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ON THE ADSORPTION OF DISSOLVED DIPOLAR MOLECULES ON SOLID METALS

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Outline:- The question of adsorption of dissolved dipolar molecules on solid metals which is particularly important in connection with lubrication in the sphere of limit friction was investigated. The relative saturation of the adsorption-layer with increasing concentration of the solution of those polar molecules in contact with the metal is investigated with the aid of static or "adhesion" friction which is particularly strongly influenced by adsorbed molecules. For this purpose a semi-automatic measuring apparatus and a form of friction element or slider was evolved suitable for obtaining clearly reproducible friction-coefficients correct to a few per cent.

The method is described and the first results of the measurements obtained with various metals, solvents and dissolved polar substances are given.

An exceedingly strong adsorption of stearic acid on metals was observed together with the "gliding-effect", consisting in the disappearance of a finite static friction when a saturated adsorption-layer of this acid was present.

The effect of oxidation and sulphiding on the static friction is numerically illustrated.

Arrangement.

I. Introduction:-

Little is known of adsorption of dissolved molecules on solid metals though it is important both practically for lubrication, flotation, painting, catalysis etc., and theoretically. It is theoretically important because though there are some investigations on the nature of the adsorption-potential on metallic boundary surfaces and in particular with dipolar molecules there is not sufficient experimental material to develop adsorption theories still further. For the adsorption measurements with gases which also could be used for this latter purpose the number of dipolar substances at our disposal is only small in spite of the fact that the methods of measurements are magnificently developed. The great number of dipolar substances capable of adsoprtion from solutions remained unused because of experimental difficulties. The difficulties of such measurements of solutions are these: it is not very easily possible to make and treat metallic powder - as used for the usual adsorption methods - with such large specific surface as e.g. the so much examined charcoal and ensure that the surface remains completely metallic before coming into contact with the solution and is not made impure by oxides etc. When working with metallic powders of small specific surface, however, very sensitive methods are required to ascertain the concentration of the solution after adsorption. So there will always be the dilemma of trying to obtain easily measurable differences in concentration with strong but therefore probably impure adsorbents - or obtaining only small differences of concentration with weak adsorbents which, however, remain pure. The first course was taken by Harkins and Gaus[1] the second by Heymann and Boye[2]. These experiments - which are only beginnings - show that those difficulties about which we talked are not insurmountable but they also are the reason that the results of such measurements are very scarce. We find in the relevant papers that those two mentioned are all that was ever written on the subject.

II. Finding the static friction ("adhesion"-friction)

We shall now report an experiment in which an attempt is made to avoid the obstacles mentioned above by measuring on macroscopic metallic surfaces the relative saturation of the adsorption-layer at a certain concentration of the solution by means of the static friction[3] ("adhesion"-friction). The advantage of macroscopic surfaces is that they are easily cleaned and readily observed. Furthermore a great variety of metals can be examined independent of whether or not they can be produced in very fine subdivision. Also, conditions for the experiment can be selected in such a way that the concentration of the solution is only so minutely changed by adsorption of a layer on to the metal as to be beyond measurement[4]. Therefore no analysis would be necessary as the concentration remains a known factor from the weighed portion. The "adhesion"-friction or friction of rest

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1) W.D. Harkins and D.M. Gaus, Journ. Americ.Chem.Soc. Vol.53 (1931) page 2804.

2) E. Heymann and E. Boye, Koll.-Zs. Vol.59 (1932), page 153.

3) Immediate adsorption measurements have also been taken in hand. The calling up of Dr. Guny who worked on them stopped those experiments for the time being.

4) An exception to this seem to be the cases of particularly strong adsorption. These are dealt with later on.

used as an indicator of the relative saturation of the adsorption-layer is measured by the friction coefficient μ_H which is defined as the quotient of the tangential frictional force and normal impressed force when two bodies in contact are given relative tangential motion. Hitherto no clear and reproducible quantitative value has been given to the "adhesion" or static friction such as one is used to with other physical quantities. That can be seen from the fact that friction-coefficients are frequently given with one digit only or within rather wide limits. Values frequently vary according to the experimental method and even measurements with a simple instrument do the same. In view of these facts it seems unsuitable to use static friction about which there is still little known in order to measure another phenomenon viz. special adsorption here considered which is equally unexplored. This objection, however, becomes void if we examine the reasons for the vagueness of the friction-coefficients. One reason for a certain vagueness of the friction-coefficients of certain pairs of materials in contact is to be found in the phenomenon of friction itself. For the individual strength of the microscopical, material junction and energy barriers and particularly under shear stress which with their resistance to movement constitute the static (adhesion) friction, must vary within large limits as these obstacles can be of different kinds and sizes whilst their specific strengths are perhaps not very different.5)

