Adsorption from Binary Solutions of Completely Miscible Liquids. Part III. Surface Activity Coefficients of Components Adsorbed from Perfect Solutions.*

By G. A. H. ELTON.

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On the basis of the present theory of the surface tensions of binary perfect solutions, it is shown that the surface activity coefficients of the components adsorbed at the liquid–air interface should vary linearly with bulk mole-fraction. Existing experimental data are shown to confirm this view. The theory is extended to include adsorption at the liquid–solid interface with similar theoretical results, which await experimental investigation.

THE main experimental method for the study of adsorption at liquid–solid interfaces in binary solutions depends on the determination of the change in concentration which occurs when a known amount of a solution is equilibrated with a known area of adsorbent. It is then possible, subject to certain assumptions, to calculate surface mole-fraction isotherms from isotherms of concentration change (Part I *; Kipling and Tester, *J.*, 1952, 4123). Two main types of surface mole-fraction isotherm are obtained: (*a*) the surface mole-fraction of one component may always be greater than or equal to its bulk mole fraction, *i.e.*, complete preferential adsorption of this component may occur (Part II *); or (*b*) the surface mole-fraction of each component is greater than its bulk mole-fraction at low mole-fractions, and less than its bulk mole fraction at high mole-fractions, the net adsorption being zero at some intermediate mole fraction. The type of surface mole-fraction isotherm obtained in any given case depends on the energies of interaction of the adsorbed molecules with the surface of the adsorbent, and how these energies change with mole fraction. It is desirable that it should be possible ultimately to give a theoretical account of the observed surface mole-fraction isotherms, and to predict the forms of the isotherms in terms of other properties of adsorbates and adsorbent.

Adsorption at liquid–air interfaces is easier to study, as the extent of adsorption may be calculated from surface-tension data by using Gibbs's adsorption equation. Also, theories of the structure of the surface zones at liquid–air interfaces have been developed (see, *e.g.*, Guggenheim, "Mixtures," Oxford Univ. Press, 1952, pp. 166—182), based on various simplified models. We will consider first the simple theory of adsorption at a liquid–air interface, based on the quasi-crystalline model of the structure of the bulk solution and the surface zone, and then show how the theory can be modified to apply to adsorption at liquid–solid interfaces.

Adsorption at a Liquid–Air Interface: Quasi-crystalline Model of a Perfect Solution.—Gibbs's adsorption equation leads, for an ideal binary liquid mixture at temperature *T*, to the expression (Guggenheim and Adam, *Proc. Roy. Soc.*, 1933, *A*, **139**, 218)

$$n_B{}^s - \frac{x_B}{x_A} \cdot n_A{}^s = -\frac{1}{kT} \cdot \frac{d\gamma}{d \ln \phi_B} = -\frac{1}{kT} \cdot \frac{d\gamma}{d \ln x_B} \quad . \quad . \quad . \quad . \quad (1)$$

where $n_A{}^s$, $n_B{}^s$ are the number of molecules of the components A and B respectively per cm.^{2} in the surface zone; x_A, x_B are the bulk mole fractions; γ is the surface tension; k is the Boltzmann constant; and ϕ_B is the fugacity of B. Hence values of $n_B{}^s - (x_B/x_A)n_A{}^s$ are obtainable directly from values of γ and x_B, and may be used as a convenient measure of the relative adsorption of B. (In order to obtain individual values of $n_A{}^s$, $n_B{}^s$, it is necessary to make some assumption concerning the total number of molecules in the surface zone: see p. 3814.)

For the purpose of this analysis we will adopt the quasi-crystalline model of the liquid state (see, *e.g.*, Guggenheim, *op. cit.*, p. 16), and for simplicity, confine our attention to perfect solutions, which possess the same properties as ideal solutions (Fowler and

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* Part I, *J.*, 1951, 2958; Part II, *J.*, 1952, 1955.

Guggenheim, " Statistical Thermodynamics," Cambridge Univ. Press, 1939, p. 353), with the further limitation that the two species have the same molecular dimensions. We assume that the molecules in the surface zone pack in the same way as in the bulk liquid, the only difference being in composition. Finally, we assume that the difference in composition from that of the bulk liquid is confined to a single layer of molecules, an assumption which is thermodynamically consistent with equation (1) (Defay and Prigogine, *Trans. Faraday Soc.*, 1950, **46**, 199).

