ADSORPTION OF NON-ELECTROLYTES FROM SOLUTION

By J. J. KIPLING, B.SC., M.A., D.PHIL.

(UNIVERSITY COLLEGE, HULL)

THE study of adsorption from solution falls into several classes, for each of which separate experimental and theoretical treatments are appropriate : (i) adsorption of simple non-electrolytes, (ii) adsorption of electrolytes, including ionic dyestuffs,[1a, b] (iii) ion-exchange,[1c] (iv) adsorption on crystals (which is largely a study of crystal growth), with which may be included the use of adsorption indicators, (v) the adsorption of coloured substances, probably of high molecular weight, in purification processes,[1d] (vi) techniques of chromatography.[1e] This Review is concerned with the first class of adsorption only, and will deal mainly with adsorption at the liquid–solid interface. In view of the connections which exist with the other branches listed above, key references are given, from which similarities to, and differences from, adsorption of the first class will become apparent.

Substances behaving as Non-electrolytes in Adsorption.—A number of experiments have shown that some substances, although they may ionise in solution, nevertheless behave non-electrolytically in the adsorption process. Phelps and Peters [2] investigated adsorption of the lower aliphatic acids and amines by charcoal over a considerable range of pH, finding in each case that the extent of adsorption followed the dissociation curve of the substance. They concluded that only the undissociated molecules were adsorbed. The Reviewer has confirmed these conclusions in a more rigorous treatment, considering the adsorption isotherm of the undissociated acid or amine in conjunction with its dissociation constant.[3] This treatment could be applied to the data of Fromageot and Wurmser,[4] who, working with oxalic acid, obtained data similar to those of Phelps and Peters, but offered no adequate interpretation ; also to the results of Anderson,[5] who showed that adsorption of phenol and of diethylbarbituric acid is greater from acid than from alkaline solutions, the reverse holding for nicotine. For sulphanilamide, adsorption is highest at the isoelectric point and falls off at both higher and lower pH. The adsorption of ethyl alcohol, as would be expected, is independent of pH.

These results are important because the study of adsorption of electrolytes has shown that the surfaces of charcoals (the most frequently-used adsorbents) have electrochemical properties which vary according to the method of preparation, thus profoundly affecting the adsorption of electro-

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[1] (*a*) Weiser, " Colloid Chemistry ", 2nd edn., New York and London, 1949, Chapter 7 ; (*b*) Miller, Colloid Symp. Monograph No. 5, 1928 ; *J. Phys. Chem.*, 1932, **36**, 2967 ; (*c*) Duncan and Lister, *Quart. Reviews*, 1948, **2**, 307 ; (*d*) Deitz, " Bibliography of Solid Adsorbents ", Washington, 1944 ; (*e*) *Discuss. Faraday Soc.*, No. **7**, 1949.

[2] *Proc. Roy. Soc.*, 1929, *A*, **124**, 554 ; Phelps, *ibid.*, 1931, *A*, **133**, 155.

[3] *J.*, 1948, 1483.

[4] *Compt. rend.*, 1924, **179**, 972.

[5] *Acta Pharmacol.*, 1947, **3**, 199.

lytes. The subject has recently been reviewed in a very useful monograph by Steenberg.[6] These changes in electrochemical properties must be connected with changes in the chemical groupings present at the charcoal surface. In general, such changes might not be expected necessarily to affect the adsorption of non-electrolytes. Thus, for steam-activated charcoals, temperature of activation does not affect the adsorption of acetic acid from aqueous solutions, provided that the degree of activation (as measured by gas-adsorption tests) is the same in all cases.[3] For oxygen-activation, a temperature effect has been found,[7] though it is claimed that this is only due to change in surface area.[8] Confirmation of a true temperature effect would not alone destroy the suggestion that acetic acid is adsorbed non-ionically, for Bartell and Lloyd [9] have shown that adsorption in the essentially non-ionic system benzene–ethyl alcohol may be varied from preferential adsorption of benzene (which is regarded as typical for charcoals) to preferential adsorption of alcohol (which is typical of silica gel [10]), by varying the temperature at which the charcoal is activated with oxygen or carbon dioxide ; see also Iliin.[11]

In this Review we shall include with true non-electrolytes those substances which behave non-electrolytically in the adsorption system being considered.

The Adsorption Isotherm.—Investigation of this class of adsorption proceeded initially by analogy with those which had earlier been carried out on gases. Thus the adsorption isotherm has been extensively studied.* In dilute solutions, a very large number of isotherms follow the so-called Freundlich equation, $x/m = kc^{1/n}$, in which x/m is adsorption per unit mass of adsorbent, c the concentration of the solution at equilibrium, and k and n are constants. Freundlich himself [14] gives many examples of this, using charcoal as adsorbent for solutions of the lower fatty acids in water, benzoic acid in benzene, bromine in ether, etc. In such work, the concentrations did not usually exceed 0·2M. The equation is often obeyed up to much higher concentrations (*e.g.*, up to 2N. with aqueous acetic acid and charcoal), but ultimately breaks down.

For work in the gas phase, the Langmuir equation [15] has now replaced the Freundlich equation. In the form $x/m = k'c/(1 + kc)$, it has been applied to solutions. It is usually obeyed over a rather wider range of

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[6] " Adsorption and Exchange of Ions on Activated Charcoal ", Uppsala, 1944.

[7] King, *J.*, 1937, 1489.

