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HYDROGEN-TREATED GRAPHITIZED CARBON BLACKS

ADSORPTION OF ACETIC ACID AND PROPYLAMINE BY GAS CHROMATOGRAPHY

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SUMMARY

The isotherms and isosteric heats of adsorption in the region of very low surface coverages have been measured for propylamine and acetic acid on two graphitized carbon blacks, graphitized Sterling FT and MT, before and after hydrogen treatment at 1000°. In order to obtain adsorption isotherms at very low coverages with good precision, a gas chromatographic method has been adopted.

The experimental results confirm the effectiveness of the hydrogen treatment in removing trace amounts of surface oxides and the usefulness of an oxygen-free carbon surface in deriving adsorption isotherms of hydrogen-bonding substances. The removal of chemical impurities causes the extent of propylamine adsorption to be sharply reduced and the shape of the isotherm to be altered. On untreated graphitized carbon blacks, the heat of adsorption of propylamine shows an uninterrupted fall as the surface coverage increases, whereas after the hydrogen treatment, a constant value of 7.5 kcal/mole is obtained. In contrast to the behaviour of propylamine, on treated carbon surfaces the adsorption of acetic acid increases and the heat-coverage curve is steeper than for untreated surfaces. This is because the adsorbate can establish strong lateral interactions on a clean surface. The surface density of chemisorbed oxygen on unpurified graphitized Sterling FT is estimated as two oxygen-containing groups per 10^4 \AA^2 .

INTRODUCTION

Graphitized carbon blacks have been widely tested in order to determine their adsorption of substances from both gaseous and liquid phases. These adsorbing materials provide surfaces that are sufficiently chemically and geometrically homogeneous to give a reliable interpretation of the adsorption data, *e.g.*, of the adsorption isotherms and heats of adsorption; this is not the case with heterogeneous surfaces such as non-graphitized carbon blacks and inorganic oxides. Graphitized carbon blacks are of even greater use in basic studies of adsorption as a result of the con-

siderable amount of information that is available on their crystal structure and particle size. In addition, although these adsorbing materials are complex in physical structure, they can be easily reproduced.

However, adsorption measurements carried out at low coverage on graphitized carbon blacks for polar^{1,2} and non-polar³ substances yield anomalously high heats of adsorption, thus indicating the presence of a small fraction of heterogeneous sites on their surface. These heterogeneities are of two types, one of which consists of geometrical irregularities and typified by the studies by GRAHAM³, and the other of oxygen groups, which are presumably bound to the peripheral carbon atoms of each layer⁴. These hydrophilic sites may comprise a burnt-off residue that remains after the heating of carbon blacks to produce graphitic carbons⁵. It is generally accepted that these chemical heterogeneities account for their strong interactions with hydrogen-bonding adsorbates.

Several authors⁶⁻⁸ have pointed out the great influence that this small fraction of chemical heterogeneities has on the adsorption process of hydrogen-bonding substances by the surfaces of graphitized carbon blacks. The need for oxygen-free carbon surfaces so as to make adsorption data more amenable to theoretical treatment has been substantiated by these earlier studies.

The first attempt to obtain an uncontaminated surface was made by MILLARD *et al.*⁸, who reported that the oxygen surface complexes on Graphon, a graphitized carbon black with a surface area of about 90-100 m²/g, could be removed by heating the adsorbent in a stream of hydrogen at 1000°. The removal of chemisorbed oxygen was indicated by the fact that, within the sensitivity limits of their experimental apparatus, the heat of adsorption of water did not show variations that were dependent on the increase in surface coverage.

In the present work, hydrogen treatment has been extended to two other examples of graphitized carbon blacks, graphitized Sterling MT and graphitized Sterling FT, both of which have a degree of chemical and geometric surface homogeneity that is appreciably higher than that of Graphon⁹. The adsorption isotherms and heats of adsorption are given for acetic acid and propylamine in the region of very low surface coverages, obtained on both treated and untreated graphitized carbon blacks. Graphon was subjected to the same treatment, but we found that the decontamination of graphitized Sterling MT and FT is more complete than that of Graphon.

In order to obtain adsorption data at very low surface coverages, the pulse chromatographic method was used, as devised by GLÜCKAUF¹⁰ and widely adopted by other workers¹¹⁻¹⁴. In addition to the advantage of a much higher sensitivity than for static methods, this technique allows measurements to be made rapidly and the apparatus consists of simple, standard types of equipment. As far as accuracy is concerned, it has been shown by KISELEV AND YASHIN¹⁵ that, provided certain experimental conditions are observed¹⁶, the results obtained from chromatographic measurements are close to those from static adsorption measurements.