Using the model defined in this way, we can relate the surface tension of such a solution to the surface tension of the pure components thus (Schuchowitzky, *Acta Physicochem. U.R.S.S.*, 1944, **19**, 176; Belton and Evans, *Trans. Faraday Soc.*, 1945, **41**, 1; Guggenheim, *ibid.*, p. 150):

$$\exp(-\gamma/N^s\mathbf{k}T) = x_A \exp(-\gamma_A{}^\circ/N^s\mathbf{k}T) + x_B \exp(-\gamma_B{}^\circ/N^s\mathbf{k}T) \quad . \quad . \quad (2)$$

where $N^s = n_A{}^s + n_B{}^s$, and $\gamma_A{}^\circ$, $\gamma_B{}^\circ$ are the surface tensions of the two pure components. Hence

$$\gamma = -N^s\mathbf{k}T \ln (x_A\psi_A + x_B\psi_B) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$\psi_A = \exp(-\gamma_A{}^\circ/N^s\mathbf{k}T) \text{ and } \psi_B = \exp(-\gamma_B{}^\circ/N^s\mathbf{k}T)$$

Differentiating (3) with respect to x_B, we obtain, for constant temperature

$$\mathrm{d}\gamma/\mathrm{d} \ln x_B = -N^s\mathbf{k}Tx_B/(c + x_B) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where

$$c = \psi_A/(\psi_B - \psi_A) = \tfrac{1}{2}\{\coth [(\gamma_A{}^\circ - \gamma_B{}^\circ)/2N^s\mathbf{k}T] - 1\} \quad . \quad . \quad . \quad (5)$$

Equations (1) and (4) then give:

$$n_B{}^s = N^s x_B(c + 1)/(c + x_B)\,;\ n_A{}^s = N^s x_A c/(c + x_B) \quad . \quad . \quad . \quad . \quad (6)$$

$$x_B{}^s = x_B(c + 1)/(c + x_B)\,;\ x_A{}^s = x_A c/(c + x_B) \quad . \quad . \quad . \quad . \quad (7)$$

Hence, if $f_A{}^s$, $f_B{}^s$ are the activity coefficients of A and B, respectively, in the surface layer, defined on the basis of standard states as follows:

$f_B = 1$ when $x_B = 1$; $f_B{}^s = 1$ when $x_B{}^s = 1$: $f_A = 1$ when $x_A = 1$; $f_A{}^s = 1$ when $x_A{}^s = 1$;

then we obtain

$$f_B{}^s = x_B/x_B{}^s = (c + x_B)/(c + 1)\,;\ f_A{}^s = x_A/x_A{}^s = (c + x_B)/c \quad . \quad . \quad (8)$$

Hence, the surface activity coefficients will vary linearly with bulk mole fraction, and

$$\mathrm{d}f_B{}^s/\mathrm{d}x_B = 1/(c + 1)\,;\ df_A{}^s/\mathrm{d}x_A = -1/c \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Some surface-tension data are available for binary liquid mixtures which obey Raoult's law, show little or no change in heat content or volume on mixing, and have molecules of approximately equal size. We may test the theory given above by using equations (8) and (9) to calculate the theoretical variation of $x_A{}^s$, $x_B{}^s$, $f_A{}^s$, $f_B{}^s$ with bulk mole fraction, and by comparing it with the "experimental" variation of these quantities, obtained from the observed surface tensions at different bulk mole fractions, using equation (1) together with the equation:

$$n_A{}^s + n_B{}^s = N^s = 1/A_A = 1/A_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where A_A, A_B are the areas occupied by single molecules of A and B in the surface. These values are calculated from the densities of the liquids, Emmett and Brunauer's equation (*J. Amer. Chem. Soc.*, 1937, **59**, 1533) being used. Comparison of values of $f_A{}^s$, $f_B{}^s$ obtained in the two ways is the more sensitive test of agreement (see below).

Fig. 1 shows graphs of $f_A{}^s$, $f_B{}^s$ for the system chlorobenzene (A)–bromobenzene (B) at 20°, the points being calculated from smoothed surface-tension data (Kremann and

Meingast, *Sitzungsber. K. Akad. Wiss. Wien,* 1914, **123**, 821), by use of $A_A = A_B = 33{\cdot}7 \times 10^{-16}$ cm.^{2}, while the broken lines are obtained from equation (8). Fig. 2 shows similar graphs for the system H_2O(A)–D_2O(B) at 25° (Jones and Ray, *J. Chem. Physics,* 1937, **5**, 505), $A_A = A_B = 10{\cdot}5 \times 10^{-16}$ cm.^{2} being used. It is seen that in each case the points follow the calculated line quite closely.

