37. *Adsorption from Binary Liquid Mixtures on Silicic Acid Gel. Part I.*

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The apparent adsorption isotherms of the following binary solutions have been determined by interferometric analysis throughout the whole concentration range : nitromethane–carbon tetrachloride; the homologous series nitromethane to 1-nitrobutane, severally, with benzene as the other component; nitromethane–nitrobenzene; ethyl alcohol and acetone, severally, with water. The last two systems gave pronounced S-shaped isotherms. We have investigated the correctness of representing these apparent isotherms by the assignment of equations of the Freundlich or Langmuir type to each component. In order to provide a more effective test the apparent isotherms were determined at as low concentrations of the preferentially adsorbed component as possible.

A second equation has been found which enables individual adsorptions to be determined as a function of the equilibrium liquid mole-fraction. These so-called individual adsorption isotherms are better considered as mutual displacement curves, since they demonstrate the competition of the two components for the available adsorption space. The shapes of these pairs of curves resemble the Brunauer adsorption types and it is shown on theoretical grounds that only certain of these types can occur together.

The vapour-pressure data for those of the above systems containing nitro-compounds have been determined at 25°. All the systems show positive deviations from Raoult's law, but these may be very marked or slight. The vapour-pressure data enable the adsorption results to be displayed and discussed in two ways. (1) The individual adsorptions or displacements are calculated as functions of the equilibrium *vapour* mole-fraction and thus *true* individual adsorption curves are constructed which are of various types, depending on the chemical character of the adsorbates in relation to the particular adsorbing surface, and reveal correctly the adsorption competition in these systems. (2) A comparison is made on the same diagram of the mole-fraction of the vapour phase that is in equilibrium with the mole-fractions of (*a*) the actual equilibrium liquid solution, (*b*) the ideal equilibrium liquid solution, and (*c*) the equilibrium adsorbed phase. Insight is thus obtained into general considerations bearing on the occurrence of S-shaped apparent adsorption curves. This is seen in the varied systems here investigated to be due to the interplay of the two factors : (1) the extent of the deviations (positive in our systems) from Raoult's law in the equilibrium liquid phase, and (2) the extent of the preferential adsorption of one of the components. Large deviations from Raoult's law produce marked examples of what we have called S-shaped *ab*sorption curves, and S-shaped *ad*sorption curves follow unless the preferential adsorption of one component is sufficiently strong on the surface concerned. The extent to which the adsorption in these saturated mixed vapour systems can be determined as a function of p for each component has been discussed.

WHEN a binary solution is shaken with a solid adsorbent, one of the components may be adsorbed preferentially. If the liquid consists of two completely miscible components, 1 and 2, either (*a*) one component is adsorbed preferentially over the whole range of concentrations, or (*b*) each component is adsorbed preferentially over different parts of the range. The adsorption shown by a system is here measured as $n(x^0 - x_1)/m$ (following Bartell and Sloan [1]), where n is the total number of moles of 1 and 2 present in the system, x^0 is the initial mole-fraction of component 1, x_1 is the mole-fraction of 1 in the bulk liquid after adsorption has occurred, and m is the weight of the adsorbent. This quantity is known as the apparent adsorption of 1, and a plot of it against x_1 is known as the apparent

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

adsorption isotherm of 1. In case (*a*) above, $(x^0 - x_1)$ is always positive, giving the type of isotherm shown in Figs. 1(*A*) to 1(*G*), and in case (*b*), $(x^0 - x)$ is successively positive, zero, and negative (or the reverse), giving the type of isotherm shown in Figs. 1(*H*) to 1(*J*).

The shape of the isotherms of the latter type can only be explained if it is assumed that both components of the binary solution are adsorbed. This idea was first adequately put

FIG. 1. *Apparent adsorption isotherms of:* (*A*) *nitromethane–carbon tetrachloride;* (*B*) *nitromethane–benzene;* (*C*) *nitroethane–benzene;* (*D*) *1-nitropropane–benzene;* (*E*) *2-nitropropane–benzene;* (*F*) *1-nitro-n-butane–benzene;* (*G*) *nitromethane–nitrobenzene;* (*H*) *ethyl alcohol–water;* (*J*) *acetone–water.*
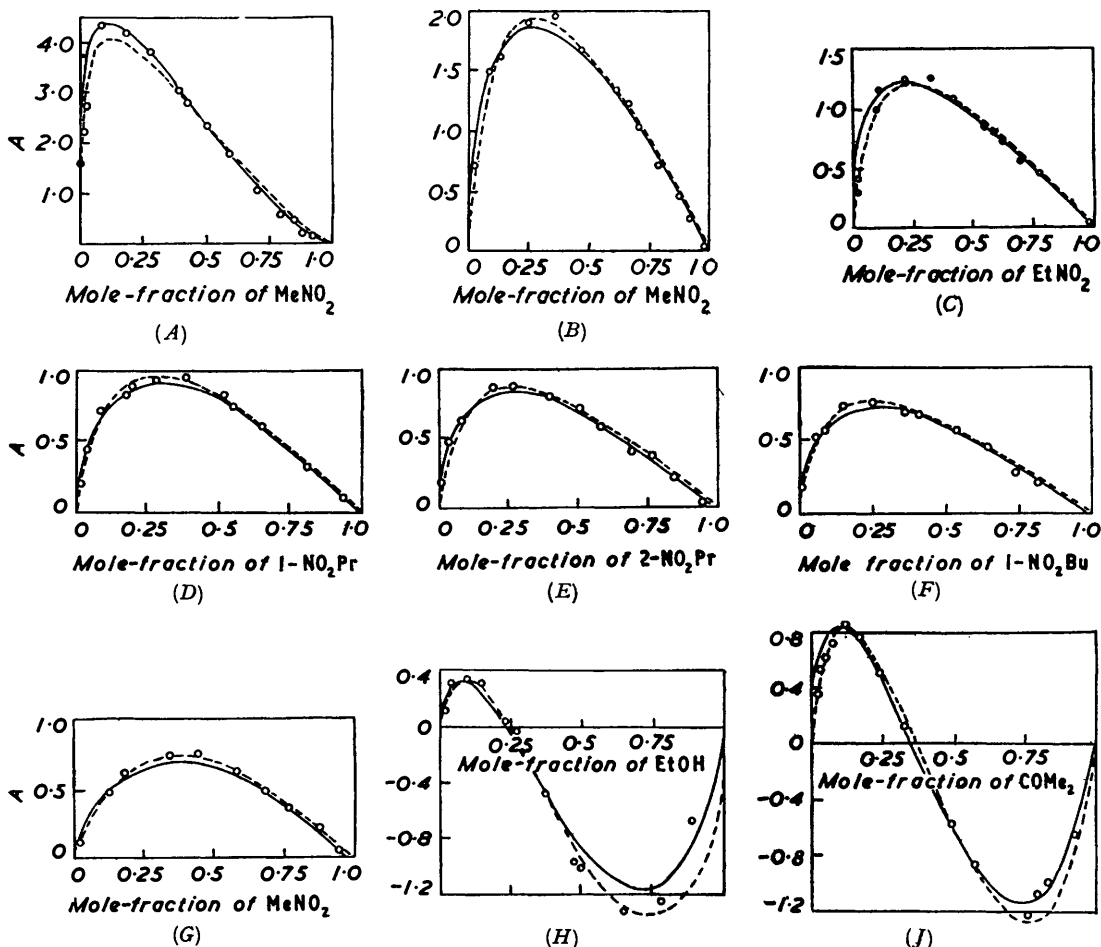
$A = n(x^0 - x)/m$ (10^{-3} mole g.$^{-1}$). —— Eqn. 2. ---- Corresponding Langmuir-type eqn. ○ Exptl. points.