EXPERIMENTAL

Research-grade propylamine and acetic acid were used (E. Merck, Darmstadt, G.F.R.).

The samples of graphitized Sterling FT and graphitized Sterling MT adsorbing materials were supplied by Dr. W. R. SMITH of the Cabot Corp., Billerica, Mass., U.S.A. These two carbons had specific surface areas of 11.5 and 8.0 m²/g, respectively, based on nitrogen adsorption (B.E.T. method) and assigning to the nitrogen cross-sectional area a value of 16.2 Å². If, as reported by PIERCE AND EWING¹⁷, a value of 20.2 Å² instead of 16.2 Å² were used, the surface areas would be amended to 14.1 and 9.8 m²/g, respectively.

The hydrogen treatment was carried out as follows. A carbon black sample, previously sieved to the desired mesh range, was placed in a piece of iron tubing, which was in turn placed in a cylindrical oven. The oven was then heated to 1000° and a stream of pure hydrogen was passed through the sample. This temperature was maintained for about 4 h. The actual time is not critical: in the original work⁸, the treatment was carried out for 12 h, but in our experiments no further significant improvement was obtained by continuing the treatment for more than 4 h. Attempts were made to put the carbon into a pure quartz tube, among others. However, after heating, the tube was found to be seriously corroded, presumably due to a reaction between hydrogen, carbon and quartz at high temperatures. In order to obtain a highly purified hydrogen stream, two traps, both containing molecular sieves, were inserted in the gas-line in front of the inlet to the oven. One of the traps was maintained at 0°, so as to eliminate trace amounts of water, and the other at -196° (liquid nitrogen), so as to eliminate trace amounts of oxygen.

After the treatment, no appreciable variation in the surface areas of the graphitized carbon blacks was found.

The procedure described by KISELEV AND YASHIN¹⁸ was used for calculating isotherms from the profile of the chromatographic peak. The gas chromatograph used was a Carlo Erba, Model GI instrument, equipped with a flame ionization detector. The use of this detector permitted the determination of amounts of desorbed substances of the order of nanograms. In the GLÜCKAUF method¹⁰, no allowance is made for the broadening of the chromatographic band due to diffusion in the gas phase, which can give rise to errors in deriving isotherms. To minimize the effect of the diffusion, we used short glass chromatographic columns (1 m × 3 mm I.D.) packed with a fine powder (60-80 B.S.S.) of the adsorbing materials being studied. Also, relatively high linear velocities of the carrier gas (12-14 cm/sec) were used. Hydrogen, with a stated purity of 99.99%, was used as the carrier gas so as to prevent any possible slight oxidation by trace amounts of oxygen, which are always present in gases of normal purity.

The temperature throughout an adsorption run could be maintained to within ± 0.1°. The samples, injected with a 10 μl syringe (S.G.E., Melbourne, Australia), were suitably split at the column inlet to obtain the desired sample size (ca. 10⁻⁶ g). Repeated measurements of the peak areas corresponding to successive injections of the same compound in any one adsorption run were in agreement to within 2-3% provided that purified graphitized Sterling FT or MT was used. However, with untreated materials, especially in the elution of propylamine, repeated measurements were in agreement only to within 8-10%. This different behaviour must be accounted for by the slow desorption of the last adsorbate molecules strongly bonded to the carbon surface. Consequently, there were difficulties in measuring the peak areas having very broad tailing edges.

RESULTS AND DISCUSSION

The isotherms for the adsorption of propylamine on both untreated and treated graphitized Sterling FT and MT are shown in Figs. 1 and 2. The hydrogen treatment removed chemisorbed oxygen from the carbon surface, as shown by the fact that the initial "knee-bend" has almost completely disappeared, thus indicating a homo-

