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THE EFFECT OF HEAT TREATMENT ON THE ADSORPTION PROPERTIES OF SOLIDS. II. THE EFFECT OF HEAT TREATMENT ON THE CHARACTER OF THE ADSORPTION ISOTHERM *

D. DOLLIMORE and P. SPOONER **

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (Gt. Britain)

A. TURNER

Lancashire Tar Distillers Ltd., Cadishead, Manchester (Gt. Britain)

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ABSTRACT

In this study the nitrogen adsorption isotherms of heat-treated zinc oxalate, sintered magnesium oxide, and some oxidised pitch resins are considered. It is shown that characterisation of the adsorption isotherm can be via the monolayer capacity, the BET constant C, or plots of the degree of coverage of the surface at various relative vapour pressures. These parameters are critically assessed and shown to be dependent upon the closeness to the manner in which the complete adsorption isotherm is described by the BET equation. In considering the complete adsorption isotherm it is considered best to characterise the adsorption data by quoting the statistical monolayer capacity and the value of C at this point on the adsorption isotherm. The adsorption isotherms are then best compared by plotting as the number of statistical layers against the relative pressure. The further characterisation by plotting the apparent variation in C or the degree of coverage of the surface against the relative pressure has a usefulness if the limitations of the method are noted.

INTRODUCTION

The BET equation [1,2] for multimolecular adsorption on a free surface is

$$\frac{(P/P_0)}{v[1-(P/P_0)]} = \frac{1}{v_m C} + \frac{(C-1)(P/P_0)}{v_m C} \tag{1}$$

where v is the volume adsorbed at pressure P and absolute temperature T; P_0 is the vapour pressure of the gas at temperature T; v_m is the volume of gas adsorbed when the entire adsorbent surface is covered with a unimolecular layer, the monolayer; and C is approximately equal to $\exp(\epsilon_1 - \epsilon_L)/RT$, where ϵ_1 is the heat of adsorption of gas in the first adsorbed layer and ϵ_L is the heat of liquefaction of the gas. If the function $(P/P_0)/v[1-(P/P_0)]$ is

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** Present address: Chemistry Department, Lakehead University, Thunder Bay, Ontario, Canada.

plotted against P/P_0, a straight line is obtained, the slope and intercept of which give the values of ν_m and C over the range $0.05 < P/P_0 < 0.35$. It is a well-known fact that the BET equation presents an extremely useful means for calculating in a reproducible way a value for the surface area from a limiting part of the adsorption isotherm. It has been discussed at length that the BET equation can only be an approximation, as in these cases where it gives acceptable results, the basic assumption of a constant heat of adsorption in the first layer and a homogeneous surface is not fulfilled, and when this is fulfilled a stepwise adsorption occurs which is not compatible with the equation. It is worthwhile quoting Brunauer [3] on the subject of the value of C, viz. "Thus, the C constant does not evaluate the average heat of adsorption for the entire first layer, but the average heat of adsorption for a part of the first layer, . . . that part which takes place on the energetically less active sites of the surface".

It is therefore not surprising that the C-value, when calculated from the straight line part of the BET plot, represents only an average. In Part I [1] it was pointed out that by substituting $P/P_0 = X$ and $V/V_m = n$ in the BET equation and rearranging, an expression for C is obtained.

$$C = \frac{n(1-x)^2}{x - nx(1-x)} \tag{2}$$

One of the assumptions of the BET equation is that ν_m and C are constants for any particular adsorption system and these two assumptions may be tested for actual systems.

It is part of the purpose of this study to determine how to characterise an adsorption isotherm on a heat-treated solid sample. Besides the determination of C, another parameter should be considered, namely the degree of coverage of the surface. A clear distinction should be drawn between the monolayer coverage and the actual fraction of the surface covered (θ). The BET equation assumes that multilayers are formed with adsorption to an extent depending upon the magnitude of C. Thus the fraction of surface covered (θ) has been expressed by Hill [4] as

$$\theta = n(1 - X) \tag{3}$$

If n is given a particular value, then eqn. (3) provides a value of θ, while eqn. (2) provides a value of C at various partial pressures (X).