[8] Linner and Williams, *J. Phys. Chem.*, 1950, **54**, 605.

[9] *J. Amer. Chem. Soc.*, 1938, **60**, 2120.

[10] Bartell, Scheffler, and Sloan, *ibid.*, 1931, **53**, 2501.

[11] *Z. physikal. Chem.*, 1931, *A*, **155**, 403.

[12] Chaplin, *J. Phys. Chem.*, 1932, **36**, 909 ; Ockrent, *Nature*, 1932, **130**, 206.

[13] Allmand, Burrage, and Chaplin, *Trans. Faraday Soc.*, 1932, **28**, 218.

[14] Freundlich, " Colloid and Capillary Chemistry ", London, 1926.

[15] Langmuir, *J. Amer. Chem. Soc.*, 1918, **40**, 1361.

* We are here concerned with isotherms in which adsorption is a continuous function of concentration. Claims to have observed discontinuous isotherms have been made,[12] but, like similar work on the gas phase,[13] do not seem to have been followed up.

concentration than the Freundlich equation (*e.g.*, up to 35% in benzene–methyl alcohol with silica gel[16]), but again is not satisfactory over a wide range.

If the Langmuir equation were followed over the complete concentration range for a binary liquid mixture, the adsorption isotherm would have

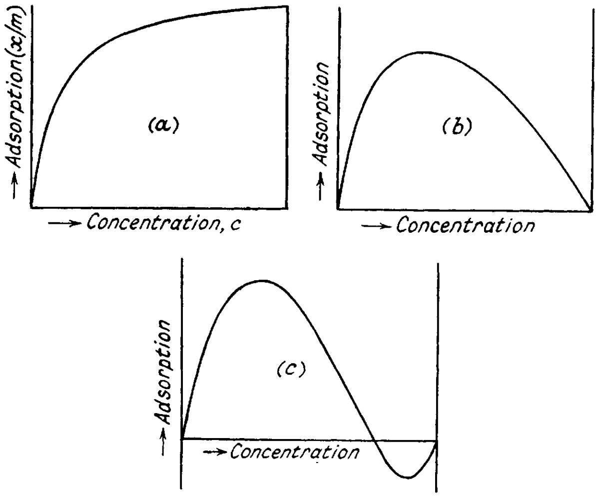

FIG. 1

Isotherms of apparent adsorption.

the form shown in Fig. 1(*a*), adsorption always increasing with concentration. Many cases have been investigated, however, in which the curve reaches a maximum and then falls, ultimately to zero at the end of the concentration range, either remaining positive at intermediate values, as in Fig. 1(*b*), or becoming negative first, as in Fig. 1(*c*). Examples are the adsorption of acetic acid on charcoal from water [17, 18] and from toluene.[17]

Apparent Adsorption and Negative Adsorption.—Several reasons have been put forward to explain the fall in the adsorption curve after it has reached a maximum. Fundamentally these all derive from the fact that there is no direct method of measuring adsorption from the liquid phase; see further, Defay.[19] The degree of "adsorption" of a solute is usually determined by comparing its concentration in a known volume (or weight) of solution before and after adsorption. It has then usually been taken that x g. of solute are adsorbed per g. of adsorbent, where

$$x = v(c_0 - c)/1000m \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

and c_0 = initial concentration of solution in g./l., c = final concentration of solution in g./l., v = volume of solution used in ml., and m = weight

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[16] Volkova, *J. Phys. Chem., U.S.S.R.*, 1933, **4**, 412.
[17] Schmidt-Walter, *Kolloid-Z.*, 1914, **14**, 242.
[18] Nestler and Cassidy, *J. Amer. Chem. Soc.*, 1950, **72**, 680.
[19] *Bull. Soc. chim. Belg.*, 1928, **37**, 63.

of adsorbent in g. Alternatively, a similar expression based on weight, instead of volume, of solution has been used.

There are two ways in which this equation is unsatisfactory. First, it was pointed out by Williams,[20] and soon afterwards by Schmidt-Walter,[17] that the equation ignores the change in total volume of the solution which is caused by the removal of the adsorbed material. Hence x does not measure the true amount of solute adsorbed ; it is based immediately on the difference between the initial and final concentrations of the solution, and is therefore referred to as the " apparent adsorption " of the solute. Williams [20] developed an equation taking into account the change of volume which takes place on adsorption : *

$$x' = M(C_0 - C)/m(1 - C) \quad . \quad . \quad . \quad . \quad (2)$$

where concentrations are expressed in g. of solute per g. of solution, M g. of solution being used in the determination. This equation can be modified for use in experiments where volumes and not weights of solution are used :

$$x' = \frac{(\rho . c_0 - \rho_0 . c) . v}{m(1000\rho - c)} \quad . \quad . \quad . \quad . \quad (3)$$

ρ_0 and ρ g./ml. being the densities of the initial and final solutions respectively. This correction is useful for extending the range over which either the Freundlich or the Langmuir equation appears to be applicable, but nevertheless is of value only in dilute solutions. The term x' may be referred to as " apparent adsorption corrected for volume change ".

