

## 792. Adsorption from Binary Mixtures : Determination of Individual Adsorption Isotherms.

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In adsorption on solid surfaces from binary liquid mixtures, the isotherms for adsorption of the individual components cannot be represented by simple Freundlich or Langmuir equations. An analysis based on the assumption that the surface is completely covered with adsorbate at all concentrations gives results in agreement with those obtained by direct adsorption from the corresponding vapour phase. A kinetic treatment is proposed for this type of adsorption. Vapour-pressure data required in this work are recorded for the systems benzene-ethyl alcohol and benzene-ethylene dichloride at 20°.

THE development of theories of adsorption on to solid surfaces from binary liquid mixtures has been traced in a recent review (Kipling, *Quart. Reviews*, 1951, 5, 60). What has conventionally been called the "adsorption isotherm" is now explained as the resultant of two individual isotherms (for the "solute" and "solvent" respectively) and is not itself a direct measure of the adsorption of either component. It could more accurately be described as the "isotherm of concentration change," as it is obtained directly from experimental measurement of this function. The term "selective adsorption" has also been proposed (Rao, *J. Phys. Chem.*, 1932, 36, 616), but in the light of the present work, it seems unlikely to have precisely the significance originally intended.

The determination of the individual isotherms now becomes of great interest, but is not possible by any direct method. Two indirect methods have been proposed: (i) the testing of theoretical equations for the individual isotherms against experimental data on their resultants, (ii) investigation of adsorption through the vapour phase in equilibrium with the binary liquid mixture.

(1) *Bartell and Sloan's Method.*—The relation between the isotherm of concentration change and the individual adsorption isotherms has been given independently by Ostwald and de Izaguirre (*Kolloid-Z.*, 1922, 30, 279) and Bartell and Sloan (*J. Amer. Chem. Soc.*, 1929, 51, 1637, 1643), and can be written in the form: \*

$$n_0(x_0 - x)/m = n_0\Delta x/m = n_1^s(1 - x) - n_2^s x \quad . \quad . \quad . \quad (1)$$

where, for a mixture of substances 1 and 2,  $x_0$  is the mole-fraction of 1 in the mixture before, and  $x$  is that after adsorption;  $n_1^s$  and  $n_2^s$  are respectively the number of moles of 1 and of 2 adsorbed per g. of charcoal;  $m$  is the weight (g.) of charcoal used, and  $n_0$  is the total number of moles in the original solution.

Bartell and Sloan assumed that the adsorption of each component followed a Freundlich equation. They thus obtained the following equation for the isotherm of concentration change:

$$n_0 \cdot \Delta x/m = k_1 \cdot x^\alpha(1 - x) - k_2(1 - x)^\beta \cdot x \quad . \quad . \quad . \quad (2)$$

By successive approximations they were able to deduce values of the four constants which made equation (2) fit their experimental results for a number of systems, and in particular the system benzene-ethyl alcohol with charcoal.

The Freundlich equation has been used empirically for adsorption from both the gaseous and the liquid phase. For the adsorption of gases it has been replaced (for unimolecular adsorption) by the more satisfactory Langmuir equation, which has kinetic, thermodynamic, and statistical derivations (Brunauer, "Physical Adsorption of Gases and Vapours," Oxford, 1944). We have therefore investigated the applicability of the

\* As the symbols used in the literature have been very varied, an attempt has been made in this paper to establish a standard in accordance with the convention recently approved for this Journal (*J.*, 1951, 1677).

Langmuir equation to liquid systems, as it might be expected to prove more satisfactory than the Freundlich equation. In place of equation (2) it gives :

$$n_0 \cdot \Delta x/m = \frac{k_1' K x(1-x)}{1+k_1' x} - \frac{k_2' K' x(1-x)}{1+k_2'(1-x)} \dots \dots \dots (3)$$

Repeating the adsorption from the system benzene-ethyl alcohol on a new sample of charcoal, we have found that the experimental data can be fitted as well by equation (3) as by equation (2), when the constants are : Freundlich,  $k_1 = 11.50$ ,  $k_2 = 7.72$ ,  $\alpha = 0.70$ ,  $\beta = 0.71$  ; Langmuir,  $k_1' = 15.6$ ,  $k_2' = 50.0$ ,  $K = 3.21$ ,  $K' = 1.00$ , giving the curves

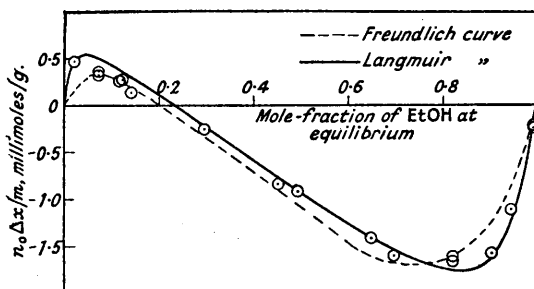


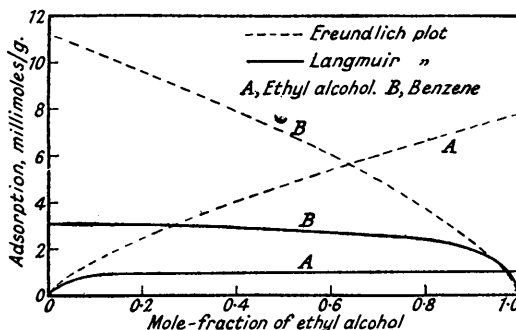
FIG. 1. Isotherms of concentration change for the system benzene-ethyl alcohol.