EXPERIMENTAL

A previous study reported the thermal decomposition of zinc oxalate [5]. This study was repeated here and a series of similar nitrogen adsorption isotherms obtained. The sintering of zinc oxide has been studied previously [6], but it was found that many of the characteristics of such a sintering treatment could be obtained with magnesium oxide; therefore, a series of nitrogen adsorption isotherms are given here for heat-sintered magnesium oxides. Nitrogen adsorption isotherms on oxidised pitch resins are also used in this study. The adsorption isotherms are shown in Figs. 1—3. All adsorption iso-

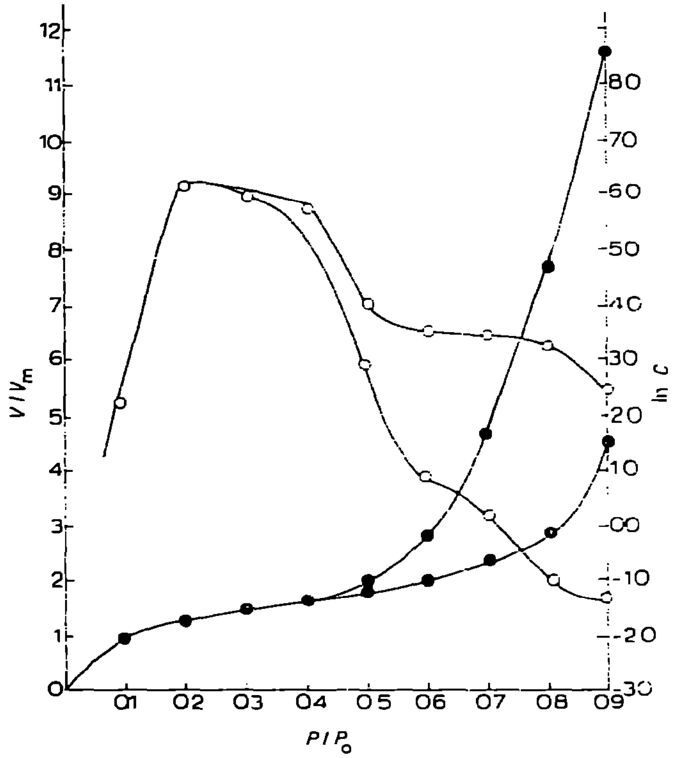


Fig. 1. The nitrogen adsorption isotherms of zinc oxalate decomposed at 400°C for various times up to 45 min. Note. (1) The specific surface area varied from 10 m^2 g^{-1} to 52 m^2 g^{-1}. (2) The points on the common adsorption isotherm are not experimental points but are drawn to help construction of the isotherm (this also applies to Figs. 2 and 3). (3). Two boundary conditions are drawn for the variation in the isotherm and in the variation of ln C. The values for all the isotherms lay within these boundary conditions.

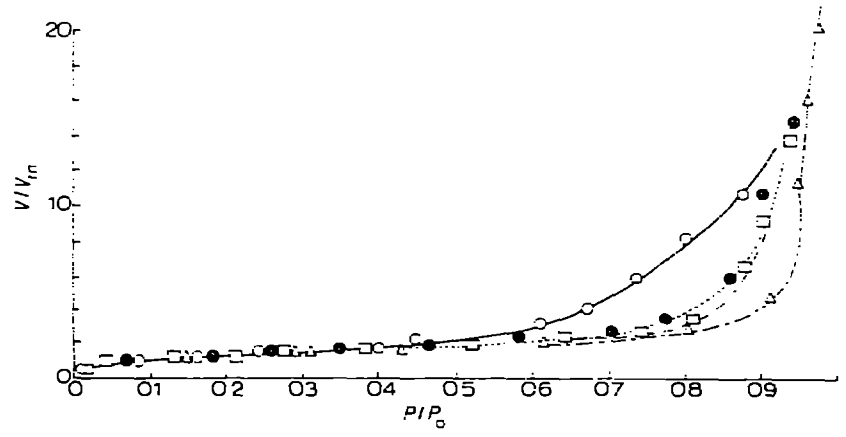


Fig. 2. Nitrogen adsorption isotherms on magnesium oxide sintered at 650°C in oxygen. Sample heated for ○, 10 min; ●, 120 min; □, 180 min; △, 4400 min.

