656. Adsorption from Binary Solutions of Completely Miscible Liquids. Part I. Calculation of Surface Mole-fraction Isotherms.

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It is shown that for adsorption by a solid from a solution of two completely miscible liquids, individual adsorption isotherms for the two components can be calculated from isotherms of apparent adsorption (concentration change), provided that allowance is made for the fact that adsorption of one component must always be accompanied by desorption of the other. The method is applied to Innes and Rowley's data on adsorption from methanol–carbon tetrachloride mixtures by charcoal, giving results in reasonably good agreement with those previously obtained by thermodynamic calculations based on vapour adsorptions.

When a binary solution is shaken with a solid adsorbent, one of the components may be preferentially adsorbed, bringing about a decrease in the mole-fraction of this component in the solution. For a solution comprising two completely miscible liquids, A and B, experiments of this kind can be carried out over the complete mole-fraction range. If component B is preferentially adsorbed, the excess of B present in the surface layer is usually calculated as $-(n_A + n_B)\Delta x_B$ (see, *e.g.*, Bartell and Sloan, *J. Amer. Chem. Soc.*, 1929, **51**, 1643), where n_A, n_B are the total number of moles of A and B, respectively, in the system, and Δx_B is the increase of mole-fraction of B in the solution. When $-(n_A + n_B)\Delta x_B$ is plotted as a function of x_B, isotherms of two types may be obtained, as shown in Figs. 1 and 2. In each case the adsorption is zero at the two extremes of mole-fraction, as is to be expected, but zero adsorption is sometimes also found at an intermediate mole-fraction, where the adsorption changes sign.

In order to interpret isotherms of the two kinds, it has been suggested (see, *e.g.*, Bartell and Sloan, *loc. cit.*; Ostwald and de Izaguirre, *Kolloid-Z.*, 1922, **30**, 279; Kipling, *Quart. Reviews*, 1951, V, 60) that simultaneous adsorption of both components occurs, the adsorption of each component following independently a Freundlich- or Langmuir-type isotherm of the type encountered in gas adsorption. Depending on the relative magnitudes of the adsorption of the two components, the net apparent adsorption of one of them, as measured by the concentration change, could be positive, negative, or zero. By using suitable empirical constants in two simultaneous Freundlich isotherms, experimental curves of both types can be reproduced (Kipling, *loc. cit.*).

Various objections to this method can be made. Adsorption from the liquid phase differs greatly from adsorption from the gas phase in that in the former case the solid is always covered with a layer of molecules of A and B, even in the absence of adsorption. One or more of these layers may be firmly bound to the adsorbent by a molecular force field, giving a surface zone in which the mole-fraction may differ from the bulk mole-fraction. If the zone is of constant thickness, extra molecules of B can be incorporated into it only at the expense of displacing some molecules of A, and the adsorption of A can only be independent of the adsorption of B if the surface zone is of continually varying thickness, which is not generally considered to be the case. In fact most available evidence indicates that such surface zones are of unimolecular thickness, except where the preferentially adsorbed component is of low solubility in the second component (McBain and Swain, *Proc. Roy. Soc.*, 1936, *A*, **154**, 608; Guggenheim and Adam, *ibid.*, 1933, *A*, 139, 218; Hansen, Fu, and Bartell, *J. Physical Chem.*, 1949, **53**, 769; Fu and Bartell, *ibid.*, 1950, **54**, 537). Hence the decrease in mole-fraction of the preferentially adsorbed component is due to two factors: first, the decrease in the number of its molecules present in the bulk solution, and secondly, the increase in the number of molecules of the second component in the bulk solution.

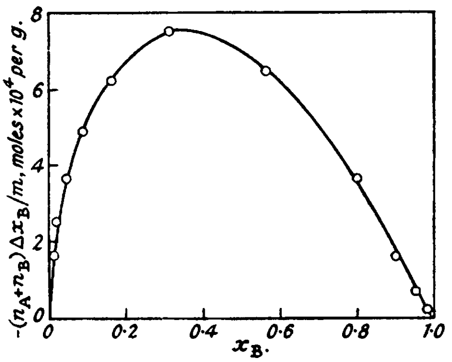


FIG. 1.
Apparent adsorption of benzene (B) *from ethyl carbonate by charcoal* (*Bartell and Sloan*).