Points : experimental.  
Curves : calculated.

shown in Fig. 1. This has already been briefly reported (Kipling and Tester, *Nature*, 1951, 167, 612). The constants have been revised slightly from those published earlier. Those for the Freundlich method are very similar to those of Bartell and Sloan, although different charcoals were used.

In spite of the close agreement of these two treatments with each other and with the experimental data, a plot of the individual isotherms given by the two methods shows a

FIG. 2. Individual adsorption isotherms for the system benzene-ethyl alcohol, plotted according to the Freundlich and the Langmuir equations.



wide discrepancy (Fig. 2). This discrepancy clearly casts doubt on the validity of both of these treatments, which is further considered on p. 4128. Both treatments require saturation values for the separate components of the mixtures which do not agree with the experimental values of Table 1. In view of this, we have turned to the vapour phase in

TABLE 1. Separate adsorption of ethyl alcohol and benzene at 20°.

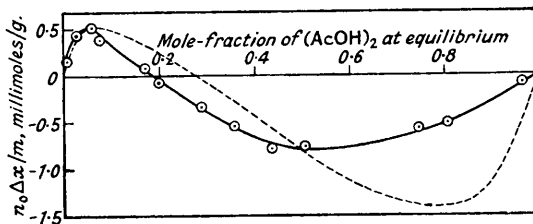
Benzene :		Ethyl alcohol :		Benzene :		Ethyl alcohol :	
$p/p^\circ$	w, %	$p/p^\circ$	w, %	$p/p^\circ$	w, %	$p/p^\circ$	w, %
0.051	22.2	0.030	13.9	0.344	25.6	0.401	22.4
0.076	23.2	0.117	19.4	0.423	26.2	0.607	23.7
0.108	24.3	0.152	20.4	0.656	26.2	0.683	23.7
0.193	23.8	0.208	20.9			0.803	23.9

the hope of obtaining reliable individual isotherms, and have then proposed two methods for describing the results.

(2) *Adsorption from the Vapour Phase.*—In adsorption from the vapour phase, measurements can be made both of the total weight of material adsorbed by the solid (which is not possible in adsorption from solutions), and of the change thus caused in the concentration of the liquid producing the vapour. It is then possible to determine the two individual adsorption isotherms directly. Provided that the mode of adsorption from the two phases is the same, then these must also be the individual isotherms for adsorption directly from

FIG. 3. Isotherm of concentration change for adsorption from benzene-acetic acid mixtures.

Points : experimental.  
Broken curve : calculated.



the liquid phase. Agreement has previously been found between isotherms of concentration change for adsorption from the vapour and liquid phases (Innes and Rowley, *J. Phys. Coll. Chem.*, 1947, **51**, 1172), but not for the individual isotherms.

Measurements of adsorption from the vapour phase are shown in Figs. 5, 6, and 7 for three systems. The corresponding isotherms of concentration change (obtained from the

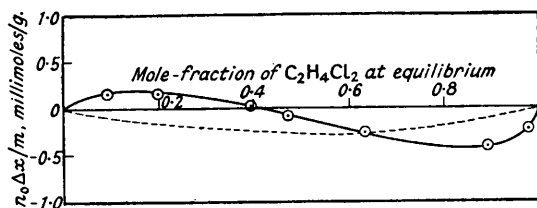


FIG. 4. Isotherm of concentration change for adsorption from benzene-ethylene dichloride mixtures.

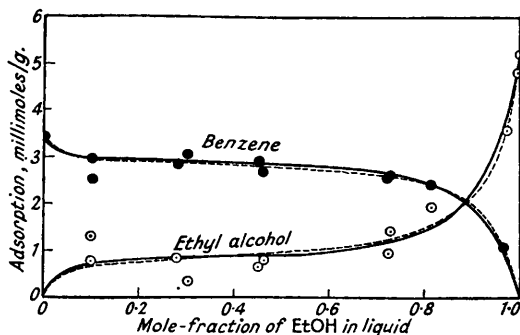
Points : experimental.  
Broken curve : calculated.

liquid phase) are given in Figs. 1, 3, and 4. In the system benzene-acetic acid, it is assumed that the acetic acid is present as the dimeric molecule over effectively the whole of the concentration range, and that it is adsorbed in that form.