By special selection of the experimental conditions particularly the formation of the adhering parts (junctions) and the surfaces finish, it is possible to diminish variation of the static friction (adhesion-friction); obviously, it is possible thus to standardize the selection of the "junctions" mentioned before. Another reason for the vagueness of static friction is that static friction depends upon a great number of different factors about which we still know little. Their nature must be left partly to chance as long as all influences are not known and as long as we cannot control them. One of these factors is the presence of foreign molecules which are bound to the surface chemically or by adsorption. And it is through these that the friction can be very greatly altered. Anologous to the principal law of photo-chemistry by Grotthus, it is true to say that foreign molecules can influence the static friction only when they are bound to the surface. Together with the assumption that the effect on the friction of such molecules bound to the surface must be in proportion to their relative covering of the surface, this principle forms the basis for the attempt to investigate the adsorption on surfaces of solid bodies by means of the static friction.

In the first place, conditions were sought under which static friction could be ascertained with that accuracy which is necessary to give reliable recognition of the effect on static friction of the concentration of the solution surrounding the friction slider. Therefore, the effect of the following factors was examined:

A. Kind of measuring apparatus.
B. Form of friction-slider.
C. Surface treatment.
D. Impurities.
E. Time.

5) After Bowden and Leben, Proc. Roy. Soc. A.169 (1939), page 371, have shown qualitative connections between friction and mechanical metal properties, it could be suggested to obtain the quantitative connections by means of the amounts of the variations of friction, and of the bulk properties which bear on it. We started on this with our distribution pictures of which two examples are given here in Figs. 1 and 2. (The friction was measured by the apparatus described above. The different results obtained for brass/brass and brass/iron are seen in the subdivision and spreading out of the distribution curves).

We aimed at being able to repeat the results of measurements in a reliable way with an average deviation of a small percentage from the mean. We also tried to develop a method for our work which was not too complicated.

A. Effect of the kind of measuring apparatus.

After a torsion apparatus had been found impracticable one of conventional construction was examined. Here a slider rests on a horizontal support and is loaded by weights whose vertical pull was directed horizontally by means of a small freely-rotating pulley. Pieces of metal in the shape of flat cylinders, lenses or watch-glasses were tried as sliders. The results showed a margin of error of at least 25% even when the average of very many single measurements was taken. There was also a great sensitivity to shocks. When the slider was under a tension just too small to cause motion, then motion could be initiated by the slightest shock. Such shocks were unavoidable when adding weights. Therefore, an apparatus was built on the principle of the inclined plane where there was reason to believe in the avoidance of shocks occurring through the measurements themselves. The angle was measured in which a body resting on an inclined plane slides down; the tangent of this angle is of course the friction coefficient. In particular a metal plate resting on three supports was examined as a slider. But results with this apparatus showed only a small improvement. In this case also, shocks caused by handling the instrument could not be avoided completely. The gliding was caused very often by making the plate rotate around an axis vertical to the plane of the plate. This phenomenon is an example of a source of error which later on could be observed in greater detail and which was due to the fact that the transition from adhesion to sliding is not clearly defined.

Based on these experiences an apparatus was constructed which works on the principle of the inclined plane, the sliding-angle of which is, in order to avoid jerking, not fixed by the person who measures but by increasing the inclination of the gliding-support steadily under the influence of the force of gravity. The construction is shown in figure No.3 and the mounting in figure No.4. The slider proper is in the measuring-apparatus "M" one foot of which is mounted in a corresponding opening of the beam "B". This beam is resting on the column "S" so as to be able to be rotated. By an overweight on the side of the measuring container it sinks down and inclines. Its movement is damped by an oil-brake consisting of a base-board and a cylinder "Z" which is able to pivot and contains a piston "K" into which a valve "V" is fitted. This valve opens when the beam is turned back to its starting position so that the reversed motion is not damped. On the right of the beam is a pointer which records the friction-coefficient on the scale "SK" at the moment when sliding is observed optically ot acoustically.