forward by Williams,[2] who deduced the following equation, put in terms of mole-fractions, relating the apparent adsorption to the individual true adsorptions of the two components.

$$n(x^0 - x_1)/m = n_1{}^S(1 - x_1) - n_2{}^S x_1 \qquad . \quad . \quad . \quad . \quad (1)$$

where $n_1{}^S$ and $n_2{}^S$ are the numbers of moles of 1 and 2 adsorbed by 1 g. of adsorbent.

In order to determine the individual adsorptions a second relation between $n_1{}^S$ and $n_2{}^S$ is required.

An indirect method of dealing with this difficulty was first suggested by Ostwald and

² Williams, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, **2**, No. 27.

Izaguirre,[3] who assumed that the adsorption of each component followed a Freundlich equation, and thus obtained the following expression for the apparent adsorption isotherm

$$n(x^0 - x_1)/m = k_1 x_1^{\alpha}(1 - x_1) - k_2(1 - x_1)^{\beta} x_1 \qquad . \quad . \quad (2)$$

where k_1, k_2, α, and β are the usual Freundlich equation constants, whose values were determined, essentially, by neglecting the second Williams correction in the range of adsorption covered by very small mole-fractions of the preferentially adsorbed component. In a number of cases the method was applied with some success.[4] Bartell and Sloan [1] used the same equation but obtained a better fit for the concentration range as a whole by a successive approximation method. The new values thus obtained for the Freundlich constants gave fairly good agreement except in the dilute region.

Kipling and Tester [5] found that their experimental data could be fitted equally well by an equation corresponding to equation (2) in which n_1^S and n_2^S are represented by Langmuir, Case I, expressions. They showed, however, that, although both treatments agreed with each other and with experiment, the individual isotherms given by the two

FIG. 2.

○ *Apparent adsorption (exptl.).*

△ *Apparent adsorption (calc. according to Bartell and Sloan [1]).*

□ *Apparent adsorption (calc. according to Ostwald and Izaguirre [3]).*

● *Apparent adsorption (calc. according to Langmuir's equation).*
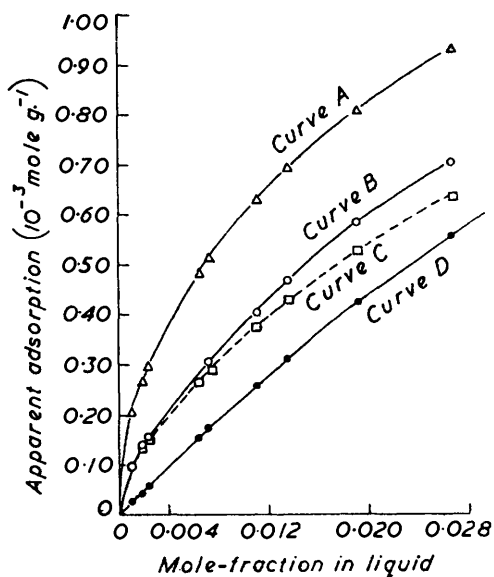
methods revealed a wide discrepancy. They did not investigate the adsorption in the very dilute range where, certainly, the Williams corrections usually become very small, and which is particularly interesting theoretically.

In all our cases these two expressions fitted the experimental results almost equally well over most of the concentration range [see Figs. 1(*A*) to 1(*J*)], but in these Figures one cannot see the very considerable deviations of the results calculated by using these empirical expressions in the region of adsorption up to *ca.* 7% of nitro-compound in the equilibrium solution, and especially in the very dilute region of *ca.* 0·1%, where both of the Williams corrections are very small. More sensitive methods of analysis, even than those used here, are required in these systems in order to test adequately Ostwald and Izaguirre's method. Fig. 2 shows the deviations from the experimental values, obtained by using (i) this method, (ii) Bartell and Sloan's adaptation, and (iii) the Langmuir expression, in the system nitromethane-benzene for concentrations of nitromethane up to *ca.* 3% : these deviations are seen to be very considerable for the last two methods of calculating the adsorption.

[3] Ostwald and Izaguirre, *Kolloid Z.*, 1922, **30**, 279.
[4] See, *e.g.*, Jones and Outridge, *J.*, 1930, 1574.
[5] Kipling and Tester, *J.*, 1952, 4123.

Further, in the cases of the five systems involving a nitroparaffin and benzene, the best fit of the Langmuir expression is obtained when the second term on the right-hand side is zero. If the Langmuir treatment were valid, this would indicate that the adsorption of benzene in these systems is zero at all concentrations, which is highly unlikely. Also, in the very dilute solutions, where the Williams corrections are small, the apparent curve does not conform at all to the Langmuir, Case I, type of equation, but is fairly closely in agreement with a Freundlich type (see Fig. 2, curves B and C).

Undoubtedly, it is much more satisfactory to determine the individual adsorptions by finding a second relation between them, which can then be solved simultaneously with equation (1). In the present work we were able to show, by an extensive series of measurements, that the adsorbent used had a constant volume available for adsorption, independent of the liquid used. A similar constancy had been found by Bachmann [6] and by Jones and Outridge.[4] The equation (3) (where $\bar{v}_1$ and $\bar{v}_2$ are the partial molar volumes of components

$$n_1{}^S \bar{v}_1 + n_2{}^S \bar{v}_2 = V \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

1 and 2 respectively, and V is the volume of the gel available for adsorption) can therefore be used with equation (1) to calculate $n_1{}^S$ and $n_2{}^S$.

If the adsorption were a monolayer, equation (4) (originally used by Adam and Guggenheim [7] as a second possible equation needed for the determination of the individual adsorptions occurring at a binary solution–vapour interface) could be used, as was suggested by Elton [8] and adopted by Kipling and Tester : [5]

$$n_1{}^S A_1 + n_2{}^S A_2 = A \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where A_1 and A_2 are the effective areas occupied per mole of 1 and 2 respectively, and A is the area of the adsorbent. However, it is improbable that adsorption from solution, *i.e.*, from mixed saturated vapour, is always as a monolayer unless the geometry of a porous adsorbent necessitates it. Further, the surface area of an adsorbent obtained, *e.g.*, by the low-temperature nitrogen-adsorption method, may differ greatly from the area involved in liquid adsorption.

