present work is 69.5°. No transition point corresponding to 65.2–65.4°, which they obtained on heating, was found in the present case but the transition point between the B and C modifications, 63.5°, does approach their value of 63.9°, which was their second transition point upon cooling.

It appears that *n*-dotriacontane like *n*-hexacosane can occur in three forms. The equation for the expansion of the C form cannot be expressed by any simple equation. In the case of the liquid over the range studied, the relationships are linear and given by the equation $d = 0.8275 - 0.00064t$ where d is the density at any temperature t.

Summary

1. It has been shown that the dilatometer method can be used to measure accurately the transition points of solid paraffin hydrocarbons such as dicetyl.

2. Pure dicetyl can be prepared from cetyl alcohol if sufficient recrystallizations are made.

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The Adsorption of Ethyl Iodide on a Plane Surface of Iron at 20°

BY MARION H. ARMBRUSTER AND J. B. AUSTIN

Although the adsorption of gases on powdered iron and on promoted iron catalysts has been studied intensively, practically no attention has been paid to adsorption on iron surfaces which are substantially plane. As the great majority of iron surfaces commonly used can be considered plane, at least from a macroscopic point of view, and as the condition of the surface presumably influences the behavior of iron and steel in pickling, in galvanizing and tinning, in painting, in lubrication, and in corrosion, a knowledge of adsorption phenomena on such surfaces is greatly to be desired. As a preliminary to a general study of the subject, measurements have been made of the adsorption at 20° of ethyl iodide on a surface of cold-rolled steel. The surface was studied in two conditions: (1) after degreasing, and (2) after degreasing and subsequent reduction in hydrogen at 450°. Ethyl iodide was selected because it is an effective inhibitor in pickling solutions and at the same time has a vapor pressure which enables it to be used conveniently in adsorption measurements.

Apparatus.—The method employed was identical with that described in earlier measurements on mica.[1] The apparatus, however, had been improved in two ways: the ratio of the volume of the adsorption bulb and trap to that of the remainder of the system had been changed to give higher accuracy, and the single McLeod gage had been replaced by a double one, one arm of which covered the range 10^{-6} to 0.2 mm., the other the range 0.2 to 2.0 mm. With these improvements pressure was deter-

mined with an accuracy of 1% over the range 10^{-6} to 2 mm. The volume of C, the main part of the system, was 521.8 cc.; the volume of A, the adsorption bulb and trap, and of B, the blank system, was 457.3 and 458.4 cc., respectively.

Materials.—Ethyl iodide from the Eastman Kodak Company was redistilled under reduced pressure and the constant boiling fraction was collected in a bulb which was subsequently connected to the gas manifold through a U-tube and vacuum stopcock. Dissolved or entrapped air was removed by first freezing the iodide in the U-tube and bulb with a mixture of carbon dioxide snow and alcohol, and then, by alternate warming of bulb and U-tube with the vacuum pump on, distilling the iodide back and forth until the pressure as read by the gage had fallen below 10^{-4} mm., which is approximately the vapor pressure of the iodide at this temperature. Ethyl iodide was then introduced into the adsorption system by allowing the U-tube to warm up with the stopcock to the gas manifold open. In spite of precautions to keep the iodide in the dark a very slight discoloration appeared after several weeks. When such discoloration was noted, a fresh sample was prepared. Measurements made with a trace of discoloration present gave, however, the same results as those made with a fresh sample.

Hydrogen, taken from a tank, was freed of traces of water vapor and oxygen by passing it through sulfuric acid and calcium chloride, then over hot platinized asbestos and finally over activated alumina and phosphorus pentoxide. Direct determination showed that hydrogen is not measurably adsorbed on the plane surface of iron at room temperature, hence its use caused no interference in the measurements with ethyl iodide.