The system benzene (A)–ethylene dichloride (B) at 14° (Whatmough, *Z. physikal. Chem.,* 1902, **39**, 129) obeys Raoult's law, but the areas of the molecules, calculated as described above, differ appreciably ($A_A = 30{\cdot}3 \times 10^{-16}$ cm.^{2}; $A_B = 28{\cdot}0 \times 10^{-16}$ cm.^{2}). Kipling and Tester's results (*loc. cit.*) lead to the values $A_A = 27{\cdot}8 \times 10^{-16}$ cm.^{2}, $A_B = 24{\cdot}4 \times 10^{-16}$ cm.^{2}. Each of these pairs of areas was used separately to calculate $f_A{}^s$, $f_B{}^s$ from the smoothed surface-tension data by using the equation

$$n_A{}^sA_A + n_B{}^sA_B = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

to obtain individual values of $n_A{}^s$ and $n_B{}^s$ from equation (1). Fig. 3 shows the two sets of values for $f_A{}^s$, $f_B{}^s$ obtained in this way, together with those obtained by using $A_A = A_B = 26{\cdot}1 \times 10^{-16}$ cm.^{2} (the mean of the latter pair of areas). There is little difference between the results obtained by use of the various assumed areas, but considerable deviations from the theoretical lines occur, the discrepancy for each component being greatest at small mole fractions. Although the system obeys Raoult's law, there is a heat of mixing $\Delta H_m = -10$ cal./mole, and also a volume change on mixing $\Delta V_m = +0{\cdot}34\%$ (Belton and Evans, *loc. cit.*), so we may conclude that an energy of interaction between the molecules exists, and the system is not strictly ideal. Deviations from the theoeretical lines are, of course, more obvious on graphs of $f_A{}^s, f_B{}^s$ against x_B (as given in Fig. 3) than on graphs of $x_A{}^s$, $x_B{}^s$ against x_B (see Fig. 4, which gives surface mole-fraction isotherms for this system).

FIG. 1.

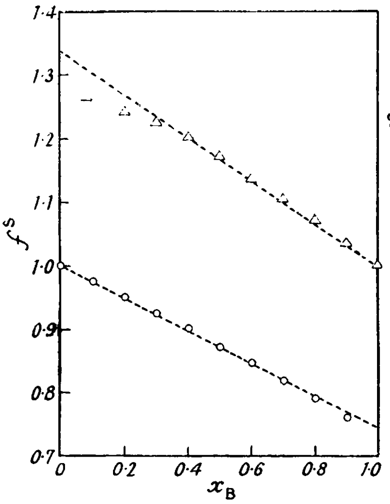
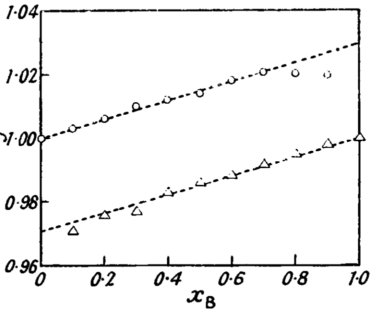


FIG. 2.



O, *A*; △, *B*.

Deviations from the theoretical values of $f_A{}^s$, $f_B{}^s$ are also found (see Fig. 5) for the system benzene (A)–chloroform (B) at 18·2° (Whatmough, *loc. cit.*). The molecular areas used in this calculation are (i) $A_A = 30{\cdot}4 \times 10^{-16}$ cm.^{2}; $A_B = 24{\cdot}1 \times 10^{-16}$ cm.^{2}, and (ii) $A_A = A_B = 27{\cdot}3 \times 10^{-16}$ cm.^{2} (the mean of the two areas). It is again seen that the surface activity coefficients obtained by using the different pairs of molecular areas agree fairly closely. Deviations from the theoretical lines again occur, and are again largest for each component at high mole fractions. Although the system follows Raoult's law closely, the heat of mixing is not zero and some association occurs (Barker and Smith, *J. Chem. Physics,* 1954, **22**, 375), so the system is not strictly ideal.

