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THE ADSORPTION ISOTHERMS AND THE HEAT OF ADSORPTION OF METHYL ACETATE ON CARBON BLACK

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Abstract. The adsorption isotherms of methyl acetate on carbon black at 10° intervals in the temperature range 10–50° have been measured and the heats of adsorption calculated as a function of coverage. The resultant curves are discussed in terms of the size of the adsorbate molecules and adsorbate, adsorbate and adsorbate-adsorbent interactions and show that the surface of an ungraphitized black behaves as if it were graphitized and uniform towards an adsorbate having large molecules which interact with each other on the surface.

Work was carried out to study the behaviour of a fairly large molecule with appreciable dipole moment towards ungraphitized carbon black surface. The molecule might be expected to occupy several sites on the surface of the adsorbent.

Experimental

Apparatus. Adsorption was measured gravimetrically using a Bakr adsorption balance, as modified by Connor, Lewis and Thomas,¹ made of Pyrex and isolated from the pumps by a metal closure valve. A pressure of better than 5×10^{-5} mm measured on an ionization gauge could be maintained indefinitely in the outgassed apparatus with the valve closed. The quartz spring had a sensitivity of approximately 32 cm/g and could carry a maximum load of 1 g. Both pressure and spring extension could be measured to 0.001 cm. The vapour pressure of the adsorbate was controlled by cryostating² an ampoule of methyl acetate sealed into the apparatus.

As much as possible the glass system was wound with nichrome wire and covered with an insulating layer of glass-wool to facilitate the degassing of the glass-walls.

Purification of Materials and Method of Measurement. Methyl acetate was purified by refluxing with a small amount of acetic anhydride and excess anhydride removed by fractionation followed by treatment with K_2CO_3 (an). The ester was then fractionated three times, only the middle fraction being kept after each fractionation (n_D^{20} 1.3613; lit.³ 1.3614). Finally the ester was outgassed in vacuum and condensed into ampoules which are subsequently sealed into the adsorption apparatus.

Philblack O was heat-treated at 500°C in an atmosphere of nitrogen for 2 hr before being loaded into a platinum bucket suspended from the quartz spring. The black was outgassed in the adsorption

apparatus at 500° for a further 20 hr. Adsorption and desorption measurements were made at 10, 20, 30, 40 and 50°C. The measurements were repeated several times at each temperature and were found to be reproducible.

The surface area of the black was determined using the standard BET procedure⁴ with nitrogen at liquid oxygen temperature and was found to be 72.59 m²/g assuming an area 17.0×10^{-20} m² at -183° for the nitrogen molecule.

Results

The plots of weight of methyl acetate adsorbed against pressure of adsorbate are shown in Fig. 1a and 1b for the given experimental temperatures.

Discussion

The adsorption isotherms were reversible and obeyed the BET and Freundlich but not the Langmuir isotherm equation. The average heat of adsorption at 30°C calculated from the BET equation was 8.86 kcal/mole, compared with about 7 kcal/mole for the heat of liquefaction of methyl acetate at 30°. It was concluded that this was a case of physical adsorption. The heat of adsorption was calculated by applying the Clausius-Clapeyron equation to the adsorption isosteres. The application of this equation assumes that the perfect gas laws are obeyed for the adsorbate and that q_{st} remains constant over the temperature range considered. Both assumptions are justified in the present work as the temperatures T_1 and T_2 differed by only 10° and the pressures were low. The plots of q_{st} at different temperatures are shown in Fig. 2(a-d). W_m , the weight per gram required for monolayer coverage was obtained from the BET plots. The average value of 20.0 mg/g was almost independent of temperature and was used to calculate coverage in terms of θ , the fraction of a monolayer.

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The plots of heat of adsorption as a function of coverage show an initial increase of heat of adsorption with θ with a maximum at $\theta = 0.6$ followed by a steady decrease and a second diffused maximum at $\theta = 0.2$. The curve for 45°C shows only the maximum at $\theta = 0.6$. The heats of adsorption vary from 6.7 to 13.9 kcal/mole. Over most of the range the value lies close to and slightly above the heat of liquefaction. The maximum value observed is nearly twice the heat of liquefaction.

Behaviour similar to this has been observed by

Beebe and Dell⁵ in the system sulphur dioxide-Spheron-6 heat treated at 2700°C where a single maximum at $\theta = 0.6$ was found by Bobka, Dininny, Diebrt and Pace⁶ and Beebe and Young⁷ for argon on Graphon, where peaks at $\theta = 0.75$ and $\theta = 2$ were observed, and by Isirikyan and Kiselev⁸ in their work on the adsorption of n-hexane on graphitized thermal black.