Iron Surface.—The adsorbent was a bundle of cold-rolled flat steel wire in strips 0.076 mm. in thickness, 110 mm. in length and 19 mm. in width. These strips were not bound together but were packed into the adsorption bulb in an upright position. The total area, determined by measuring the dimensions of each strip, was 11,129

(1) Armbruster and Austin, THIS JOURNAL, **60**, 467 (1938).

sq. cm. and the bundle weighed 357.1 g. The surface was degreased with absolute alcohol and anhydrous ether before use. The chemical composition of the metal was C 0.39, Mn 0.70, S 0.049, P 0.016, Si 0.128.

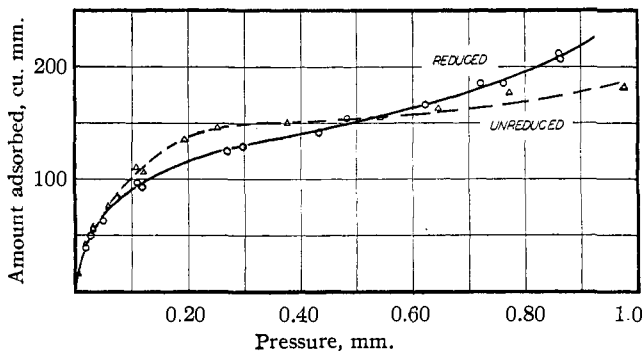**Treatment of Surface.**—The first set of measurements was made on the degreased surface after baking for two

Fig. 1.—Typical adsorption isotherms of ethyl iodide on a reduced and unreduced surface of iron.

hours at 300° under a pressure of 10^{-6} mm. This treatment, which gave a surface on which adsorption was reproducible, was adopted as standard after tests using longer time or higher temperature failed to show a significant difference in the results. In this first set no attempt was made to remove any invisible "oxide" film because it was desired to study the behavior of the iron surface in the condition in which it ordinarily exists. This degreased and baked surface is therefore referred to as "unreduced iron." After measurements with ethyl iodide, nitrogen, argon, carbon monoxide, carbon dioxide and oxygen, the surface was reduced at 450° in a stream of purified hydrogen introduced at the bottom of the adsorption bulb, and was freshly reduced before each run. The period of reduction was usually about twenty-four hours, was never less than eighteen hours, and was occasionally as long as sixty hours. Following reduction the adsorption bulb was sealed off and the sample was given the standard degassing treatment, producing a surface that appeared to be oxygen free. The adsorbent was cooled either in hydrogen or in vacuum. The conditions of cooling did not influence the magnitude of the adsorption but did affect the rate of approach to the equilibirum temperature. The adsorption bulb and liquid air trap in front of it were kept in water at 20° during all measurements. The trap between the system and the diffusion pump was immersed in liquid air from the middle of the baking period to the end of each run.

TABLE I

TYPICAL ADSORPTION OF ETHYL IODIDE ON DEGREASED UNREDUCED SURFACE OF IRON (CORRECTED FOR BLANK)

Pressure, mm.	Adsorption, cu. mm.	Pressure, mm.	Adsorption, cu. mm.
0.0133	41.4	0.250	145
.030	60.0	.375	150
.0603	93.4	.540	156
.105	111	.642	167.5
.120	106	.770	179
.190	135	.975	183.5

Results and Discussion.—Typical data for adsorption on the "unreduced iron," the reduced iron and the glass blank are given in Tables I, II and III. The results for the iron surfaces are also shown in Fig. 1, the initial adsorption being plotted on a larger scale in Fig. 2. Adsorption equilibrium was attained instantaneously on both the reduced and unreduced surface and was reproducible in successive runs.

Form of the Isotherms.—Isotherms for the iron surface in its two different conditions are given in Fig. 3 in the form of p/a against p, where a is the amount of gas adsorbed at pressure p. This method of plotting, which was suggested by Langmuir, yields a straight line if the data follow his isotherm, and is therefore useful in showing how closely the measurements fit his equation. It is evident from the diagram that the Langmuir relation holds for the middle pressure range but that it is not followed at either the highest or lowest pressures. Moreover, the range over which Langmuir's equation holds is much smaller for the reduced iron than for the unreduced surface.