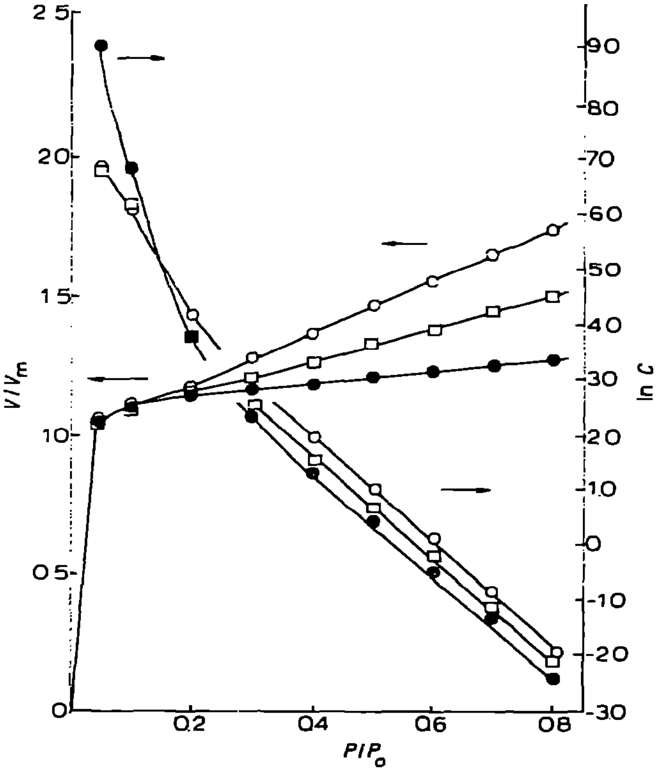


Fig. 3. Nitrogen adsorption isotherms on pitch 100 resins precarbonised at 950°C in nitrogen and then oxidised at 450°C. Adsorption points; ●, sample oxidised to 25% burn off; □, sample oxidised to 52% burn off; ○, sample oxidised to 76% burn off.

therms were determined at a temperature of —195.8°C using conventional volumetric adsorption equipment [7].

RESULTS AND DISCUSSION

Test of the constancy of the BET term C

The partially decomposed samples of zinc oxalate produced a common adsorption isotherm when plotted in the reduced form of the number of statistical layers against the relative vapour pressure. The application of eqn. (2) to give the value of C at different pressures is also shown in Fig. 1. Table 1 gives the variation in C, also found by using eqn. (2), for adsorption isotherms on sintered magnesium oxide (see Fig. 2). It can be seen that for these adsorption isotherms there is a maximum in the value of C. The pitch resin samples carbonised at 950°C and oxidised at 450°C produced steadily decreasing values of C as the relative pressure increased (Fig. 3). The heat treatment causes various patterns of behaviour both in the adsorption isotherms (plotted in the form of statistical monolayers against the relative pressure) and in the value of C calculated at various pressures by the use of eqn. (2) The two patterns of behaviour, easily recognised in the heat-treated

TABLE 1

The variation of C (from eqn. 2) for sintered magnesium oxide

Relative vapour pressure X	No. of statistical layers N	ln C
0.1	1	2.20
0.2	1.24	6.21
0.3	1.42	5.96
0.4	1.66	5.92
0.5	1.90	2.94
0.6	2.00	0.98
0.7	2.60	0.42
0.8	3.92	1.90

The above data are for the sample heated for 120 min. All sintered samples give indentical data up to X = 0.4.

samples reported in this study, are simply a decreasing value of C with increasing pressure, or a maximum in the value of C at a point just beyond the monolayer.

The same kind of analysis was also applied to the standard adsorption isotherm result of de Boer for nitrogen adsorption at liquid nitrogen temperature on alumina [8]. The variation of ln C thus calculated is shown plotted against P/P_0 in Fig. 4; the standard adsorption isotherm is also shown. Thus it can be seen that the value of C varies during and after the monolayer region. It reaches a peak at a value of 1.34 monolayers and $P/P_0 = 0.26$. This is inside $P/P_0 = 0.35$, the upper limit for the fitting of the BET equation to experimental data.