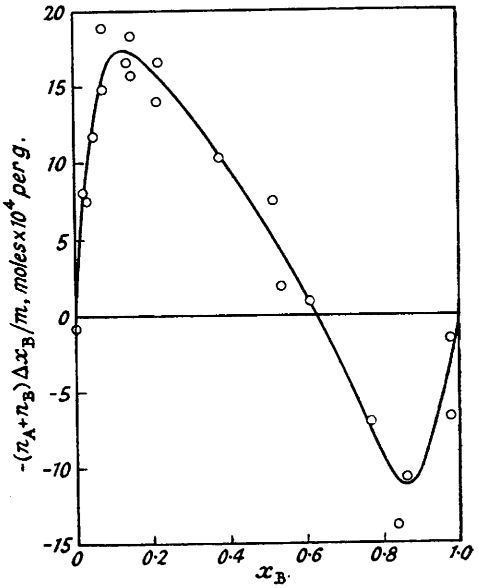


FIG. 2.
Apparent adsorption of carbon tetrachloride (B) *from methanol by charcoal* (*Innes and Rowley*).

In many practical adsorption experiments, the change in concentration produced by the adsorption is of principal importance, but from a theoretical point of view, a knowledge of the actual composition of the adsorbed layer is desirable, in order that the forces producing the adsorption, and the relative attraction of the adsorbent for the two components, can be assessed.

For a unimolecular surface layer, we have

$$n^s_A a_A + n^s_B a_B = A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n^s_A, n^s_B are the number of moles of components A and B respectively in the surface layer, a_A and a_B the corresponding effective areas occupied per mole, and A is the area of adsorbent available. In a solution containing in all n_A moles of A and n_B moles of B, the surface layer would, in the absence of adsorption, contain kn_A and kn_B moles respectively where

$$k(n_A a_A + n_B a_B) = A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In a similar solution where the surface layer contains an excess δ moles of component B, there will be a deficiency $\delta a_B/a_A$ moles of component A in the layer, these having been displaced by the excess of component B. Thus equation (1) becomes

$$(kn_A - \delta a_B/a_A) + (kn_B + \delta) = A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence from an initial mole-fraction

$$x^0_B = n_B/(n_A + n_B) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

an equilibrium mole-fraction x_B in the bulk solution is obtained where

$$x_B = \frac{n_B - n^s_B}{(n_A + n_B) - (n^s_A + n^s_B)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Then, from equations (1) and (5)

$$x_{\mathrm{B}} = \frac{a_{\mathrm{A}}\{n_{\mathrm{B}}(1-k)-\delta\}}{a_{\mathrm{A}}(n_{\mathrm{A}}+n_{\mathrm{B}})(1-k)+\delta(a_{\mathrm{B}}-a_{\mathrm{A}})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If the mole-fraction of the solution is measured before and after adsorption, we obtain

$$\Delta x_{\mathrm{B}} = x_{\mathrm{B}} - x^{0}_{\mathrm{B}} = \frac{-\delta(n_{\mathrm{A}}a_{\mathrm{A}}+n_{\mathrm{B}}a_{\mathrm{B}})}{(n_{\mathrm{A}}+n_{\mathrm{B}})\{a_{\mathrm{A}}(n_{\mathrm{A}}+n_{\mathrm{B}})(1-k)+\delta(a_{\mathrm{B}}-a_{\mathrm{A}})\}} \quad . \quad . \quad . \quad (7)$$

whence

$$\delta = \frac{-a_{\mathrm{A}}(n_{\mathrm{A}}+n_{\mathrm{B}})^2(1-k)\Delta x_{\mathrm{B}}}{n_{\mathrm{A}}a_{\mathrm{A}}+n_{\mathrm{B}}a_{\mathrm{B}}+\Delta x_{\mathrm{B}}(a_{\mathrm{B}}-a_{\mathrm{A}})(n_{\mathrm{A}}+n_{\mathrm{B}})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Therefore