Secondly, in some experiments the concentration of the solute is greater after adsorption than before. Equation (1) then gives a negative value for the adsorption of the solute, as is seen in Fig. 1(*c*). Such " negative adsorption " can only be interpreted by assuming that the solvent is adsorbed, and to a greater extent than the solute in relation to their respective molecular concentrations in the original solution. This leads to the concept, first adequately put forward by Williams,[20] that in liquid systems of the type being considered, both solute and solvent are probably adsorbed simultaneously. For completely miscible liquids, it follows that if the whole concentration range is being considered, the distinction between " solute " and " solvent " is completely arbitrary.† It has been pointed out [21] that one may almost speak, not of adsorption " from " or " in " solutions, but " of " solutions, emphasising that both components are adsorbed.

Equation (1) does not, therefore, give a true measure of the adsorption of either component, nor (as will be seen below) is it likely that any method can be devised to give such information directly. In this respect there

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[20] *Medd. K. Vetenskapsakad. Nobelinst.*, 1913, **2**, No. 27.

[21] *Kolloid-Z.*, 1922, **30**, 279.

* Units and symbols have been changed, where necessary, to bring them into conformity with those used throughout this Review.

† The distinction may be useful in dilute solutions, but undue emphasis on adsorption of solute may well have led to early misunderstanding of the real phenomenon of simultaneous adsorption of both components.

is an important difference between adsorption from solution and from the gas phase, where, even for a mixture of adsorbates, the adsorption of each component can be measured directly.[22] A further difference may also be noted. At room temperature, one component of a binary gaseous mixture may be a permanent gas to which the adsorbent may be " indifferent ".[23] It seems unlikely that an adsorbent might be " indifferent " to any component of a binary liquid mixture.

True Adsorption Isotherms.—The above analysis shows that the isotherm which has been discussed so far is an isotherm of concentration change and does not give the true adsorption of either solvent or solute. It is a composite isotherm, the resultant of combining the isotherms for the true adsorption of each component. An interesting arithmetical analysis has been made by Ostwald and de Izaguirre[21] of the shapes which such composite isotherms may have when different types of " true " isotherms are combined; the results are shown in Figs. 2(*a*)—(*f*). In each case the adsorption of the solute follows an exponential law with regard to concentration, but this is not assumed in all cases for the adsorption of the

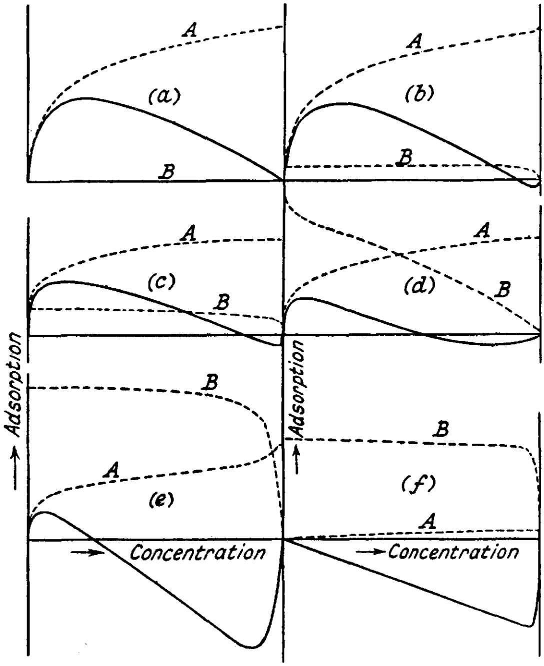

FIG. 2

" Composite " adsorption isotherms.

Full line—" resultant " isotherm.
Broken lines—A, " solute " ; B, " solvent ".

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[22] Lambert and Peel, *Proc. Roy. Soc.*, 1934, *A*, **144**, 205.

[23] Brunauer, " Physical Adsorption of Gases and Vapours ", Oxford, 1944, p. 477.

solvent. Fig. 2(*a*) is interesting in showing that adsorption of the solvent does not have to be postulated to explain a maximum in the composite isotherm, even though adsorption of the solute rises over the whole concentration range. This shows again the inadequacy of using $(c_0 - c)$ as a measure of true adsorption. The shape of the composite isotherm is here purely an arithmetical consequence of the change in volume of the solution which accompanies adsorption. It is clear, however, that " negative " adsorption is only possible if the solvent is adsorbed.

Attempts to Measure True Adsorption.—The realisation that each component in a binary system is likely to be adsorbed brought forward many attempts to measure the individual adsorption values. It now seems rather unlikely that any direct measurements are possible. A direct method would involve a knowledge of the volume change in the solution caused by adsorption. Most adsorbents used in this work are porous (activated charcoal, silica gel, etc.) and hence an appreciable volume of the solution is retained mechanically in the pores in addition to that which is adsorbed at the actual surface. So far it has not been found possible to distinguish between these two volumes of solution. A method has been suggested by Defay,[19] based on the displacement, by another liquid, of the solution held mechanically, but the method does not seem to have been applied satisfactorily. The use of non-porous adsorbates, although less difficult to deal with in this particular way, suffers from the disadvantage that the surface area per g. available for adsorption is so small that the changes in concentration are small and can only be measured with considerably reduced accuracy.