The variation of C has also been found for the adsorption of nitrogen onto powdered zinc oxide (Fig. 5) [6]. The peak corresponds again to an adsorption of 1.34 monolayers, with a shift in relative adsorption pressure from 0.26 for the de Boer standard isotherm, to 0.27 here. There is, however, a smaller variation in the value of C for this adsorption isotherm than that for the de Boer isotherm, which indicates that the position of this peak in the isotherms of this kind varies with P/P_0, as does the position of the monolayer which occurs at 0.085 for the de Boer adsorption isotherm and 0.10 for the zinc oxide isotherm of Fig. 5. This is a reflection of the fact [9] that the position of ν_m is determined by the value of C. This is demonstrated in Fig. 6 which gives the BET C-value for monolayer completion at particular values of P/P_0. In the zinc oxide adsorption isotherm a broadening of the peak in Fig. 5 would be expected at lower C-values because the attractive forces do not bind the adsorbate molecules as strongly to the surface of the adsorbent.

The immediate significance of the variations in C is that it is a convenient parameter to show how far the isotherm deviates from the BET isotherm. Further, it is one of the purposes of this paper to indicate that any discussion on the variation of C can be conducted as a separate point, in no way invalidating the normal application of the BET plot to calculate the mono-

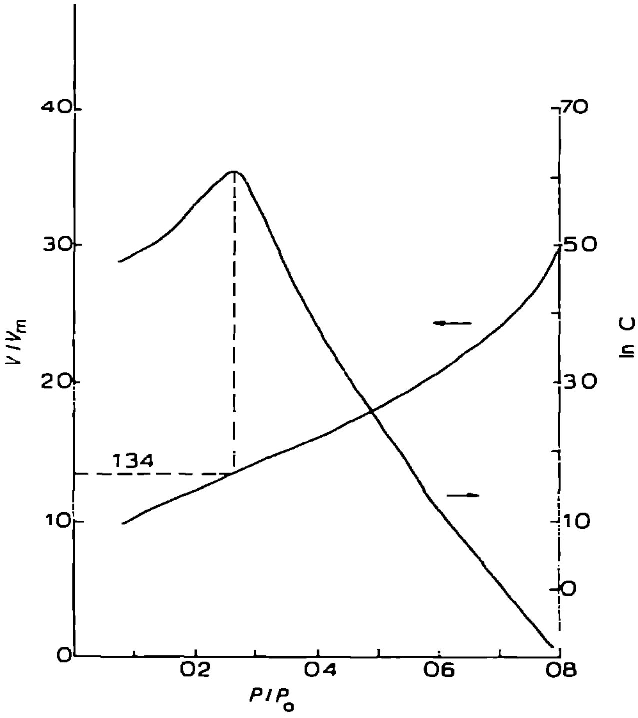
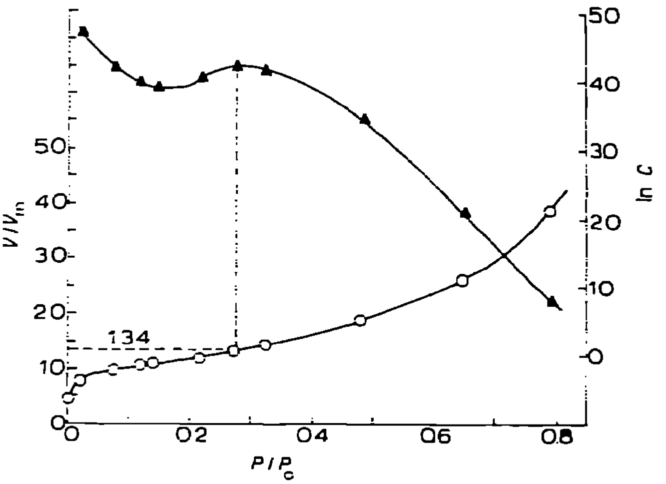


Fig. 4. The variation of ln C throughout the isotherm for de Boer's standard points.



