A General Treatment and Classification of the Solute Adsorption Isotherm

I. Theoretical

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A theoretical basis is developed for the classification of adsorption isotherms for solutes in dilute solution, which relates their characteristic shapes to parameters of the solvent and any second solute.

Three of the four main classes (S, L, H) are accounted for by differences in relative magnitude of the activation energies of desorption of solutes and solvent. The S-shaped isotherm is also accounted for by an additional concentration-dependence of this parameter, implying cooperative adsorption. The subgroups of each class are also explained.

The linear (C) isotherm is explained by penetration of substrate micropores by solute, with or without solvent, whereby new adsorption sites are opened up; the theory predicts the experimentally found sharp inflection to a plateau in the C-curves. Curves of the other classes can also in some cases show a linear branch above the turning point, representing conditions like those for C-curves.

The theoretical treatment is valid whether the adsorbing surface is energetically uniform, or, as in most systems, nonuniform.

INTRODUCTION

All three states of matter can be adsorbed at a solid surface (1, 2): gases (3–5), liquids (6) and (dissolved) solids, respectively, can form the adsorbate. In the case of the two last-named particularly, the adsorbate under study is necessarily applied from solution in a liquid. Adsorption of liquids is thus studied from single-phase mixtures ("composite liquids"). For convenience we can therefore specify three general systems embracing: VPA (vapor or gas phase adsorption), CLA (composite liquid adsorption) and SSA (solid solute adsorption).

Many treatments have been developed to describe the three types of adsorption process, most of them dealing with VPA. These can be classified under four headings: kinetic theories, thermodynamic theories, "potential" theories, and theories of capillary condensation (2, 3). Langmuir pioneered the kinetic approach to the subject in his classic papers (7). His equation for VPA in monolayers and the more generalized form developed by Brunauer, Emmett and Teller (8) to include multilayer adsorption are probably the best known theoretical treatments, though the literature on the subject is extensive [see, for example, for VPA (2–5, 7–11); for CLA and SSA (2, 6, 12–19)]. The last named authors (8) developed the so-called "BET" equation, well known for its use in specific surface measurement by VPA of finely divided solids; it has also been used in a modified form by Ewing and Liu (20) for measuring specific surface of powders by dye solutions.
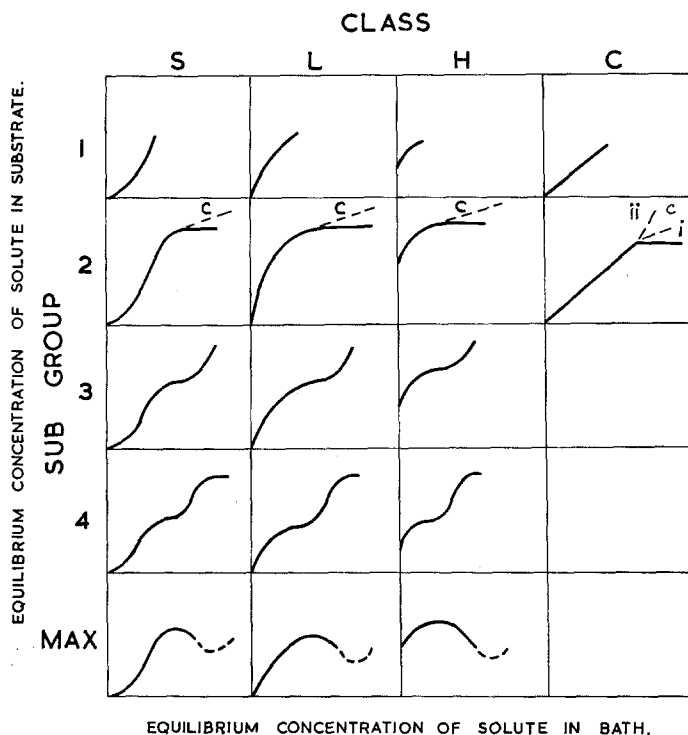
FIG. 1. System of isotherm classification. The 2c subgroup indicates microporosity in the substrate, and in the C-class, the second branch of the curve in the subgroup 2 may be horizontal, or have a less steep (ci) or a steeper (cii) slope than the main portion, according to the nature of the system. These slight variations from the earlier diagram (23) are made in the light of later results. Though only subgroups progressing from 1 through 4 are shown these obviously can be extended to 5 or beyond if further rises and steps occur.

