455. *Adsorption on Carbons from Binary Liquid Mixtures: Some Surface Activity Coefficients.*

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Surface activity coefficients are compared for a range of binary liquid mixtures adsorbed on charcoal. The curves of surface activity coefficient against surface mole-fraction are of three types, corresponding to the types of isotherm of concentration change and of individual adsorption isotherm. In general, there is no correlation between the surface activity coefficients and those for the corresponding liquid phase. Surface forces are the most important in most cases, though absolute volatility is also important and may become the over-riding factor in extreme cases. In a special series, charcoal shows a preference for the less polar methyl group over the more polar chlorine atom. A comparison is made of the behaviour of one system on charcoal, on carbon black, and on graphite.

THE forces of physical adsorption which hold the molecules of a substance to a solid surface and prevent their return to the liquid or vapour phase have been likened to those holding together the molecules in the liquid phase, so preventing their escape into the vapour phase. When a binary mixture is involved, the adsorbate has, in general, a different composition from that of the liquid in equilibrium with it, just as the liquid usually has a different composition from that of its saturated vapour. It is interesting, therefore, to investigate the "surface activity coefficients" for such systems, *i.e.*, the activity coefficients of the two components in the adsorbed layer. These should show the relative tendencies of the two substances to escape from the surface.

Surface activity coefficients have been considered from a theoretical standpoint by Elton [1] for such systems. We now present the data obtained from a series of experimental investigations and use them to draw a number of simple qualitative conclusions about the forces responsible for adsorption.

Two conventions have been used for expressing surface activity coefficients. Elton's convention, which we shall follow, is that the surface activity of either component, and hence its surface activity coefficient, is 1 when its surface mole-fraction is 1. This convention seems particularly suited to a comparison of activity coefficients for the adsorbed layer and for the bulk liquid when completely miscible liquids are being considered. In particular, it is more appropriate than the convention used by Fu, Hansen, and Bartell [2] in dealing with partially miscible systems.

We have $f_1 = a_1/x_1$ and $f_1^s = a_1^s/x_1^s$ where f_1 and f_1^s are the activity coefficients of substance 1 in the liquid and the surface phase respectively, a_1 and a_1^s are the corresponding activities, and x_1 and x_1^s the corresponding mole-fractions. The surface mole-fractions are obtained from the individual adsorption isotherms, the derivation of which has been discussed previously.[3-6] With the present convention, $a_1 = a_1^s$ for any mixture. The value of a_1 is obtained from vapour-pressure measurements; hence values of f_1 and of f_1^s can be calculated. Calculations have been made for: (1) A series of mixtures adsorbed on charcoal, for which the individual isotherms have been recorded previously,[3-6] and (2) two further series, isotherms for which are recorded in this paper, in which (*a*) pairs are taken from the group carbon tetrachloride, chloroform, 1 : 1 : 1-trichloroethane (methylchloroform), *tert.*-butyl chloride [these substances have molecules of very similar size and shape, and it was hoped to derive information about the relative effects in adsorption of the chlorine atom, hydrogen atom, and methyl group], and (*b*) a comparison is made, for one

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[1] Elton, *J.*, 1954, 3813.

[2] Fu, Hansen, and Bartell, *J. Phys. Colloid Chem.*, 1948, **52**, 374.

[3] Kipling and Tester, *J.*, 1952, 4123.

[4] Blackburn and Kipling, *J.*, 1954, 3819.

[5] *Idem*, *J.*, 1955, 1493.

[6] *Idem*, *J.*, 1955, 4103.

liquid mixture, of adsorption on the porous charcoal used throughout this work with adsorption on a non-porous carbon black, and on a non-porous graphite.

The results of adsorption measurements which have not been published previously are shown in Figs. 1—4. The individual adsorption isotherms have been calculated as described previously[3, 4] from the monolayer values recorded in the Tables; from these were obtained the values of x_1^s and x_2^s. The partial-pressure data are recorded, for convenience, in the form of activity coefficients, together with the vapour pressures of the pure components.