Dobine [24] claims to have measured the individual adsorption isotherms of water and acetic acid, using charcoal as adsorbent. His method uses the difference between the adsorptive capacities of dry and moist charcoals. His papers, however, do not give full details, and it is difficult to understand how an experiment with moist charcoal differs from one with dry charcoal added to a solution of lower concentration ; see further Nestler and Cassidy.[18]

In the absence of direct methods, various indirect methods have been proposed. Williams,[20] studying the adsorption on charcoal from aqueous solution, measured the total uptake from the vapour phase above solutions of acetic acid of known concentration. By assuming that the same amounts of water and acetic acid were adsorbed from the vapour phase as from the solution in equilibrium with the vapour, he was able to combine two sets of data to determine individual adsorption values. Only a few points were obtained by this method, but from them Williams claimed to establish the relationship :

$$x/x_\infty + y/y_\infty = 1 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where x and y g. of acetic acid and water respectively are adsorbed per g. of charcoal at any given concentration, and x_∞ and y_∞ g. are the maximum amounts adsorbed (*i.e.*, from the pure components). Williams

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[24] *Compt. rend.*, 1937, **205**, 1388 ; 1938, **206**, 430 ; 1941, **212**, 155, 339.

did not comment on these results. His equation would imply, however that (as might be expected) the surface of the charcoal is completely covered at all concentrations, and further that the adsorbed layer is only one molecule thick. Such a relation might be expected to apply widely, provided that the molecular sizes of the two adsorbates are such that replacement of the smaller by the larger does not leave areas of the surface which cannot be covered. A similar equation has recently been shown to apply to adsorption from mixtures of gaseous hydrocarbons.[25]

Williams did not plot the adsorption values, but this was later done by Gustafson,[26] as in Fig. 3. The same author later,[27] and also Bakr and King,[28] questioned the value of Williams's method on the ground that the material taken up from the vapour phase might include liquid condensed in capillaries, in addition to the material truly adsorbed. Davis [29] had earlier obtained adequate results for the system iodine–ethyl acetate. Bakr and McBain [30] attempted to apply it to the system toluene–acetic acid–charcoal, but their results scarcely seem accurate enough to lead to any definite conclusion. Jones and Outridge [31] have also used the method for the system n-butyl alcohol–benzene–silica gel, and have compared the results with those obtained by Ostwald and de Izaguirre's method (see below); they conclude that, in this system, the material adsorbed from the vapour phase includes some which is held by capillary condensation. This reinforces Gustaver's criticism of Williams's statement that " the equilibrium between charcoal and water vapour is of course the same as that between charcoal and water at the same temperature ", in so far as it is applied to this problem. The equilibrium must be the same so long as the type of adsorption involved is the same, but it appears that, for some systems, two forms of " adsorption " take place in the vapour phase, but only one in solution.

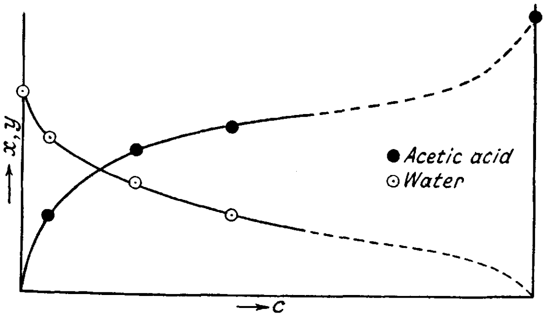

FIG. 3

Adsorption from aqueous solutions of acetic acid.

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[25] Lewis, Gilliland, Chertow, and Cadogan, *Ind. Eng. Chem.*, 1950, **42**, 1319.

[26] *Z. physikal. Chem.*, 1916, **91**, 385.

[27] Gustaver (formerly Gustafson), *Kolloid-Z.*, 1922, **31**, 358.

[28] *J.*, 1921, **119**, 454.

[29] *J.*, 1907, **91**, 1666.

[30] *J. Amer. Chem. Soc.*, 1924, **46**, 2718.

[31] *J.*, 1930, 1574.

Theories of Adsorption from Binary Systems.—The alternative method of obtaining true adsorption values is to put forward a theory of adsorption which embodies an equation relating the true adsorption of each component to the concentration of the equilibrium solution. Then, if x and y g. are the actual amounts of solute and solvent adsorbed from M g. of solution, the concentrations being initially C_0 and finally C g. of solute per g. of solution, we have

$$C = (MC_0 - \mathrm{x})/(M - \mathrm{x} - \mathrm{y}) \quad . \quad . \quad . \quad . \quad (5)$$

as an equation which allows for change in volume due to adsorption. Ostwald and de Izaguirre [21] have considered five cases, in each case assuming that the adsorption of the solute follows the Freundlich equation. It should be noted that this assumption is only used in the last stage of the derivation of the following five equations, and that the derivations up to this stage are fundamental.

Case 1 : the solvent is not adsorbed. This case is most unlikely to occur in practice, but the mathematical treatment is useful later. We have :

$$M(C_0 - C) = \mathrm{x}(1 - C)$$

Hence

$$M(C_0 - C)/m = kC^{\alpha}(1 - C) \quad . \quad . \quad . \quad . \quad (6)$$

Case 2 : the solvent is adsorbed. In this case,

$$M(C_0 - C) = \mathrm{x}(1 - C) - \mathrm{y}C \quad . \quad . \quad . \quad (7)$$

If it is now assumed that adsorption of the solvent as well as of the solute follows the exponential law, so that $\mathrm{y} = mk_2(1 - C)^{\beta}$, then

$$M(C_0 - C)/m = k_1C^{\alpha}(1 - C) - k_2(1 - C)^{\beta}C \quad . \quad . \quad (8)$$

[This equation agrees in form with an equation derived by Williams [20] to relate apparent adsorption to true adsorption. Williams, however, only related $(C_0 - C)$ to x and y, without making further assumptions about the relation between x, y, and C.] The constants in equation (8) are obtained as follows. For small values of C, the term $k_2(1 - C)^{\beta}C$ is neglected and the values of k_1 and α are obtained. At higher concentrations, the difference, Δ, between $k_1C^{\alpha}(1 - C)$ and the observed value of $M(C_0 - C)/m$ gives $\Delta = k_2(1 - C)^{\beta}C$. A plot of $\log(\Delta/C)$ against $\log(1 - C)$ thus gives the values of k_2 and β.