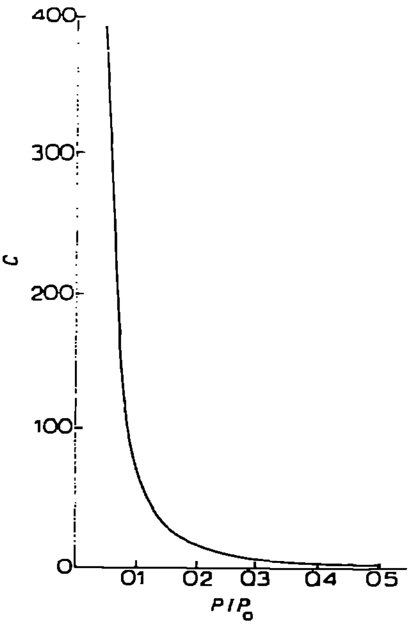


Fig. 5. The variation of ln C during the adsorption isotherm of nitrogen on zinc oxide.

Fig. 6. The BET C-value for monolayer completion ($V/V_m = 1$) at particular values of P/P_0.

layer capacity. This is because, as pointed out in Part I [1], the slope of the BET plot is $(1/\nu_m)[(C-1)/C)]$. It follows that this will be linear not only for a high value of C, as commonly stated, but for variable and high values of C. The extrapolation of the BET plot produced an intercept that is put equal to $1/(\nu_m C)$. This means that the value of C actually determined from the intercept represents the value of C at zero pressure.

It also follows that if C is to be quoted it should be the value that corresponds to the other parameter determined from the BET equation, namely the monolayer capacity ν_m. From eqn. (2) this is given by

$$C = \frac{(1-X_m)^2}{X_m^2} \tag{4}$$

It can be seen that this has the extra advantage that C is related to an experimental parameter X_m, the relative pressure at the monolayer capacity V_m. It also avoids the temptation to quote C to an accuracy beyond the limits of the experimental parameters. It would seem wiser to characterise the adsorption isotherm by quoting V_m and X_m in place of ν_m and C.

In practice, most physical adsorption isotherms when plotted as the "linear" form of the BET equation show a downward deviation at $P/P_0 < 0.05$ and an upward deviation at $P/P_0 > 0.30$. The method of calculating C based on eqn. (2) is limited in practice by the fact that only slightly misplaced estimates of the monolayer capacity cause large changes in the apparent behaviour of C. In these cases where C does not show a maximum, it quite often shows a steep variation at $n < 0.6$, which could indicate the existence of active sites on the surface. There is, however, an analytical reason why the method may not always be applicable. First, for C to be large then

$$n(1-X)^2 >> X - nX(1-X) \tag{5}$$

However, more important, for C to be positive

$$X > nX(1-X) \tag{6}$$

or

$$n\,(1-X) < 1$$

When $n(1-X) = 1$, this is equivalent to putting $C = \infty$ in the BET equation. This is illustrated in Fig. 7. All positions above the line in this graph will give negative C-values, while all positions below the line will produce positive values.

Small variations from this line can produce quite startling changes in C with often a change in sign. Thus the characterisation of the isotherm by plotting the apparent change in C with relative vapour pressure has restricted usefulness, depending first on a comparison made by superimposing the experimental isotherm over that drawn for $C = \infty$ in Fig. 7.

Analytical determination of fraction of surface covered

The distinction was drawn in the introduction between the statistical monolayer and the fraction of surface covered. The relationship between the