It must be remembered that the volume of the gel, V, will contain, as well as material adsorbed by the solid in mono- or multi-layers, that corresponding to so-called capillary adsorption. Work bearing on this point will be published later.

The individual isotherms are shown in Figs. 3(A) to 3(J), and it can be seen that in general they correspond more to the B.E.T. multimolecular isotherm types than to Langmuir (Case I) isotherms. Moreover, since in equation (4) A_1, A_2, and A are constant, not varying with the mole-fraction of the equilibrium solution, it follows that $A_1 \cdot \mathrm{d}n_1{}^S = -A_2 \cdot \mathrm{d}n_2{}^S$ for all x values, and therefore

$$A_1 (\mathrm{d}n_1{}^S/\mathrm{d}x_1) = -A_2 (\mathrm{d}n_2{}^S/\mathrm{d}x_1) \text{ or } A_1 (\mathrm{d}n_1{}^S/\mathrm{d}x_1) = A_2 (\mathrm{d}n_2{}^S/\mathrm{d}x_2) \quad . \quad (5)$$

and further that

$$A_1 (\mathrm{d}^2 n_1{}^S/\mathrm{d}x_1{}^2) = -A_2 (\mathrm{d}^2 n_2{}^S/\mathrm{d}x_1{}^2) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Therefore it is necessary that in the individual isotherms (plots of $n_1{}^S$ against x_1, and $n_2{}^S$ against x_1) the gradients increase or decrease together, but that their signs are opposite, *i.e.*, if one curve is convex the other is concave. If points of inflection occur they must be at the same value of x_1, for in equation (6) when $\mathrm{d}^2 n_1{}^S/\mathrm{d}x_1{}^2 = 0$, $\mathrm{d}^2 n_2{}^S/\mathrm{d}x_1{}^2 = 0$ also. It is clear that, in consequence, certain important limitations are imposed on the shapes of the corresponding pairs of isotherms concerned in systems where one relation between the values of $n_1{}^S$ and $n_2{}^S$ is as in equation (4). The individual isotherms or displacement curves that are found in this work belong to one or other of the five Brunauer types [see

[6] Bachmann, *Z. anorg. Chem.*, 1913, **79**, 202.
[7] Adam and Guggenheim, *Proc. Roy. Soc.*, 1933, **139**, *A*, 218.
[8] Elton, *J.*, 1951, 2958.

FIG. 3. *Individual adsorption isotherms : key letters refer to corresponding letters in Fig. 1 except that* (H) *and* (J) *are interchanged.*
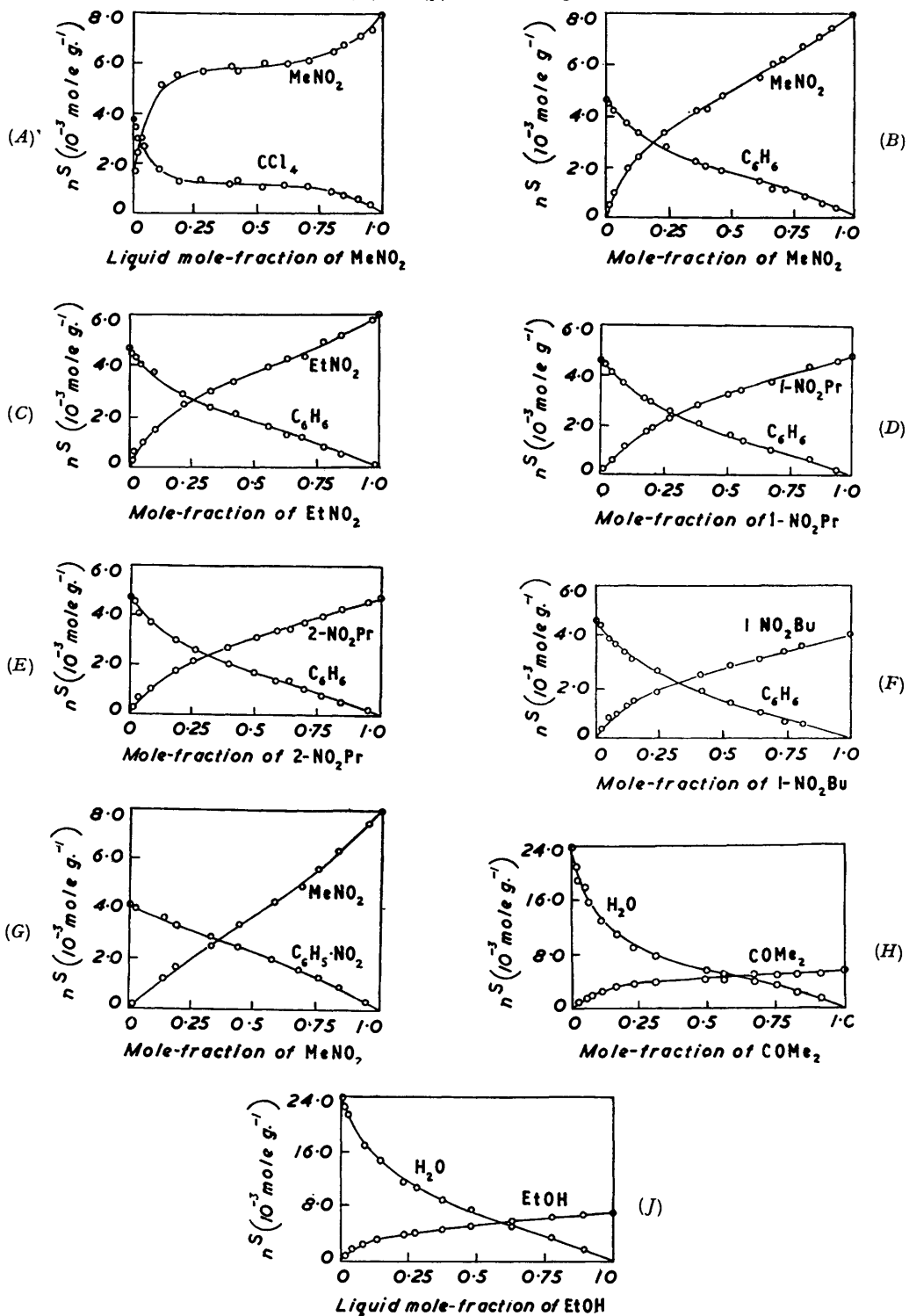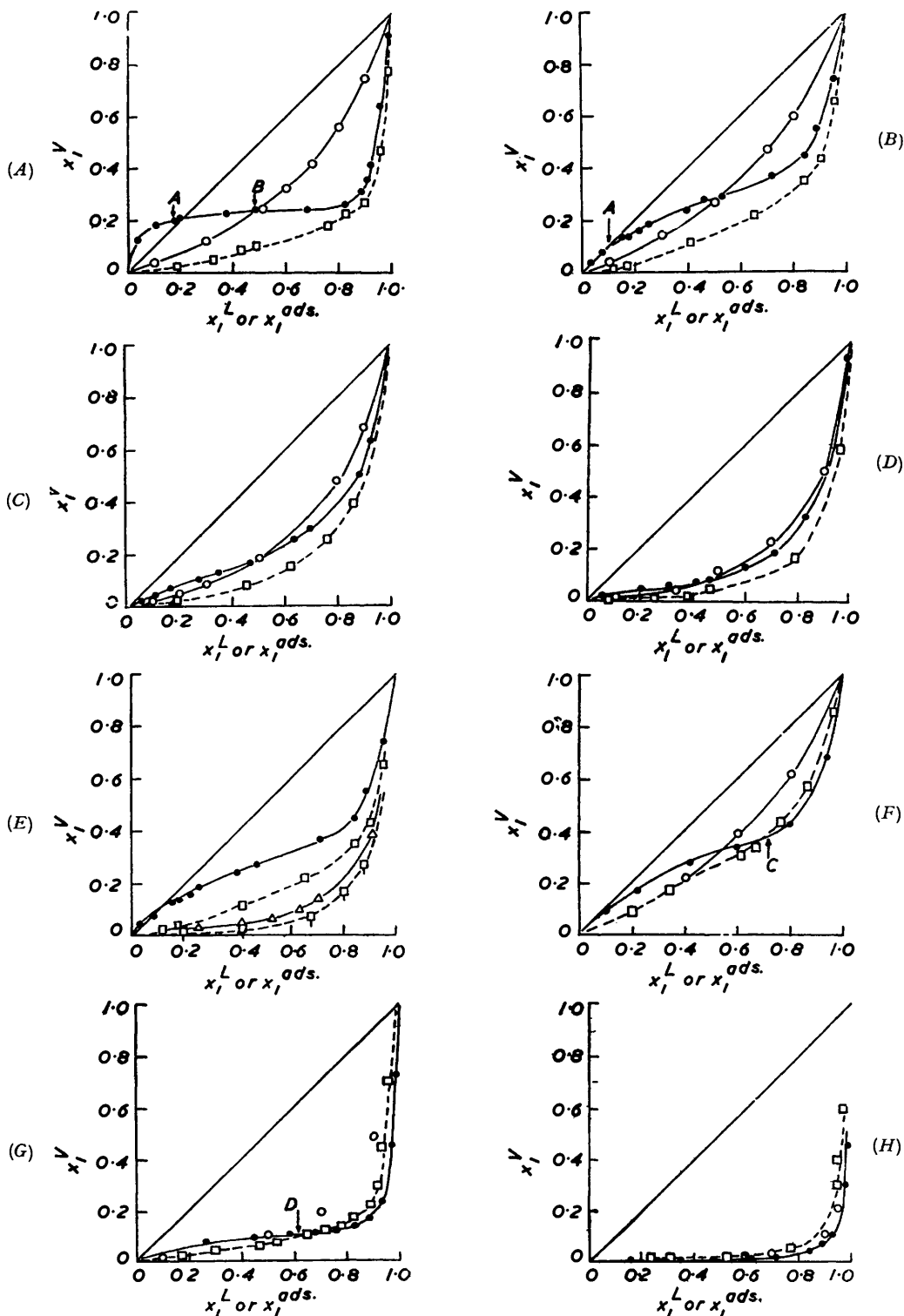
FIG. 4.