TABLE II

TYPICAL ADSORPTION OF ETHYL IODIDE ON REDUCED IRON SURFACE (CORRECTED FOR BLANK)

Pressure, mm.	Adsorption, cu. mm.	Pressure, mm.	Adsorption, cu. mm.
0.0019	21	0.0010	15
.0109	39	.025	51
.0468	61	.267	125
.114	97	.430	141
.117	94	.620	167
.297	129	.760	184
.481	154	.860	211
.720	184		
.860	207		

TABLE III

TYPICAL ADSORPTION OF ETHYL IODIDE ON GLASS BLANK

Pressure, mm.	Adsorption, cu. mm.
0.0243	—0.7
.073	0.0
.0385	+0.9
.431	1.9
.785	2.5

The use of the more general isotherm given by Brunauer, Emmett and Teller[2] results in curves which are substantially identical with those shown in Fig. 3. This is not surprising because the pressure never exceeded about 0.01 the saturation pressure and, as shown below, the layer of adsorbed gas was only one molecule thick over

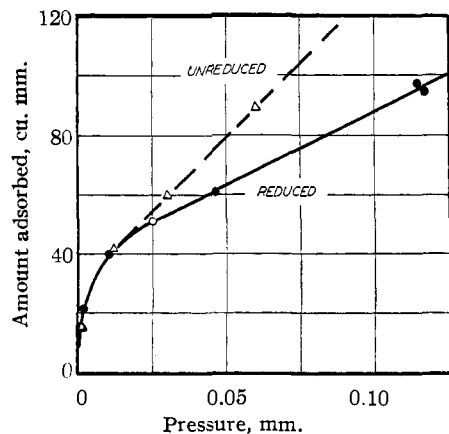(2) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

Fig. 2.—Typical initial adsorption shown on a larger scale. On curve for reduced surface, circles and dots represent different runs.

most of the pressure range studied. Under these conditions the equation of Brunauer, Emmett and Teller is substantially identical with Langmuir's.

The amount of gas adsorbed at the apparent saturation indicated by the horizontal portion of the curve for unreduced iron in Fig. 1 is about 150 cu. mm. The saturation calculated by means of the Langmuir equation from the linear part of the curve in Fig. 3, is 170 cu. mm., which is believed to be a better value. If it is assumed that the geometric area of the surface, that is, 11,129 sq. cm., is also the true area, and if the cross-sectional area of the ethyl iodide molecule is taken as 26.1 sq. Å., which is the two-thirds power of the volume per molecule in the liquid at 20°, then the surface is 100% covered at these pressures. This method of estimating the cross section of an adsorbed molecule has been widely used with generally satisfactory results, but its accuracy when used with organic compounds whose molecules are far from being cubic in shape is open to some question. Another method of obtaining the cross-sectional area of ethyl iodide is by means of the equation given by Emmett and Brunauer.[3] Taking the density of the liquid at 20° as 1.93 g. per cc., this relation gives 28.5 sq. Å., which, on the basis of 170 cu. mm. adsorbed at saturation, corresponds to a coverage of 110%. On either basis, therefore, it is clear that saturation corresponds to the completion of a monomolecular layer, and, further, that the cold-rolled surface is substantially plane. This conclusion is confirmed by unpublished data for the adsorption of argon on the same surface, which show that the

(3) Emmett and Brunauer, THIS JOURNAL, **59**, 1558 (1937).