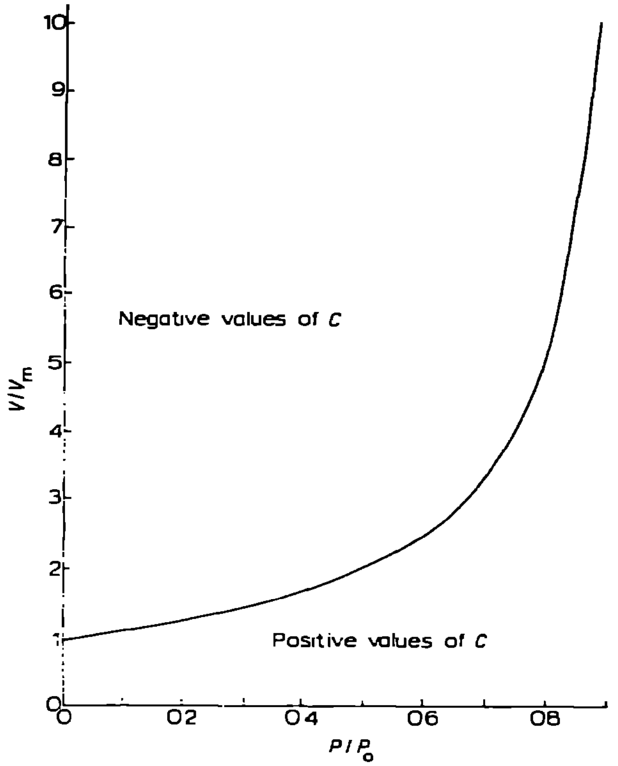


Fig. 7. The adsorption isotherm for $C = \infty$, and the sign and value of C at various places on the graph. Notes. (1) Areas of + and — value for C on the graph are indicated. (2) The further away from the line that a real adsorption point lies then the smaller the value of C. (3) The line represents the condition $C = \infty$. (4) Values of $C > 100$ give adsorption points identical with $C = \infty$ on this scale beyond $P/P_0 = 0.15$.

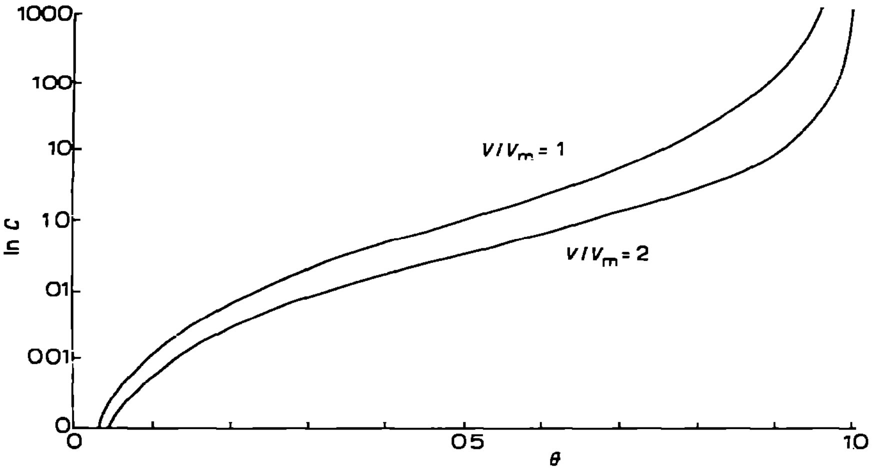


Fig. 8. The variation of C with fraction of surface covered.

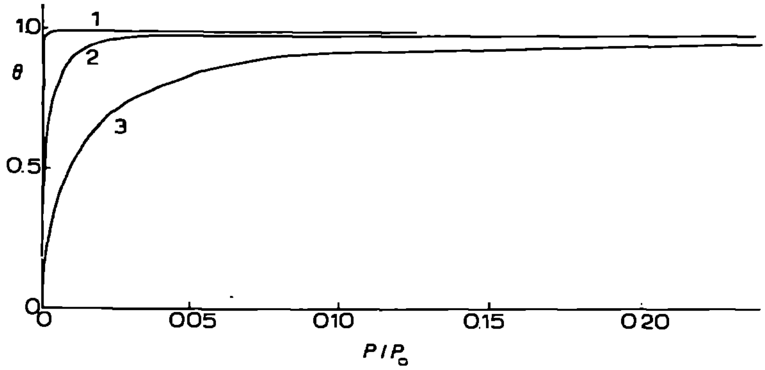


Fig. 9. Fraction of surface covered with increasing P/P_0 for various BET C-values. 1, C = 100 000; 2, C = 1000; 3, C = 100.