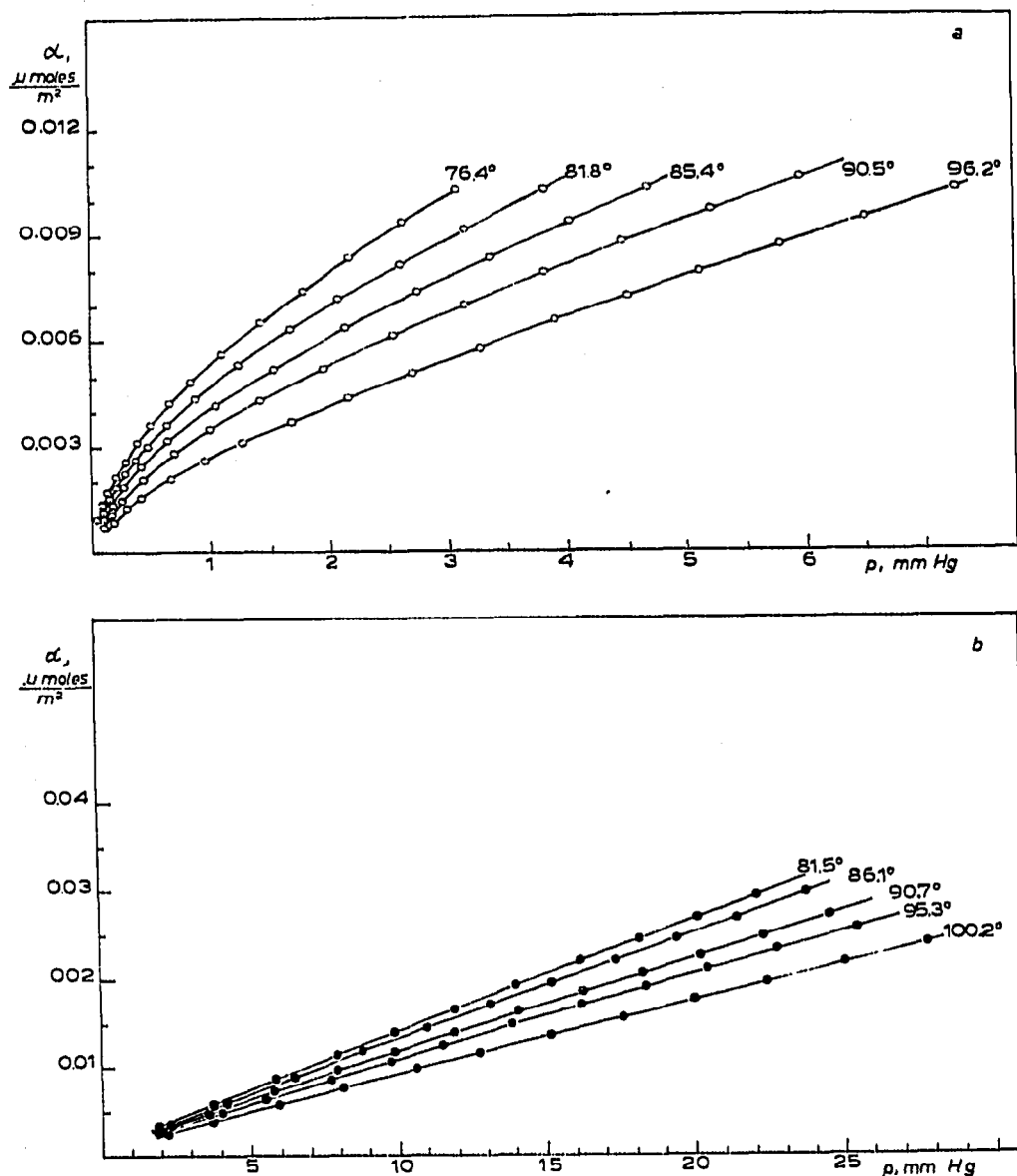


Fig. 1. (a) Isotherms for propylamine on graphitized Sterling FT. (b) Isotherms for propylamine on hydrogen-treated graphitized Sterling FT.