It will be seen that the individual isotherms for the benzene-ethyl alcohol system (Fig. 5) bear little resemblance to either set shown in Fig. 2. It follows that equations

FIG. 5. Adsorption from benzene-ethyl alcohol vapour mixtures : individual isotherms.

Points : experimental.  
Full curves : calculated (Section 3).  
Broken curves : calculated (Section 4).



different from the simple Freundlich or Langmuir equations are required to describe them. To this end, we suggest two theoretical treatments, one based on a consideration of the nature of the adsorbed phase, the second a possible kinetic mechanism by which adsorption equilibrium is reached.

(3) *Nature of the Adsorbed Phase.*—Elton (*J.*, 1951, 2958) has recently pointed out an essential difference between adsorption from the liquid phase and most cases of adsorption from the gaseous phase, *viz.*, that the surface of the adsorbent is completely covered by liquid at all concentrations. We have, independently, reached the same conclusion, and



where  $x^v$  is the mole-fraction of vapour<sub>1</sub> in the vapour phase. Similarly

$$\sigma_2 = Kp_2/(p_1 + Kp_2) = p_2/(p_2 + p_1/K)$$

Two methods are available for the determination of  $K$ . For  $\sigma_1$  we can write  $m_1/(m_1)^\circ$ , where  $m_1$  and  $(m_1)^\circ$  g. are the weights of vapour<sub>1</sub> adsorbed per g. of adsorbent from a given mixture and from the pure component, respectively. Then

$$[(m_1)^\circ/m_1 - 1]p_1/p_2 = K \quad \dots \quad (8)$$

Alternatively,  $K$  can be obtained from the isotherms of the separate components when adsorbed alone on the same solid. If the equations for these adsorption isotherms are written in the form  $m/m^\circ = p/(1 + \beta p)$ , then from the derivation of the Langmuir equation, we have

$$\beta_1 = N/[(2\pi M_1 RT)^{1/2} k_0 e^{-Q_1/RT}]$$

$$\beta_2 = N/[(2\pi M_2 RT)^{1/2} k_0' e^{-Q_1/RT}]$$

and

$$K(k_0 M_1^{1/2} e^{-Q_1/RT} / k_0' M_2^{1/2} e^{-Q_1/RT}) = \beta_2/\beta_1$$

(b) *Adaptation to liquid-phase adsorption.* Equation (6) can be modified for use in liquid-phase adsorption by relating  $p_1$  to  $x$ . Two important cases arise.

Case 1. In the ideal case, in which Raoult's law is obeyed, *i.e.*,  $p_1 = p_1^\circ x$ , equation (6) becomes

$$\sigma_1 = p_1^\circ x / [p_1^\circ x + Kp_2^\circ(1 - x)]$$

or

$$\sigma_1 = x / [x + K'(1 - x)] \quad \dots \quad (9)$$

The equation for the isotherm of concentration change now becomes :

$$\begin{aligned} \frac{n_0 \Delta x}{m} &= \frac{Ax(1-x)/A_1}{x + K'(1-x)} - \frac{AK'x(1-x)/A_2}{x + K'(1-x)} \\ &= \frac{x(1-x)A \left[ \frac{1}{A_1} - \frac{K'}{A_2} \right]}{x + K'(1-x)} \quad \dots \quad (10) \end{aligned}$$

The form of this equation should be noted. It gives zero apparent adsorption only when  $x = 0$ ,  $x = 1$ , or when  $1/A_1 = K'A_2$ . It follows that, unless this last condition is fortuitously obeyed, the isotherm of concentration change must have the form of the calculated curve in Fig. 4, *i.e.*, the adsorption of one component will appear positive and that of the other component negative at all concentrations.

Case 2. For most systems, Raoult's law is not obeyed, and a different relationship between  $p_1$  and  $x$  is required. Margules's equation (*Sitzungsber. Akad. Wiss. Wien*, 1895, 104, 1243) may then be appropriate. The form of this equation which has been used in vapour studies of most such systems contains two terms in the exponential factor. This form is likely to have the most general application to adsorption studies. The alternative forms of the equation, with one, or with three or more terms, could, of course, be used where appropriate, as could any other equation having the same effect. The equation

$$p_1 = p_1^\circ x e^{\frac{1}{2}\alpha_2(1-x)^2 + \frac{1}{2}\alpha_3(1-x)^3}$$

leads to

$$\sigma_1 = x / \{x + K'(1-x)e^{[-\frac{1}{2}\alpha_2 x^2 + (\alpha_2 + \alpha_3)x - \frac{1}{2}\alpha_2 - \frac{1}{2}\alpha_3]}\} \quad \dots \quad (11)$$

and hence

$$n_0 \Delta x / m = \frac{x(1-x)A \left\{ \frac{1}{A_1} - \frac{K'e^{[-\frac{1}{2}\alpha_2 x^2 + (\alpha_2 + \alpha_3)x - \frac{1}{2}\alpha_2 - \frac{1}{2}\alpha_3]}}{A_2} \right\}}{\{x + K'(1-x)e^{[-\frac{1}{2}\alpha_2 x^2 + (\alpha_2 + \alpha_3)x - \frac{1}{2}\alpha_2 - \frac{1}{2}\alpha_3]}\}} \quad \dots \quad (12)$$