B. Effect of the form of the friction element.

Figure 5 shows the measuring apparatus with the friction insertion, a U-rail as a base and a cylinder as a slider. The friction insertion is shown alone in Fig. 6. This form proved to be the most suitable. By its use, coefficients of friction could be measured to an accuracy of 2 to 4%. The idea of this form of friction element was derived through various intermediate stages from the cross-wire experiments of Holm [9]. An intermediate stage of a friction-body put on a U-rail in which the principle of crossed wires can still be clearly recognised is shown in figure No.7. We can obtain with such a body results as good as with the cylinder but friction-coefficients higher than unity cannot be measured with it because the lower ring will then lift, causing disturbances through

vibrations. The edges of the rail on which the cylinder rests are rounded off. Sharp edges result in irregular values because after some sliding a succession of "saddle-like" deformities is caused. The arrangement shown here enables work with exclusion of air as the glider can be returned to its starting position by an inclination of the beam towards the side with the pointer without the necessity of opening the container. The object of shutting the measuring container with a glass-plate and a threaded ring is not only to exclude air but also to prevent evaporation of the liquid and its running out of the container when inclined. Heating is provided. Metals other than brass, iron and aluminium have as yet only been used for measurements in the form of electrolytic coatings.

C. Effect of the conditions of the surface.

If at least one surface of the adhering metal parts with which friction shall be measured is flat, the friction-coefficient and its variation depends essentially upon the condition of the surface. According to our observations polished surfaces as well as rough surfaces are unsuitable for exact measurements. When rail and cylinder are used the friction-coefficient is to a large extent independent of the condition of the surface. It did not matter if the surface was polished with emery cloth No.1/0 or finished with a polishing paper or a soft leather cloth. The upper limit of roughness permissible with metals differs, e.g. brass may be rubbed with a rougher grade of emery than silver without affecting friction measurement.

D. Effect of impurities.

While at first clean metallic surfaces only were to be examined, some observations about the influence of oxidation were made 6) by measuring freshly polished surfaces which had been oxidized by air. Friction of brass on brass was the same in cyclohexane whether the brass was polished under cyclohexane and did not come into contact with air until the measurement, or whether it was polished in air and for some minutes was in contact with air. A brass sur ace grew distinctly darker in colour after having been in contact with air for one day and friction became lower. Fatty (greasy) impurities can be removed by solvents through repeated rinsing. The most efficient solvents are ethylacetate and acetone. Rinsing must continue until the friction no longer alters in the presence of the cleansing agent. Then the cleansing agent must be removed by rinsing with the liquid under test. Here again the test liquid must be renewed again and again until the friction no longer changes.

E. Effect of time.

Quite often alterations of friction may be observed after some lapse of time. If for instance the container had not been rinsed sufficiently with the test-liquid a friction-value may at first be observed which is near that of the cleansing agent. After some time - ranging from some minutes to some hours - the friction alters to a constant value, which, however, need not yet be the value of the test liquid which will perhaps not be obtained before a renewed filling. In this case the time of desorption is observed. The time of adsorption can be observed if the measurement is changed from the

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6) ... the influence of which is reported in greater detail in the work of T.P. Hughes and G. Wittingham (cf. Transactions of the Faraday Society, Vol. 38 (1942) page 9.

solvent to the solution. When using low viscosity substances it is of such a magnitude that the equilibrium of adsorption is reached after approximately 5 minutes. When using concentrated solutions the adsorption time is so short that it could not be measured. Very dilute solutions also gave a final adjustment of the friction value very quickly which leads to the conclusion that there are at least two phenomena influencing the speed of adsorption. Perhaps they are the speed of diffusion and the real speed of adsorption. A time effect of very high magnitude can be observed when the cylinder, shortly before it slides, is turned around its longitudinal axis into a new position. A small lowering of the friction to approximately 0.05 could be observed if sliding takes place within the next 20 seconds. When, however, the cylinder was in its new position for 30 to 60 seconds the higher value of friction was obtained again, which does not alter any curve even if one waits very much longer. Using stearic acid/carbon tetrachloride this behaviour was examined more closely, when the relation of concentration to the static (adhesion) friction was measured after 2 intervals of rest. No systematic difference could be observed whether the interval of rest was one of 20 or one of 300 seconds. The time effect just described can be observed with solutions only, which leads to the conclusion that we are dealing with an adsorption phenomenon. It cannot be observed with pure liquids. If there is no air-bubble in the measuring container the friction will remain unaltered for weeks. This experiment was made with brass/brass in cyclohexane. The highest demands must be made as to the purity of solvents and the substances to be dissolved.