completion of a monomolecular layer corresponds to a coverage of about 130%. As the argon atom is smaller than the ethyl iodide molecule and may therefore be able to enter minute irregularities which ethyl iodide cannot penetrate, and as there is less uncertainty in the cross-sectional area, this result probably gives a better indication of the size of the surface than that obtained with ethyl iodide. There can be no doubt, therefore, that the surface is substantially plane.
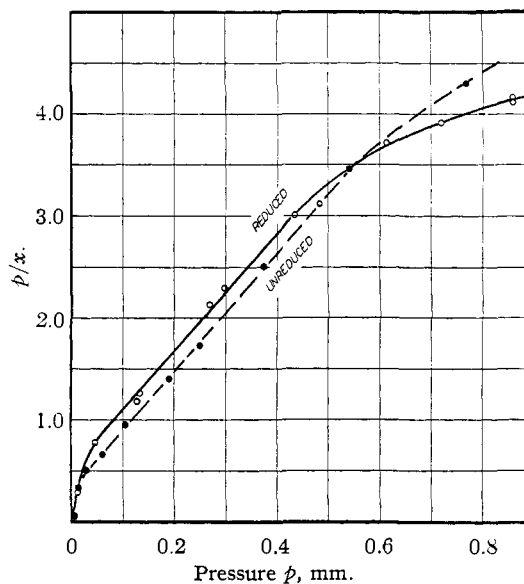

Fig. 3.—Isotherms of Fig. 1 plotted to show deviation from Langmuir's equation.

It is also of interest to note that the point on the isotherm in Fig. 1 at which the monomolecular layer is substantially complete, that is, the point at which the curve levels off, corresponds very well with the point which Emmett and Brunauer[3] (p. 1553), on the basis of other evidence, have chosen on their isotherms as representing completion of a monolayer. This is the point they call B and our data confirm the correctness of their conclusions. The increased adsorption at the highest pressure studied, above 0.60 mm., represents almost certainly the beginning of a second layer of adsorbed gas.

In Fig. 3 the linear portion of the curve for the reduced surface has the same slope as that for the unreduced iron, so that the amount of gas required to complete a monomolecular layer is the same for both kinds of surface. The deviation from linearity in the curve for reduced iron begins at a lower pressure than for the unreduced surface, and the curves cross at a pressure of about

0.50 mm., indicating that for a given pressure above this value the concentration of adsorbed ethyl iodide is greater on the reduced surface.

Measurements made in the region of very small adsorption indicate that on the unreduced surface, Langmuir's equation is not followed until approximately 20 cu. mm. of gas is adsorbed. Below this amount, which corresponds to a coverage of about one-eighth of the surface, adsorption increases more rapidly with pressure than it does in the range in which Langmuir's isotherm is valid. The reason for this is not clear. One possible explanation is that at low pressures adsorption may take place on active points such as grain boundaries, or patches of impurity, but the behavior of the reduced surface casts some doubt on this view, for on the reduced iron departure from the Langmuir equation extends up to an adsorption of 60 cu. mm., which corresponds to a coverage of about one-third of the surface and it is hardly likely that grain boundaries or particles of carbide or oxide constitute so large a proportion of the exposed area.
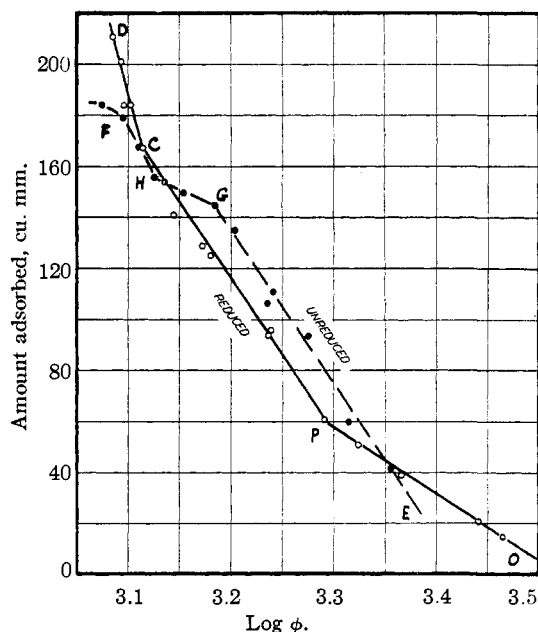

Fig. 4.—Isotherms of Fig. 1 plotted to show deviation from Palmer's isotherm.