These results could all be explained by assuming that the surface of a graphitized black was uniform and consequently the heat of physical adsorption would

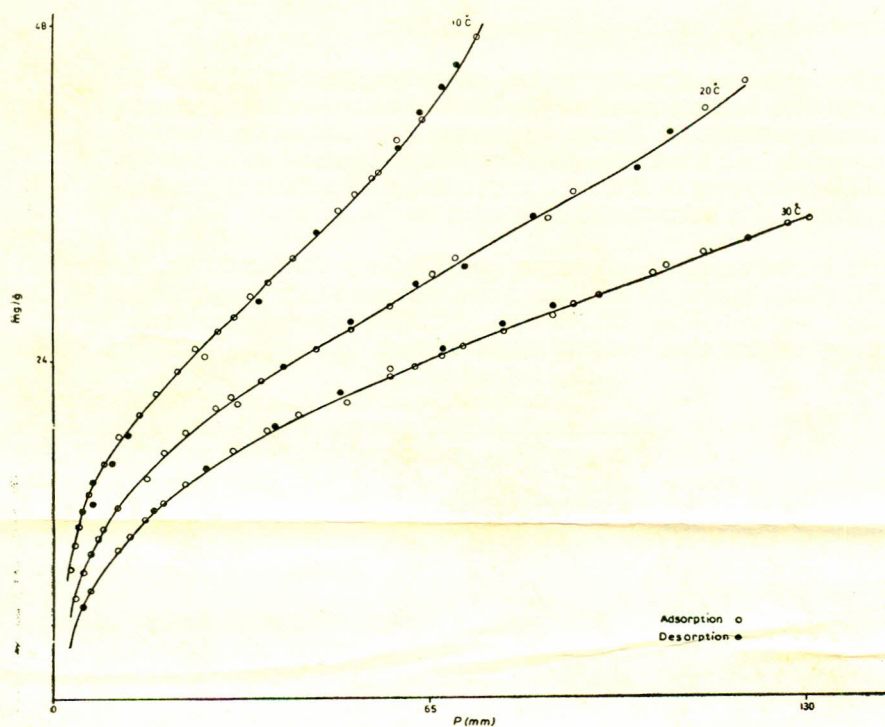


Fig. 1a. Adsorption isotherms.

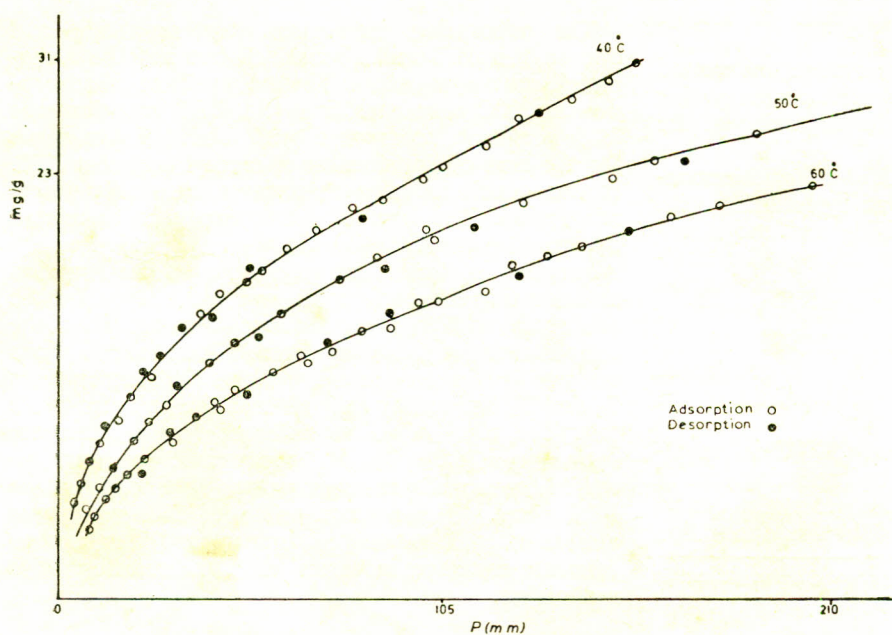


Fig. 1b. Adsorption isotherms.

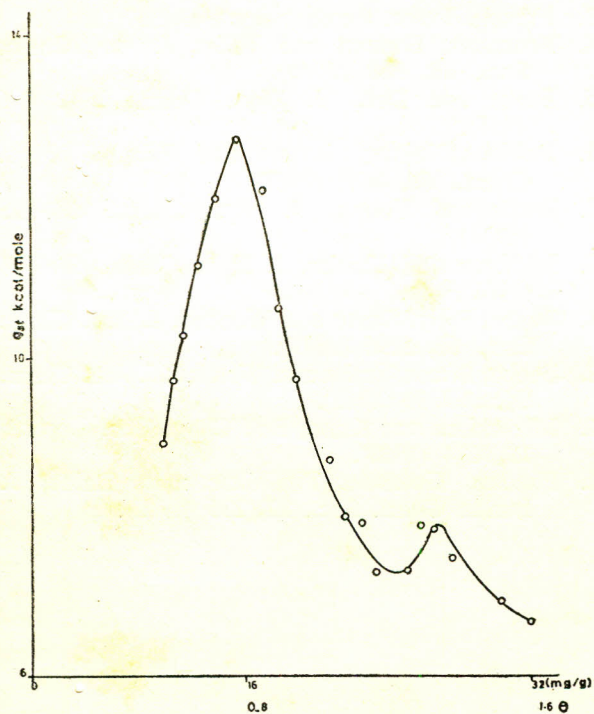


Fig. 2a. Heats of adsorption at 15°C.