Possibly the most favored approach to the theoretical aspects of all adsorption systems is the study of the isotherm, in which the amount adsorbed is plotted against the pressure (or concentration) in the external phase, at constant temperature, and usually under equilibrium conditions (21). A necessary preliminary is the classification of isotherm shapes, because these are largely determined by the adsorption mechanism and can therefore be used to diagnose the nature of the adsorption. Thus Brunauer et al. (22) divided all vapor adsorption isotherms into five types. The BET equation applies to three of these, and in certain conditions to the other two also; the Langmuir equation applies to one type only. In CLA systems two completely miscible liquids A and B are usually employed in a series of binary mixtures covering the whole

range of possible concentrations from pure A to pure B. Isotherms for these systems also have been classified (6).

There are several marked differences between CLA and SSA. For instance, in SSA from aqueous solutions the adsorbed species is often a micelle, especially an ionic micelle, but this does not occur in CLA. In SSA, multilayers often form and there may also be changes of orientation of the adsorbed molecules as they increase in concentration at the adsorbent surface. These effects are seldom observed in CLA.

SOLUTE ADSORPTION: DESCRIPTION AND BASIC ASSUMPTIONS

Solute adsorption is a factor in domestic life, and the basis of a great number of industries;

it is familiar in all laboratories and essential in many life processes. Its industrial applications include detergency, dyeing, froth flotation of minerals, pollution control, ion-exchange and other purification processes for solutions, the sensitization of photographic emulsions, the measurement of specific surface of powders, liquid–solid chromatographic techniques, and tanning. Adsorption of solutes is also of fundamental importance in soil science.

The term *solute adsorption* here describes the many systems in which adsorption of a solute with a limited solubility occurs. In practice the solute is usually though not necessarily a solid, and its solubility is often very low—in most cases of technical importance the most concentrated solutions used are 0.001–0.1 M—and the concentration of solvent relative to the adsorbent surface can be considered constant throughout. The isotherm is complete when the solute has reached its saturation value in the solvent.

Classification of isotherms is as stated necessary to their theoretical treatment and interpretation. A classification system of SSA isotherms has been described (23). This divides them all, by their initial slope, into four main classes, termed for convenience the S, L (i.e., "Langmuir"), H ("high affinity"), and C ("constant partition") classes, and further into several subgroups, 1, 2, 3, etc., or *max*, by subsequent variations as shown in Fig. 1. A wide range of experimental data was given and interpreted qualitatively according to the classification (23).

Our aim in this study is to develop a theoretical treatment of solute adsorption which can interpret all the above shapes, and be capable of experimental verification. We develop our approach on the classical kinetic model first adopted by Langmuir.

Further experimental evidence supporting the present theoretical treatment is given in Part II (24).

In VPA, Langmuir's treatment takes into account only forces between adsorbate and substrate and is confined to monolayer coverage, but the BET treatment allows also for multilayer coverage originating of course in adsorbate–adsorbate interaction. In solute adsorption other types of interaction are superimposed on these two and consequently the situation is more complex. It involves substrate–solvent, solvent–solute, substrate–solute, solvent–solvent and possibly other forces involved in adsorption of micelles or aggregates of solute. A complete theoretical description is therefore highly complex. (Hei, *et al.* (13), using a thermodynamic treatment show that if substrate–solvent and substrate–solute interactions occur at the same sites, the Langmuir VPA isotherm can still theoretically be fitted to solute adsorption data.)

We have used reasonable assumptions to simplify our treatment. We do not claim therefore that it is exhaustive, but only that it can be expressed in a form consistent with the available experimental evidence, and suitable for use as a basis for further experiment and theoretical examination.

The kinetic situation in solute adsorption is very similar to that in gas adsorption, the difference being in the free path of the molecules (4). We therefore commence with the equation Langmuir developed for gas adsorption,

$$\frac{y}{y_m} = \frac{bp}{1 + bp}, \qquad [1]$$

where y is the amount of substance in the adsorbed monolayer at pressure p, and y_m is the amount in the completed monolayer.