This equation can give the sigmoid form usually observed, the curve cutting the concentration axis when

$$1/A_1 = K'e^{[-\frac{1}{2}\alpha_2 x^2 + (\alpha_2 + \alpha_3)x - \frac{1}{2}\alpha_2 - \frac{1}{2}\alpha_3]} / A_2,$$

*i.e.*, when

$$x = \left[ (\alpha_3 + \alpha_2) \pm \sqrt{\alpha_3^2 + 2\alpha_2\alpha_3 + \alpha_2^2 - 2\alpha_3 \left( \frac{\alpha_2}{2} + \frac{\alpha_3}{3} + \ln \frac{A_2}{A_1 K_1} \right)} \right] / \alpha_3$$

provided that this gives one positive root. The constants may be such that there is no real root between 0 and 1, in which case a sigmoid curve will not be obtained. Curves have been published in which there is no negative branch, even though the system in question does not obey Raoult's law, e.g., for the system methyl alcohol-benzene with silica gel (Bartell and Scheffler, *J. Amer. Chem. Soc.*, 1931, **53**, 2507).

(c) *Direct application to the liquid-phase adsorption.* An equation having the same form as (6) can be derived directly by applying the same kinetic treatment to the liquid phase. Then

$$\sigma_1 k_0 e^{-Q_3/RT} / (1 - \sigma_1) k_0' e^{-Q_4/RT} = (a_1 M_1^{\ddagger}) / (a_2 / M_2^{\ddagger}) \quad \dots \quad (13)$$

where  $a_1$  and  $a_2$  are the activities of the first and the second component, respectively, in the liquid phase, and  $Q_3$  and  $Q_4$  the respective heats of desorption into the liquid phase. Then

$$\sigma_1 = a_1 / (a_1 + K'' a_2) \quad \dots \quad (14)$$

where

$$K'' = (k_0 M_1^{\ddagger} / k_0' M_2^{\ddagger}) e^{(Q_4 - Q_3)/RT}$$

This is of the same form as equation (6) for adsorption from the vapour phase.  $K$  and  $K''$  are not equal, but can be related as follows. Let  $L_1$  and  $L_2$  be the molar heats of vaporisation of the two components. Then

$$Q_4 - Q_3 = (Q_2 - L_2) - (Q_1 - L_1)$$

From the Clapeyron-Clausius equation,

$$d \ln p_1^\circ / dT = L_1 / RT^2 \quad \text{and} \quad d \ln p_2^\circ / dT = L_2 / RT^2$$

whence  $\ln p_1^\circ = -L_1/RT + c_1$ , and  $\ln p_2^\circ = -L_2/RT + c_2$ , on the assumption that  $L_1$  and  $L_2$  vary only slightly with temperature,  $c_1$  and  $c_2$  being constants. Then

$$p_1^\circ / c_1' = e^{-L_1/RT} \quad \text{and} \quad p_2^\circ / c_2' = e^{-L_2/RT}$$

where

$$\ln c_1' = c_1, \quad \text{and} \quad \ln c_2' = c_2.$$

Hence

$$c_2' p_1^\circ / c_1' p_2^\circ = e^{(L_1 - L_2)/RT}$$

and

$$K'' = (k_0 M_1^{\ddagger} p_2^\circ c_1' / k_0' M_2^{\ddagger} p_1^\circ c_2') e^{(Q_4 - Q_3)/RT} = K p_2^\circ c_1' / p_1^\circ c_2'$$

For most simple pairs of organic liquids,  $c_1' / c_2' = 1$  as a first approximation, so that  $K'' \sim p_2^\circ K / p_1^\circ = K'$ . As  $a_1 = p_1 / p_1^\circ$ , equation (14) becomes identical with equation (9) if Raoult's law is obeyed, and with equation (11) if Margules's equation is appropriate.

#### DISCUSSION

*Nature of the Adsorbed Phase.*—As the treatment proposed in Section (3) seems to offer a satisfactory interpretation of the experimental data, it may be relevant to examine the deficiencies of those used in Section (1). The argument is based on the assumption that the adsorbing surface is completely covered at all liquid concentrations. If the Langmuir equations are used in the form

$$n_1^s = \frac{k_1 K_1 x}{1 + k_1 x}, \quad n_2^s = \frac{k_2 K_2 (1 - x)}{1 + k_2 (1 - x)} \quad \dots \quad (15)$$

then equation (4) becomes

$$\frac{A_1 k_1 K_1 x}{1 + k_1 x} + \frac{A_2 k_2 K_2 (1 - x)}{1 + k_2 (1 - x)} = A$$

This is a quadratic equation in terms of  $x$ , and hence can, in general, only have two solutions for  $x$ . The experimental data, however, require an equation which will give a number of solutions for  $x$  which approaches infinity. It therefore follows that the Langmuir equation cannot be used in this form in the present theory of adsorption. A similar difficulty confronts the use of the Freundlich equation. This conclusion had been foreshadowed (Kipling and Tester, *loc. cit.*).

