336. *The Adsorption Isotherm of Langmuir and of Brunauer, Emmett, and Teller for Multilayers where* n = 3.

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An analysis of the adsorption isotherm of Langmuir and of Brunauer, Emmett, and Teller for multilayers, where the number of such layers is limited to 3, is made. The isotherms are shown to change from Type I through IV and V and then to VA as the values of c change from just greater than 2·16 to *ca.* 0·25. *Three* is thus the smallest value of n where all the known isotherm types for a limited number of multilayers can be encountered as c varies. At high values of c ($c > 1000$) the change of adsorption type from I to IV again occurs in this case. The $x/(V/V_m)$ against x curves are analysed, especially in relation to approximations which hold at low values of x.

IT has been shown recently (Jones and Birks, *J.*, 1951, 1127) that an analysis of the case when $n = 2$ in the Langmuir–Brunauer, Emmett, and Teller (B.E.T.) theories for multilayer adsorption leads to realisable isotherms which change from Type I to Type V as the value of c changes from $c > 2$ to $2 > c >$ *ca.* 0·2, and then to a type that may be called VA if *ca.* $0{\cdot}2 > c > 0$. The case when $n = 3$ is analysed in this paper.

When $n = 3$ the Langmuir equation becomes

$$\frac{N\eta}{N_0} = \frac{\sigma_1\mu[1 + 2(\sigma_2\mu) + 3(\sigma_2\mu)^2]}{1 + \sigma_1\mu[1 + \sigma_2\mu + (\sigma_2\mu)^2]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the Brunauer equation

$$\frac{V}{V_m} = \frac{cx(1 + 2x + 3x^2)}{1 + cx(1 + x + x^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

These equations are identical if $\sigma_1\mu = cx$ and $\sigma_2\mu = x$; c then $= \sigma_1/\sigma_2$; σ_3 is considered equal to σ_2. It is not necessary to assume for the purpose of this analysis that $\sigma_2 = \sigma_L$ as in the further B.E.T. treatment.

From equation (2), $V/V_m = 0$ only when $x = 0$, the factor in parentheses in the numerator having no real roots. V/V_m approaches 3 as x approaches ∞ (see Jones, *J.*, 1951, 126).

$V/V_m = \infty$ if $1 + cx + cx^2 + cx^3 = 0$; this equation has no real positive roots ($c > 0$); if x is negative it can be shown that there is one real root; *i.e.*, V/V_m passes to infinity at one negative value of x only. This is typical of all cases in this model where n is an odd number, and may be contrasted with the cases where n is even, *e.g.*, $n = 2$ (Jones and Birks, *loc. cit.*).

Differentiating equation (2), we obtain

$$\frac{1}{c}\cdot\frac{\mathrm{d}}{\mathrm{d}x}\frac{V}{V_m} = \frac{1 + 4x + (c + 9)x^2 + 4cx^3 + cx^4}{[1 + cx(1 + x + x^2)]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The numerator here, if equated to zero, has no real positive root ($c > 0$) and therefore for values of $x > 0$ no maximum or minimum occurs on the isotherm; such values do occur for values of $x < 0$. The gradient at the origin $= c$.