● $x_1^V - x_1^L$; ○ $x_1^V - x_1^L$ (*calc. according to Raoult's law*); □ $x_1^V - x_1^{ads}$. (*A*) *Nitromethane–carbon tetra-chloride*; (*B*) *nitromethane–benzene*; (*C*) *nitroethane–benzene*; (*D*) *1-nitropropane–benzene*; (*E*) ● and □ *from* 4 (*B*), △ $x_1^V - x_1^L$ and □ $x_1^V - x_1^{ads}$ *for* 1-nitro-n-butane–benzene; (*F*) *water–ethyl alcohol*; (*G*) *water–acetone*; (*H*) *nitromethane–nitrobenzene*.

Figs. 3(*A*) to 3(*J*)[1] : this is interesting but to be expected, since these types of isotherms represent some of the simplest kinds of curves obtainable when adsorption increases continuously with increase of concentration. It is important to see which of these isotherm types can occur together as pairs if equation (4) holds: (*a*) $n_1{}^S$ can increase linearly while $n_2{}^S$ decreases linearly with x_1; (*b*) isotherms of Type I cannot occur as a *pair*, so that Langmuir (Case I) curves cannot be found for any two components—neither can Freundlich curves, unless the exponent in one of the two Freundlich equations has values between 0 and 1, when the curve is concave to the x_1 axis, and in the other Freundlich equation, the exponent is >1, when the curvature is reversed; (*c*) isotherms of Type III cannot occur as a *pair*; (*d*) a Type I curve and a Type III curve can however form a pair of isotherms; (*e*) when a single point of inflection occurs, as in Type II and Type V isotherms, it can be seen that the corresponding pairs must be of the same Type, *i.e.*, if the $n_1{}^S$–x_1 curve is of Type II or V then the $n_2{}^S$–x_2 curve is also of the Type II or V respectively; (*f*) the remaining Type IV, with its double point of inflection, could not occur with the other component having the same type of isotherm—the isotherm with which it could occur is not listed in this classification and would probably not be found in any actual system.

The possible pairs of isotherms that could occur are thus very limited, and it is interesting to see how far they are exemplified in our experiments. Equation (3), for which we have considerable experimental justification and which is the second relation between $n_1{}^S$ and $n_2{}^S$ that we require and have used in this work, would, of course, lead to the same consequences as outlined above if the partial molar volumes did not vary much with mole-fraction. In many of our systems this variation is quite small and the calculated values of $n_1{}^S$ and $n_2{}^S$ are not very different from those that would be obtained if the molar volume of the pure components had been used. The pairs of isotherms we have found are shown in Figs. 3(*A*)—3(*J*) and this set of diagrams shows the true adsorption or displacement curves for the two components $n_1{}^S$ and $n_2{}^S$ separately plotted against the mole-fraction in the equilibrium liquid phase. Fig. 3(*A*) shows a very clear example of a pair of Type II isotherms, and this occurs also in Figs. 3(*B*), 3(*C*), and 3(*D*), although the inflection in the curves becomes indistinct as the homologous series of nitro-compounds is ascended. In Figs. 3(*E*) to 3(*J*) [excluding 3(*G*)] the two pairs can be considered as examples of Types I and III occurring together. In Fig. 3(*G*) (for nitromethane–nitrobenzene) the pair of isotherms are almost linear. There is no instance, of course [see paragraph (*b*) above], of a " double Langmuir " or a " double Freundlich " type if in the latter *both* exponents are between 0 and 1.