two is given by eqn. (3). This is based on a thermodynamic consideration of the BET adsorption isotherm equation [4]. Using the BET equation and eqn. (3) it is possible to show the variation of fractional surface covered with the value of C for fixed values of V/V_m (Fig. 8). The variation of the fraction of surface covered θ with relative pressure P/P_0, predicted by application of the Hill equation to the BET isotherm for various C-values, is shown in Fig. 9. Experimentally, nearly complete coverage might be postulated at the point where the experimental isotherms show a maximum in the value of C, while the BET equation predicts complete coverage only at saturation ($P/P_0 = 1$). In Fig. 10 experimental values for the de Boer and zinc oxide adsorption isotherms have been used to obtain θ, and these show a different pattern of behaviour to the theoretical BET isotherms given in Fig. 9. In fact, $\theta = 1$ is not reached but a peak in the value is obtained for the de Boer data corresponding to the peak in the ln C curve. The zinc oxide curve shows a much wider peak which has a maximum at a higher value of P/P_0 than the maximum of the C-value plots given in Fig. 5. Comparison of the "experimental" plots of ln C vs. P/P_0 and θ vs. P/P_0 suggest that the maximum surface coverage occurs where the heat of adsorption is a maximum or nearly so. It then

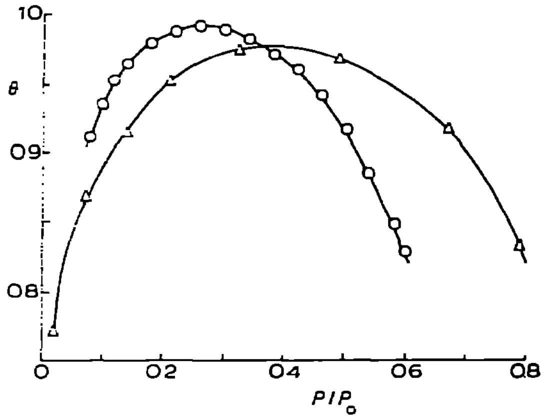


Fig. 10. The variation of the fraction of surface covered (according to Hill) during the adsorption isotherm. ○, de Boer standard isotherm; △, zinc oxide.

follows that it would be erroneous to identify a maximum in the heat of adsorption plotted against P/P_0 as corresponding to the pressure at which ν_m — the monolayer capacity — is reached.

Applied to the heat-treated materials reported here, this kind of analysis produces a maximum in the value of θ at $P/P_0 = 0.3$ for the common "reduced" adsorption isotherms on residues from the decomposition of zinc oxalate (Fig. 1). While the sintered magnesium oxides all produced different adsorption isotherms (Fig. 2), all of them showed maximum values of θ at $P/P_0 = 0.4$. In these two cases the plots of ln C vs. pressure produce maximum values of ln C at low relative pressures in the same region as the recorded maximum in θ. The oxidised pitch resins, however, showed a maximum in θ at very low relative pressures ($P/P_0 < 0.05$), and a continuous decrease in the value of ln C with increasing relative pressure. The plots of ln C vs. P/P_0 and θ vs. P/P_0 would help characterise the changes that take place in the adsorption isotherm over and above the change in the monolayer coverage. Although the theoretical implications of θ as the fraction of surface covered, and C as a function of the heat of adsorption have limitations, these definitions of the terms may be noted when considering the variations observed when they are plotted against relative pressure.

The "single point" method of determining the value of ν_m introduced by Halasz and Schay [10] depends on the BET equation being rearranged to give

$$\nu_m = \nu(1 - x)\left(1 + \frac{1 - x}{cx}\right) \tag{7}$$

For large values of C this reduces to

$$\nu_m = \nu(1 - x)$$

or

$$1 = n(1 - x)$$

which is the function plotted against P/P_0 in Figs. 9 and 10. The behaviour observed for the experimental data has also been observed for micro-porous carbons prepared from poly-vinylidene chloride [11]. Formally it occurs when the high pressure region of the adsorption isotherm has a lower adsorptive capacity than that predicted by the corresponding BET equation. In the cases considered here, it can be seen from Fig. 10 that the behaviour approximates to BET behaviour and that values of ν_m calculated by the single point methods from values between 0.2 and 0.35 are within 2% error. The exact range in which this approximation holds varies from sample to sample (see the zinc oxide data). This kind of analysis would seem to provide data indicating a variation in the value of C, and hence the heat of adsorption (see Figs. 4 and 5), and to demonstrate that the complete coverage, as opposed to the monolayer capacity, is probably achieved or very nearly achieved in the relative pressure region where the maximum value of C is also recorded, but certainly in a region of somewhat higher P/P_0 values than that needed to achieve the statistical monolayer capacity.