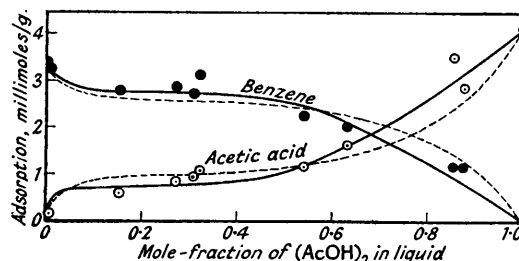
*Kinetic Treatment.*—The suggested kinetic treatment shows some similarity to that of Tryhorn and Wyatt (*Trans. Faraday Soc.*, 1928, **24**, 36) which appears, implicitly, also to

have been based on the assumption that the adsorbing surface is at all times completely covered. This treatment, however, neglected any consideration of the desorption process and did not therefore give a picture of kinetic equilibrium as usually understood.

Equation (6) is also similar to that of Markham and Benton (*J. Amer. Chem. Soc.*, 1931, **53**, 497; cf. also Kemball, Rideal, and Guggenheim, *Trans. Faraday Soc.*, 1948, **44**, 948), which is, however, normally used for cases in which the surface is only fractionally covered. The present treatment is put forward to emphasise the specific conditions applying to saturated vapours, but can be regarded as the limiting case of Markham and Benton's treatment when the free surface tends to zero. In the form of equation (6) it can more usefully be applied to deriving an equation for the isotherm of concentration change.

FIG. 6. Adsorption from benzene-acetic acid vapour mixtures: individual isotherms.

Points: experimental.  
Full curves: calculated (Section 3).  
Broken curves: calculated (Section 4).



A preliminary investigation of the usefulness of equation (6), and those which follow from it, has been made by reference to data on the three systems already discussed. Calculations of  $K$  have been made and are presented in Tables 2, 3, and 4. There is considerable variation in all three cases, from which we deduce that the activity coefficients for the adsorbed substances depart considerably from unity. This is not entirely unexpected when such factors as molecular interaction and difference in packing of the two components in relation to adsorption sites are considered.

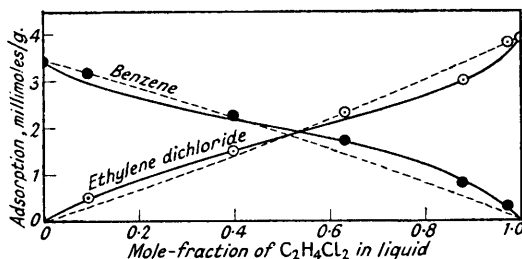


FIG. 7. Adsorption from benzene-ethylene dichloride mixtures. True adsorption isotherms.

Points: adsorption from vapour.  
Full curves: calculated (Section 4).  
Broken curves: calculated (Section 5).

In spite of this limitation, we have used mean values of  $K$  in further calculations, in order to draw a number of qualitative conclusions. First, the individual adsorption isotherms have been calculated, as a function of liquid-phase concentration, for the three systems, equations (9) and (11) being used. The resulting curves are shown in Figs. 5, 6, and 7. They are of substantially the same form as those obtained experimentally, which suggests that the activity-concentration relationship for the liquid mixtures plays a major part in determining the shape of the individual adsorption isotherms. A less precise form of this conclusion was suggested earlier by Tryhorn and Wyatt (*loc. cit.*).

TABLE 2. Adsorption of ethyl alcohol vapour from mixtures with benzene.

Mole-fraction of EtOH in liquid	$(m_1)^{\circ}/m_1$	$p_1$	$p_2$	$K$	Mole-fraction of EtOH in liquid	$(m_1)^{\circ}/m_1$	$p_1$	$p_2$	$K$
0.05	10.4	18.4	73.4	2.66	0.5	6.04	32.5	65.0	2.51
0.1	7.54	22.4	72.5	2.02	0.6	5.00	33.8	61.0	2.22
0.2	6.75	25.6	71.0	2.08	0.7	3.91	35.0	54.0	1.89
0.3	6.57	28.3	69.5	2.27	0.8	2.87	37.5	42.5	1.65
0.4	6.50	30.5	67.5	2.49	0.9	2.08	41.0	27.2	1.63