Case 3 : a solvated solute is adsorbed ; solvent is not adsorbed. Here $\mathrm{y} = S\mathrm{x}$, where S is a solvation factor which may be a function of concentration. Ostwald and de Izaguirre deal with the case where $S = (1 - C)^{\gamma}$, and derive the equation :

$$M(C_0 - C)/m = kC^{\alpha}\{1 - C[1 + S(1 - C)^{\gamma}]\} \quad . \quad . \quad (9)$$

As in case 2, the values of S and γ can be obtained from the difference between $M(C_0 - C)/m$ and $kC^{\alpha}(1 - C)$.

Case 4 : the solute is solvated and the solvent is adsorbed. This is a combination of cases 2 and 3, giving :

$$M(C_0 - C)/m = k_1C^{\alpha}\{1 - C[1 + S(1 - C)^{\gamma}]\} - k_2.(1 - C)^{\beta}C \quad . \quad (10)$$

It is more difficult to deal with this case unless S is known as a function of C from a separate experiment.

Case 5 : solvent only is adsorbed. This is equivalent to case 1.

Experimental Tests.—In attempting to test the above equations, Ostwald and de Izaguirre found few data in the literature which extended over the complete concentration range. These only applied to case 2. An analysis of Schmidt-Walter's results [17] on aqueous acetic acid and charcoal gave isotherms for adsorption of solute and solvent not entirely similar to those shown in Fig. 3. It can be calculated that the values obtained for x and y only obey equation (4) with a tolerance of 25%. Equation (8), however, was found to reproduce the apparent adsorption isotherm faithfully. Gustafson's apparent isotherm for adsorption from the alcohol–phenol system by charcoal [26, 32] was also reproduced. Adsorption from the system acetic acid–ethylene, however, did not obey the equation, and Ostwald and Schulze postulated adsorption of a eutectic.[33]

The above approach has been developed slightly differently and independently by Bartell and his co-workers.[10, 34, 35] It is assumed that each component is adsorbed according to an equation of the Freundlich type. The composite equation is expressed in terms of mole fraction, instead of weight concentration :

$$(H.\Delta N)/m = k_1N^{\alpha}(1 - N) - k_2(1 - N)^{\beta}N \quad . \quad . \quad (11)$$

where H represents the number of millimoles of original solution, N is the mole fraction of solute at equilibrium, and ΔN is the change in mole fraction observed during adsorption. The two terms on the right-hand side of the equation refer to the adsorption of the two components respectively. The four constants are found by the procedure of Ostwald and de Izaguirre, except that it is continued as a series of successive approximations until steady values for the constants are obtained. Equation (11) then fits the experimental curve. This has been done for a series of binary organic liquid mixtures, charcoal [34] and silica gel [10, 35] being used as adsorbents.

The validity of this method has been questioned. It has been seen above that the Langmuir equation has been used with some success to represent adsorption from dilute solutions. It can also be used in deriving an equation based on (7) :

$$\frac{H.\Delta N}{m} = \frac{k'_1K'N(1 - N)}{1 + k'_1N} - \frac{k'_2K'N(1 - N)}{1 + k'_2(1 - N)} \cdot \quad . \quad . \quad . \quad (12)$$

Equation (12) can be made to fit the experimental curves as accurately as equation (11) for the system benzene–ethyl alcohol–charcoal.[36] If, however, the isotherms for the adsorption of the individual components are plotted, there is no agreement between the two treatments. This disagreement has focussed attention on the mathematical forms of these equations, and it seems unlikely that either is strictly applicable. A fresh approach is almost certainly needed.

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[32] Gustafson, *Z. Elektrochem.*, 1915, **21**, 459.

[33] *Kolloid-Z.*, 1925, **36**, 289.

[34] Bartell and Sloan, *J. Amer. Chem. Soc.*, 1929, **51**, 1637, 1643.

[35] Bartell and Scheffler, *ibid.*, 1931, **53**, 2507.

[36] Kipling and Tester, *Nature*, in the press.

Multilayer Adsorption.—In the work which has been discussed so far there has been little consideration of the way in which the molecules are adsorbed at the surface. It may have been assumed, by analogy with the phenomena in the gas phase described by the Freundlich and the Langmuir equations, that the adsorbed material forms a monolayer on the adsorbing surface. Analogy with "soluble" films at gas–liquid interfaces would also suggest this (but see also below).