Initial adsorption of this sort, though unusual, is not unknown. Its existence was predicted by Polanyi[4] on the basis of his adsorption theory and it has been observed experimentally. For example, a somewhat similar isotherm was obtained

(4) Polanyi, *Verhdl. deuts. phys. Ges.*, **18**, 55 (1916).

by Tompkins[5] and a precisely similar behavior was observed with cyclopentane on vitreous silica by Palmer and Clark.[6]

As Palmer and Clark point out, an isotherm of this form is obtained if the adsorbing surface is initially contaminated by a substance of high adsorptive power, but it is difficult to see what this second substance might be in the present measurements. Moreover, if this anomaly were due to contamination, successive determinations should yield a more normal curve, yet the behavior observed appeared to be reproducible. Palmer and Clark attempted to explain this behavior by assuming that at low pressures a molecule condenses on a point of high potential and that this molecule may, if polar, enhance the surface potential in its immediate neighborhood so that a second molecule tends to condense next to the first, although the normal potential of the surface might be too small to permit this with non-polar molecules. This explanation, which fits well in some cases, is not as satisfactory in others. For example, in their own measurements it is difficult to see why a molecule such as cyclohexane should show this effect much more markedly than more polar molecules such as alcohols.

The data also have been plotted in the form recommended by Palmer,[7] namely, as a, the amount adsorbed, against log φ, where φ is the adsorption potential calculated from the relation $\varphi = RT \log P_s/p$, p being the pressure corresponding to adsorption a, and P_s being the saturation pressure at the temperature in question. Isotherms of this form obtained by Palmer for the adsorption of organic vapors on vitreous silica are straight lines all having the same slope. The data for ethyl iodide on iron are plotted in this manner in Fig. 4. As with the Langmuir isotherm, the lines are straight and parallel in the intermediate range of pressure but show deviations from the common slope in both high and low pressure ranges. The kinks in the curves at the high pressure region are believed to be associated with the completion of a monomolecular layer. On this basis the volume of ethyl iodide required is between 145 and 170 cu. mm., in fair agreement with the value of 170 cu. mm. deduced from the Langmuir equation.

Spreading Force and Equation of State.— Palmer has also shown[7] that his adsorption isotherm can be combined with Gibbs' adsorption

(5) Tompkins, *Trans. Faraday Soc.*, **32**, 643 (1936).
(6) Palmer and Clark, *Proc. Roy. Soc.* (London), **A149**, 360 (1935).
(7) Palmer, *ibid.*, **A160**, 254 (1937).

isotherm to give a relation from which the lateral spreading force, F, of the adsorbed gas can be calculated. This equation is

$$F = f\varphi_0 e^{-sa}(a + 1/s) + I \qquad (1)$$

where f is a dimensional constant for adjusting units, φ_0 is the potential of the surface at zero adsorption, s is the slope of the log φ-a curve, that is, the slope of the lines in Fig. 4, a is the amount adsorbed and I is a constant of integration. This relation has been used to calculate the variation of spreading force with the effective surface area per molecule, with results shown in Fig. 5, which also includes (dash and dot line) the force–area curve for a two-dimensional perfect gas at the same temperature. In this calculation, the area per molecule has been taken as the geometric area, 11,129 sq. cm., divided by the number of molecules adsorbed. For the reduced surface the lower part of the curve (AB in Fig. 4) was extrapolated to $a = 0$ to obtain φ_0, and it was assumed that $F = 0$ when $a = 0$. The second section (BC) was again extrapolated to zero adsorption to obtain a new φ_0, but the integration constant, I, was adjusted so that the value of the spreading force at point B corresponded with that obtained from calculations on the section AB. A similar adjustment of the constant was made for section CD. The calculation for the unreduced surface is based on a value of φ_0 obtained by extrapolating section EG to $a = 0$, and on the assumption that $F = 0$ when $a = 0$. It is possible, perhaps likely, that at still lower pressures, there may be a change of slope corresponding to that found at B on the curve for the reduced surface, so that there is some uncertainty as to the exact values of F, but this uncertainty is believed to be small. The variation of F with a is, of course, not subject to this uncertainty. The results for sections GH and HJ were obtained by adjusting the constant of integration as before.