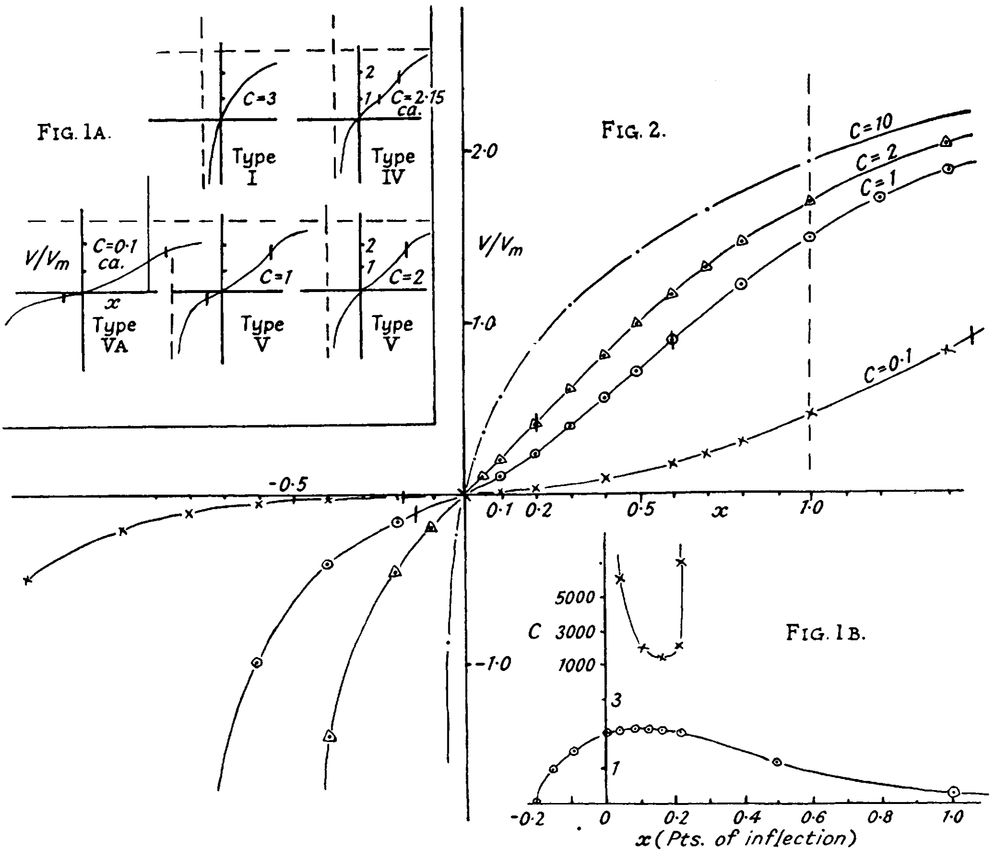
Differentiating again, we obtain

$$\frac{1}{c}\cdot\frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{V}{V_m} = \frac{(c - 2) + 3(c - 3)x + 3cx^2 - c(c - 17)x^3 + 3c(c + 6)x^4 + 6c^2x^5 + c^2x^6}{[1 + cx(1 + x + x^2)]^3} \quad . \quad (4)$$

The investigation of this equation for the occurrence of points of inflection on the isotherm can proceed best as follows: the sign changes of the coefficients of x ($x > 0$) as c varies can be considered from the point of view of Descartes's rule of signs (see, *e.g.*, "The Theory of Equations," J. V. Uspensky, McGraw-Hill, 1948, p. 121) which can give preliminary information as to the general location of the roots. If $0 < c < 2$ there is one sign change and therefore there is one real positive root only; if $c = 2$ the absolute term is zero, giving a root at the origin and, excluding zero, there is now one sign change, again giving one real positive root only; if $3 > c > 2$ there are two sign changes and therefore either two real positive roots or none; if $3 < c < 17$ there are no sign changes and therefore no positive roots, *i.e.*, between $c = 3$ and $c = 17$ there can be no points of inflection on the isotherm. But if c is greater than

17 the term in x^3 is negative and again there are two sign changes and therefore either two real positive roots or none. Descartes's rule of signs is of particular value in this case because of the small number of sign changes involved and by its aid alone the occurrences of points of inflection, and so of isotherm types, can be mapped out.

The actual positions of the points of inflection can then be located by a combination of the methods of solving the polynomial in x graphically, which will give values of x corresponding to chosen values of c, and of treating the equation as a quadratic in c, which will give values of c corresponding to chosen values of x. In this way the following results have been obtained (illustrated in Fig. 1A). If $c >$ *ca.* 2·16 there are no real positive roots (it will be shown later that this does not apply when $c >$ *ca.* 1000); if $c =$ *ca.* 2·16 there are two equal positive roots when x has the value *ca.* 0·1; if $2{\cdot}16 > c > 2$ the two roots separate, until when $c = 2$ one root is at the origin and the other at $x =$ *ca.* 0·21; if $2 > c > 0{\cdot}2$ one point of inflection is now at



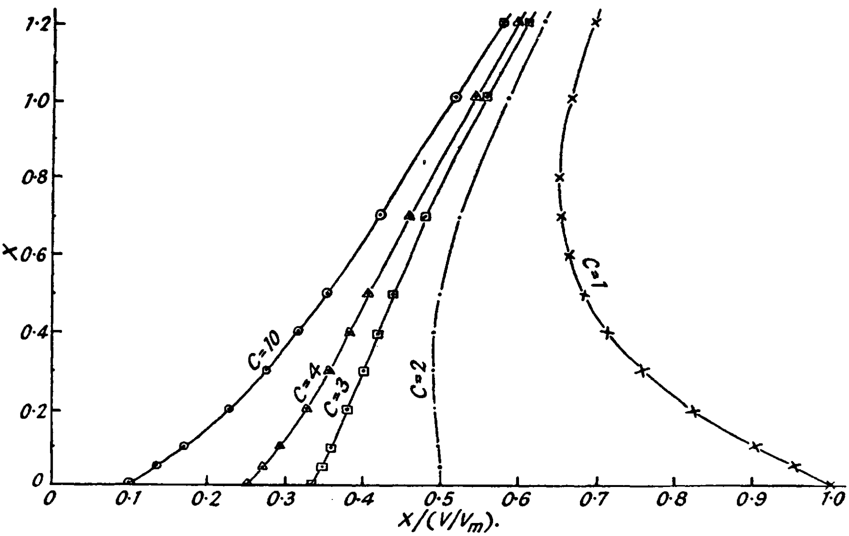
negative values of x and the other at higher positive values of x; if $c =$ *ca.* 0·25, $x = 1$, and if *ca.* $0{\cdot}25 > c > 0$ one point of inflection is negative and the other is at an x value greater than the saturation value (if $x = p/p_0$). For this case then there is the appearance on some of the realisable isotherms of two points of inflection, giving the type of curve that has been labelled by Brunauer Type IV, these two points having their genesis at $c =$ *ca.* 2·16 and then rapidly diverging as c gets smaller; the type changes involved are shown in Fig. 1A. This case does not occur when $n = 1$ (Type I only) or with $n = 2$ (see above). When $n = 3$ it occurs only within the narrow range of c values as described here; when $n > 3$ this range is widened.