We replace p by solute A concentration c_A. (Strictly, the activity should be used, but in the present case we are considering only dilute solutions, and we shall therefore speak of concentrations.) Thus

$$y = by_m c_A (1 + bc_A)^{-1}. \qquad [2]$$

The term b, the derivation of which is described by Langmuir (7), includes various constants and is dependent on temperature (2, 3, 7). Thus

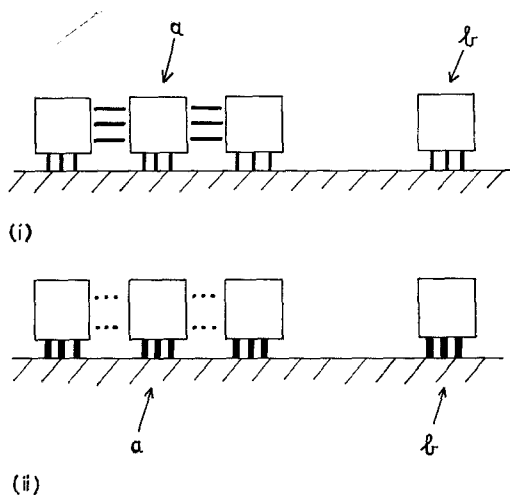$$b = \frac{Ne^{E/RT}}{y_m \nu \sqrt{(2\pi MRT)}}, \qquad [2a]$$

(i)

(ii)

FIG 2. Sketch illustrating bonding effects at the substrate surface. (i) The solute–solute forces (illustrated by heavy lines) are strong relative to those between solute and substrate. Consequently a solute molecule would be more stable at a than at b. In this case the energy of activation for removal of solute from substrate is concentration-dependent and "cooperative adsorption" occurs, revealed by S-isotherms. (ii) There are relatively strong attractive forces (illustrated by heavy lines) between solute molecules and substrate, but very weak forces (illustrated by broken lines) between solute molecules themselves. Consequently a solute molecule would be equally stable if located at b as at a. This is the most common situation, and produces L- (or H-) isotherms.

where N is the Avogadro number, E the energy of activation for removal of the solute from the substrate (on the assumption that the adsorption process has zero activation energy at low coverage for solutes as for gases), y_m is expressed as the number of adsorbate molecules per square centimeter of completed monolayer, ν is the frequency of oscillation of the adsorbate molecules perpendicular to the surface, M the molecular weight of the adsorbate, R the gas constant, and T is the absolute temperature.

THE ACTIVATION ENERGY FOR REMOVAL (LIFT-OFF) OF SOLUTE FROM THE SURFACE

As stated, in the classic kinetic treatments it is assumed that interaction of the adsorbate molecules themselves at the surface is negligible. We find that in theory and experimentally

the shape of some of the isotherms can be accounted for by postulating that this type of interaction does occur under particular conditions.

Consider the situations shown in Fig. 2, where a molecule of solute is shown in process of being captured by a surface. If the molecule is strongly attracted by the surface, and its interaction with neighboring molecules is negligible, then the activation energy required to remove it or to give "lift-off" from the surface is independent of the presence of neighboring adsorbed solute molecules. This situation is illustrated at (ii) in Fig. 2. If however the solute–solute forces at the substrate surface are significant relative to the solute–substrate ones, as in the situation illustrated by Fig. 2 (i), then the activation energy E_A for lifting a molecule of A will clearly be raised by the presence of its neighbors, and "cooperative adsorption" occurs.

Therefore we assume that E_A varies with the concentration of A to some power $n(n > 1)$, or

$$E_A = \Delta E_A c_A{}^n + E_A{}^0,$$

where ΔE_A is the increment of E_A and $E_A{}^0$ is a constant. Strictly ΔE_A should be shown to vary with y, the concentration of A at the substrate surface, but we find that on this assumption an explicit equation is obtained which can only be solved numerically. We are however dealing only with the initial part of the isotherm and here y and c_A are always both increasing. Therefore to simplify the treatment we use c_A in preference to y, and obtain a more manageable expression.

We now consider the influence of various factors upon the activation energy for removal of the solute from the substrate, assuming that the general system consists of a dilute solution of a solute A in a solvent B, containing also a second dissolved substance C. C might be another solvent or a solute, such as an unsuspected impurity in A or B, or a planned additional solute which affects the adsorption of A by competition, or by reaction with A or B. Usually, of course, the concentration of A alone in the solution and in the adsorbent is

actually measured. [Adsorption of A may dislodge more than one molecule of B or C (see below) but this does not affect the general treatment.]

Each of the species A, B, and C has an activation energy for removal, say E_A, E_B, and E_C, respectively. The concentration of B is by definition constant throughout the range of experiments which give the data plotted in the isotherm, and we assume for simplicity that the concentration of C also is constant.