Algebraic form of the relationship $C = f(X)$

The characteristic form of the plot of ln C vs. relative pressure (P/P_0) both for the standard isotherm of de Boer and the experimentally determined adsorption isotherm on zinc oxide has been given in Figs. 4 and 5. The curves showed a maximum at $P/P_0 = 0.26$, approximately at which point in the standard isotherm ln C had a value of 6. It has been possible to express C as a function of P/P_0 by the relationship

$$\ln C = \frac{A}{[1 + B(P/P_0)^4 - C(P/P_0)^2]^{1/2}} \tag{8}$$

Then, in order to fit the data on the standard isotherm, $A = 4.4$, $B = 118.6$, and $C = 14.8$ (see Fig. 11).

There is no adsorption isotherm for which C is constant from $P = 0$ to $P = P_0$, but for experimental purposes, in the BET analysis C is considered to be constant over the very important region $P/P_0 = 0.05$—0.35 for the majority of type II isotherms. So far as we are aware, it is not yet certain whether this limited validity in the BET equation is due to shortcomings in the model itself or to lack of knowledge of the various parameters, such as the number of layers, variations in heat of adsorption or frequencies of oscillation, etc. in the higher layers.

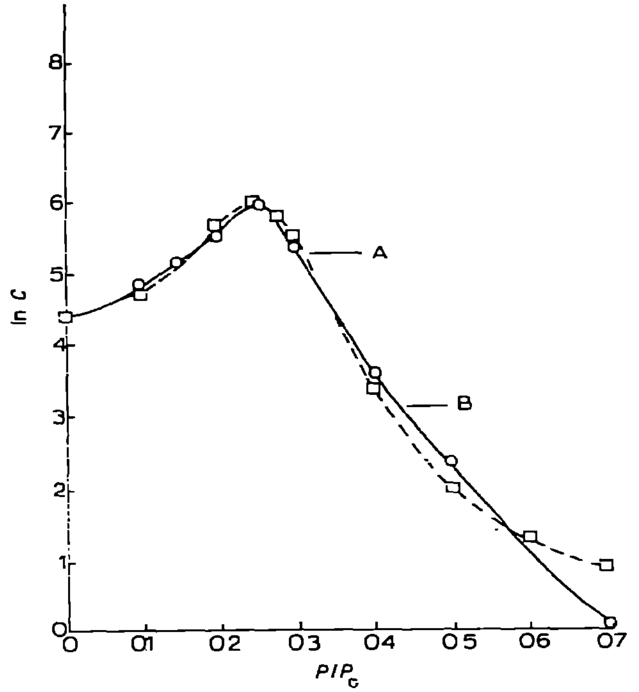


Fig. 11. The variation of ln C as a function of relative pressure.

Curve A. $\ln C = \dfrac{4.4}{[1 + 118.6(P/P_0)^4 - 14.8(P/P_0)^2]^{1/2}}$.

Curve B, ln C vs. P/P_0 (from standard adsorption isotherm of de Boer).

Attempts have been made to calculate the C-factor from theoretical considerations, but these have only been looked on as crude approximations [12]. The factor in the quantity C has been called the "entropy factor" [13], and considered as a function of the entropy change in the transfer of the vapour from the liquid state to the adsorbed state. It was held to compensate for the fact that the heat of adsorption in the second and higher layers is greater than the heat of condensation. The entropy term in C could then be responsible for the too-large adsorption predicted by the BET equation for $P/P_0 > 0.35$. It would also play a significant part in causing the variation in the value of C with pressure reported in this study.

CONCLUSIONS

In order to characterise the adsorption isotherms on heat-treated materials, the statistical monolayer capacity and hence the specific surface area should be recorded. However, it would seem better to record the value of the BET "constant" C at the monolayer value rather than from the slope of the BET plot. It is also shown that this "constant" C shows an apparent variation with relative pressure, and that the fractional surface coverage reaches its maximum values at a pressure higher than that recorded for the statistical monolayer capacity. The adsorption isotherms on heat-treated materials may best be compared by plotting in the reduced form of the number of statistical layers against the relative vapour pressure. There is, however, some further usefulness in plotting the apparent variations in the constant C and the fractional surface coverage against relative pressure, provided the limitations on the interpretation of these terms are noted.

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