Further insight is given into these phenomena by comparing the mole-fractions of the condensed liquid and of the adsorbed phases, with that of the corresponding vapour phase mole-fraction which represents an almost ideal phase in equilibrium with the other two. In Figs. 4(*A*) to 4(*E*), the vapour mole-fractions, $x_1{}^V$, of the nitro-compounds are plotted as ordinates, and their mole-fractions in the liquid phase, $x_1{}^L$, and in the adsorbed phase, $x_1{}^{ads}$, respectively, as abscissæ. Points on the straight line from the origin to $(1{\cdot}0)(1{\cdot}0)$ indicate when the mole-fractions in the condensed phases are identical with those in the vapour phase in equilibrium. In addition, the curve representing the mole-fractions in the liquid phase if Raoult's law were obeyed, *viz.*, $x_1{}^L$ (calc.), is drawn through the circled points.

Fig. 4(*A*) shows these relationships for the system nitromethane–carbon tetrachloride. At vapour mole-fractions $< ca.$ 0·2, the liquid equilibrium mole-fraction contains carbon tetrachloride in excess of the vapour mole-fraction. The deviations from Raoult's law are so great that at the point *A* the mole-fractions $x_1{}^V$ and $x_1{}^L$ are the same, forming here an azeotropic mixture. At a vapour mole-fraction of $x_1{}^V = ca.$ 0·24 the $x_1{}^L$ curve cuts the Raoult's law curve at *ca.* 0·5 (point *B*); at values of $x_1{}^V < 0\cdot24$, the liquid phase contains carbon tetrachloride in excess of the quantity corresponding to an ideal solution, and at values of $x_1{}^V > 0\cdot24$ it contains nitromethane in excess. The greater concentration of carbon tetrachloride at values of $x_1{}^V < B$ or of nitromethane at values $> B$ in the solution, compared with these values in an ideal solution, is analogous to the type of apparent adsorption curve shown in Fig. 1(*H*) and could be referred to as an S-shaped *absorption* curve. The mole-fractions of the adsorbed phase in equilibrium with its vapour correspond

to a strong preferential adsorption throughout, either from the vapour or from the liquid (ideal or actual). This is particularly noticeable up to $x_1^V = ca.\ 0.24$; e.g., when $x_1^V = 0.1$, $x_1^L = 0.03$, but $x_1^{ads} = 0.5$ (x_1^L calc. being 0.28). It must be remembered that at this temperature this system is close to the condition of separating into two liquid layers, one of which would have a high mole-fraction of nitromethane. The molecular interactions producing these effects in the liquid phase, the most important being the powerful tendency to aggregation of the strongly polar nitromethane, do not seem to be present to any large extent in the adsorbed phase, where the surface may enforce a degree of orientation and disaggregation, although by comparison with other systems, e.g., Fig. 4(C), there seems to be a flattening of the x_1^{ads} curve; the capillary-condensed portions of the adsorbed solution would also tend to bring together the x_1^L and x_1^{ads} curves to an extent depending on the proportions of this type of retained adsorbed solution. At values of $x_1^V > ca.\ 0.24$, the liquid phase now shows strong preferential absorption of the nitromethane, an effect of the positive deviation of this system from Raoult's law, and although the corresponding values of x_1^{ads} are always greater than x_1^L, these two compositions are not greatly disparate in the region of x_1^V from *ca.* 0.3 to 1.0. The preferential adsorption of the nitromethane from the mixed vapour phase is always sufficient to prevent the crossing of the x_1^L and x_1^{ads} curves that produces an S-shaped apparent adsorption curve.

The systems nitromethane, nitroethane, and 1-nitropropane, with benzene as the second component [Figs. 4(B)—4(D)], form an interesting group because they all show a positive deviation from Raoult's law, which, however, diminishes rapidly with increase in the length of the attached hydrocarbon chain. The system nitromethane–benzene still deviates sufficiently to produce a not very clearly indicated azeotropic mixture [point *A*, Fig. 4(B)]. There are the familiar x_1^L departures from Raoult's law, giving at x_1^V values $< ca.\ 0.28$, solutions richer in benzene, and at x_1^V values between *ca.* 0.28 and 1.0 solutions richer in nitromethane, than correspond to an ideal mixture. As before, the adsorbed-phase concentrations do not seem to be affected noticeably by the molecular interactions which produce the x_1^L–x_1^V curve with its marked point of inflection. The x_1^{ads} curve shows the same strong preferential adsorption of the nitromethane through the whole mixed vapour range. It seems that the marked disparity between the x_1^L and x_1^{ads} curves in the lower ranges of x_1^V, as compared with the greater resemblance for the higher ranges, is to be ascribed largely to the positive deviation effects in the liquid phase.

In Figs. 4(C) and 4(D) can be seen : (1) the decreasing positive deviation of the liquid phase from Raoult's law as the homologous nitro-compound series is ascended; (2) the increasing mole-fraction of the nitro-compound in the liquid phase, Raoult's law being assumed, as the series is ascended, and the vapour pressure of the nitro-compound decreases; and (3) the strong preferential adsorption of the nitro-compound from both the vapour and the liquid throughout. Increasing preferential adsorption of the nitro-compound follows its increasing preferential absorption in the homologous series; the positive deviation from Raoult's law in all cases produces S-shaped absorption curves, but no S-shaped adsorption curves occur.

In Fig. 4(E) are shown the x_1^V–x_1^L and the x_1^V–x_1^{ads} curves in the nitromethane–benzene and 1-nitrobutane–benzene systems. For clarity the intermediate systems are omitted. It will be noticed how considerably the values of x_1^{ads} increase at a given value of x_1^V, with the longer-chain nitro-compound, although the *difference* between the corresponding values of x_1^L and x_1^{ads} has considerably decreased.

Figs. 4(F) and 4(G) show the same relationships for the systems ethyl alcohol–water and acetone–water, water being taken as component 1; in both cases there occurs an S-shaped apparent adsorption curve. It is interesting that the ethyl alcohol–water system has x_1^V–x_1^L (calc.) and x_1^V–x_1^L curves very similar to those in the nitromethane–benzene system [Fig. 4(B)]; the positive deviation from Raoult's law is considerable and almost the same in both cases. At x_1^V values $< ca.\ 0.3$, the x_1^L values show considerable excess of ethyl alcohol, while at x_1^V values $> ca.\ 0.3$ there is an excess of water in the equilibrium liquid phase above that calculated for an ideal solution—a strongly S-shaped absorption curve. But in the adsorbed phase, while there is always a preferential adsorption of water as compared with the equilibrium vapour phase, this is not sufficiently

great here [in contrast with the conditions shown in Fig. 4(*B*)] to avoid the cutting of this curve by the $x_1^V - x_1^L$ curve (point *C*). It appears that either a greater preferential adsorption of water on the gel surface, or a smaller positive deviation from Raoult's law in the liquid system, would have produced an apparent adsorption curve *without* a so-called negative branch, or S-shaped curve.