If $x >$ *ca.* 0·226, there are two real roots of c, one positive and one negative; if *ca.* $0{\cdot}226 > x > 0$ there are two real positive roots of c, one of which (near $c = 2$) has already been discussed in this paper, and the other occurs when $c > 1100$. It has been found that the two positive roots have their genesis at a value of $c =$ *ca.* 1100 corresponding to a value of $x =$ *ca.* 0·16; as c increases again these values diverge (apparently approaching the values of $x = 0$ and $x = 0{\cdot}226$). Thus at high c values a change of isotherm from Type I to Type IV again occurs between certain x values, which however may be difficult to observe experimentally. In Fig. 1B the curves show the changes in the location of the points of inflection with changes in the value of c for this case. Attention should be drawn here to the fact that, as pointed out before (Jones, *loc. cit.*), this analysis would apply also to a monolayer (Langmuir's Case IV) where there are three molecules accommodated per elementary space and when $\sigma_1 \neq \sigma_2$ but $\sigma_2 = \sigma_3$.

In Fig. 2 are illustrated theoretical isotherms for typical values of c; and in view of the considerable use made by experimenters of the plots $x/(V/V_m)$ against x, which are of course tests of the agreement of the isotherm with a rectangular hyperbola whose asymptotes are parallel to the axes and which passes through the origin (compare Langmuir's Case I), these corresponding graphs are given in Fig. 3. For $n = 3$, as contrasted with $n = 2$, the isotherm is never a rectangular hyperbola, although in certain concentration ranges, as seen in Fig. 3, a straight line could be drawn passing fairly well through the points.

It can be deduced from simple calculus that the gradient of the $x/(V/V_m)$ against x curve at $x = 0$ is $(c - 2)/c$, and that this applies to all values of $n > 1$. Therefore when $c = 2$ the gradient at $x = 0$ is 0; it is positive if $c > 2$ and negative if $c < 2$ (see Fig. 3 for illustrations of these points when $n = 3$). Further, in view of the importance of results determined at low

FIG. 3.



pressures (*e.g.*, Foster, *J.*, 1945, 773), suitable approximations to the isotherms at low values of x are here investigated. From the equation

$$\frac{x}{V/V_m} = \frac{1 + cx + cx^2 + cx^3}{c(1 + 2x + 3x^2)}$$

it is seen that when $x = 0$, $x/(V/V_m) = 1/c$; dividing the bracketed factor in the denominator into the numerator, we obtain

$$\frac{x}{V/V_m} = \frac{1 + x(c - 2) + x^2(1 - c) + \ldots\ldots}{c} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where there are further terms in the numerator involving higher powers of x. The same expression is obtained for all values of $n > 2$, for the terms involving x and x^2. [For $n = 2$ all the coefficients of x^2 and higher powers of x include the factor $(4 - c)$.] This means that for small values of x, where cx^2 can be neglected in comparison with cx, there is a linear relation whose gradient is $(c - 2)/c$ (the gradient at $x = 0$), and this applies to all values of $n > 1$. If $n = \infty$ the further terms in the numerator of equation (5), involving higher powers of x than x^2, are absent. Therefore the plot of $x/(V/V_m)$ against x for certain values of c, starting from $x/(V/V_m) = 1/c$ when $x = 0$, has then the same gradient for small x values, whatever the n values ($n > 1$).

Returning now to the isotherm, it can be seen that it follows that at these small values of x the curves are hyperbolæ of the same type as before; in fact the isotherm can be written in these regions for all values of $n > 1$, $V/V_m = [cx/(1 + x(c - 2)]$, the asymptote equations being $V/V_m = c/(c - 2)$ and $x = -1/(c - 2)$. If $c > 2$ there is in this region of x values a Type I isotherm (in the sense that it is concave to the x axis); if $c < 2$ there is a Type III curve in this region (convex to the x axis). If $c = 2$ the term in x in the denominator is zero and $V/V_m = 2x$ (*i.e.*, a straight line of gradient 2). It is thus clear why the approximately linear portion of the isotherm for $c = 2$ extends for some distance from the origin (see Fig. 2); this linear portion is further extended because of the incidence of the second point of inflection at $x =$ *ca.* 0·21 for $n = 3$. For $c = 1$ the curve is convex to the x axis at first, but later has an approximately linear region located round the point of inflection at $x =$ *ca.* 0·6. If c is large the approximation $V/V_m = cx/(1 + cx)$ will be satisfactory at these sufficiently low values of x.

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