242. *Theory of Chromatography. Part V. Separation of Two Solutes Following a Freundlich Isotherm.*

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An attempt is made to predict the behaviour during chromatographic separation of solutes following individually a Freundlich isotherm $ac = q^n$. A method is shown for the graphical solution of the fundamental chromatographic equation $dq_1/dc_1 = dq_2/dc_2$, which makes it possible to calculate the distribution of solutes in binary chromatograms for any type of isotherm. It is shown that in the case of Freundlich isotherms two essentially different types of chromatogram must be expected (see Figs. 4 and 6). In order to obtain complete separability into two adjoining bands the condition must be fulfilled that the molar phase ratio at the point of separation of the bands

$$\left[\frac{q_2}{c_2}\cdot\frac{c_1}{q_2}\right]_0 > n_2$$

If the leading solute has the lower value of n, *i.e.*, if $n_1 < n_2$, this can always be achieved by working at low enough concentrations. If this condition is not fulfilled, solute 2 cannot be obtained pure, but can only be enriched. Pure solute 1 can always be obtained, though in the latter case not quantitatively. Chromatographic separation is the easier the smaller the ratio n_1/n_2 of the Freundlich exponent.

(a) *An Isotherm for Multiple Solutes.*—The case of the Langmuir isotherm has been dealt with in considerable detail in an earlier publication. In deducing what happens in the case of two substances each following a Freundlich isotherm, the difficulty arises that no isotherm of the Freundlich type has so far been suggested for multiple solutes. Nevertheless, we may assume that, just as the simple Freundlich isotherm $q = (ac)^n$ can be replaced by a sum of Langmuir equations

$$q = \sum_1^{\nu} \frac{a_\nu c}{1 + b_\nu c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

as has been suggested by Hinshelwood (" Kinetics of Chemical Change in Gaseous Systems ", 2nd edition, p. 195), the multiple Freundlich isotherm, if it existed, might be synthesised as

$$q_1 = \sum_1^{\nu} \frac{a_{1\nu}c_1}{1 + b_{1\nu}c_1 + b_{2\nu}c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

An isotherm of this type, which still has a finite slope (dq/dc) at $c_1 = 0$ would show little difference in principle from the chromatographic behaviour of a " pure " Langmuir isotherm, and such differences would be confined mainly to a smaller rate of separation at the rear end (see, *e.g.*, Part III, Fig. 2).

Another possibility is to write the Freundlich equation in the form

$$ac = q(q)^{n-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and compare it with the Langmuir equation in the form

$$ac = q(1 - \beta q)^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\beta = b/a$ represents the amount of adsorbent occupied at saturation by 1 mol. of adsorbate. If the mechanism of adsorption is similar, we may reasonably assume that in both cases the concentration of the solute is in the first instance proportional to the concentration in the adsorbed state (q), modified by a factor which is dependent on the amount of free adsorbing space still available, which is a function of the amount absorbed. In the case of the multiple Langmuir isotherm this modifying function is

$$\left[1 - \beta_1\left(q_1 + \frac{\beta_2}{\beta_1}q_2\right)\right]^{-1}$$

We may assume that a similar additivity would exist for the occupied surface areas in the case of the modifying function of a multiple Freundlich isotherm, which would then have the form, analogous to eqn. (3) :

$$\left.\begin{aligned} a_1c_1 &= q_1\left(q_1 + \frac{\beta_2}{\beta_1}q_2\right)^{n_1-1} \\ a_2c_2 &= q_2\left(\frac{\beta_1}{\beta_2}q_1 + q_2\right)^{n\;-1} \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5a, b)$$

Equation (5*a*, *b*), which, like the Freundlich equation, can only be considered as empirical, should make it possible to predict the conditions of mixed adsorption when the single-solute isotherms are known, at least if the surface requirements β can be considered identical.

Actually it is possible to make physical assumptions which link the Freundlich isotherm with the theoretically deduced Langmuir equation (though it cannot be discussed here how far these assumptions are justified). We may assume that every part of the surface can become an actively adsorbing spot, if raised temporarily to a higher energy level P which in this case corresponds to a state of unsaturation. The higher this degree of unsaturation, the larger must be the activation energy P, but the greater will be the amount of desorption energy Q which an adsorbed solute requires for its removal from this activated spot. The simplest assumption would be that P and Q form, at a given temperature, a definite ratio $P/Q = m$, where $m < 1$, so that activation + adsorption results in an exothermic process.