The curve for the unreduced surface (Fig. 5) bears a striking resemblance to the force–area curves for insoluble films on water. The sudden change in the curve beginning at $A = 30$ sq. Å. is particularly significant and suggests the completion of a monomolecular layer at this point, and the flattening off below 28 sq. Å. suggests the formation of a second layer. This inference is further strengthened by the fact that the area per molecule at which the break occurs, that is, 30 sq. Å., is in reasonable agreement with the

cross-sectional area of 26 sq. Å. calculated from the volume per molecule in the liquid.

The deviation of this curve from that for a two-dimensional perfect gas (dot and dash line) is the same as the deviation from ideality shown by a real three-dimensional gas, which suggests that the data should fit a two-dimensional analog of van der Waals equation of the form $(F + c/A^2) \cdot (A - A_0) = kT$, where k is the Boltzmann constant, T is the temperature on the absolute scale, and c and A_0 are constants. An attempt to fit the data to this equation shows that although it describes the results approximately it does not represent them accurately. The difficulty may arise from the uncertainty in F resulting from the
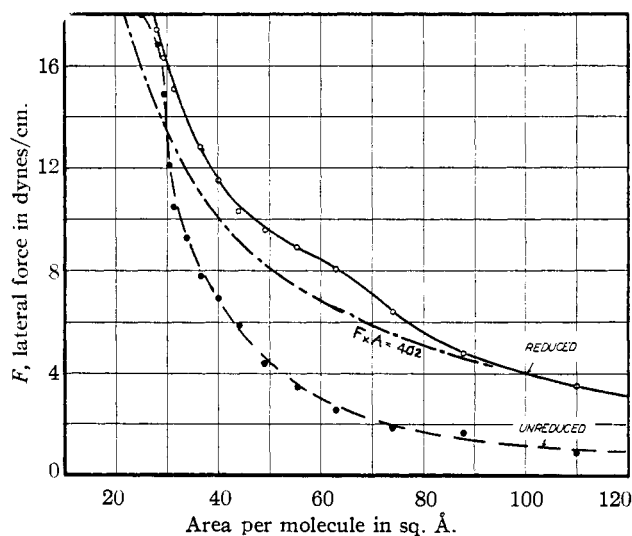

Fig. 5.—Force–area curves calculated from data of Fig. 4.

choice of a constant of integration but it seems more likely that it is a real effect—possibly due to the influence of dipole forces. The equation of state assumes that the only force acting between molecules is the van der Waals force, whereas there must certainly be some dipole interaction between molecules which have such a large dipole moment.

The curve for the reduced surface lies above that for a two-dimensional ideal gas, except at the lowest pressures where the two coincide. Under these circumstances the equation of state has the form $(F - c/A^2)(A - A_0) = kT$, which is the relation obtained if the spreading force is largely due to dipole repulsion, and it has been found that the relation $(F - 2700/A^2)A = kT$ fits the data with satisfactory accuracy. Although it is not clear why the quantity A_0 should be sub-

stantially zero, there is little room to doubt that on the reduced surface dipole interaction is a significant factor in the spreading force.