We may conclude from the study of these four systems that for binary liquid mixtures which fulfil the requirements of a perfect solution the surface activity coefficients at liquid–air interfaces agree well with those predicted by equation (8). Surface activity coefficients for systems which obey Raoult's law owing to a cancelling of two or more "non-ideal" factors may deviate considerably from those calculated from equation (8). In each of the two systems of this type considered here, the deviations occur in such a way that the surface activity coefficient for the component which is negatively adsorbed tends towards unity at low mole-fractions, instead of towards the higher value predicted for perfect solutions. Also the surface activity coefficient of the positively adsorbed component is lower at low mole-fractions than predicted. That is, near each extreme of composition a greater degree of mixing occurs in the surface layer than that given by equation (7).

Adsorption at a Liquid–Solid Interface.—The theory of adsorption at a liquid–solid interface is more complicated than for a liquid–air interface since, for a full treatment, specific properties of the solid (*e.g.*, magnitude of lattice parameters, electronic nature of adsorption sites, etc.) must be considered. For a preliminary treatment, however, various assumptions will be made, which enable a fairly simple equation to be derived.

FIG. 3.

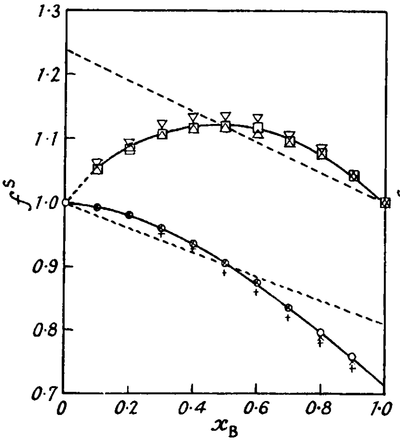
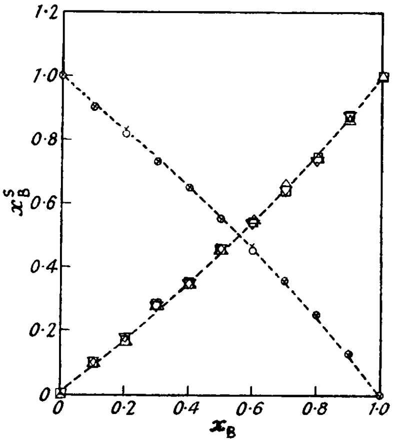


FIG. 4.



○, *A*; △, *B*, for $A_A = 27{\cdot}8$, $A_B = 24{\cdot}4$: ×, *A*; □, *B*, for $A_A = A_B = 26{\cdot}1$: +, *A*; ▽, *B*, for $A_A = 30{\cdot}3$, $A_B = 28{\cdot}0$.

We adopt the quasi-crystalline model of a perfect solution, and again assume that the molecules in the surface zone (confined to a single layer of molecules) pack in the same way as in the bulk liquid. These assumptions were made in the treatment of the liquid–air interface; the additional assumption for the liquid–solid interface is that when the surface layer contains n_A^s and n_B^s molecules of A and B respectively per cm.^{2}, each molecule possesses an excess of energy w_A^s or w_B^s by virtue of its interaction with the solid surface. We may then formulate the grand partition function for 1 cm.^{2} of the surface layer (Ξ^s) thus:

$$\Xi^s = \sum_{x_B^s} \frac{N^s!}{n_A^s!\,n_B^s!} (\lambda_A q_A^s)^{n_A^s} (\lambda_B q_B^s)^{n_B^s} \exp(-W^s/kT) \quad . \quad . \quad . \quad (12)$$

where the summation is for all values of x_B^s; λ_A and λ_B are the absolute activities of A and B; q_A^s and q_B^s are the molecular partition functions per cm.^{2} of the surface layer, and

$$W^s = n_A^s w_A^s + n_B^s w_B^s = N^s[x_B^s(w_B^s - w_A^s) + w_A^s] \quad . \quad . \quad . \quad (13)$$

Using Stirling's approximation for factorials, we obtain from equation (12):

$$\Xi^s = \sum_{x_B^s} \left(\frac{\lambda_A q_A^s}{x_A^s}\right)^{n_A^s} \left(\frac{\lambda_B q_B^s}{x_B^s}\right)^{n_B^s} \exp(-W^s/kT) \quad . \quad . \quad . \quad . \quad (14)$$