A Maxwell–Boltzmann distribution being assumed for the P levels, the proportion of active surface ΔS_Q adsorbing with an adsorption energy between Q and $Q + \Delta Q$ is

$$\frac{\Delta S_Q}{\Delta Q} = \frac{m}{\boldsymbol{R}T}\cdot \mathrm{e}^{-mQ/\boldsymbol{R}T} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a1)$$

There is no reason why in normal cases a group of active spots of uniform properties should not adsorb according to the Langmuir isotherm :

$$\Delta q_Q = \frac{\Delta S_Q}{\beta}\cdot\frac{Kc\,\mathrm{e}^{Q/\boldsymbol{R}T}}{(1 + Kc\,\mathrm{e}^{Q/\boldsymbol{R}T})} = \frac{\Delta S_Q}{\beta}\cdot\frac{b_Qc}{1 + b_Qc} \quad . \; . \; . \; . \; . \; . \; . \quad (a2)$$

Replacement of ΔS_Q in (a2) by means of (a1) and elimination of Q by b_Q leads to the equation

$$\Delta q_Q = \frac{mK^mc}{\beta\,.\,b_Q^{\,m}(1 + b_Qc)}\cdot\Delta b_Q \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a3)$$

and integrating over all values of Q, *i.e.*, for all adsorption factors b from 0 to ∞, we have

$$q = \frac{mK^mc}{\beta}\int_0^\infty \frac{\mathrm{d}b}{b^m(1 + bc)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a4)$$

which for $0 < m < 1$ results in

$$q = \frac{m\pi K^m}{\beta\sin m\pi}\cdot c^m = Ac^m \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a5)$$

This is the well-known form of the Freundlich isotherm.

The same considerations can be applied to the case of two solutes. This leads eventually to

$$q_1 = \frac{m_1K_1^{\,m_1}c_1}{\beta_1}\int_0^\infty \frac{\mathrm{d}b_1}{b_1^{\,m_1}\left[1 + b_1c_1 + \left(\dfrac{b_1}{K_1}\right)^{m_2/m_1}K_2c_2\right]} \quad . \; . \; . \; . \; . \; . \quad (a6)$$

which integral appears to be soluble only for the case $m_1 = m_2$. In this case, integration leads to equations for q_1 and q_2 which are almost identical with the equations 5*c*, *d*. This gives some theoretical support for the multiple adsorption isotherms 5*a*, *b*, though only in the case $n_1 = n_2$.

Unfortunately, very few experimental data on mixed adsorption are available to test the usefulness of equation (5*a*, *b*), one of the best examples being the adsorption of oxalic (1) and succinic (2) acids on charcoal (probably by Masius; see Freundlich, "Colloid and Capillary Chemistry," Methuen, Fig. 39, p. 200). The Freundlich isotherms of the single solutes obtained from the experimental data are $40c_1 = (q_1)^{2\cdot1}$ and $216c_2 = (q_2)^{3\cdot6}$, where c is measured in mol./l. and q in millimol. per g. of charcoal, from which would follow in accordance with eqn. (5*a*, *b*), the multiple isotherms

$$40c_1 = q_1\left(q_1 + \frac{\beta_2}{\beta_1}q_2\right)^{1\cdot1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5a')$$

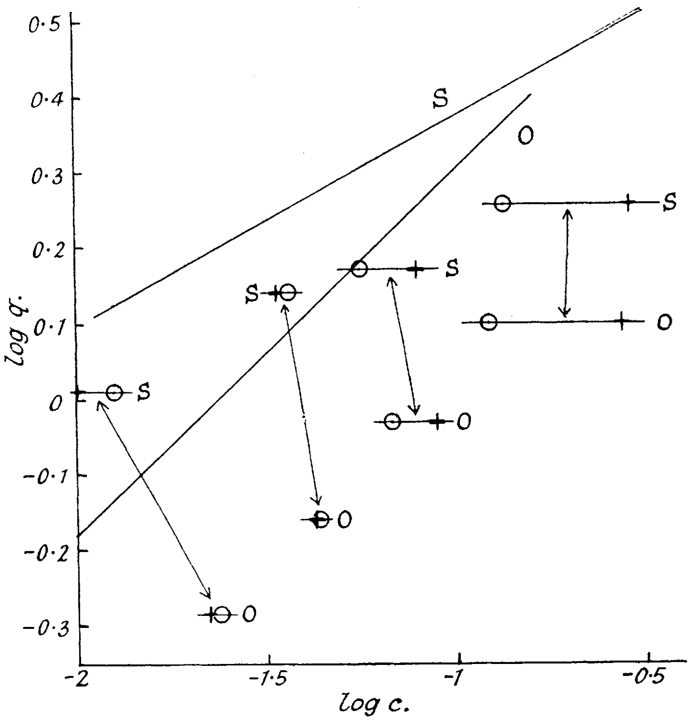
$$216c_2 = q_2\left(\frac{\beta_1}{\beta_2}q_1 + q_2\right)^{2\cdot6} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5b')$$