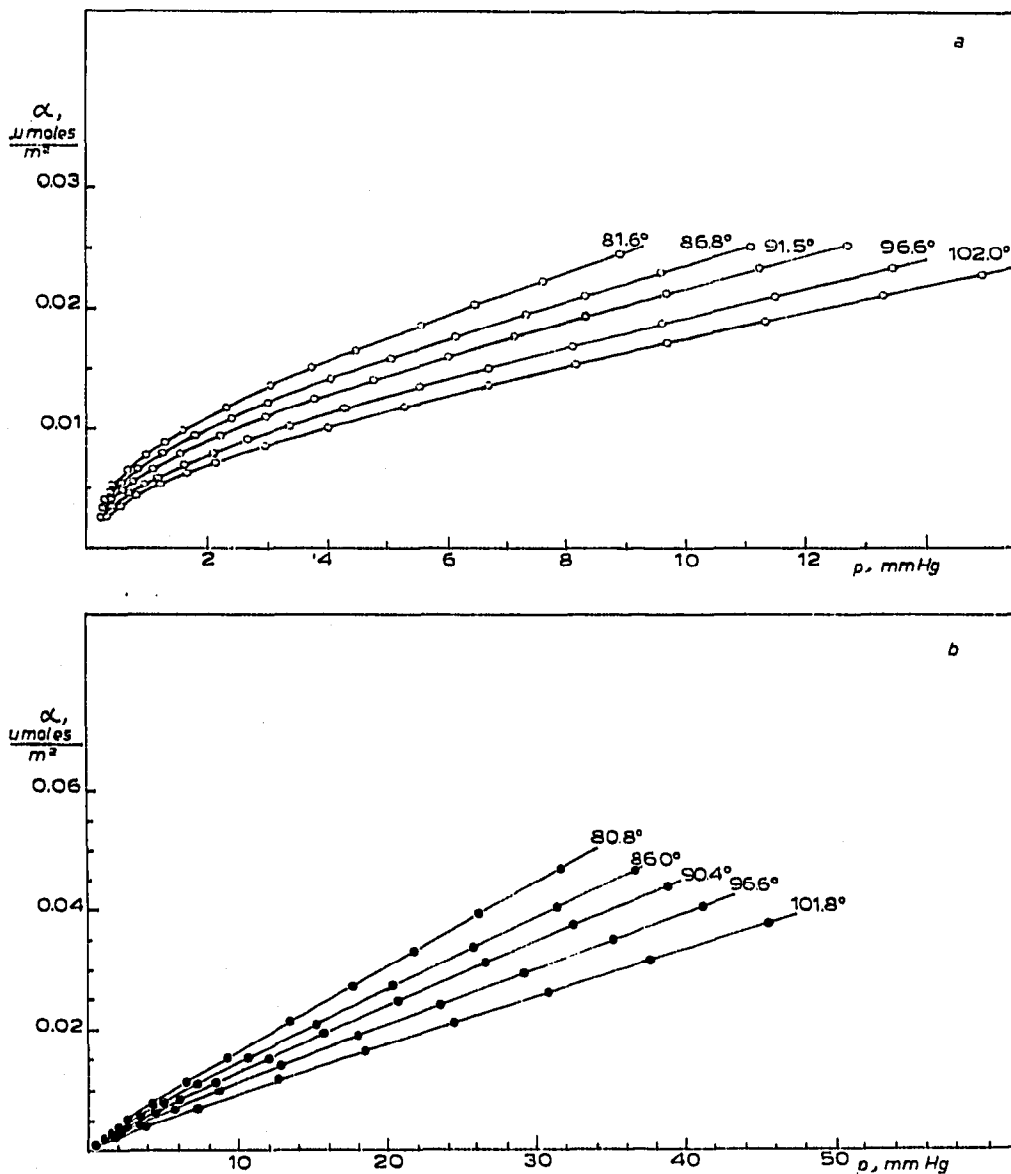


Fig. 2. (a) Isotherms for propylamine on graphitized Sterling MT. (b) Isotherms for propylamine on hydrogen-treated graphitized Sterling MT.

geneous distribution of the adsorptive sites. Also, at the same temperature and partial pressure in the gas phase where the comparison can be made, the concentration of propylamine in the adsorbed phase is clearly always much lower on purified adsorbents than on unpurified adsorbents. It can be seen that isotherms for propylamine on untreated surfaces are obtained over a narrower pressure range than for treated surfaces. This is because equal amounts of propylamine were injected into

all of the chromatographic columns and because untreated surfaces possess a higher affinity than treated surfaces for propylamine. Therefore, in the former instance the maximum of the chromatographic peak, corresponding to the maximum gas phase concentration of the adsorbate in equilibrium with the adsorbed layer, is systematically lower than in the latter instance.

The isotherms corresponding to unpurified adsorbing materials show that in some instances, at the same temperature and gas phase concentration, graphitized Sterling MT appears to adsorb a higher amount of propylamine per square meter of adsorbent than graphitized Sterling FT. However, it has been previously demonstrated that oxygen is almost completely chemisorbed at the periphery of the graphitic crystallites¹ and that graphitized Sterling FT is composed of particles that are smaller than those of the graphitized Sterling MT¹⁹. It follows that the former graphitized carbon black will have a higher degree of chemical heterogeneity than the latter, and graphitized Sterling FT will consequently adsorb a larger amount of propylamine than graphitized Sterling MT. These discrepancies can be accounted for by the great difficulty in obtaining reliable data from the adsorption of hydrogen-bonding compounds on oxidized surfaces at very low coverages. On the contrary, after chemical purification, at the same temperature and gas phase concentration, both of the graphitized carbon blacks adsorb the same amount of propylamine per unit surface area, which is to be expected as both of the surfaces consist of carbon atoms arranged as in graphite²⁰.