In the acetone–water system [Fig. 4(*G*)] there is much greater disparity in the vapour pressures of the pure components than in the ethyl alcohol–water system, and also considerable positive deviation from Raoult's law, giving, as seen from the graph, an S-shaped absorption curve. Throughout, there is strong preferential adsorption on the gel surface of the water; *e.g.*, when $x_1^V = ca.$ 0·1, $x_1^{ads} = ca.$ 0·6, but, as in the previous case, this preferential adsorption of water is not sufficiently great to prevent the $x_1^V - x_1^L$ and the $x_1^V - x_1^{ads}$ curves from crossing (at the point *D*) and thus producing an S-shaped apparent adsorption curve. Again it appears that either a greater preferential adsorption of water, or a smaller positive deviation from Raoult's law in the liquid, would have meant the absence of a negative branch in the apparent adsorption curve. In comparing this case with 1-nitrobutane–benzene, where there are somewhat similar differences of volatility of the pure components, the absence of the S-shaped apparent adsorption curve in that case would be expected because of the small positive deviation from Raoult's law and the strong preferential adsorption of the nitro-compound from the vapour phase.

In Fig. 4(*H*) are shown these same relationships for the system nitromethane–nitrobenzene, with the less volatile component again labelled 1. Nitrobenzene was chosen instead of, *e.g.*, nitrobutane because much greater analytical accuracy could be obtained with the interferometer, and the apparent adsorption was likely to be small in any case. As is seen, the $x_1^V - x_1^L$ curve is fairly close to what would be expected if Raoult's law held. There is naturally a very heavy concentration of nitrobenzene in the equilibrium liquid phase; *e.g.*, when $x_1^V = 0·1$, $x_1^L = 0·92$, which is not greatly different from x_1^L (calc.), *viz.*, 0·89. The x_1^{ads} curve shows, however, that although the nitrobenzene is always very strongly preferentially adsorbed from the vapour phase, there is at *all* mole-fractions a small preferential adsorption of nitromethane from the liquid phase, and although this preferential adsorption is not marked, the absence of serious deviation from Raoult's law in the liquid phase accounts for the absence here of an S-shaped apparent adsorption curve. The mean life-time of the nitromethane, relatively to that of the nitrobenzene, is slightly greater on the polar surface than in the bulk liquid phase, owing to the larger polar proportion in the nitromethane molecule and its, probably partial, orientation on the surface.

Some general considerations have been put forward above which are frequently decisive in determining whether S-shaped apparent adsorption curves occur or not. Their presence would be expected when strong positive deviation from ideality in the liquid phase occurs in systems where the adsorbing surface is sufficiently similar in its attraction for both components; for instance, on the silicic acid gel surface, the nitromethane–benzene and nitromethane–carbon tetrachloride solutions show such strong deviations as to give azeotropic mixtures and yet do not give S-shaped adsorption curves, the nitro-compound being too strongly preferentially adsorbed; the ethyl alcohol–water system also gives azeotropic mixtures, although it shows much less positive deviation from Raoult's law, and yet S-shaped adsorption curves occur, the surface having rather similar attraction for these two components. On the other hand, in the nitromethane–nitrobenzene system, although the attractions of both components for the surface are similar, an S-shaped adsorption curve does not occur because there is little positive deviation from ideality in the equilibrium liquid phase.

It is now possible to see how the individual adsorptions n_1^S and n_2^S change with the mole-fraction in the equilibrium vapour phase, and this will be shown in some typical systems. These curves should give a truer picture of the adsorption process, since the concentrations are expressed in terms of the ideal vapour-phase mole-fraction. Fig. 5 shows this for nitromethane with carbon tetrachloride and with benzene, and should be compared with Figs. 3(*A*) and 3(*B*). The shapes of the adsorption curves for each component are seen to be greatly altered, the points of inflection in these curves, so very marked in the case of carbon tetrachloride, disappear, and they could be described as

belonging to types I and III of the Brunauer classification, although the early part of the curve is almost linear. Clearly, then, the Type II shapes of the individual adsorption curves, when adsorption is plotted against liquid mole-fraction, are to be ascribed not to surface effects but to the deviation from ideality in the equilibrium liquid solution. The strongly adsorbed nitro-compound has a curve of Type I with a high initial slope, whereas the weakly adsorbed benzene has one of Type III with a low initial slope. It is tempting to consider these disparate initial slopes as corresponding to the large and small values of
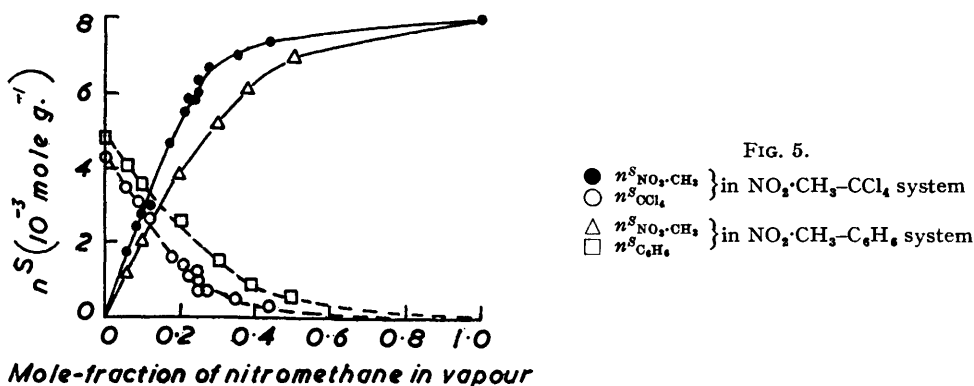
FIG. 5.

● $n^S_{NO_2 \cdot CH_3}$ ⎫ in $NO_2 \cdot CH_3$–CCl_4 system
○ $n^S_{CCl_4}$ ⎭

△ $n^S_{NO_2 \cdot CH_3}$ ⎫ in $NO_2 \cdot CH_3$–C_6H_6 system
□ $n^S_{C_6H_6}$ ⎭

Mole-fraction of nitromethane in vapour

mean life-time on the surface, and this would probably be a correct deduction in this case, but it must be remembered that these curves are really pairs of displacement isotherms and the character of each is affected by that of the other.

In Fig. 6 the 1-nitrobutane–benzene system is shown in this way; the types of individual isotherms are similar to the previous system, but are not different in type from the same systems depicted in Fig. 3(F), where the abscissæ are equilibrium liquid mole-fractions,

FIG. 6.