Fig. 1 shows the straight lines of the single-solute isotherms of succinic acid (S) and oxalic acid (O), as well as a number of points giving the measured adsorption equilibria for approximately equimolar solutions of the mixed solutes, the points of coexisting concentrations being tied by arrows. From the values of q_1 and q_2 of these points the "theoretical" values of c_1 and c_2 have been calculated by means of eqns. (5*a*′) and (5*b*′), and the resulting points are shown in Fig. 1 as circles : β_2/β_1 has been chosen as 1·2 which slightly improves the agreement as compared with the assumption of equal surface requirements. Though the deviations of the calculated values of c_1 and c_2 from the observed values are not negligible, it is apparent that the equations (5*a*′) and (5*b*′), the constants of which are taken from the single-solute isotherm, express the conditions of mixed adsorption with reasonable approximation.

Much better is the agreement with the experimental values if we consider the effect of the total adsorbate on the molar phase ratio ξ obtained from eqns. (5*a*) and (5*b*) :

$$\xi = \frac{c_1}{c_2}\Big/\frac{q_1}{q_2} = \frac{a_2}{a_1}\left(\frac{\beta_2}{\beta_1}\right)^{n_1-1} \cdot \left(\frac{\beta_1}{\beta_2}q_1 + q_2\right)^{n_1-n_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Fig. 1.



Adsorption of succinic and oxalic acid on charcoal. The lines represent the adsorption of the single solutes ; the points show the data of mixed adsorption of the two acids, coexisting concentrations being tied by arrows. (+) *observed data,* ○ *calculated from single solute isotherms by eqn.* (5*a*′, *b*′).

(see Fig. 2). Here the points correspond to the experimental values of c_1, c_2, q_1, q_2, and the line is obtained from eqn. (6) with $\beta_2/\beta_1 = 1{\cdot}2$, and all the other constants are taken from the single-solute isotherms. ξ is the separation factor and its importance for the chromatographic separation is similar to that of the molar phase ratio of the gaseous and the liquid phase for fractional distillation. The agreement is so much better here because any effects of mutual attraction or repulsion between the different adsorbed solutes, *e.g.*, due to the heat of mixing in the surface, which are not considered in eqn. (5*a*, *b*), are greatly reduced in ξ. This, too, has its parallel in the vapour pressures of binary liquids, where the agreement between theory and experiment is always better for the molar phase ratio than for the concentration–pressure curves.

Very similar conditions exist in the case of the binary adsorption of acetone (i) and acetic acid (ii) on charcoal. The single-solute isotherms are here (see experiments by Michaelis and Rona, *Biochem. Z.*, 1909, **15**, 204—207)

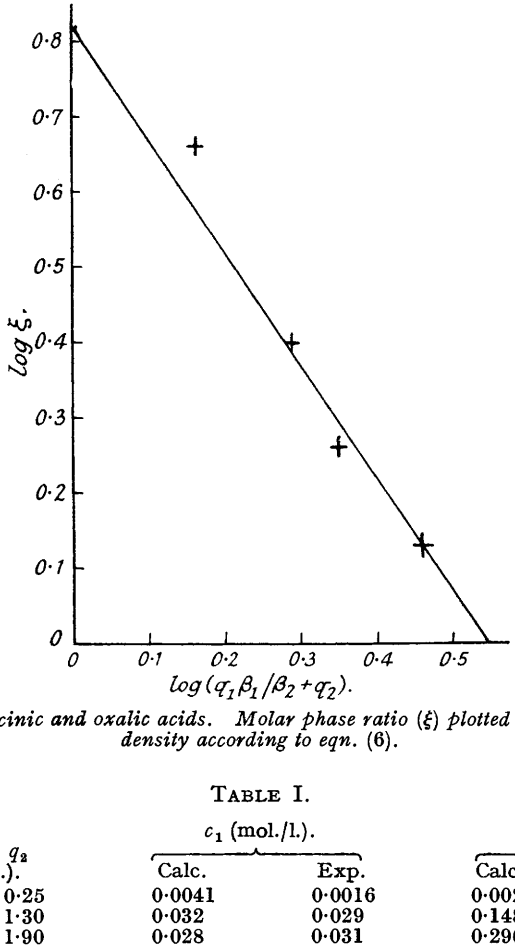
$$25c_1 = q_1^{2\cdot0} \text{ and } 41{\cdot}5c_2 = q_2^{3\cdot0}$$

so that one might expect the multiple isotherms

$$25c_1 = q_1(q_1 + \varepsilon q_2) \text{ and } 41{\cdot}5c_2 = q_2\left(\frac{q_1}{\varepsilon} + q_2\right)^2$$

At high concentrations of acetone, deviations due to the heat of mixing in the surface are again very marked, but at lower concentrations of acetone agreement is quite good (see Table I, where the concentrations in the solvent have been calculated for given quantities of adsorbate, using a value of $\varepsilon = 0{\cdot}65$), and Table II, where the amount of acetic acid required to produce a given distribution of solute 1 between 50 c.c. of water and 1 g. of charcoal has been calculated from the adsorption data of solute 1.