In order to evaluate Ξ^s we replace the summation in equation (14) by its maximum term, and to determine the value of this it is necessary to make some assumption concerning the variation of $w_A{}^s$ and $w_B{}^s$ with $x_B{}^s$. The simplest possible assumption is that $w_A{}^s$ and $w_B{}^s$ are independent of the composition of the surface layer. Differentiating the summation term, and using this assumption, we find that its maximum value occurs when

$$\frac{\lambda_A q_A{}^s}{x_A{}^s}\exp(-w_A{}^s/\boldsymbol{k}T) = \frac{\lambda_B q_B{}^s}{x_A{}^s}\exp(-w_B{}^s/\boldsymbol{k}T) = \lambda_A q_A{}^s \exp(-w_A{}^s/\boldsymbol{k}T) + \lambda_B q_B{}^s \exp(-w_B{}^s/\boldsymbol{k}T) \quad . \quad (15)$$

Hence

$$\Xi^s = \left[\frac{\lambda_A q_A{}^s}{x_A{}^s}\exp(-w_A{}^s/\boldsymbol{k}T)\right]^{n_A{}^s}\left[\frac{\lambda_B q_B{}^s}{x_B{}^s}\exp(-w_B{}^s/kT)\right]^{n_B{}^s} = [\lambda_A q_A{}^s \exp(-w_A{}^s/\boldsymbol{k}T) + \lambda_B q_B{}^s \exp(-w_B{}^s/\boldsymbol{k}T)]^{N^s} \quad . \quad (16)$$

Now

$$\Xi^s = \exp(-\gamma^x/\boldsymbol{k}T);\ \lambda_A q_A{}^s = x_A \exp(-\gamma_A{}^x/N^s\boldsymbol{k}T);\ \text{and}\ \lambda_B q_B{}^s = x_B \exp(-\gamma_B{}^x/N^s\boldsymbol{k}T) \quad . \quad . \quad (17)$$

where γ^x, $\gamma_A{}^x$, $\gamma_B{}^x$ are the excess free energies per cm.^{2} of the surface layer, for the solution, pure A, and pure B, respectively (for analogous relations for a liquid–air interface, see, *e.g.*, Guggenheim, *op. cit.*, pp. 173—175). Hence from equations (16) and (17) we obtain

$$\exp(-\gamma^x/N^s\boldsymbol{k}T) = x_A \exp[-(\gamma_A{}^x + N^s w_A{}^s)/N^s\boldsymbol{k}T] + x_B \exp[-(\gamma_B{}^x + N^s w_B{}^s)/N^s\boldsymbol{k}T] \quad . \quad . \quad (18)$$

$$\therefore \quad \gamma^x = -N^s\boldsymbol{k}T \ln (x_A\sigma_A + x_B\sigma_B) \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where

$$\sigma_A = \exp[-(\gamma_A{}^x + N^s w_A{}^s)/N^s\boldsymbol{k}T];\ \sigma_B = \exp[-(\gamma_B{}^x + N^s w_B{}^s)/N^s\boldsymbol{k}T] \quad . \quad (20)$$

Differentiating equation (19) with respect to x_B (at constant T), and combining the result with equation (1), as for the liquid–air interface, we obtain

$$n_B{}^s = N^s x_B(K + 1)/(K + x_B);\ n_A{}^s = N^s x_A K/(K + x_B) \quad . \quad . \quad . \quad (21)$$

where $K = \sigma_A/(\sigma_B - \sigma_A)$. At present, K must be regarded as an empirical constant for a given solution and adsorbant. Also

$$x_B{}^s = x_B(K + 1)/(K + x_B);\ x_A{}^s = x_A K/(K + x_B) \quad . \quad . \quad . \quad (22)$$

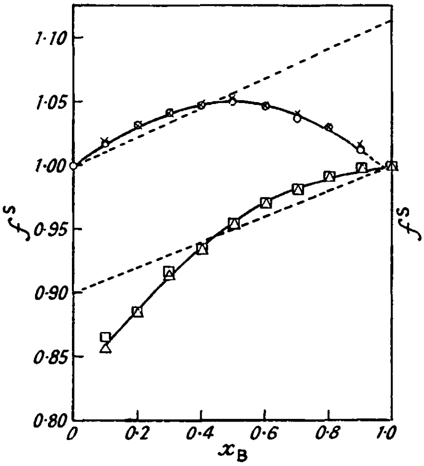
and

$$f_B{}^s = (K + x_B)/(K + 1);\ f_A{}^s = (K + x_B)/K \quad . \quad . \quad . \quad . \quad (23)$$

Hence this simplified theory leads to the conclusion that for systems of the type considered the surface activity coefficients at the liquid–solid interface should vary linearly with bulk mole-fraction, and that complete preferential adsorption of A should occur if K is positive, and complete preferential adsorption of B if K is negative, with no adsorption if K is zero.