E_A is a measure of the energy which the molecules of A require before they lift off from the adsorbent surface and diffuse away into the solution. Clearly E_A will be influenced by the nature of both B and C. B competes with

A for sites on the adsorbent surface and C also may do so. Thus effectively in [2a] we can write $E_A - E_B - E_C$ in the energy term of the exponent.

Influence of Activation Energy Variations on Isotherm Shape

We now consider the consequence of allowing the activation energy E_A to increase as mentioned above with the concentration of the solute A. We shall denote the increment in E_A by ΔE_A, with increase taking place above some base level E_A^0. The model now becomes

$$E = E_A^0 + \Delta E_A c_A{}^n - E_B - E_C \qquad [3]$$

and b can be written

$$b = \frac{k}{y_m} \exp\left[\frac{1}{RT}(E_A^0 + \Delta E_A c_A{}^n - E_B - E_C)\right] \qquad [4]$$

Writing $E_B + E_C - E_A^0 = \mu$ and $(K/y_m)e^{-\mu/RT} = \alpha$ and substituting in [2] we get

$$y = y_m \alpha c_A e^{\Delta E_A c_A{}^n/RT}(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})^{-1} \qquad [5]$$

$$\frac{dy}{dc_A} = \frac{\alpha y_m\{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})(e^{\Delta E_A c_A{}^n/RT} + c_A e^{\Delta E_A c_A{}^n/RT} \cdot n\Delta E_A c_A{}^{n-1}/RT) - c_A e^{\Delta E_A c_A{}^n/RT}(\alpha e^{\Delta E_A c_A{}^n/RT} + \alpha c_A e^{\Delta E_A c_A{}^n/RT} \cdot n\Delta E_A c_A{}^{n-1}/RT)\}}{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})^2}$$

$$= \frac{\alpha y_m\{(e^{\Delta E_A c_A{}^n/RT} + e^{\Delta E_A c_A{}^n/RT} \cdot n\Delta E_A c_A{}^{n-1}/RT)\}}{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})^2}$$

$$= \frac{\alpha y_m e^{\Delta E_A c_A{}^n/RT}(1 + n\Delta E_A c_A{}^n/RT)}{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})^2}, \qquad [6]$$

and the second derivative becomes:

$$\frac{d^2y}{dc_A{}^2} = \frac{\alpha y_m\{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})^2[e^{\Delta E_A c_A{}^n/RT} \cdot n\Delta E_A c_A{}^{n-1}/RT + e^{\Delta E_A c_A{}^n/RT} \cdot c_A(n\Delta E_A c_A{}^{n-1}/RT)^2 + e^{\Delta E_A c_A{}^n/RT} \cdot n^2(\Delta E_A c_A{}^{n-1}/RT)^2] - 2e^{\Delta E_A c_A{}^n/RT}(1 + n\Delta E_A c_A{}^n/RT) \times (1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})(\alpha e^{\Delta E_A c_A{}^n/RT} + \alpha c_A e^{\Delta E_A c_A{}^n/RT} \cdot n\Delta E_A c_A{}^{n-1}/RT)\}}{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})^4}$$

$$= \frac{\alpha y_m\{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})e^{\Delta E_A c_A{}^n/RT} \cdot n\Delta E_A c_A{}^{n-1}/RT(1 + n + n\Delta E_A c_A{}^n/RT) - 2e^{\Delta E_A c_A{}^n/RT}(1 + n\Delta E_A c_A{}^n/RT) \times \alpha e^{\Delta E_A c_A{}^n/RT}(1 + n\Delta E_A c_A{}^n/RT)\}}{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})^3}$$

$$= \frac{\alpha y_m e^{\Delta E_A c_A{}^n/RT}\{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})n\Delta E_A c_A{}^{n-1}/RT(1 + n + n\Delta E_A c_A{}^n/RT) - 2\alpha e^{\Delta E_A c_A{}^n/RT}(1 + n\Delta E_A c_A{}^n/RT)^2\}}{(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})^3} \qquad [7]$$