FIG. 2.



Mixed adsorption of succinic and oxalic acids. Molar phase ratio (ξ) plotted against mixed adsorption density according to eqn. (6).

TABLE I.

q_1	q_2	c_1 (mol./l.).		c_2 (mol./l.).	
(milli-mol./g.).		Calc.	Exp.	Calc.	Exp.
0·25	0·25	0·0041	0·0016	0·0024	0·0010
0·57	1·30	0·032	0·029	0·148	0·144
0·42	1·90	0·028	0·031	0·296	0·302
0·51	2·04	0·037	0·030	0·39	0·30
0·37	2·60	0·030	0·033	0·625	0·628

TABLE II.

Total acetone used (milli-mol.).	q_1 (milli-mol./g.).	c_1 (mol./l.).	Acetic acid added (milli-mol.).	
			Calc.	Exper.
0·209	0·043	0·0033	33·4	34·2
,,	0·055	0·0031	13·9	17·1
,,	0·061	0·0030	10·1	8·6
,,	0·129	0·0016	0·4	0

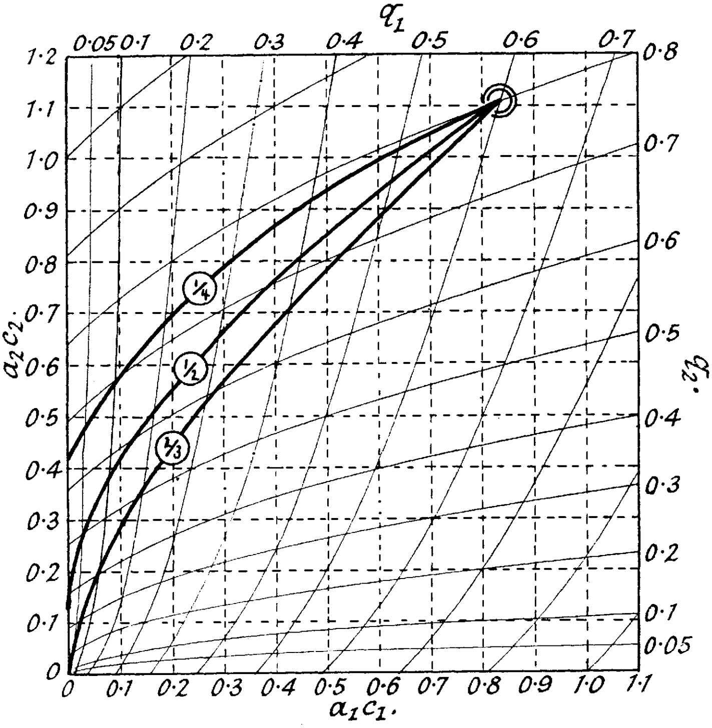
These considerations should make it clear that substances separately obeying a Freundlich isotherm do not necessarily follow the binary isotherm (5*a*, *b*), but that this equation represents a function which contains many, though not necessarily all, the essential features, which may be expected from a multiple adsorption isotherm of such solutes. In particular, it contains the typical feature of the Freundlich isotherm of infinite slope at zero concentration.

For $n_1 = n_2$, $\beta_1 = \beta_2$. Eqn. (5*a*, *b*) can also be written in the form

$$\left.\begin{aligned} q_1 &= \frac{a_1c_1}{(a_1c_1 + a_2c_2)^{1-1/n}} \\ q_2 &= \frac{a_2c_2}{(a_1c_1 + a_2c_2)^{1-1/n}} \end{aligned}\right\} \quad \text{- . - - . . . .} \quad (5\ c,\ d)$$

which shows at the same time the formal resemblance to and also the essential difference from the multiple Langmuir isotherms.

FIG. 3.



Contour lines of the q_1–c_1–c_2 *and of the* q_2–c_1–c_2 *surfaces, as required for obtaining the curve of coexistent values of* c_1 *and* c_2 *in the mixed part of the chromatogram for a given case of initial concentrations* c_1^0, c^0_2 (◎). *The three lines refer to three different values of* a_1/a_2 (= $\frac{1}{4}$, $\frac{1}{2}$, *and* $\frac{1}{3}$).