Mean value of  $K = 2.1$

TABLE 3. *Adsorption of ethylene dichloride vapour from mixtures with benzene.*

Mole-fraction of $C_2H_4Cl_2$ in liquid					Mole-fraction of $C_2H_4Cl_2$ in liquid				
$(m_1)^{\circ}/m_1$	$p_1$	$p_2$	$K$		$(m_1)^{\circ}/m_1$	$p_1$	$p_2$	$K$	
0.1	7.37	6.2	66.75	0.59	0.6	1.80	36.7	29.5	1.00
0.2	4.83	12.25	59.25	0.79	0.7	1.59	43.0	22.1	1.15
0.3	3.13	18.5	52.0	0.76	0.8	1.42	49.0	15.0	1.37
0.4	2.49	24.5	44.5	0.82	0.9	1.245	55.0	7.5	1.80
0.5	2.09	30.6	37.0	0.90					

Mean value of  $K = 1.0$

TABLE 4. *Adsorption of acetic acid vapour from mixtures with benzene.*

Mole-fraction of AcOH (dimer) in liquid					Mole-fraction of AcOH (dimer) in liquid				
$(m_1)^{\circ}/m_1$	$p_1$	$p_2$	$K$		$(m_1)^{\circ}/m_1$	$p_1$	$p_2$	$K$	
0.1	7.23	8.0	67.0	0.74	0.6	2.85	9.5	45.0	0.39
0.2	5.28	8.5	65.6	0.55	0.7	2.01	10.0	35.0	0.29
0.3	4.58	9.0	63.0	0.51	0.8	1.53	10.9	24.0	0.24
0.4	3.93	9.0	59.0	0.45	0.9	1.23	12.0	13.0	0.21
0.5	3.75	9.2	53.0	0.48					

Mean value of  $K = 0.43$

Of the several systems recorded in the literature, we have chosen as an example that of methyl alcohol-carbon tetrachloride with charcoal (Innes and Rowley, *J. Phys. Coll. Chem.*, 1947, **51**, 1154, 1172). The data here require a modification of equation (7) to the form

$$x_1^s = x^v/[x^v + kK(1 - x^v)] \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where  $x_1^s$  is the mole-fraction of component 1 in the adsorbed phase. Then

$$x^v/x_1^s = kK + (1 - kK)x^v$$

where  $k$  is the ratio  $(n_2^s)/(n_1^s)^{\circ}$  of the number of moles of the two components required to cover 1 g. of the surface completely. Table 5 shows the derivation of the value of  $kK$ ,

TABLE 5. *Adsorption of carbon tetrachloride vapour from mixtures with methyl alcohol.*

Mole-fraction of $CCl_4$ in vapour ( $x^v$ )				Mole-fraction of $CCl_4$ in vapour ( $x^v$ )			
$x^v$	$x^v/x^s$	$kK$		$x^v$	$x^v/x^s$	$kK$	
0.11	0.115	0.96	0.96	0.43	0.49	0.88	0.79
0.12	0.185	0.65	0.60	0.49	0.56	0.88	0.76
0.16	0.20	0.80	0.76	0.58	0.62	0.94	0.86
0.23	0.29	0.79	0.73				

Mean value of  $kK = 0.78$

from which the curve in Fig. 8 has been calculated. It agrees very well with the experimental data and is also in close agreement with Fig. 3 of Elton's recent paper (*loc. cit.*), which gives the corresponding curve for adsorption from the liquid phase for the same system.

For comparison, Fig. 9(b) gives our results for the ethyl alcohol-benzene system, also plotted in terms of  $x_1^s$ . Fig. 9(a) shows the fraction of the surface covered by each component as a function of vapour composition.

We have also examined the use of equations (10) and (12) for constructing the isotherm of concentration change. The result for the benzene-ethyl alcohol system (Fig. 10) is slightly better than those derived on the earlier basis (Fig. 1). The values of  $\alpha_2$  and  $\alpha_3$ , the Margules constants, have been derived from vapour-pressure data given on p. 4132.

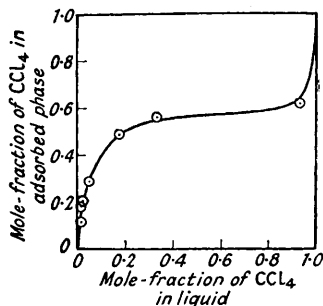
The benzene-ethylene dichloride system obeys Raoult's law very closely, and thus the calculated curve shows only one branch. The experimental curve, however, shows two branches, though these rise to only very small values, as will be seen from a comparison of Figs. 4 and 1, which are plotted on the same scale. We conclude that the behaviour of the system in the adsorbed phase is not ideal. As it has been suggested that the behaviour of this system in the liquid phase is only pseudo-ideal, it is hoped later to investigate systems in which more nearly ideal behaviour might be expected in both the liquid and the adsorbed phase.