$$\begin{aligned} n^{s}_{\mathrm{B}} &= kn_{\mathrm{B}} + \delta \\ &= \frac{An_{\mathrm{B}}+(n_{\mathrm{A}}+n_{\mathrm{B}})\Delta x_{\mathrm{B}}\{A-a_{\mathrm{A}}(n_{\mathrm{A}}+n_{\mathrm{B}})\}}{n_{\mathrm{A}}a_{\mathrm{A}}+n_{\mathrm{B}}a_{\mathrm{B}}+\Delta x_{\mathrm{B}}(a_{\mathrm{B}}-a_{\mathrm{A}})(n_{\mathrm{A}}+n_{\mathrm{B}})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9) \end{aligned}$$

Hence the mole-fraction of component B in the surface layer is given by

$$\begin{aligned} x^{s}_{\mathrm{B}} &= n^{s}_{\mathrm{B}}/(n^{s}_{\mathrm{A}}+n^{s}_{\mathrm{B}}) \\ &= \frac{Ax_{\mathrm{B}}-a_{\mathrm{A}}(n_{\mathrm{A}}+n_{\mathrm{B}})\Delta x_{\mathrm{B}}}{A+(n_{\mathrm{A}}+n_{\mathrm{B}})(a_{\mathrm{B}}-a_{\mathrm{A}})\Delta x_{\mathrm{B}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10) \end{aligned}$$

The surface mole-fraction of component A may then be obtained from

$$x^{s}_{\mathrm{A}} = 1 - x^{s}_{\mathrm{B}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Equations (10) and (11) render possible the calculation of the individual surface mole-fractions corresponding to any given bulk mole-fractions, provided that the surface area of the adsorbent and the effective areas occupied by the two adsorbed components are known. However, the surface area of the adsorbent has not generally been given in published work on this subject (*e.g.*, Bartell and Sloan, *loc. cit.*), and as is seen from equation (10), the shape of the surface mole-fraction isotherm will depend markedly on the value of A. Urbanic and Damerell (*J. Physical Chem.*, 1941, **45**, 1245) studied adsorption of iodine from carbon tetrachloride on glass spheres of known surface area, but only three points, all in dilute solution, were obtained, not sufficient for the calculation of an isotherm. Further work of this kind, over a larger range of concentration, would be of value, but the difficulty lies in obtaining a sufficiently large surface area of spherical particles to produce measurable concentration changes in concentrated solutions. On the other hand, some adsorbents which are of high surface area, such as silica gel, may produce other complications, due to the occurrence of absorption of one or both of the components into the interior of the adsorbent.

Innes and Rowley (*ibid.*, 1947, **51**, 1172) have evaluated individual surface mole-fraction isotherms for the system methanol (A)–carbon tetrachloride (B)–charcoal by means of a thermodynamic calculation based on measurements of adsorption both from binary solution and from the mixed vapours (*ibid.*, p. 1154). It had previously been shown (*idem*, *ibid.*, 1945, **49**, 411) that the amounts of the two components present in the surface layer were related to the surface pressure, or spreading pressure in the layer, by the approximate expression

$$A\left(\frac{\partial F}{\partial \mu_{\mathrm{B}}}\right)_{T} = -\frac{(n^{s}_{\mathrm{A}}+n^{s}_{\mathrm{B}})(x^{L}_{\mathrm{B}}-x^{s}_{\mathrm{B}})}{x^{L}_{\mathrm{A}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where F is the spreading pressure, μ_{B} the chemical potential of component B in the solution, and x^{L}_{A}, x^{L}_{B} the mole-fractions of components A and B, respectively, in the solution. For any given solution (the partial pressures of the components being p_{A} and p_{B}), the spreading pressure F is given by the equation