(b) *Chromatographic Separation in the Case* $n_1 = n_2$.—In order to apply chromatographic equations to either eqn. (2) or (5), it is necessary to solve the fundamental differential equations governing the chromatographic process $dq_1/dc_1 = dq_2/dc_2$. As has been pointed out in Part I (*Proc. Roy. Soc.*, 1946, *A*, **186**, 54), a general solution is so far only possible in the case of the " pure " Langmuir isotherm. We can, however, solve this equation by graphical evaluation and thus obtain the relationships between coexistent values in the chromatogram of c_1 and c_2 or q_1 and q_2 in any numerical case.

For this purpose lines of equal q_1 and of equal q_2 are plotted on a system with the co-ordinates a_1c_1 and a_2c_2 (or c_1 and c_2) (see Fig. 3). These represent the contour lines of the three-dimensional q_1–a_1c_1–a_2c_2 and q_2–a_1c_1–a_2c_2 diagrams. We may then start with a point [representing the conditions of the original solution (c_1^0, c_2^0) to be chromatographed] and, by a method of trial and error, find a neighbouring point which obeys the condition $\Delta q_1/\Delta c_1 = \Delta q_2/\Delta c_2$. Thence we proceed from point to point until one of the concentrations becomes zero. The resulting curve (thickly marked in Fig. 3) then represents the relationships between coexistent values in the mixed chromatogram of q_1 and q_2, c_1 and c_2.

In order to make a wider use of this diagram the evaluation has been made for three different values of a_1/a_2 ($= \frac{1}{4}, \frac{1}{2}, \frac{2}{3}$) which thus represent three different isotherms of the same type. The contour lines of Fig. 3 have been calculated for eqn. (5*a*, *b*) with $n_1 = n_2 = 2$ and $\beta_1/\beta_2 = 1$. In this case the position of the " coexistence line " depends on the ratio a_1/a_2 only, so no individual values need be assigned to these constants.

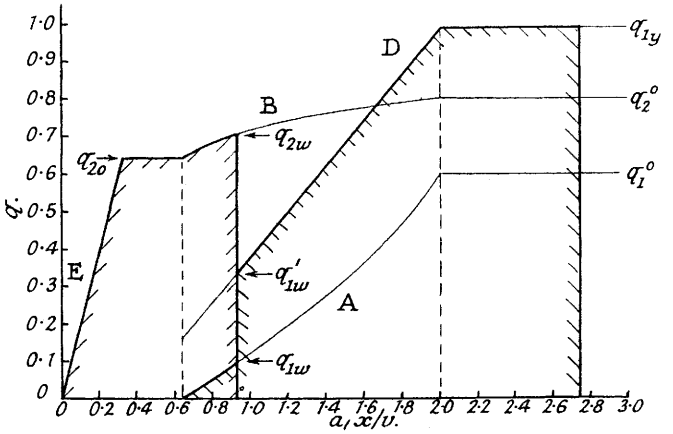
The starting concentrations of the adsorbate q_1^0 and q_2^0 have been chosen at random ($q_1^0 = 0{\cdot}6$, $q_2^0 = 0{\cdot}8$) and consequently $c_1^0 = 0{\cdot}84/a_1$, $c_2^0 = 0{\cdot}12/a_2$.

Each case of a_1/a_2 results in a function of coexistent values of c_1 and c_2 (and of q_1 and q_2, respectively) and these functions differ greatly in their characteristics. It can be shown that different starting points c_1^0, c_2^0, q_1^0, q_2^0 do not affect these characteristics, but that these depend on the ratio a_1/a_2 only. We always get types of function for coexistent values which can be represented with good approximation by the empirical equations (6*a*), (6*b*) and (6*c*), the value of the constants depending on the starting point.

a_1/a_2.	Equations for coexistent values of q_1, q_2.	Constants for $q_1^0 = 0{\cdot}6$, $q_2^0 = 0{\cdot}8$.			
		k_1.	k_2.	k_3.	
$\frac{1}{4}$	$q_2 = k_1 + k_2q_1 + k_3q_1^2$	0·64	0·5	0·5	(6*a*)
$\frac{1}{2}$	$q_2 = k_1 + k_2\sqrt{q_1}$	0·37	0·55	—	(6*b*)
$\frac{2}{3}$	$q_2 = k_1{}^3\sqrt{q_1} + k_2q_1$	0·77	0·25	—	(6*c*)

These relationships for coexistent values of q_1 and q_2 make it possible to substitute q_2 in the mixed isotherm (5*a*, *b*). This leads to the " pseudo-single-solute " isotherm $q_1 = \mathrm{F}_{(c_1)}$ required for the construction of the binary chromatograms according to the general equations given in Part III.