The benzene-acetic acid system was chosen in order to investigate the effect of



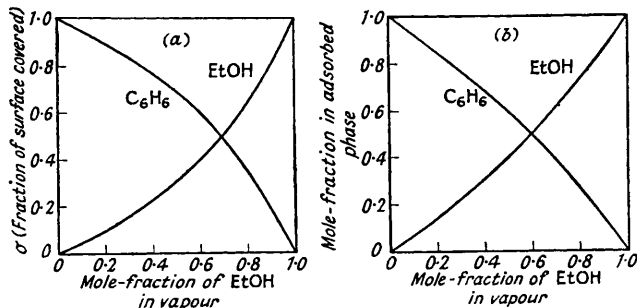
dimerisation of one component. We are satisfied that the acetic acid is essentially dimeric throughout, and that the presence of monomer can be neglected, except in very dilute solutions. The calculated isotherm of concentration change (Fig. 3) departs considerably from the experimental points in concentrated acetic acid solutions, more acetic acid being adsorbed than predicted theoretically. It is possible that the "excess" is adsorbed chemically by the small amount of alkaline ash in the charcoal, the presence of which has been demonstrated.

FIG. 8. Adsorption from carbon tetrachloride-methyl alcohol vapour mixtures.



Points : experimental.  
Curve : calculated.

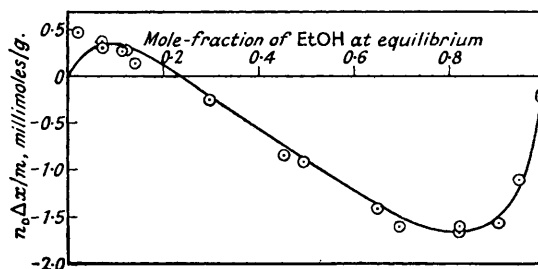
FIG. 9. Adsorption from benzene-ethyl alcohol vapour mixtures.



Finally, it may be noticed that equations (10) and (12) assume approximately the form of a Langmuir equation for dilute solutions, when both  $(1 - x)$  and the exponential term approach 1. This explains the success which has been found in the past in applying Langmuir- or Freundlich-type equations to isotherms of concentration change. Such work has usually been done on dilute solutions, with a very small range of mole-fractions. This has been particularly the case with aqueous solutions, in which the small molecular weight of water makes a solution much more dilute in terms of mole fraction than it appears

FIG. 10. Isotherm of concentration change for adsorption from benzene-ethyl alcohol mixtures.

Points : experimental.  
Curves : calculated.



when considered in terms of weight fraction or normality. Even for dilute solutions, it should be emphasised that the equations have not the same significance as has the true Langmuir equation for gaseous adsorption. Thus the constants do not give immediately a value for the surface area of the adsorbent in the way that is familiar for gaseous adsorption. Attention has already been drawn, in general terms, to the inadequacies of apparent adsorption data for determinations of surface areas (Kipling, *loc. cit.*).

#### EXPERIMENTAL

**Materials.**—The adsorbent was a commercial steam-activated coconut-shell charcoal, used in B.S.S. grading 20—40. Before use it was dried at 120°.

Benzene was dried over phosphoric oxide and fractionally distilled. Further impurities were removed by fractional crystallisation, until the whole yield froze at 5.5°. The purified benzene had  $d_4^{20}$  0.8788,  $n_D^{20}$  1.5010, in agreement with values quoted by Timmermans ("Physico-Chemical Constants of Pure Organic Compounds," London, 1950).

Ethyl alcohol was dried over calcium oxide. Remaining traces of water were removed by refluxing the alcohol with sodium wire and ethyl phthalate. The alcohol was then distilled; it had b. p.  $78.2^{\circ}$ ,  $d_4^{20}$  0.7895,  $n_D^{20}$  1.3617.

Ethylene dichloride was fractionally distilled, the fraction used having  $n_D^{20}$  1.4449, in good agreement with Coulson, Hales, and Herington's value (*Trans. Faraday Soc.*, 1948, **44**, 636).

Acetic acid, purified by Orton and Bradfield's method (*J.*, 1927, 983), had m. p.  $16.6^{\circ}$ ,  $n_D^{20}$  1.3718.

*Procedure.*—The determinations were all carried out in a  $20^{\circ}$  thermostat. For the liquid-phase experiments, sealed tubes containing charcoal and the mixtures were shaken in the thermostat for not less than 12 hours. For vapour-phase experiments, charcoal, in a small container, was suspended in the vapour above the appropriate liquid mixture, contained in a sealed vessel, and was weighed at intervals until equilibrium was attained.

Concentrations were determined by using a Pulfrich refractometer. A calibration curve was prepared for each system studied. Differences in concentration were determined accurately by direct comparison of the solutions before and after adsorption had taken place, by means of a differential reading on the instrument. The detailed procedure has been described earlier, *e.g.*, by Kane and Jatkar (*J. Indian Inst. Sci.*, 1938, **21**, A, 331).