On both treated and untreated graphitized Sterling FT and MT, the isosteric heats of adsorption of propylamine were calculated from the isotherms, and are shown in Fig. 3. The sharp decrease and the flatness of the heat of adsorption curves after the hydrogen treatment confirm that the oxygen surface complex has disappeared and that the adsorption of propylamine occurs only on the graphitic planes, giving an initial adsorption heat of 7.5 kcal/mole. The slight initial variation in the heat of adsorption curves corresponding to hydrogen-treated materials may be due to a residual surface heterogeneity or, more likely, to the very slight adsorption of propylamine in the apparatus.

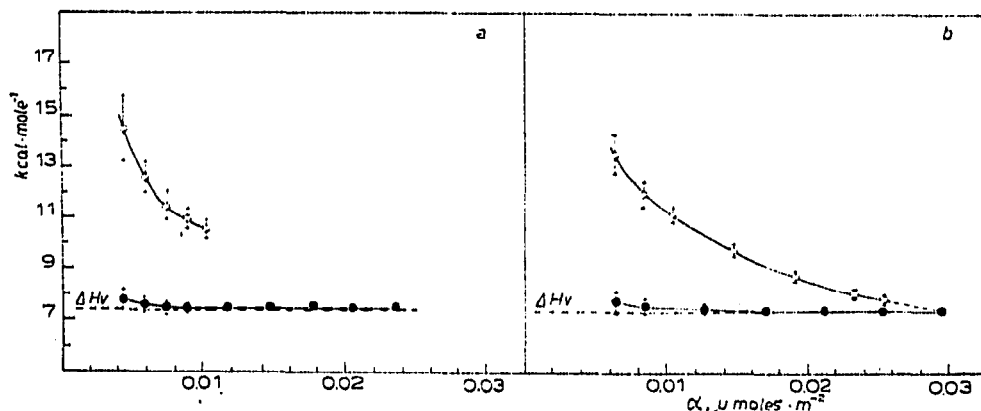


Fig. 3. (a) Isosteric heats of adsorption of propylamine on graphitized Sterling FT (○) and on hydrogen-treated graphitized Sterling FT (●). (b) Isosteric heats of adsorption of propylamine on graphitized Sterling MT (○) and on hydrogen-treated graphitized Sterling MT (●).

Apparently, the fact that the heats of adsorption and of vaporization have virtually the same values is completely fortuitous, as the forces that are operative in the adsorption and in the bulk liquid propylamine are very different.

As the heats of adsorption of the separate molecules are sums of the terms for individual structural groups, then by assigning the values of $Q_{C_2H_6} = 2.1$ kcal/mole and $Q_{CH_4} = 1.6$ kcal/mole for the adsorption on graphitized carbon black, as reported by KISELEV²¹ and verified by us ($Q_{C_4H_{10}} = 7.40$ kcal/mole), a value of $Q_{NH_3} = 2.2$ kcal/mole is deduced.

The fact that on untreated carbon surfaces a basic adsorbate, such as propylamine, shows a high heat of adsorption, which sharply increases as the coverage decreases, can be accounted for by the formation of some kind of chemical complex between the adsorbate and the acidic fraction of surface oxides²², which in extreme instances yields a "salt formation". Strong chemical interactions, which caused almost irreversible adsorption, were shown to occur by injecting very small amounts of propylamine, e.g., about $1 \cdot 10^{-7}$ g, into the chromatographic columns. In this instance, in spite of the use of a very sensitive detector, eluate desorbed from the packing material could not be detected.

Fig. 3b shows that at a surface coverage of about $0.03 \mu\text{mole/m}^2$, the heat of adsorption curves yield the same value of 7.5 kcal/mole. It can be assumed that at lower surface coverages propylamine is adsorbed only on the surface oxide groups, which conventionally are assumed to be hydroxyl groups. With increasing surface coverage, for values higher than $0.03 \mu\text{mole/m}^2$, the basal planes of graphite crystals are the only ones responsible for the adsorption of propylamine. Therefore, this surface coverage value should correspond to the surface density of hydroxyl groups. The value calculated in this manner is about $2 \cdot 10^{-2}$ hydroxyl groups per 100 \AA^2 . This value is, however, a very low surface concentration compared with the corresponding value of about one hydroxyl group per 100 \AA^2 corresponding to a silica gel, as highly dehydroxylated as possible²³.