III. Carrying out the measurement.

The reason for a full exposition of the performance of the measurement apart from the description hitherto made is that precise statements about the carrying out of friction measurements can be found only very rarely so that it is not always possible to judge the values which are given.

After the surface has been treated, the slider is inserted into the measuring container and the cleansing done in the way described before. After the solvent has been poured in, measurements are taken which are repeated with fresh solvent until the friction-value no longer alters. With one filling - i.e. for one point on the curve - 10 single measurements are carried out. The deviation of the single measurements from the average value is 4 per cent on the average so that the error of the mean value itself is 2 per cent. The solutions are made by pipetting the substances to be dissolved or stock solutions of them into the measuring container. After the dilution the container is shaken and then one must wait for about 5 minutes before commencing measurement. The viscosity of the fluid in the oil-brake is adjusted to fix the duration of settling at 30 seconds. The scale is marked in units of 0.01 and the accuracy of reading is 0.005 units or more according to the skill of the measurer.

IV. Results of measurements.

The dependence of static-friction on the concentration of solutions of alcohols and fatty acids in hydrocarbons or carbon tetrachlorides were examined for several metals. The results may be roughly classified into those which show a relatively small adsorption and those which show a very strong adsorption.

A. Weak adsorption.

In graph No. 8 the results of solutions of n-propanol and n-butanol in benzol on brass and silver are shown. Whilst on brass alcohol is adsorbed from the solution in both cases, silver appears to adsorb only propanol whilst the straight line of the curve measured with butanol does not show any adsorption. As to the two curves for

brass, a small fall of the friction is characteristic after maximum saturation of the adsorption-layer has been reached. We may suppose that this is so because of the development of further layers of adsorbed molecules on top of the first layer.

B. Strong adsorption.

In graph No.9 we have the results obtained with stearic acid in various solvents on brass. When comparing the concentration-data of graphs 8 and 9 the reason for the classification into strong and weak adsorption becomes clear. Saturation of metallic surfaces with acid moleculed is already reached with normalities of 10^{-5} as compared to the normalities of 2 to 3 of the alcohols.

1. Effect of solvents.

As the three solvents cyclohexane, benzol and carbon tetrachloride give almost the same static friction for brass on brass and the final value obtained at higher concentrations also is the same, viz. 0.1, the intensity of adsorption can be read immediately off the curves for the static friction which decreases in the case of stearic acid with the solvents in the order given. The same order of solvents is obtained when they are arranged according to the strength of their adhesion on mercury - 128, 143 and 149 erg/cm^2. When it is kept in mind that - when dealing with adsorption from solutions - there is always competition between molecules of both substances contained in the solution to occupy the surface this connection between adhesion reaction of the solvent and the desorbing effect appears understandable.

2. Influence of metals.

Adsorption of stearic acid from cyclohexane on various metals was examined. Apart from the fact that after the same treatment of the surface the static friction of metals starts at different values, no other essential difference in behaviour can be observed. Roughly all curves (see graph No.10) show 3 different stages. First a very steep decline with smallest concentrations [7], followed secondly by a much smaller inclination and thirdly the stage of the "sliding-effect" about which we will speak later on. From these results it may reasonably be supposed that the change of the initial steep decline to the small inclination gives us the saturation of the adsorption-layer. This saturation means the formation of a monomolecular layer. Now the area of the macroscopic inner surface of the measuring container and the rails and slider is 104 cm^2. In order to cover this surface with stearic acid molecules the diameter of which is 20×10^{-16} cm^2, we need 0.8×10^{-7} Mole. With a normality of 5 to 10×10^{-6}, however, the amount of the molecules contained in the 20 ccm. of measuring liquid is the same, viz. 1 to 2×10^{-7} Mole. This means that in cyclohexane stearic acid is adsorbed so strongly that all molecules brought into the container are fixed until the metallic surface is occupied. We are of course easily made to think that there is a chemical reaction. But by using solvents the stearic acid can be completely desorbed again; we could, however, not yet see if the desorption takes place as a salt. We also must mention the measurement in carbon tetrachloride as an argument against a chemical reaction which in comparison with the measurement in cyclohexane points to a shifting of an adsorption equilibrium.