To obtain an L-type curve we require this expression to be negative i.e., we require

$$2\alpha e^{\Delta E_A c_A{}^n/RT}(1 + n\Delta E_A c_A{}^n/RT)^2 > n\Delta E_A c_A{}^{n-1}/RT(1 + \alpha c_A e^{\Delta E_A c_A{}^n/RT})(1 + n + n\Delta E_A c_A{}^n/RT)$$

i.e.,

$$2\alpha e^{\Delta E_A c_A{}^n/RT}(1 + 2n\Delta E_A c_A{}^n/RT + n^2(\Delta E_A{}^2 c_A{}^{2n}/R^2 T^2) > \frac{n\Delta E_A c_A{}^{n-1}}{RT}$$

$$\times (1 + n + n\Delta E_A c_A{}^n/RT + \alpha c_A e^{\Delta E_A c_A{}^n/RT} + n\alpha c_A e^{\Delta E_A c_A{}^n/RT} + n\Delta E_A c_A{}^n/RT\alpha c_A e^{\Delta E_A c_A{}^n/RT})$$

i.e.,

$$2\alpha e^{\Delta E_A c_A{}^n/RT} + 3\alpha e^{\Delta E_A c_A{}^n/RT} \cdot n\Delta E_A c_A{}^n/RT + \alpha e^{\Delta E_A c_A{}^n/RT} \cdot n^2(\Delta E_A{}^2 c_A{}^{2n}/R^2 T^2)$$

$$> \frac{n\Delta E_A c_A{}^{n-1}}{RT}(1 + n + n\Delta E_A c_A{}^n/RT + n\alpha c_A e^{\Delta E_A c_A{}^n/RT}). \quad [8]$$

A reversal of this inequality will yield an S-type curve as stated earlier.

For small values of c_A, inequality [8] becomes:

$$2\alpha > n(n+1)\frac{\Delta E_A c_A{}^{n-1}}{RT}$$

i.e.,

$$\frac{k}{y_m}e^{[E_A{}^0 - E_B - E_c]/RT} > \frac{n(n+1)}{2}\frac{\Delta E_A c_A{}^{n-1}}{RT} \quad [9]$$

for an L-type curve.

If we assume as a first approximation that $n = 1$, then [9] reduces to

$$\frac{k}{y_m}e^{[E_A{}^0 - E_B - E_c]/RT} > \frac{\Delta E_A}{RT}. \quad [10]$$

An examination of the inequalities [9] and [10] shows that we can move from an L-type to an S-type curve either by increasing ΔE_A or by increasing one or both of E_B and E_C. As we shall show in Part II (24), these changes can be demonstrated experimentally.

Activation Energy Independent of Concentration

If we consider the special case when E_A is independent of c_A we can deduce an inequality from [9] by putting $\Delta E_A = 0$, when $E_A{}^0$ be-

comes E_A, i.e.,

$$\frac{k}{y_m}e^{[E_A - E_B - E_c]/RT} > 0 \quad [11]$$

This is always true, hence we deduce that for those cases in which the energy terms are all independent of concentration, an L-type curve should always be produced.

Relative Size of A and B Molecules

If there is a difference in size of the molecules of the component A and the solvent B, there will be some relationship between their respective activation energy terms of the form $mE_A{}^0 = lE_B$ if l molecules of B are displaced by m molecules of A occupying the same area. Hence we can write

$$E_B = \frac{m}{l}E_A{}^0,$$

and the inequality [10] becomes

$$\frac{k}{y_m}e^{\{E_A{}^0[1-(m/l)]-Ec\}/RT} > \frac{\Delta E_A}{RT},$$

but the statement following [10] still applies.

THE H-CURVE

This arises in special cases where the adsorbate–substrate affinity is especially high

and $E_A \gg (E_B + E_C)$, so that dy/dc_A has a very high value.

THE C–CURVE

This curve shown in Fig. 1 has received little theoretical attention, yet it is, in some respects, the most interesting of the SSA isotherms and is almost unknown in the other forms of adsorption. Even in SSA it occurs in only a few systems. The feature common to these systems is a substrate which is microporous and a solute which on general chemical considerations is expected to have higher affinity for the substrate than has the solvent (23).

To understand the significance of this curve, consider first the S- or L-isotherms. The tangent of the angle, relative to the y-axis, of any portion of these curves represents the increment of concentration of solute (or vapor) in the external phase, necessary to maintain a constant increment of concentration, at equilibrium, in the substrate. The complement of this angle, i.e., the slope of the isotherm at any point, may thus be regarded as a measure of the ease with which bombarding solute molecules can find vacant sites in the surface. In the normal, or L-curve, the slope steadily falls with rise in concentration because vacant sites become more difficult to find with the progressive covering of the surface. In the S-curve the slope at first increases with concentration, because in cooperative adsorption, sites capable of retaining a solute molecule increase. Eventually, in all cases, the slope falls and becomes nil at the saturation point, when no vacant sites remain.