In one case, however, the definite suggestion has been put forward that the adsorbate may be present in a multimolecular form. Hansen, Fu, and Bartell [37] have investigated adsorption by graphite from aqueous solutions of *n*-hexanoic and *n*-valeric acids, *n*-amyl and *n*-butyl alcohols, aniline, *cyclo*hexane, and phenol. It will be noted that these solutes differ from those hitherto considered in having only a limited solubility in the solvent used. By neglecting the last term in an equation similar to (7), these authors obtained approximate values for the individual adsorption of these solutes, which they claimed to be within 3% of the true values. These values, if it is assumed that the molecules form a monolayer on the surface, give cross-sectional areas for the adsorbed molecules considerably smaller than the close-packing values recorded by Adam [38] for the same molecules adsorbed at air–liquid interfaces. As any error in calculating the amount of substance adsorbed would make this smaller than the true value, it was concluded that some of the adsorbate must be in layers beyond the first. The adsorption isotherms in these cases can be fitted by an equation analogous to that used by Brunauer, Emmett, and Teller (ref. 23, p. 149) for multimolecular gaseous adsorption. The term p/p_0 of the B.E.T. equation is replaced by c/c_0, where c_0 is the concentration of a saturated solution. From this equation, values ranging from one to four were obtained for the molecular thickness of the adsorbed layer. Non-porous carbon blacks behaved similarly, but a porous charcoal in no case gave more than a monolayer. The adsorption of the solvent was not investigated. An earlier paper [39] had referred to the possibility of multilayer adsorption from solution, but apparently without recognition of the possibility of adsorption of the solvent.

Thermodynamic Considerations.—Bartell has arrived at a similar conclusion from a thermodynamic approach.[40] The chemical potential of the solute is considered in the bulk solution and in the adsorbed phase:

$$\mu = \mu_0 + RT \ln a \quad \text{for the bulk solution}$$

$$\mu^s = \mu_0^s + RT \ln a^s \quad \text{for the adsorbed phase}$$

where a and a^s refer to the activities in these two phases respectively. For equilibrium,

$$\mu_0 + RT \ln a = \mu_0^s + RT \ln a^s$$

whence

$$\ln a^s = \ln a + (\mu_0 - \mu_0^s)/RT \quad . \quad . \quad . \quad (13)$$

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[37] *J. Phys. Chem.*, 1949, **53**, 769.

[38] "The Physics and Chemistry of Surfaces", Oxford, 1941.

[39] Garner, McKie, and Knight, *J. Phys. Chem.*, 1927, **31**, 641.

[40] Fu, Hansen, and Bartell. *ibid.*, 1948, **52**, 374.

Under ideal conditions, we can replace a^s by m^s, the molality in the ideal layer, so that the value of $(\mu_0 - \mu_0^s)/RT$ can be obtained from the intercept of the limiting slope of a curve of $\log m^s$ against $\log a$. When this term is known, a^s can be evaluated for any value of a, and hence f^s, the activity coefficient of the solute in the adsorbed phase. An approximation gives m^s to within 5%.

The plot of m^s against a is S-shaped and there is a break in the plot of $\log f^s$ against $\log m^s$. This was interpreted as caused by the formation of a second layer of adsorbate. The adsorption isotherm can again be fitted by a modified B.E.T. equation. In a subsequent paper [41] an alternative convention for calculating m^s was discussed, but it was shown that the general conclusions are not affected by changing the convention. Similar work considering the surface excess in terms of the Gibbs adsorption equation also led to the conclusion that adsorption may be multimolecular on non-porous graphites but only unimolecular on porous materials.[42]

It has usually been assumed (see *e.g.*, ref. 38) that adsorbed films at air–liquid interfaces are unimolecular, especially in view of McBain and Swain's microtome investigations.[43] Recent extension of the above work, however, has shown that multilayer adsorption at air–liquid interfaces may also occur in some cases.[44]

Innes and Rowley have also used a thermodynamic approach for binary systems in which there is complete miscibility. Using the system carbon tetrachloride–methyl alcohol–charcoal, they have compared data for adsorption from solution in two ways : [45] (i) directly, as described above, using a form of equation (7), (ii) using an equation [47] similar to the Guggenheim and Adam form [48] of the Gibbs equation. The results do not show perfect agreement, but qualitatively give the same shape for the composite isotherm. The individual isotherms are not considered separately.

Nature of Selective Adsorption.—In many of the composite isotherms, the S-shape is unsymmetrical, which points to a preference of the surface for one component of the binary mixture. A sufficient number of such systems has now been investigated for it to be clear that the direction of preferential adsorption depends on the chemical natures of the adsorbate and adsorbent. Thus many charcoals show a preference for hydrocarbons over hydroxylic substances and for aromatic over aliphatic compounds, *e.g.*, benzene over alcohols,[10] toluene over acetic acid,[17, 49] phenol over ethyl alcohol.[26] This accords with the structure of charcoal as composed of graphitic fragments.[50] Silica gel, on the other hand, usually shows precisely the opposite preferences, particularly as regards hydroxylic compounds : alcohols over benzene,[10, 31, 35] acetic acid over toluene,[49]

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[41] Fu, Hansen, and Bartell, *J. Phys. Chem.*, 1949, **53**, 454.

[42] *Idem, ibid.*, p. 1141.

[43] *Proc. Roy. Soc.*, 1936, *A*, **154**, 608.

[44] Fu and Bartell, *J. Phys. Chem.*, 1950, **54**, 537.

[45] *Ibid.*, 1947, **51**, 1172.

[47] *Idem, ibid.*, 1945, **49**, 411.

[48] *Proc. Roy. Soc.*, 1933, *A*, **139**, 218.

[49] Kane and Jatkar, *J. Indian Inst. Sci.*, 1938, **21**, *A*, 331.

[50] Blayden, Gibson, and Riley, B.C.U.R.A. Conference, 1944.

acetic acid over carbon disulphide.[51] These preferences may be likened to hydrophobic and hydrophilic behaviour of colloids.