FIG. 4.



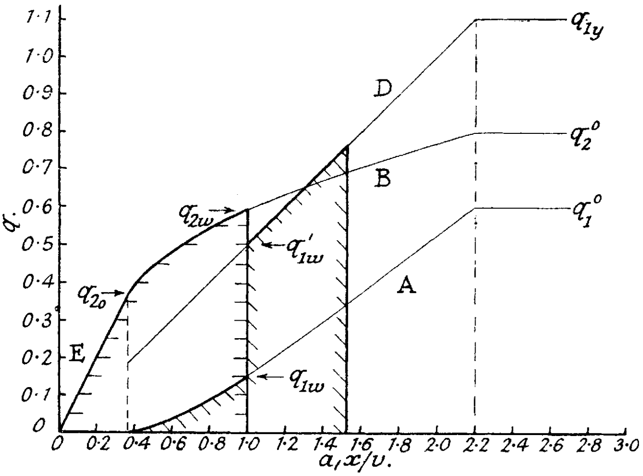
Boundary lines of chromatograms calculated for mixed isotherm with the constants $n_1 = n_2 = 2$ *and mixed* $a_1/a_2 = \frac{1}{4}$. *Note similarity with the case of the Langmuir isotherm. Complete separation is attainable.*

Figs. 4, 5, and 6 show the calculated loci of the chromatographic boundaries for the three cases considered ($a_1/a_2 = \frac{1}{4}, \frac{1}{2}, \frac{2}{3}$). Curves *A* and *B* represent the loci of the rear boundary of the mixed band for solute I and II respectively; curve *D* shows the rear slope of the pure frontal band of solute I, and curve *E* gives the diffuse rear boundary of the pure rear band of solute II. All the curves show the values of q_1 or q_2 plotted against the parameter a_1x/v as abscissa.

From these curves the actual form of the chromatograms can be obtained by fixing numerical values for the quantities of solutes (m_1, m_2) and for the volume v of solvent used. This defines the position x of the front boundaries of the mixed band and of the pure band of solute I. To make things clearer, these boundaries (for given cases of m and v) have been cross hatched; with these boundaries the abscissa represents the length of column (x) in an arbitrary unit.

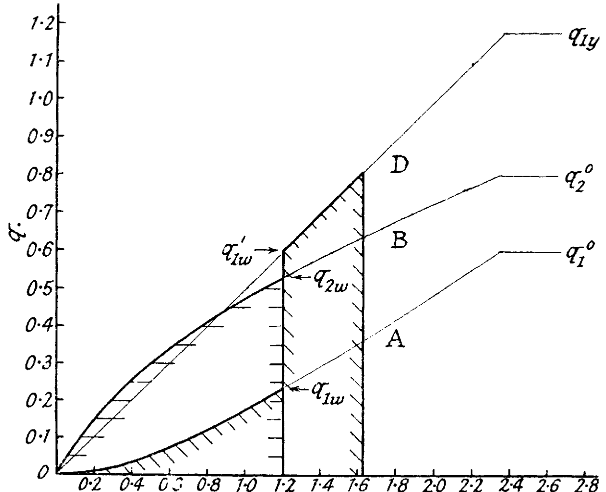
We then see from Fig. 4 that, for solutes with values of $a_1/a_2 < \frac{1}{2}$, the general arrangement of the binary chromatogram shows little difference from that arising from a Langmuir isotherm (see Part I or Part III, Figs. 1*a–e*, Fig. 1*A*, *B*). The principal differences are that (*a*) the rear band does not separate from the top of the column, a known feature for Freundlich isotherms (see Weiss, *loc. cit.*, Fig. 4), and consequently is only very incompletely eluted, and (*b*) the frontal band of solute 1 never completely separates from the rear band of solute 2, even after the mixed band has disappeared, because on account of the infinite value of dq/dc at $c_1 = 0$, the tail of the frontal band moves infinitely slowly and thus would always be overtaken by any other substance with $c > 0$ (see Fig. 5 of Part IV). The complete separation into two distinct bands of two solutes can therefore always be taken as a sign that the strict Freundlich isotherm does not apply to the faster-moving solute at very low concentrations, but that a pseudo-Freundlich isotherm of the type of eqn. (1) applies, which, as has been shown by a similar diagrammatic investigation, always permits separation into two distinct bands.

FIG. 5.