A linear isotherm is therefore consistent with conditions in which the number of sites (not necessarily of equal energy) *remains constant* throughout the whole range of solute concentrations up to saturation of the substrate. This means that the surface available for adsorption expands proportionally with y, the amount of solute adsorbed. We may describe this condition by two models.

Model (i)

The surface expansion is expressed thus,

$$y_m = y_0(1 + \beta c),$$

where y_0 is a constant, equivalent to the extent of surface available before adsorption starts, and β is a coefficient of expansion of the surface on which adsorption occurs. The general Langmuir equation [2] can then be written

$$y = by_m c_A(1 + bc_A)^{-1} = sc_A, \qquad [12]$$

where s is a constant. Thus

$$b = s/(y_0 + y_0\beta c_A - sc_A) \qquad [13]$$

Equation [13] is valid only up to a critical value c_A^*, where

$$c_A^* = y_0(s - y_0\beta)^{-1},$$

because if c_A were greater than c_A^* the sign of b would change from positive to negative, which is impossible because the components of b are positive. Thus at $c_A = c_A^*$, $b = \infty$, i.e., the rate of escape of adsorbed solute from the surface is zero (1–3). Therefore when the concentration c_A^* is reached the value of y will remain fixed, provided no fresh surface is formed, and the curve will change abruptly to the horizontal, as shown in Fig. 1.

Model (ii)

Consider the model as an adsorbing surface with an area which expands by an opening-up or disentangling of the structure. (This can be likened to the opening of a zip fastener, with the slider as the first entering adsorbate molecule and the fastener as the substrate.) We may then assume that the rate of adsorption is independent of the available area of substrate at any given time, because each molecule as it becomes adsorbed can readily generate a new vacant site; it is therefore dependent only on the concentration c_A of the solute A in the solution in contact with it. The rate of desorption or removal of the solute from the substrate will however be proportional to the area of substrate covered by adsorbed solute molecules,

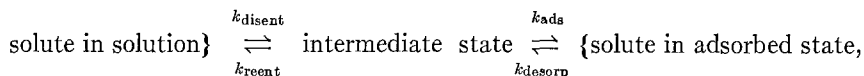and hence to a first approximation to their concentration y in the substrate.

Thus, rate of adsorption $= k'c_A$ [14]

and rate of desorption $= k''y$ [15]

where k', k'' are constants, and at equilibrium.

$$k'c_A = k''y. \qquad [16]$$

So that $y/c_A =$ constant and the isotherm has a constant slope. In more detail, the process can be shown as follows:

$$\text{solute in solution} \} \; \underset{k_{\text{reent}}}{\overset{k_{\text{disent}}}{\rightleftharpoons}} \; \text{intermediate state} \; \underset{k_{\text{desorp}}}{\overset{k_{\text{ads}}}{\rightleftharpoons}} \; \{\text{solute in adsorbed state,}$$

where the k's refer to disentanglement and reentanglement of substrate/substrate, and adsorption and desorption.

If k_{disent} is small compared with k_{ads} the first step can be rate-controlling. This is likely since the energy of activation for adsorption is assumed to be zero in the present work, and that for disentanglement of the substrate must therefore be larger.

Similarly in the reverse process k_{desorb} may be small and k_{reent} large, since the respective energies of activation must be relatively high and low.

Of course this expansion of structure cannot continue indefinitely and a situation can be envisaged where the primary expansion gives way to a secondary or even tertiary structure expansion, occurring at a slower, or perhaps at a faster rate. Thus, a change in slope will occur, the sharpness of which will depend on the degree of disparity in the relevant rates. A horizontal plateau indicates saturation of all the internal area of substrate which can be opened up by the solute, as in model (i) above. A second branch in the curve, of different slope (a rare but not an unknown occurrence), (curves C2ci, ii in Fig. 1) indicates a change in internal structure caused by pressure of the adsorbed solute, whereby a new portion of the solid, possibly with a different type of crystal lattice, starts to become accessible.

The adsorption picture suggested by the above model is consistent with the observation that many of the solutes giving C-curves for adsorption on synthetic polymers cause the polymer to disintegrate completely and even

to dissolve, if used at sufficiently high concentration, e.g., phenols applied to polyamides from water.

If conditions disturb the adsorption rate so that Eq. [14] does not exactly apply, the process will tend to revert to a normal adsorption and give S- or L-curves, even though at first sight the system appears favorable for C-curve adsorption. This sometimes occurs in practice.