In a previous paper¹⁰ it was shown that no significant change occurs in the adsorption of a basic adsorbate, such as ammonia, on graphitized Sterling MT before and after hydrogen treatment. Our experimental data are, therefore, in sharp disagreement with those results. This discrepancy is probably due to the hydrogen being insufficiently purified in the work of SPENCER *et al.*¹⁰.

As already known, the lateral interaction contributions are not clearly seen in adsorption on a non-uniform surface, as localization due to the preferential filling of hot sites tends to keep ad-atoms apart so that they do not interact. In order to obtain information on the extent to which traces of chemical heterogeneity on the carbon surface modify adsorbate-adsorbate interactions for substances that are capable of forming strong hydrogen bonds, the adsorption of acetic acid was also studied.

The isotherms for acetic acid on both untreated and treated graphitized Sterling FT and MT are shown in Figs. 4 and 5. In all instances the isotherms are convex to the pressure axis, showing that even at very low surface coverages adsorbate-adsorbate interactions take place. After the hydrogen treatment at 1000° , in contrast to the behaviour of propylamine, it can be seen that the removal of oxygen complexes from the carbon surface causes the extent of adsorption of acetic acid to be increased. Moreover, the heat-coverage curves for acetic acid, shown in Fig. 6, differ from those for propylamine, in that the heats of adsorption after the hydrogen