A similar comment was made by Holmes and McKelvey, who pointed out that Traube's rule, as modified by Freundlich,[14] requires increased adsorption of fatty acids by charcoal from aqueous solution on ascending the homologous series. If the polar solvent is replaced by a non-polar solvent, and the non-polar adsorbent by a polar adsorbent, the order should be reversed. This was found when the same series of acids was adsorbed on silica gel from toluene solution ;[52] see also ref. 53.

Orders of increasing adsorption on silica gel in the case of organic acids have been related to the order of increasing ease of formation of hydrogen bonds between the carboxyl groups and the solid surface, *viz.*, palmitic < propionic < acetic < formic. This, however, is not the only factor controlling adsorption. Benzoic acid does not fit into this series, possibly through the operation of a size factor. The adsorption of any one acid also decreases as the power of hydrogen-bonding of the solvent increases (carbon tetrachloride < toluene < nitrobenzene < dioxan < water).[54] Adsorption of single substances has also been related to the dipole moments and molecular polarisations of the solvents and to the effect of mixing solvents of different polarities.[55]

Adsorption from Ternary Mixtures.—Adsorption from mixtures containing more than two components has been studied in three ways. The isolation of one or more components from a complex solution was usually empirical until the advent of chromatographic techniques. On the other hand, a few studies have deliberately been made on the effect of competition for adsorption sites between two solutes. It is now clear that such systems should properly be regarded as ternary systems, in which the adsorption of the solvent as well as of the two solutes should be considered. These investigations, however, have mainly been carried out in dilute solution. This means that although the adsorption of the solvent has wrongly been neglected, it is just conceivable that, particularly in the case of water, it was approximately constant in each set of experiments, in which case the " apparent adsorption " figures for the solutes could be compared on a relative scale.

In an early paper Michaelis and Rona [56] showed that adsorption on charcoal of acetone from dilute aqueous solution was reduced in the presence of an excess of acetic acid. Similarly the adsorption of acetic acid was reduced in the presence of aliphatic alcohols, the reduction becoming more pronounced as the homologous series was ascended, in accordance with Traube's rule ; the corresponding esters, however, showed a constant effect ; cf. also Amiot.[57] It is interesting that, whereas the adsorption

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[51] Patrick and Jones, *J. Phys. Chem.*, 1925, **29**, 1.

[52] Holmes and McKelvey, *ibid.*, 1928, **32**, 1522.

[53] Nekrassow, *Z. physikal. Chem.*, 1928, *A*, **136**, 379.

[54] Elder and Springer, *J. Phys. Chem.*, 1940, **44**, 943.

[55] Heymann and Boye, *Z. physikal. Chem.*, 1930, *A*, **150**, 219 ; *Kolloid-Z.*, 1932, **59**, 151.

[56] *Biochem. Z.*, 1908, **15**, 196.

[57] *Compt. rend.*, 1936, **202**, 1852.

of sucrose decreases in the presence of phenol, that of phenol remains unaltered in the presence of sucrose.[58]

An extension of the Langmuir treatment can be applied to the adsorption of such solutes, provided that it is assumed, either that the solvent is not adsorbed, or that it occupies a constant fraction of the surface and that the solution is so dilute that adsorption has a negligible effect on the solvent concentration. Ockrent,[59] apparently making the first assumption, derived the equation:

$$(x/m)_1/(x/m)_2 = k_2c_1/k_1c_2 \qquad . \quad . \quad . \quad . \quad (14)$$

in which subscripts 1 and 2 refer to the two solutes. For dilute aqueous solutions of an aliphatic and an aromatic acid, the observed value of k_2/k_1 is larger than the calculated value, where k_2 refers to the larger molecule. This suggests that there may be adsorption sites small enough to give an extra advantage to the smaller molecule in competition for the surface, or that the effect of adsorption of solvent is different in the two cases.

The extended Langmuir treatment was also used by Markham and Benton [60] to derive isotherms for the adsorption of the components of a binary mixture of gases. Jones, Hudson, and Jones [61] investigated the applicability of this equation to the adsorption, from dilute aqueous solutions, of various ketones mixed with either phenol or aniline. The equation did not fit the results. Mutual displacement, however, was found in all cases. In the aniline series it was further found that the adsorption of the ketones followed an inflected isotherm, but no decisive reason for this has been advanced.

The third type of ternary system is that in which one solute is regarded as dissolved in a mixture of two solvents. Trividic [62] found that the apparent adsorption of iodine on charcoal from mixed solvents followed the Freundlich equation and that the plot of adsorption against composition of the solvent was linear. This contrasts with Schilow and Pewsner's findings [63] for adsorption of organic acids on charcoal; a linear relation is not found in any case. For water–alcohol mixtures, the values lie between those for the pure components, but for non-aqueous mixtures (alcohol–ether, toluene–alcohol, toluene–ether) may pass through a minimum. The situation here is far from clear.

Such investigations have been continued to one further stage of complexity by Ermolenko and Bokhvala [64] in investigations of the adsorption of mixtures of acids from mixed solvents. The use of mixed solvents did not change the form of the adsorption isotherm.

Measurement of Surface Area.—One method which has been used for measuring the surface areas of adsorbents has been to observe the maximum uptake of a solute from solution. This has been done either directly, or by using the Langmuir equation to extrapolate from a series of dilute

[58] Amiot, *Compt. rend.*, 1934, **199**, 636.