It appears then that on the unreduced surface, which must be essentially an oxide surface, the adsorbed molecules are held chiefly by van der Waals forces and that the forces acting between the adsorbed molecules are primarily of the same kind. The fact that the data do not exactly fit an equation of the van der Waals type for a two-dimensional phase, suggests the existence of other intermolecular forces which, considering the large dipole moment of ethyl iodide, are probably dipole interactions. On the reduced surface, however, it is clear that dipole forces are the most significant. It is likely that the adsorbed molecules are held to the surface by mirror-image forces and the force–area curve indicates clearly that dipole repulsion accounts for a large part of the lateral spreading force. A large dipole repulsion, however, requires oriented dipoles and implies that the adsorbed molecules may be oriented perpendicular to the surface.

Although the agreement between the cross-sectional area per molecule taken from the break in the force–area curve for the unreduced surface (30 sq. Å.) and that calculated from the molar volume of the liquid (26.1 sq. Å.) is reasonable, the difference deserves some consideration. In the first place it is interesting that the area indicated by the force–area curve is larger than the other. This cannot be due to an error in the estimated size of the surface, because the geometric surface area is smaller rather than larger than the true area, and increasing the value assumed for the surface area would lead to a still larger value of the cross-sectional area per molecule and an even greater discrepancy.

Rate of Adsorption.—The adsorbed gas was taken up instantaneously on each kind of iron surface. Such extremely rapid adsorption is ordinarily taken as a criterion of physical adsorption, as contrasted with chemisorption, and this conclusion is amply justified by other evidence in this case.

Critical Phenomena.—In spite of the fact that the temperature of measurement must be well below the critical temperature of ethyl iodide (281°), the force–area curves in Fig. 5 do not show any evidence of true critical phenomena. It is evident, therefore, that the critical temperature of the adsorbed iodide is below 20°, which

supports the calculations of Devonshire,[8] who estimates that the critical temperature of a two-dimensional gas is approximately $1/2$ of that of the corresponding three-dimensional gas when both temperatures are expressed on the absolute scale. The curve for reduced iron shows, however, a change in direction at about 8 dynes per cm. which strongly suggests the change in P-V isotherms for gases at temperatures approaching the critical, which, in our opinion, indicates that the critical temperature for the gas adsorbed on such a surface is not far below 20°.

Heat of Adsorption.—Brunauer, Emmett and Teller[2] have derived an equation for the adsorption isotherm which permits the calculation of the difference between E_1, the average heat of adsorption on the less active part of the surface, and E_2, the heat of liquefaction of the gas being adsorbed, and they have shown that for a given gas this difference, and hence E_1, is approximately constant for a large number of different adsorbing surfaces. The heat of adsorption should therefore be very nearly the same for both reduced and unreduced iron, which is confirmed by calculation, for $E_1 - E_2$ is 4460 cal. per mole for the unreduced surface and 4120 cal. per mole for the reduced surface. Taking E_2 at 20° as 7700 cal., E_1 is 12,200 and 11,800 cal., respectively. The heat of adsorption is therefore about 50% greater than the heat of liquefaction. It is also interesting to note that these calculated heats are of the same order of magnitude as the heat of adsorption of ethyl iodide on coconut charcoal determined calorimetrically by Lamb and Coolidge.[9]

Adsorption and Inhibitor Action.—The difference between the adsorption on the unreduced and reduced surfaces tempts one to speculate on the action of ethyl iodide as an inhibitor. It is admittedly not justifiable to draw conclusions regarding action in aqueous solution from measurements in a gas, yet it is not impossible that a study of behavior in the gaseous phase may elucidate the action in solution. The investigations of Mann and his colleagues[10] give strong support to the view that inhibitors are adsorbed on the metal surface, and that the size and chemical nature of the adsorbate determine the effectiveness of the inhibition. Machu[11] claims further that if an adsorbed layer is thick enough to have an

(8) Devonshire, *Proc. Roy. Soc.* (London), **163**, 132 (1937).
(9) Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).
(10) Mann, *Trans. Electrochem. Soc.*, **69**, 115 (1936).
(11) Machu. *ibid.*, **72**, 333 (1937).