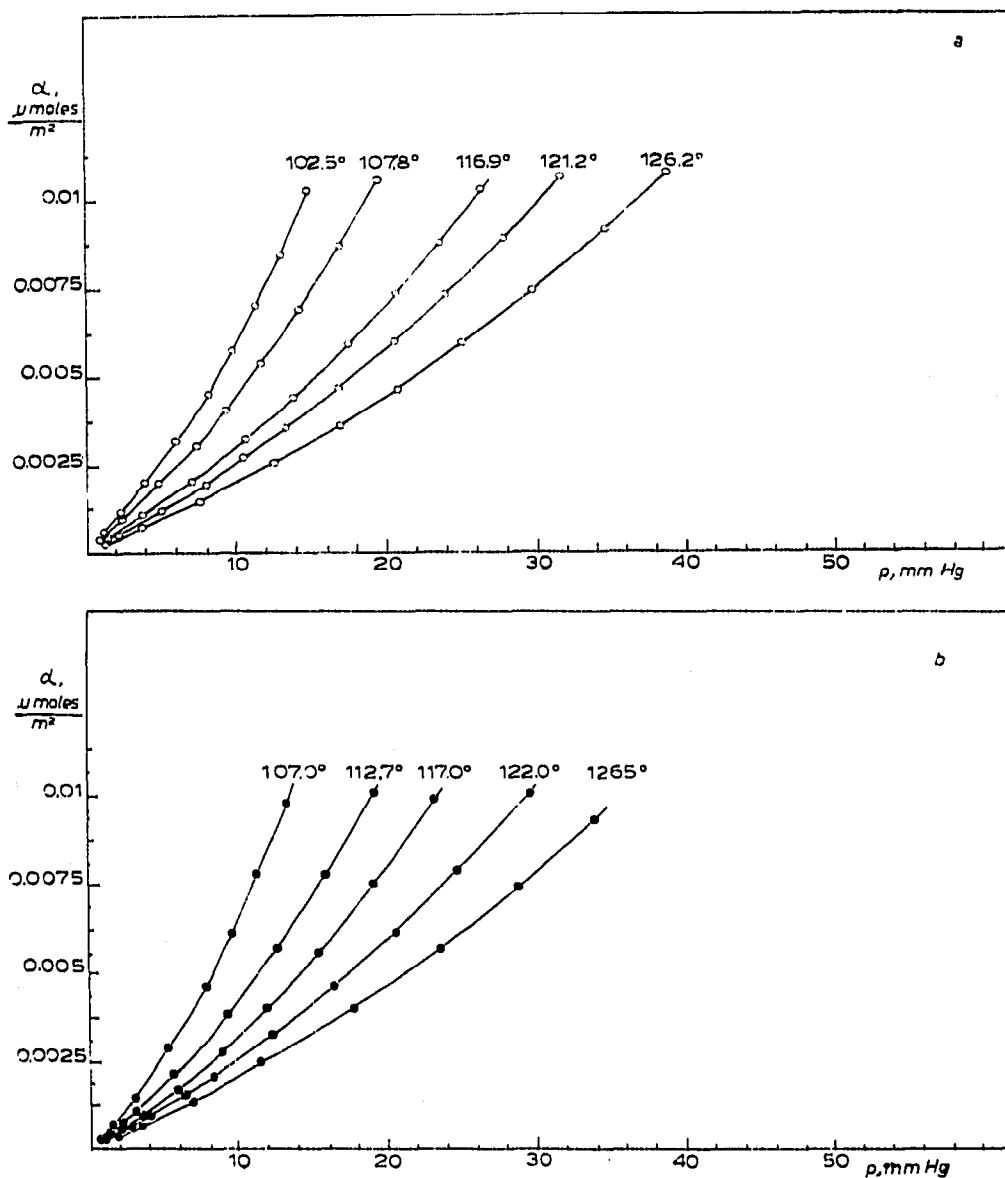


Fig. 4. (a) Isotherms for acetic acid on graphitized Sterling FT. (b) Isotherms for acetic acid on hydrogen-treated graphitized Sterling FT.

treatment show an initial increment of about 1.5–2.0 kcal/mole, which increases with increasing surface coverage. This behaviour can be explained by considering that: (1) a highly homogeneous adsorption surface enhances the effect of the lateral interactions between adjacent adsorbed molecules, causing an increase in the heat of adsorption *versus* coverage; and (2) adsorbed acetic acid molecules, even at low surface coverages, are capable of forming stronger lateral hydrogen bonds than adsorbate-heterogeneous sites.