1-Nitrobutane

Benzene

Mole-fraction of 1-nitrobutane in vapour

FIG. 7.

H_2O

EtOH

Mole-fraction of EtOH in vapour
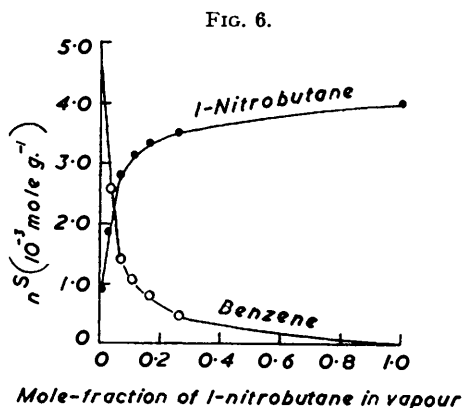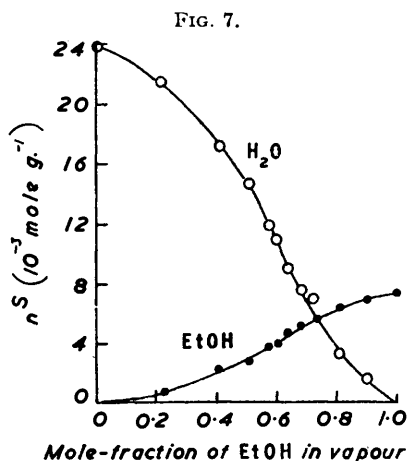
because the deviations from ideality in the solutions are small; however, because of the considerable difference in volatility between the components in this system, the changes in n_1^S and n_2^S with vapour mole-fraction of the nitro-compound are very striking, and these curves give a clear picture of the competition of the two components for the adsorbent surface; e.g., in Fig. 6 the substantial replacement of the benzene on the adsorbent by the nitrobutane is seen to occur at quite small vapour mole-fractions of the latter.

Fig. 7 shows the different effects occurring in the ethyl alcohol–water system. The adsorption curves of *both* components are of Type V; this similarity of type would be expected with components such as these that have similar adsorbabilities on this surface.

The reason for the occurrence here of two Type V curves is, however, not quite clear; it may be that the inflection points and the curvatures at high values of vapour mole-fractions of the alcohol may be caused by the same kind of interactions, in part, perhaps, in the adsorbed phase as occurs in the same circumstances in the equilibrium liquid phase.

These relationships, when the confusion introduced by the deviation from ideality in the liquid phase has been removed by this method of plotting the individual isotherms, enable the competition for the surface and the interactions occurring there, to be seen in much clearer perspective.

Fig. 8 illustrates the relationships between $n_1{}^S$ and p_1 obtained in the nitro-compound series with benzene as component 2. It can be seen that the adsorption at a given p_1 increases as the homologous series is ascended, although the final adsorptions are in the
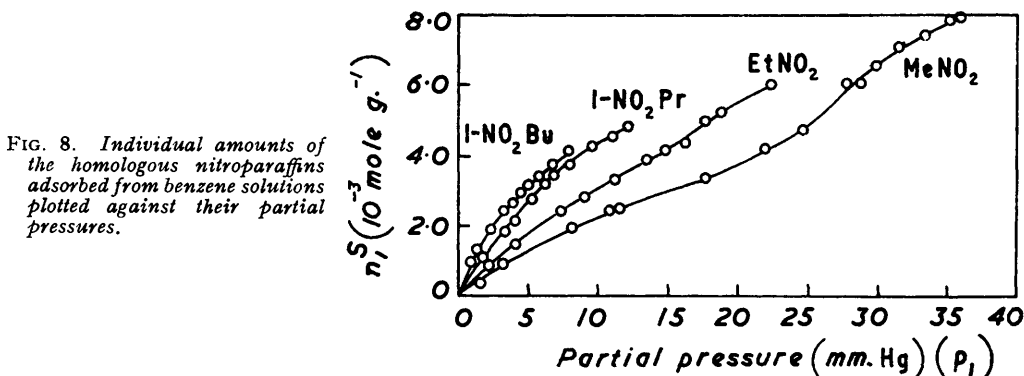
Fig. 8. *Individual amounts of the homologous nitroparaffins adsorbed from benzene solutions plotted against their partial pressures.*
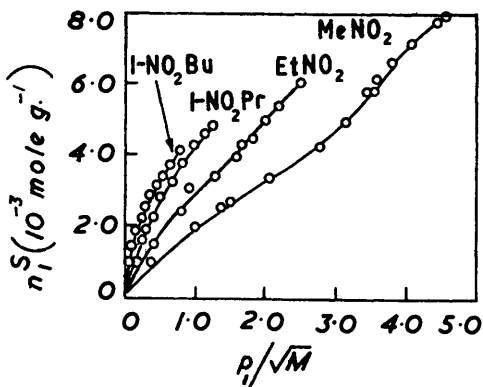
Fig. 9. *Individual amounts of the homologous nitroparaffins adsorbed from benzene solutions plotted against their relative collision numbers.*

reverse order. These results, although not strictly comparable, recall those obtained by Jones and Ottewill[9] in the adsorption of the vapours of the lower members of the homologous series of saturated hydrocarbons on a water surface. These higher final values of $n_1{}^S$ are possible with the lower members of the series because they can reach higher values of partial pressure.

Similar results are seen in Fig. 9, where $n_1{}^S$ is plotted against $p_1/\sqrt{M}$, a quantity proportional to the collision numbers.

This endeavour to elucidate these adsorptions further by observing the changes in the individual adsorptions with either p_1 or p_2, or the corresponding reduced pressures, encounters the difficulty in experiments on adsorption from mixed *saturated* vapours that p_1 and p_2 are not independently variable, and so a comparison for different adsorbates of the individual adsorptions at a certain value of p_1 is complicated by the fact that there is also occurring an adsorption of component 2, at varying values of p_2, even when

⁹ Jones and Ottewill, *J.*, 1955, 4076.

components 2 are the same substance. In general, these relationships cannot be shown correctly on a plane diagram as can those between the individual adsorptions and the mole-fractions. However, at low values of vapour pressure of the nitro-compounds, $n_1{}^S$ can be compared at approximately the same values of p_2, so that this important comparison is possible at these low pressures; *e.g.*, if (see Fig. 8) $p_1 = 1$ mm., the values of p_2 vary from 95 mm. in the nitromethane to 89 mm. in the 1-nitrobutane system. The corresponding values of $n_1{}^S$ range from *ca.* 0·46 to 0·94, whereas $n_2{}^S$ varies only from 4·5 to 3·8. These results show the true qualitative application of Traube's rule to these systems, the apparent adsorptions being, as has been shown, in the reverse order.