[59] *J.*, 1932, 613.

[60] *J. Amer. Chem. Soc.*, 1931, **53**, 497.

[61] *J.*, 1938, 269.

[62] *Compt. rend.*, 1928, **186**, 865, 1358.

[63] *Z. physikal. Chem.*, 1925, **118**, 361.

[64] *Acta Physicochem.*, *U.R.S.S.*, 1940, **13**, 839.

solutions in a way already established for gaseous adsorption.[23] Many solutes have been used for this purpose, particularly dyes, which can be estimated colorimetrically and are thus especially appropriate for routine determinations. As most of such dyes are electrolytes, however, they are excluded from the present survey.

From the foregoing discussion it is clear that the adsorption of non-electrolytic solutes is accompanied by adsorption of the solvent. Measurements of the adsorption of the solute, especially measurements of the apparent adsorption, cannot therefore give the absolute surface area of the adsorbent. At best such figures can only give comparative values for a series of adsorbents tested under the same conditions.

This conclusion should have been clear for many years, but the Reviewer has only recently come across reference to it in the literature.[37] It is borne out by a number of experiments in which areas obtained from solution measurements are compared with those given by gaseous adsorption. (The latter are now thought to give as true a value as can be obtained for the surface areas of most solids, though the term can only have a precise meaning in relation to the molecular size of the adsorbate used.) Such comparisons have not usually been made with the realisation that the solution method is unsatisfactory. Recent work by Lemieux and Morrison [65] on the adsorption of the lower fatty acids on charcoal from aqueous solutions gave surface areas varying, for different acids and charcoals, between 31% and 77% of the low-temperature nitrogen-adsorption values. The authors concluded that the acids are adsorbed only on part of the surface, but did not refer to the possibility that the remainder might be occupied by water molecules. Similar results have been expressed by saying that the effective cross-sections of fatty acids in adsorption (on carbon blacks) are often much greater than the expected value of 20·5 sq. A.

The apparent adsorption of iodine on glass spheres from carbon tetrachloride solution gave a surface area only 39·2% of the value obtained microscopically.[66] Adsorption of the large carbon tetrachloride molecules might well account for most of the remaining 60%. The same method, applied to samples of activated magnesia, gave areas about 35% lower than those obtained from low-temperature nitrogen adsorption; [67] the latter agreed with, or were smaller than, the values given by X-ray diffraction.[68] An apparent exception to this is found in the adsorption of iodine from aqueous solutions of potassium iodide on carbon blacks, where the areas from solution measurements agree with those given by gaseous adsorption and by electron-microscopy.[69] Here, however, it is not certain to what extent simple adsorption is complicated by the occurrence of electrolytic adsorption.

Two systems have been investigated to which the above generalisations

[65] *Canad. J. Res.*, 1947, **25,** *B*, 440.

[66] Urbanic and Damerell, *J. Phys. Chem.*, 1941, **45,** 1245.

[67] Zettlemoyer and Walker, *Ind. Eng. Chem.*, 1947, **39,** 69.

[68] *Idem*, *J. Phys. Chem.*, 1947, **51,** 763.

[69] Besson and Sanlaville, *J. Chim. physique*, 1950, **47,** 108.

do not seem to apply. The apparent adsorption of acetic acid from *cyclo*hexane gave areas of carbon blacks in agreement with those from gaseous adsorption. It is no doubt significant, however, that these workers [70] did not consider the effect on their results of the dimerisation of acetic acid which undoubtedly occurs in *cyclo*hexane.

The adsorption of the higher fatty acids (*e.g.*, lauric and palmitic) on Raney nickel appears to give a complete monolayer even at high dilution.[71] This raises the question whether the solvent may be unable to compete effectively for adsorption sites with a solute which is normally solid at the temperature of the experiment. Similar, but less well-established, results have been obtained in adsorption of heptanoic acid from water on alumina,[72] though in this case specific (chemical) interaction between adsorbate and surface may be possible. In general, however, it is probably fair to say that much greater attention should be paid to the adsorption of solvent than appears to have been done in the past.

It may be added that the apparent adsorption isotherm, though it was originally wrongly interpreted in terms of the adsorption of the " solute " only, is, of course, a plot of experimental observations, *i.e.*, is an isotherm of concentration change. It therefore has a considerable significance when rightly used, as in cases in which the extent to which a solution is freed from solute by adsorption is the prime consideration. One such particular example is its use to calculate the theoretical behaviour of adsorbents in flow systems, in which the changes in concentration caused by successive sections of a column or bed of adsorbent form the basis of the calculations.[73]

In conclusion, it may be suggested that the apparent reluctance of chemists to realise the limitations of the composite isotherm may possibly be due to the fact that the Freundlich and the Langmuir equation appear to be satisfactory over the small range of concentrations to which most work has been confined. This applies especially to aqueous solutions, in which, because of the low molecular weight of water, a solution appears much more concentrated in terms of weight concentration or normality than in terms of mole fraction. An adequate treatment superseding the use of the composite isotherm has, however, yet to be made.

[70] Smith and Hurley, *J. Phys. Chem.*, 1949, **53,** 1409.

[71] Smith and Fuzek, *J. Amer. Chem. Soc.*, 1946, **68,** 229.

[72] Saunders, *J.*, 1948, 969.

[73] Kipling, *J.*, 1948, 1487.