular films in a position parallel to the surface of ferric oxide. Since both carboxyls of the dimer acid are presumably chemisorbed, it would be predicted that it would desorb less readily than the monobasic acids, since both carboxyls would have to desorb at the same time for the dibasic to leave the surface completely. This, along with the high ratio of carbon chain to carboxy, might explain the corrosion inhibition properties reported for dimer acid, assuming that a film of oxide is present or is formed on the iron surface.

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