Adsorption isotherms for the separate components were determined by a flow method. The charcoal, contained in a perforated aluminium "bucket," was suspended from a spiral spring in a chamber in a thermostat. Adsorption took place from air streams containing the vapours at known partial pressures. A stream of pure, dry air was passed through a saturator containing the liquid under investigation. It was then mixed with a second air stream in proportions determined by calibrated flow-meters, to give a combined stream having the desired partial pressure of the substance to be adsorbed. The weight of the adsorbate was calculated from the extension of the spiral spring, which was read by means of a cathetometer.

*Partial Pressures.*—Partial pressures at  $20^{\circ}$  were required for each of the systems studied. Tryhorn and Wyatt (*Trans. Faraday Soc.*, 1926, **21**, 399) recorded the composition of the vapour phase in the benzene-ethyl alcohol system as a function of that of the liquid phase, but did not give the total pressures from which the partial pressures could be deduced. These were therefore determined by Rosanoff's method (*J. Amer. Chem. Soc.*, 1914, **36**, 1803), by using a simplified form of the apparatus described by Hovorka and Dreisbach (*ibid.*, 1934, **56**, 1664). The results are given in Table 6. When expressed in terms of mole-fractions, they agree closely with Tryhorn and Wyatt's data.

TABLE 6. *Partial pressures for benzene-ethyl alcohol mixtures at  $20^{\circ}$ .*

Mole-fraction of EtOH :		Total v. p.	$p_{EtOH}$	$p_{C_6H_6}$	Mole-fraction of EtOH :		Total v. p.	$p_{EtOH}$	$p_{C_6H_6}$
in liquid	in vapour	(mm.)	(mm.)	(mm.)	in liquid	in vapour	(mm.)	(mm.)	(mm.)
0.000	0.000	74.3	0.0	74.3	0.4975	0.330	97.8	32.3	65.5
0.015	0.064	78.0	5.0	73.0	0.525	0.340	96.7	32.9	63.8
0.0275	0.058	85.7	12.7	73.0	0.640	0.368	92.7	34.1	58.6
0.065	0.216	93.6	20.2	73.4	0.724	0.604	87.6	35.4	52.2
0.210	0.269	96.2	25.9	70.3	0.806	0.490	80.0	39.2	40.8
0.231	0.272	97.5	26.4	71.0	0.935	0.686	62.8	43.1	19.7
0.320	0.295	97.5	28.8	68.7	1.000	1.000	44.7	44.7	0.0
0.335	0.2975	97.4	29.0	68.4					

TABLE 7. *Partial pressures for benzene-ethylene dichloride mixtures at  $20^{\circ}$ .*

Mole-fraction of $C_2H_4Cl_2$ :		Total v. p.	$p_{C_2H_4Cl_2}$	$p_{C_6H_6}$	Mole-fraction of $C_2H_4Cl_2$ :		Total v. p.	$p_{C_2H_4Cl_2}$	$p_{C_6H_6}$
in liquid	in vapour	(mm.)	(mm.)	(mm.)	in liquid	in vapour	(mm.)	(mm.)	(mm.)
0.000	0.000	74.3	0.0	74.3	0.6325	0.595	65.5	39.0	26.5
0.040	0.0325	73.8	2.4	71.4	0.680	0.635	65.0	41.3	23.7
0.0465	0.041	73.6	3.0	70.6	0.773	0.741	64.5	47.8	16.7
0.2875	0.254	70.5	17.9	52.6	0.793	0.756	64.1	48.5	15.6
0.344	0.305	70.1	21.4	48.7	0.9475	0.935	61.8	57.8	4.0
0.450	0.402	68.6	27.6	41.0	0.973	0.9575	61.5	58.9	2.6
0.461	0.412	68.5	28.2	40.3	1.000	1.000	61.0	61.0	0.0
0.6225	0.585	66.7	39.0	27.7					

Total and partial pressures have also been determined for the system benzene-ethylene dichloride (Table 7). A close approximation to Raoult's law is found, as is the case at  $50^{\circ}$  (Zawidski, *Z. physikal. Chem.*, 1900, **35**, 129).

The calculations above for the benzene-acetic acid system are based on Schmidt's vapour-pressure data (*ibid.*, 1926, 121, 221). Although these have been criticised (Hovorka and Dreisbach, *loc. cit.*), a smoothed curve plotted in terms of dimeric acetic acid seemed adequate for the present purpose.

We acknowledge with gratitude the gifts of chemicals from Imperial Chemical Industries, Limited, of charcoal from Messrs. Sutcliffe, Speakman, Ltd., and of beryllium-copper springs from Messrs. Instrument Specialities Co. Inc., of New Jersey. We are also grateful to Imperial Chemical Industries, Limited, for the loan of apparatus, and to The Distillers Co. Ltd., for a grant to the Department, which made this work possible.

One of us (D. A. T.) is grateful to the Department of Scientific and Industrial Research for the award of a maintenance grant, during the tenure of which the present work was carried out.

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[Received, December 4th, 1951.]

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