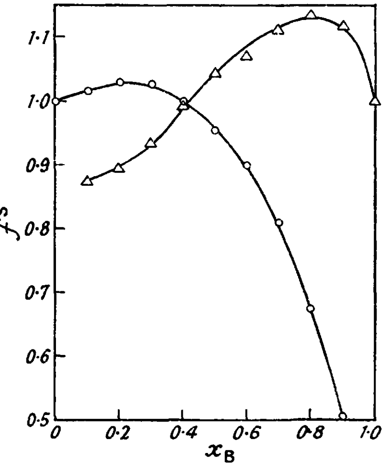
Few experimental measurements which can be used to calculate surface mole-fraction isotherms at liquid–solid interfaces are reported in the literature. Although many workers (for summary, see Kipling, *Quart. Reviews*, 1951, **5**, 60) give isotherms of concentration change for binary liquid mixtures on equilibration with various solids, the surface areas of the latter are rarely given. Innes and Rowley (*J. Phys. Chem.*, 1947, **51**, 1172) give the necessary data for adsorption by charcoal from methanol–carbon tetrachloride mixtures at 25°, but the simple theory given above is not applicable to this system, as Raoult's law is not obeyed, and the molecules are of widely different size. Kipling and Tester (*loc. cit.*) studied adsorption by charcoal from benzene (A)–ethylene dichloride (B) mixtures at 20°. This system followed Raoult's law closely, and on the basis of a simple kinetic calculation Kipling and Tester deduced that complete preferential adsorption of benzene should be observed. This was not found to be the case, each component being preferentially adsorbed from solutions in which its mole-fraction was low. The considerations given above indicate why the deviation from Kipling and Tester's prediction should occur. Although the system obeys Raoult's law, it is not strictly an ideal solution (see p. 3815), and we have already noted that it does not obey the " perfect " equations for adsorption at the liquid–air interface. Fig. 6 shows the calculated values of the surface activity coefficients in this system at the liquid–solid interface, Kipling and Tester's experimental results being used, with $A_A = A_B = 26{\cdot}1 \times 10^{-16}$ cm.^{2}. It is seen by comparison of Figs. 3 and 6 that replacement of the air phase by charcoal modifies the surface activity coefficients considerably. Each component when present at low mole-fractions has a higher surface activity coefficient at the liquid–solid than at the liquid–air interface. As the mole-fraction of either component is raised to high values, a decrease in the surface activity coefficient occurs, lower values being reached at the liquid–solid interface than at the liquid–air interface. At a bulk mole-fraction $x_B = 0{\cdot}41$, both surface activity coefficients are unity, and zero net adsorption occurs.

Fig. 5.



×, *A*; □, *B*, for $A_A = 30{\cdot}4$, $A_B = 24{\cdot}1$.
○, *A*; △, *B*, for $A_A = A_B = 27{\cdot}3$.

Fig. 6.



○, *A*; △, *B*.

In order that the theory of adsorption from solution by solids can be developed, it is desirable that adsorption from perfect solutions should be studied experimentally, and surface activity coefficients obtained for comparison with equation (23). It is possible that equation (23) may not correctly represent the surface activity coefficients for adsorption by a given solid, even for liquid mixtures which may be considered perfect, owing to the fact that the assumption that $w_A{}^s$, $w_B{}^s$ are constants may not be valid for the system considered. For example, although there may be no net energy of interaction between the molecules of the two components in the bulk solution, their properties may be modified in the surface layer so that an energy of interaction depending on $x_B{}^s$ might occur. Also, the energy of adsorption of a species may vary with $x_B{}^s$ owing to the presence of adsorption sites of different energies. When experimental data are available, it may be possible to make allowance for such factors. For example, Halsey and Taylor (*J. Chem. Phys.*, 1947, **15**, 624; Halsey, *ibid.*, 1948, **16**, 931) showed that the Freundlich adsorption isotherm for gases could be derived theoretically by assuming an exponential distribution of energy among the adsorption sites. It does not, however, seem profitable at this stage to experiment with assumptions concerning the possible variation of $w_A{}^s$, $w_B{}^s$ with $x_B{}^s$ for the case of adsorption from solution.

Battersea Polytechnic, S.W.11.

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