General Comments

Some authors have likened C-isotherm adsorption to the partition of a solute between two immiscible solvents, say P and Q, as treated by Nernst (25). The comparison is not strictly justified. In the Nernst conditions, if say the liquid Q is considered to be the substrate, there are in Q in effect an infinite number of sites available for the solute. The conditions therefore resemble those in the earliest stages of Langmuir adsorption, where a linear portion of the isotherm is observed (5, 23).

Known examples of C-curve systems are: (i) non-ionic dyes which are highly polar, applied from water to polyethylene terephthalate, which has very low affinity for water; and (ii) water applied as a solute to wool from solution in n-butanol (23), which does not readily penetrate wool, whereas water does.

In these and all other C-curve systems so far discovered there is good reason to believe that the solute initiates the adsorption by penetrating into the structure of the substrate, probably, though not necessarily always, without
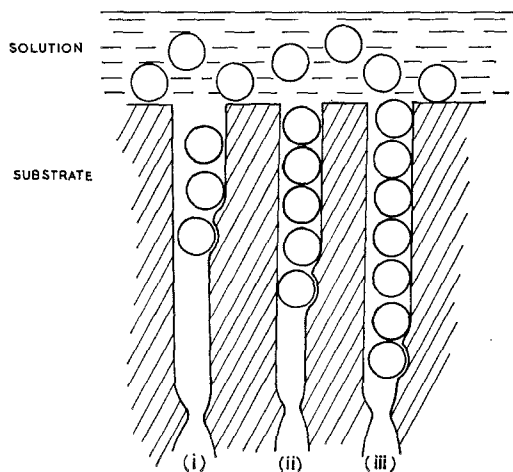
Fig. 3. Sketch illustrating the conditions producing C-isotherms. The substrate is microporous. The solute molecules (circles) have higher affinity for the substrate than have those of the solvent. The entering solute may be likened to a molecular wedge, forcing its way into the micropores of the substrate, which are thereby opened to access by following solute molecules. (i), (ii) and (iii) show stages in this penetration of substrate. Solvent may in some cases accompany the solute into the pores. When the pores are filled, the solute may break into new regions (below the lower constrictions here) and the adsorption process is then repeated.

solvent. This is illustrated diagrammatically in Fig. 3. The process of penetration of the micropores thus proceeds steadily since the "sites," i.e., the entrances to the pores, remain constant in number until they are filled.

The above theoretical treatment is thus consistent with the experimental facts.

The c-Subgroup

There are also a few cases known in which the curve at first has the normal L-form and at the turning point the curve continues to rise, but linearly. These are placed in a subgroup 2c shown in Fig. 1. The substrates are microporous (26) but probably the accessible internal area is relatively low and comparable with the external area. After normal adsorption on the latter is complete, the solute begins to penetrate pores in the manner described above. One case is known (benzyl alcohol on cellulose triacetate, from water) where the C-curve itself has this

second rise, with a steeper slope. This is believed to be due to a breakdown of the polymer structure, whereby fresh internal surface is made accessible.

Anomalous Isotherms: the "Z" Curve

From time to time isotherms may be discovered which do not fit readily into the present classification. We have encountered the unusual shape, which we term a "Z" curve shown in Fig. 4, for certain tests under short-term, non-equilibrium conditions (27). The solute was p-nitrophenol applied to dry cellulose from an organic solvent, and the curve was found to be readily repeatable. An explanation is as follows.

There is a sudden partial breakdown of the cellulose structure, due to solute penetration, when the solute concentration is raised beyond a given value. Consider, the points marked A, B in Fig. 4. A was obtained from the more concentrated initial solution, but because this higher concentration was sufficient to start the structural breakdown of the fiber, the surface available to it was larger than that available to the weaker solution; so much larger in fact that the extra amount of solute adsorbed
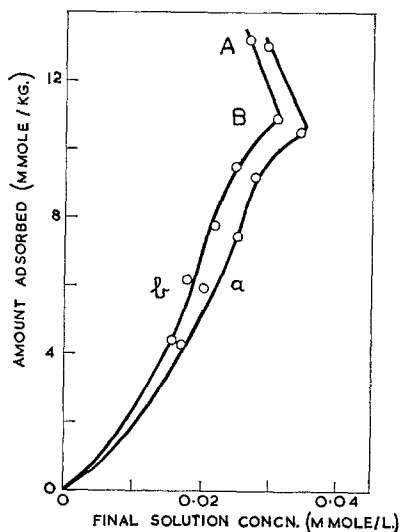

Fig. 4. Isotherms ("Z" class) for nonequilibrium adsorption [(a, b) 15, 30 min, respectively] of p-nitrophenol from 2,2,4-trimethylpentane on dry cellulose (paper pulp) (27).

reduces the final concentration below that of the initially weaker solution; hence the curve reverses.