electrical resistance higher than a critical value which he believes is about 3 ohms, it becomes effective in inhibiting further attack whereas a thinner film with a smaller resistance is not effective. The data of Fig. 1 are at least qualitatively consistent with these general views because it is evident that in the range of higher concentration (pressure) the amount adsorbed at a given concentration (pressure) is greater on the reduced surface. That is, any fresh iron exposed by acid attack in a pickling bath may become covered with a relatively thick layer of inhibitor whereas the oxide surfaces are covered with a thinner film. Moreover, if there is orientation on the iron surface the exposed part may be the relatively inert ethyl group. This suggests that dipole moment and polarizability may be significant factors in inhibitor action and that a study of these properties may show some correlation with the effectiveness of different organic compounds.

Summary

The adsorption of ethyl iodide on a plane surface of unreduced and reduced iron has been determined at 20° over the pressure range 10^{-6} to 1 mm. The adsorption isotherms fit Langmuir's equation and Palmer's relation only at intermediate pressures. The coverage at apparent saturation is about 100% based on the geometric area of the sample, which indicates that the iron surface is substantially plane.

Force–area curves for the two surfaces are quite different; that on the unreduced surface resembles the curves for insoluble films on water and shows a break at an area of about 30 sq. Å. per molecule whereas that on the reduced surface shows no such break. Comparison of the curves with that for an ideal two-dimensional gas suggests that on the unreduced surface the intermolecular forces are predominantly of the van der Waals type whereas on the reduced surface dipole repulsion seems to be the primary factor.

The molar heat of adsorption calculated from the isotherms is 11,800 cal. for the reduced iron and 12,200 cal. for the unreduced surface.

Although the temperature of measurement was well below the critical temperature, no critical phenomena were observed.

The possible bearing of the results on the action of inhibitors is discussed.

Kearny, N. J.   Received November 9, 1938

The Boiling Point Elevation. III. Sodium Chloride 1.0 to 4.0 M and 60 to 100°[1]

By Rodney P. Smith and Donald S. Hirtle[2]

The activity coefficient of sodium chloride has been determined at 0° from measurements of the freezing point depression,[3] and at 25° from electromotive force[4,5] and isopiestic vapor pressure measurements.[6,7] In 1932 Harned and Nims[8] extended the electromotive force measurements over the temperature range 0 to 40°. Harned and Cook[9] have reconsidered the calculation of the activity coefficient from the data of Harned and Nims,[8] and shown that the activity coefficients so obtained are consistent with the values given by other investigators at 0 to 25°. The data for sodium chloride have been extended further to cover the temperature range 60 to 100° by a determination of the boiling point elevation.[10] These results have been shown to be consistent with those of Harned and Cook[9] for the concentration range 0.05 to 1.0 M. To complete the measurements we have determined the boiling point elevation of sodium chloride solutions for the concentration range 1.0 to 4.0 M and at temperatures between 60 and 100°. It has been pointed out by Harned and Cook[9] that the values of $\overline{L}_2$ derived from the temperature coefficients of the electromotive force measurements appear to change too rapidly with the temperature. A consideration of all of these results not only allows a more reliable estimation of $\overline{L}_2$ and $\overline{C}_p - \overline{C}_{p_0}$, but

(1) This communication embodies part of the experimental material contained in the thesis submitted by Donald S. Hirtle to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1937.

(2) Present address: Calco Chemical Company, Bound Brook, New Jersey.

(3) Scatchard and Prentiss, This Journal, 55, 4355 (1933).

(4) Harned, ibid., 51, 416 (1929).

(5) Brown and MacInnes, ibid., 57, 1356 (1935).

(6) Robinson and Sinclair, ibid., 56, 1830 (1934).

(7) Scatchard, Hamer and Wood, ibid., 60, 3061 (1938).

(8) Harned and Nims, ibid., 54, 423 (1932).

(9) Harned and Cook, ibid., 61, 495 (1939).

(10) Smith, ibid., 61, 500 (1939).