EXPERIMENTAL

Materials.—These were carefully purified and some physical properties determined in e: case. M. p.s were observed in a double-jacketed tube, about 5 ml. of liquid being used; densities were measured in a double-bulb pyknometer of 20 ml. capacity; refractive indices were determined by using a Hilger–Chance V-block refractometer, and b. p.s were observed in an apparatus similar to that described by Jones and Betts.[10]

Adsorbent. This was a commercial granular silicic acid gel. Before use it was activated for 3 hr. at 120°. The water content was then 4·66%.

Water. This was distilled twice from a Bousfield type of conductivity still, having a block-tin condenser. It had n_D^{20} 1·3329.

Benzene. B.D.H. extra pure benzene was shaken with sulphuric acid, washed with water, fractionally frozen in the manner described by Rybicka and Wynne-Jones,[11] dried over sodium, and fractionally distilled. It had m. p. 5·5°, b. p. 80·1°/760·5 mm., d_4^{25} 0·8735, n_D^{20} 1·5012.

Carbon tetrachloride. "AnalaR" material was dried (K_2CO_3) and fractionally distilled through a Towers type column. It had m. p. −23·0°, b. p. 76·7°/760·2 mm., d_4^{25} 1·5844, n_D^{20} 1·4603.

Nitrobenzene. "AnalaR" material was fractionally frozen, dried (P_2O_5), and fractionally distilled under reduced pressure through a Towers type column. It had m. p. 5·6°, b. p. 210·2°/758·5 mm., d_4^{25} 1·1985, n_D^{20} 1·5525.

Acetone. This was an "AnalaR" product which had been purified previously, stored over small quantities of phosphoric oxide, frequently renewed, for 12-hr. periods, and distilled between each period. Finally it was fractionally distilled over potassium carbonate. It had b. p. 56·2°/759·8 mm., d_4^{25} 0·7847, n_D^{20} 1·3592.

Ethyl alcohol. Anhydrous material, prepared in the manner described by Lund and Bjerrum,[12] had b. p. 78·2°/759·8 mm., d_4^{25} 0·7851, n_D^{20} 1·3615.

Nitro-compounds. Nitromethane and nitroethane were obtained commercially; 1- and 2-nitropropane were given to us by Dr. N. Levy of Imperial Chemical Industries Limited; 1-nitrobutane was synthesised from the corresponding bromide and silver nitrite. They were dissolved in cold sulphuric acid,[13] separated by slow addition of ice-water, washed with a saturated solution of sodium sulphate, dried ($MgSO_4$), and fractionally distilled. The pure liquids were colourless, neutral to litmus, and had pleasant ethereal odours. Their physical properties are tabulated.

	B. p./mm.	d_4^{25}	n_D^{20}		B. p./mm.	d_4^{25}	n_D^{20}
$MeNO_2$	101·2°/760·0	1·1312	1·3818	Pr^iNO_2	120·5°/761·0	0·9845	1·3941
$EtNO_2$	113·6°/758·5	1·0447	1·3917	Bu^nNO_2 ...	152·0°/760·0	0·9662	1·4107
Pr^nNO_2	131·5°/759·5	0·9960	1·4016				

Procedure.—The liquid mixtures used for the experiments were prepared previously, analysed by means of a Zeiss portable water interferometer, and kept in well-stoppered bottles until required. The manipulation and transference of these liquid mixtures to the adsorbent were carried out in deep desiccators containing phosphoric oxide, and the adsorbent and solution were then shaken mechanically in an air thermostat at 25° for 24 hr., equilibrium then always being established. A sample of each purified liquid was shaken in an adsorption vessel with

[10] Jones and Betts, *J.*, 1928, 1177.
[11] Rybicka and Wynne-Jones, *J.*, 1950, 3671.
[12] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.
[13] See Kornblum *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 307; 1948, **70**, 745.

the adsorbent and in each case it was found that the interferometric reading was unaltered by contact with the gel. In this way it was shown that no impurity, perhaps small in amount, was itself interfering with the main adsorption process.

Detailed accounts of the procedure and difficulties involved in the analysis of non-aqueous solutions with this instrument have been given.[14] These difficulties are not present in the analysis of aqueous solutions. Used properly, it proved very sensitive for the analyses required in this work, *e.g.*, in the nitromethane–benzene system, a change of one scale division on the drum of the instrument corresponded to a mole-fraction change of approximately 10^{-5}. Considerable experience is, however, required in using the instrument accurately. Two additional precautions were found useful. (*a*) The whole instrument was placed in a closely fitting copper cylinder let into the side of a large water-thermostat kept at $20° \pm 0·005°$, for although one of the advantages of an interferometer for analysis lies in the fact that the actual temperature of the bath and cell, as a whole, has little effect on the readings, within certain limits, since both compartments of the cell are at the same temperature, nevertheless the small water-bath provided within the instrument was found to be too small to accomplish this always. The copper cylinder had an extension above the surface of the water in the thermostat with a tightly fitting lid, through which the cells could be reached. (*b*) The cells were sealed after filling—this must be done carefully in a dry atmosphere—by the use of two closely fitting brass plugs which extended down inside the compartments, almost to the top of the cell windows. These plugs were found to prevent absorption of water by the organic liquids, changes of concentration due to unequal evaporation of the components, and also the " creeping " of the liquid out of the cell compartments.

Volume of the gel. Three methods were used in the determination of this quantity.

(*a*) Bachmann's method.[6] The gel was immersed in each liquid at 25° for 1 hr., removed, rapidly dried externally with filter paper, and weighed.

(*b*) The adsorbent was suspended in a gauze basket above the liquid and weighed at intervals until equilibrium was reached.[15]

(*c*) Several points on the vapour isotherm of each liquid, at 25°, in the neighbourhood of the saturation vapour pressure, were determined with a high-vacuum technique, and the isotherm extrapolated to saturation vapour pressure.

In each case the weight of the liquid held by 1 g. of the gel, divided by the normal density of the liquid, gave the gel volume. Each method was used with each liquid, and the mean value obtained was 0·431 c.c. g.$^{-1}$. No individual value differed from this figure by more than 3% ; McKee,[16] using a large range of, mainly, aliphatic hydrocarbons, obtained a value of 0·430 c.c. g.$^{-1}$ for the same adsorbent.

Partial pressure. The partial pressures needed were determined in an apparatus which was a modification of that described by Hovorka and Dreisbach.[17] Details of this work and the results will be described in a later communication.

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[14] Adams, *J. Amer. Chem. Soc.*, 1915, **37**, 1181; Cohen and Bruins, *Z. phys. Chem.*, 1923, **103**, 337.
[15] See Tryhorn and Wyatt, *Trans. Faraday Soc.*, 1925, **21**, 399.
[16] McKee, personal communication.
[17] Hovorka and Dreisbach, *J. Amer. Chem. Soc.*, 1934, **56**, 1664.

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