The Presence of Solvent in the Monolayer

It has often been stated that in solute adsorption solvent remains in the monolayer. Certainly this must sometimes be so, but data from many high affinity adsorption systems used in specific surface measurement (28) show that the monolayer is there a condensed one without solvent. Experimental evidence of this, of a more direct kind, was reported by Dawson, Rich and Haydon (29), who found that formic acid is adsorbed to the same extent by various samples of titanium dioxide (rutile) from the vapor phase as from solution in benzene.

Variation in Energy Over the Surface

The curve relating heat of adsorption (in VPA) to proportion of sites filled at first falls and then in most cases tends to level out, with increase in amount adsorbed. Thus the later stages of adsorption take place on a more uniform energy surface than the early stages. The exact relation between heat and amount of adsorption differs from system to system (2, 3) but always the numerical value of the heat (strictly, the *differential* heat) decreases with increase in coverage of the surface. Langmuir tacitly assumed that the adsorbing surface has uniform energy.

As stated, we equate the activation energy of desorption with the heat of adsorption; thus E_A will tend to decrease with increase in surface coverage and ΔE_A in [3] is negative. Examination of [10] then shows that this condition will give the L-curve. To obtain the S-curve ΔE_A must be positive, so that this curve cannot be accounted for merely by the energetic nonuniformity of the surface. The variation in energy over the surface does not, therefore, affect the present treatment.

The Subgroups 1–4 · · ·

Curves in subgroup 1 represent systems in which the adsorbate monolayer has not been completed, probably because of experimental difficulties. In the subgroups 2 and higher we can identify the plateau or the "Point B" (3, 30), which is the end of the turning point, with completion of the first monolayer. [In special cases the turning point may represent a change in mode of packing of the adsorbate (31).] The subsequent rise represents the development of a second layer and in subgroup 4 this is completed. The nomenclature can readily be extended, e.g., systems giving subgroup 6 curves represent a completed third layer, and so on, but such cases seem to be extremely rare.

The present treatment as stated applies to conditions where c_A is small. Where c_A is large and the monolayer approaches completion, $y \rightarrow y_m$ and $dy/dc_A \rightarrow 0$, i.e., the curve becomes steadily less steep.

The development of a second layer can be treated as that of the first, with the difference that in place of the bare substrate surface, the adsorbate is attracted by a layer of its own molecules, in a particular orientation, and of course the value of E_A will differ from that for the first layer.

The forces generating the second and subsequent layers usually are weaker than those generating the first. Hence in effect in the inequalities [9] and [10] $E_A{}^0$ decreases and the exponent may be dominated by E_B. This means that the second rising portion of the isotherm, which changes subgroup 2 to 3 or 4, is likely to be S-shaped, having a "toe," as indeed it appears usually to do. In adsorptions of ionic micelles the curve is usually L2 or H2 in type and the plateau as shown in Fig. 1 is often long (28). Apparently the second layer is reluctant to form because of the coulombic repulsive forces from the micelles in the first layer.

The Subgroup max

In the known cases a curve with a maximum occurs with aqueous solutions of solutes which associate in solution, such as detergents and certain types of dye, possibly due to a trace of highly surface-active impurity. It therefore appears that with increase in solution concentration a point is reached at which the solute–

solute van der Waals interactions overcome substrate–solute interactions so that some solute is desorbed from the surface and incorporated in solvated micelles possibly including some highly surface-active impurity, until a new equilibrium is reached. We assume that this situation can be represented in [3] by expanding the activation energy term for the solute A, thus

$$E_A = E_A{}^0 + \Delta E_A c_A - \phi E_A c_A{}^m, \quad [17]$$

where ϕ is a constant and m is >1.

This is a reasonable assumption, since as the CMC is approached the aggregation number of solutes of the type involved here rises very rapidly with concentration. As c_A increases, the negative term in [17] becomes more important and eventually dominates so that dy/dc_A becomes negative.

ACKNOWLEDGMENTS

These are given in Part II (24).

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