Boundary lines of chromatograms calculated for mixed isotherm with the constants $n_1 = n_2 = 2$ *and* $a_1/a_2 = \frac{1}{2}$. *Intermediate case between Figs. 4 and 6.*

FIG. 6.



Boundary lines of chromatograms calculated fo. mixed isotherm with the constants $n_1 = n_2 = 2$ *and* $a_1/a_2 = \frac{2}{3}$. *Note that no pure solute II is separable , consequently no complete separation is attainable.*

This conclusion agrees with the experimental findings by Schwab and Jockers (*Z. angew. Chem.*, 1937, **50**, 646) that no white zones between coloured bands can be obtained when mixed inorganic solutes are chromatographed on alumina, where isotherms with Freundlich characteristics obtain.

The difference of the chromatograms from those of Langmuir isotherms becomes marked for small separability of the two solutes ($1 > q_1/q_2 > 0{\cdot}5$) (see Fig. 6). Here the flat portion at the front of the pure tail band of solute II and the discontinuity at this point disappear. On the other hand, there is no longer a point of complete separation, as the curve representing q_1 now runs right back to the top of the chromatographic column ($x = 0$). In this case, solute II cannot even partially be obtained in the pure state, though a certain amount of solute I can be obtained pure at the front boundary.

Between these two extremes lies the intermediate case, $a_1/a_2 = \frac{1}{2}$ (see Fig. 5). Here we have the very rare, and in practice never realised case where a pure rear band can form without a discontinuity at its forward boundary, and where, consequently, the equations (in particular 6 and 7) suggested by Offord and Weiss (*Nature*, 1945, **155**, 725), which do not normally hold good, become identical with those of Glueckauf (*ibid.*, **156**, 205).

(c) *The Case of* $n_1 \neq n_2$.—It can be shown by a graphical integration (as in Fig. 3) that the two types of chromatographic behaviour as shown in Figs. 4 and 6 will also occur if $n_1 \neq n_2$. As in the case shown in Fig. 4, separation of a pure rear band of solute 2 (with a discontinuity at x_0) is confined to the essential conditions

$$\left[\frac{\mathrm{d}c_1}{\mathrm{d}c_2}\right]_{c_1=0} > 0 \quad \text{and} \quad \left[\frac{\mathrm{d}q_1}{\mathrm{d}q_2}\right]_{q_1=0} > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This gives the possibility of discussing, not only the case of the isotherm (5*a*, *b*), but also the general isotherm of the type

$$c_1 = q_1\,\phi(q_1, q_2) \qquad\qquad c_2 = q_2\,\psi(a_1q_1, a_2q_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a, b)$$

where ϕ and ψ are any functions, the latter being a symmetrical function with respect to α_1q_1 and α_2q_2. Then

$$\left[\frac{\mathrm{d}c_1}{\mathrm{d}q_1}\right]_{q_1=0} = \phi(0,q_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\left[\frac{\mathrm{d}c_2}{\mathrm{d}q_2}\right]_{q_1=0} = \psi(0,q_2) + q_{2o}\left[\frac{\mathrm{d}\psi}{\mathrm{d}q_2}\right]_{q_1=0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Equating (9) and (10) results in

$$\left[\frac{c_1}{q_1}\cdot\frac{q_2}{c_2}\right]_{q_1=0} = \xi_o = 1 + \frac{q_{2o}{}^2}{c_{2o}}\left[\frac{\mathrm{d}\psi}{\mathrm{d}q_2}\right]_{q_1=} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which, after partial differentiation, leads to

$$\left[\frac{\mathrm{d}q_1}{\mathrm{d}q_2}\right]_{q_1=0} = \left(\xi_o - \left[\frac{\partial \log c_2}{\partial \log q_2}\right]_{q_1=0}\right) \Big/ \frac{a_1}{a_1}\left(\left[\frac{\partial \log c_2}{\partial \log q_2}\right]_{q_1=0} - 1\right) \quad . \quad . \quad . \quad . \quad (12)$$

As $\mathrm{d}q_1/\mathrm{d}q_2 > 0$, the condition for complete separability of the solutes is

$$\xi_o > \left[\frac{\partial \log c_2}{\partial \log q_2}\right]_{q_1=0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