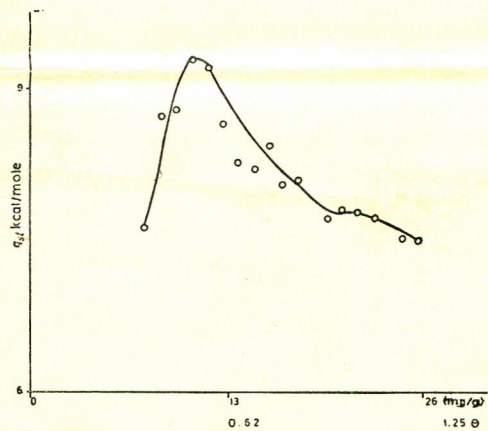


Fig. 2b. Heats of adsorption at 25°C.

not vary with coverage except for peaks which would arise as a result of lateral interaction between the adsorbed molecules.

These results may be contrasted with the measurement of Beebe and his coworkers^{5,9} on the heats of adsorption of sulphur dioxide, butane and butenes, pentane and pentenes on non heat-treated Spheron-6 which has no uniform surface.

Here the heats of adsorption fell steadily with increasing coverage from a value as high as three times the heat of liquefaction at zero coverage to nearly the heat of liquefaction at large coverage. This ratio of roughly three to one was also observed for the physical adsorption of nitrogen on carbon black.¹⁰ These results were explainable in terms of the heterogeneity of the carbon black surface.

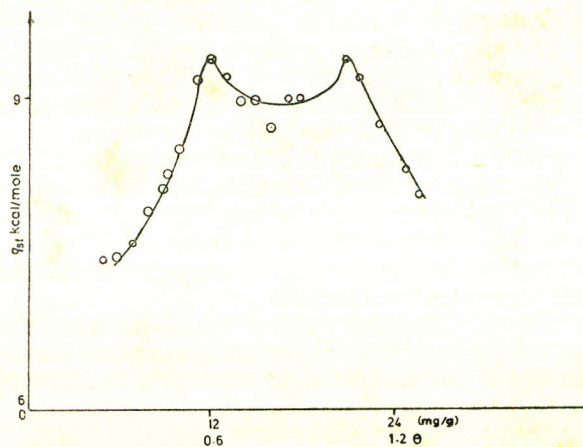


Fig. 2c. Heats of adsorption at 35°C.

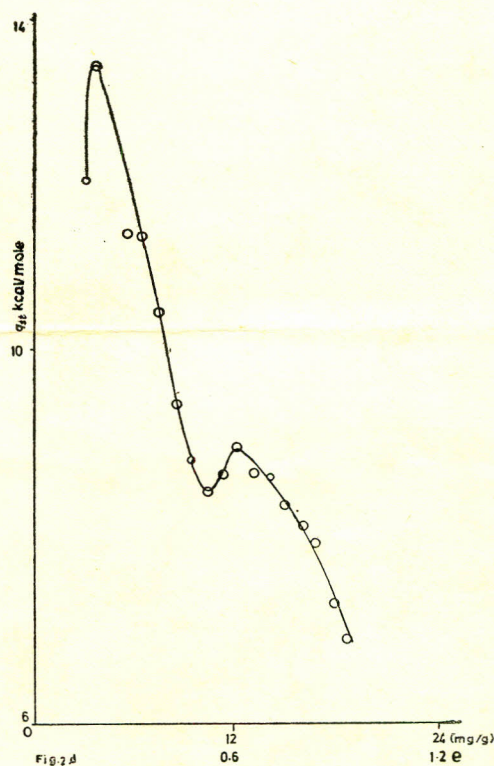


Fig. 2d. Heats of adsorption at 45°C.

The difference between the heat of adsorption curves observed here and those to be expected on the basis of a black with a heterogeneous surface requires explanation.

The anomaly can be accounted for by noting that the area per molecule of the methyl acetate was determined as 43.4 \AA^2 from the W_m value and the surface area of the black. This agrees with a value of 35 \AA^2 molecule obtained from a model assuming free rotation on the surface. A molecule of methyl acetate would, therefore, be expected to occupy several sites on the black which would be of different activity.

The result would be a smoothing of the heat of adsorption, giving rise to behaviour similar to that to be expected from a uniform surface. In addition the large dipole moment¹¹ of 1.74 D would lead to strong interaction between the molecules, thus giving rise to peaks in the heat of adsorption curves.

Additional evidence for the corrections of this hypothesis is obtained from the heat of adsorption curve for butene which shows signs of a small maximum near $\theta = 0.6$. This also is a large molecule but the weaker dipolar interaction would in this case lead to a much smaller peak.

It is concluded that the size and dipole moment of the test molecule is an important factor when the uniformity of the surface of an adsorbent is discussed.

References

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