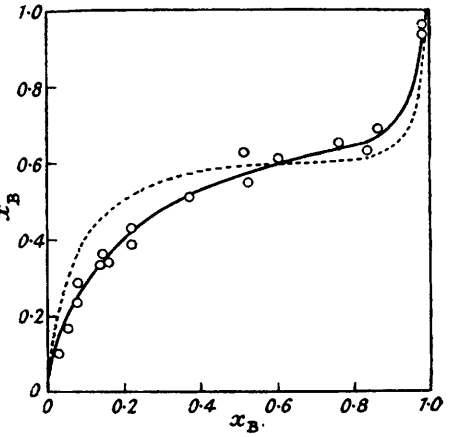
$$FA/RT = \int_0^{p_{\mathrm{A}}} n^{s}_{\mathrm{A}}\mathrm{d}\ln p_{\mathrm{A}} + \int_0^{p_{\mathrm{B}}} n^{s}_{\mathrm{B}}\mathrm{d}\ln p_{\mathrm{B}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The integrals were evaluated from the areas under graphs of n^{s}_{A} against $\ln p_{\mathrm{A}}$ and n^{s}_{B} against $\ln p_{\mathrm{B}}$, such graphs being obtained from the data on the adsorption from the vapours. The chemical potential of B as a function of its mole-fraction in the solution was determined from measurements of its partial vapour pressure in solutions of various mole-fractions. The values of $(\partial F/\partial\mu_{\mathrm{B}})_T$, n^{s}_{A}, and n^{s}_{B} corresponding to a number of values of x^{L}_{B} were then read off from smoothed curves, and used to calculate the corresponding x^{s}_{B} values from equation (12). The isotherm of apparent adsorption from solution is shown in Fig. 2, and the calculated surface mole-fraction isotherm for component B (carbon tetrachloride) as the dotted line in Fig. 3.

On the other hand, when equation (10) is applied to the data shown in Fig. 2, the only other data required apart from the mole-fraction changes produced by adsorption are the effective areas per mole occupied by A and B in the surface layer, taken by Innes and Rowley as $7{\cdot}66 \times 10^8$ cm.^{2}/mole and $17{\cdot}85 \times 10^8$ cm.^{2}/mole, respectively, and the surface area, obtained from the limiting vapour adsorption as $8{\cdot}3 \times 10^6$ cm.^{2}/g. These values being used, the isotherm of surface mole-fraction of B indicated by the points and the full line in Fig. 3 is obtained directly. The higher degree of scatter shown in the original experimental results (Fig. 2) is due to the fact that the ratio $(n_A + n_B)/m$ was allowed to vary in a random manner, a fact which is allowed for in equation (10), but not in calculating the adsorption as $-(n_A + n_B)\Delta x_B/m$. The isotherm of surface mole-fraction so obtained is seen to be in reasonable agreement with that of Innes and Rowley, the large and varied number of data used in the latters' calculations being borne in mind. Innes and Rowley stated that their results could only be considered as semiquantitative, but it is seen from Fig. 3 that the shapes of the isotherms calculated by the two different methods are very similar. The use of equation (10) in calculating surface mole-fraction isotherms seems much to be preferred in view of the smaller amount of labour involved, and the greater probable accuracy. It is of limited application at present, since, as previously mentioned, sufficient data are rarely available.

FIG. 3.

Surface mole-fraction of carbon tetrachloride (B) *in experiments of Innes and Rowley.*



O——O *Calculated for each point from equation* (10).

------ *Smoothed curve obtained by Innes and Rowley using vapour adsorption data.*

It may be stated that, in general, isotherms of apparent adsorption of the type shown in Fig. 2, will correspond to surface-mole-fraction isotherms which, as shown in Fig. 3, cut the line $x_B^s = x_B$ at the mole-fraction corresponding to zero adsorption. The type shown in Fig. 1, will lead to a surface mole fraction isotherm which does not cut the line $x_B^s = x_B$, since $x_B^{s\prime} > x_B$ at all mole-fractions other than zero and unity. Adsorption of this kind is obtained when the adsorbent has a marked " preference " for one of the components of the solution (see, *e.g.* Kipling, *loc. cit.*).

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