A useful application of (12) and (13) will in general be prevented by lack of knowledge of the value of q_{2o}. But in the case of the isotherm (5*a*, *b*), $[\partial \log c_2/\partial \log q_2]_{q_1=0}$ is independent of q_{2o} and results in

$$\left[\frac{\mathrm{d}q_1}{\mathrm{d}q_2}\right]_{q_1=0} = a_2(\xi_o - n_2)/a_1(n_2 - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

and in the condition:

$$\xi_o > n_2 > 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13a)$$

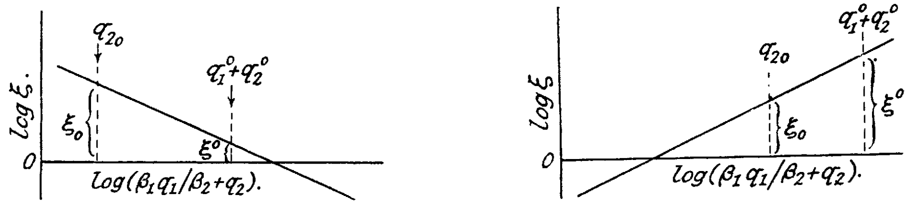
If, as in the case of Fig. 3, $n_1 = n_2$, ξ_o has the simple value a_2/a_1.

For a mixed adsorption isotherm of the type (5*a*, *b*) log ξ is a linear function of log $\left(\frac{\beta_1}{\beta_2}q_1 + q_2\right)$, and we can have two different cases, according to whether n_1 (less adsorbed solute) is smaller or larger than n_2 (rear solute). In the first case when $n_1 < n_2$ (or more generally, when ξ increases with decreasing concentration) the condition $\xi_o > n_2$ is always fulfilled, as development can be continued until ξ is large enough (see Fig. 7*a*). The separation will be the more efficient the smaller ($q_1{}^0 + q_2{}^0$), as this results in larger values of ξ^0 and ξ_o. This case behaves thus quite differently from that of the Langmuir isotherm, where separation is accelerated by working at high adsorption densities.

For the second case, when $n_1 > n_2$ (or more generally, when ξ decreases with diminishing concentration) (see Fig. 7*b*), it is apparent that the separation, which increases with ξ, improves with increasing concentrations of the solutes. If, however, they are not high enough to result in a value of $\xi_o > n_2$ $\left(\text{or more generally } \xi_o > \left[\frac{\partial \log c_2}{\partial \log q_2}\right]_{q_1 = 0}\right)$, which is essential for a clean separation of the solutes, the lowering of the concentrations in the course of the development will result in values of $\xi < 1$, at first for the rear, and eventually also for the front of the band. Thus, in the beginning, solute 1 will separate both in the front and in the rear with enrichment of solute 2 in the middle section of the band. Then, as the concentrations fall in the course of development, separation of solute 1 at the front will come to an end ($\xi_w = 1$) and will even be reversed ($\xi_w < 1$), whereby solute 2 again enters into the pure frontal band of solute 1 and eventually forms a frontal band of pure solute 2.

In this case, it is obviously much more economical to work from the start at such low concentrations that ξ^0 becomes < 1. This means that the solutes change their subscript and order in the chromatogram, reverting thereby to the case shown in Fig. 7*a*. It follows from this that chromatography at low enough concentrations will always lead to some kind of separation or enrichment in the case of Freundlich isotherms, though, if $n_1 > n_2$, chromatographic separation at high concentrations may in some cases ($\xi^0 \gg n_2$) result in a faster and more efficient separation, particularly, when $c_1^0 \ll c_2^0$, which would result in a relatively large value of c_{2o} and hence also of ξ_o (of same order of magnitude as c_2^0 and ξ^0 respectively; this follows strictly for the Langmuir isotherm, and can be shown to be true for other isotherms by the graphical method).

FIG. 7 *a*. FIG. 7 *b*.



The separation factor ξ *as function of the adsorption density.* (a) $n_1 < n_2$: *separation improves with the use of lower concentrations.* (b) $n_1 > n_2$: *separation improves with increasing concentration of the solutes.*

The first of these conclusions is confirmed by the chromatographic practice, where low concentrations are generally favoured. The second case, where high concentrations improve the separation, and which has apparently so far not been looked for, will be investigated experimentally in due course.

It is also apparent from Fig. 7*a* and *b* that, if ξ^0 is identical for two pairs of solutes, where one has $n_1 < n_2$, and the other $n_1 > n_2$. separation will be far easier in the first case where the leading solute has the lower value of n, since during the process of development the value of ξ increases, while the converse is true if the leading solute has the higher n. More generally, it can be said that pairs of solutes with equal ξ can be separated the more easily the smaller the value of n_1/n_2.

These conclusions might be elaborated more quantitatively, if the proposed binary isotherm (5*a*, *b*) were more than a rough working model which, apart from the displacement effect, does not consider mutual influences on each other of the two solutes. The present state of our knowledge concerning binary adsorption isotherms, however, is such that much preliminary work must be directed towards establishing the mutual influence of adsorbed solutes on each other and the mathematical form of mixed isotherms, before further theoretical guidance can be given to the practical chromatographer.

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