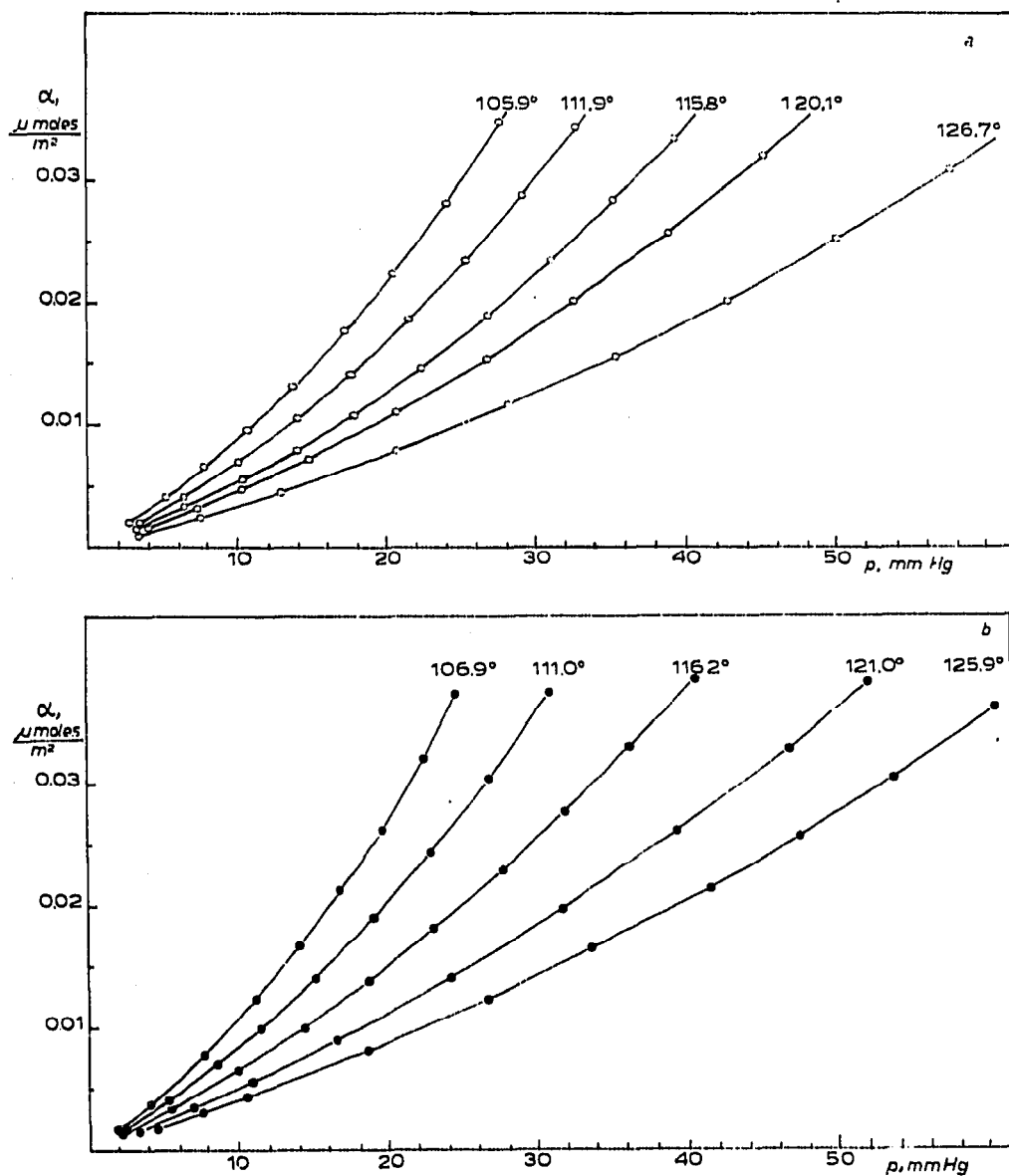


Fig. 5. (a) Isotherms for acetic acid on graphitized Sterling MT. (b) Isotherms for acetic acid on hydrogen-treated graphitized Sterling MT.

The heat-coverage curves for acetic acid on both treated and untreated adsorbing materials are analogous to those reported for hexane⁹ on graphitized carbon blacks with different degrees of surface homogeneity, such as Graphon and Sterling MT (3100). In both instances surface heterogeneity hinders the clear-cut manifestation of adsorbate-adsorbate interactions and, at least for small surface coverages, increases the localization of the adsorbate molecules. On the basis of the high heat of adsorption

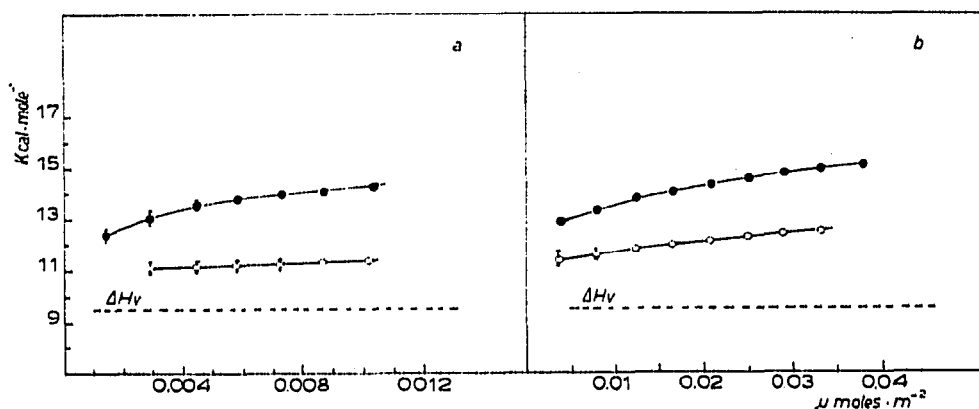
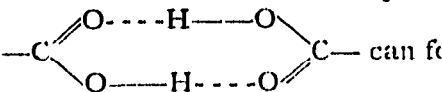


Fig. 6. (a) Isosteric heats of adsorption of acetic acid on graphitized Sterling FT (●) and on hydrogen-treated graphitized Sterling FT (○). (b) Isosteric heats of adsorption of acetic acid on graphitized Sterling MT (○) and on hydrogen-treated graphitized Sterling MT (●).

value obtained and the large difference between this value and the heat of vaporization, it can be concluded that adsorbed acetic acid molecules lie in a "flat" position,

so that very strong hydrogen bonds of the type



CONCLUSION

The present study makes possible a definitive assessment of the effects of hydrogen treatment at high temperature on microcrystalline carbon surfaces. By comparing adsorption data before and after hydrogen treatment, it can be concluded that the treatment is very effective in breaking down the carbon-oxygen surface complex. This is clearly demonstrated by the fact that the isotherms and heat-coverage curves are rather profoundly altered by the hydrogen treatment. The results make it evident that completely oxygen-free carbon surfaces can make an important contribution to the study of the adsorption of polar molecules on hydrophobic substrates. Such a study is more difficult to carry out when slightly oxidized carbon surfaces are used. In fact, as shown above, the continuous fall in heat of adsorption with increasing surface coverage does not permit correct thermodynamic data on the energy of interaction between an isolated polar molecule and a semi-infinite graphite lattice to be obtained. Also, the energy of lateral interaction for polar molecules is seriously affected by the presence of even trace amounts of surface oxides. This study was restricted to adsorption in the region of low surface coverages; we believe, however, that by extending the range of surface coverages, purified carbon surfaces would also give precise information on the contribution of lateral interactions to the adsorption and on the multi-layer build-up of polar molecules on non-polar substrates.

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