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7) A demonstrable lowering of friction takes place already at a normality of 10^{-7}, i.e. at a concentration corresponding to that of the hydrogen ions in water.

C. Limit friction.

Though it was not the aim of this research to explore the nature of limit friction itself but only to enable us to measure static friction for a very special purpose, we will give some information about an observation which appears to be not entirely unimportant. After the lowering of static friction with increasing concentration to a value of approximately 0.1 a further slight lowering of static friction with a further increase of concentration can be observed until at μ_H - approximately equalling 0.08 - an entirely new phenomenon can be found, viz. the disappearance of static friction altogether sd observed at first by Ch. Jacobs [8] and then again described by R. Holm [9]. A gliding takes place at very small angles with a speed which is lower the smaller the angle. The liquid - like behaviour of the adsorption-layer appears to happen only after the adsorption-layer has reached a greater thickness than that of one molecular layer. For this "sliding-effect" is not observed if intentionally only a single molecular layer is fixed on the metal according to the Blodgett method frequently applied by Japanese or English scientists who, however, never described the "sliding-effect". The procedure applied by Holm to produce an "epilamen" (several layers) makes it possible to form several molecular layers. The circumstances which cause a sliding-effect are not fully clear yet: the solvent has something to do with them as e.g. no effect was seen in a benzol solution. We were equally unable to find it with all metals which were examined. The influence of chemical changes of the metallic surface which was investigated thoroughly by Hughes and Wittingham [10] can also be tested by our measurements. Graph No.11 shows the difference between the relation of the static friction to concentration of silver with a pure surface and a surface which became oxidic and so impure probably through lying in the air. Sulphiding of silver up to a discolouring just visible lowers the static friction with cyclohexane from 0.62 to 0.52, and with 2×10^{-5} normal stearic acid solution in cyclohexane from 0.36 to 0.17.

V. Summary.

In the way just described systematic measurements of the adsorption of dissolved molecules on solid metals have been possible for the first time and have been made now as the results show. The variety of phenomena which are possible in the interaction of dissolved molecules with a metal, as already seen in the experiments on mercury, becomes thereby greater and more puzzling. In conjunction with our knowledge of the molecular and super-molecular structure in liquids as well as with a further development of the theory of adsorption on metals there soon will be a chance of obtaining results useful to industry.

Headings of illustrations:

Fig. 1 - (graph): distribution of errors of static friction of brass to brass in benzol.

Fig. 2 - (graph): distribution of errors of static friction of brass to iron in benzol.

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8) Ch. Jacobs, Annals of Physics Vol. 38 (1912) page 126.

9) R. Holm: Technical Physics of electrical contacts Berlin 1941.

10) cf. Footnote No. 6.

Fig. 3 - diagram of the structure of the measuring apparatus.

Fig. 4 - The measuring apparatus.

Fig. 5 - measuring container and friction-insertion.

Fig. 6 - friction insertion.

Fig. 7 - (right): intermediate stage in the development of a friction slider.

Fig. 8 - (graph): Results with solutions of n-propanol and n-butanol.
(a) propanol - benzol/brass
(b) butanol - benzol/brass
(c) butanol - benzol/silver
(d) propanol - benzol/silver.

Fig. 9 - (graph): Effect of the solvent on the adsorption of stearic acid on brass.
(a) cyclohexane
(b) benzol
(c) carbon tetrachloride

Fig. 10 - Effect of metal on the adsorption of stearic acid from cyclohexane
(a) brass
(b) iron
(c) aluminium
(d) silver

Fig. 11 - Static friction ("adhesion"-friction) of silver on silver in the presence of stearic acid in cyclohexane.

(a) metallic surface
(b) oxidic surface.