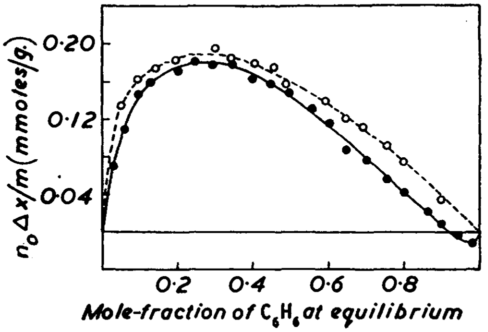


FIG. 1. *Isotherms of concentration change for adsorption from mixtures of benzene and* cyclo*hexane on* (○) *Spheron* 6, (●) *graphite.*

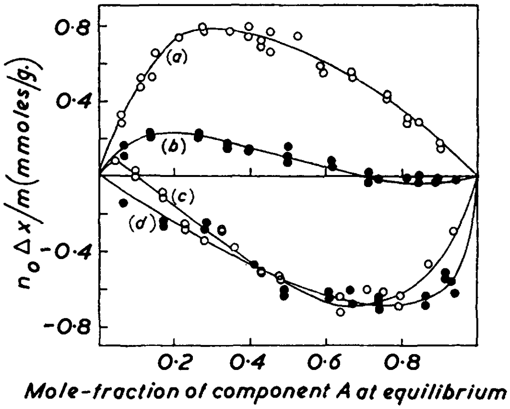


FIG. 2. *Isotherms of concentration change for adsorption on charcoal from mixtures of* (*a*) *methylchloroform* (*A*) *and* tert.*-butyl chloride,* (*b*) *methylchloroform* (*A*) *and carbon tetrachloride,* (*c*) tert.*-butyl chloride* (*A*) *and carbon tetrachloride,* (*d*) *chloroform* (*A*) *and carbon tetrachloride.*

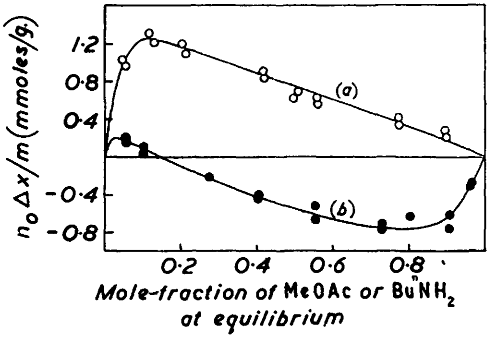


FIG. 3. *Isotherms of concentration change for adsorption on charcoal from mixtures on* (*a*) n*-butylamine and benzene,* (*b*) *methyl acetate and benzene.*

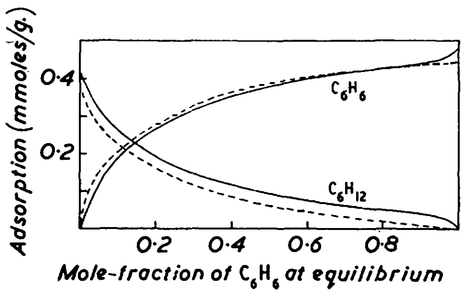


FIG. 4. *Adsorption* (*individual isotherms*) *from mixtures of benzene and* cyclo*hexane on graphite and on Spheron* 6. *Full curves, graphite: broken curves, Spheron* 6.

DISCUSSION

Examination of the Tables shows that the systems investigated can be divided into three types, representatives of which are illustrated in Figs. 5—8, where surface activity coefficients are plotted against *surface* mole-fractions. The figures also show the activity coefficients for the liquid phase plotted against mole-fractions in the *liquid* phase. This method of presentation enables a direct comparison to be made of the "escaping tendencies" of a given component from the surface layer into the liquid, and from the liquid into the vapour. The three types of behaviour are: (I) The curves of surface activity coefficient against surface mole-fraction show no point of inflexion (Fig. 5). (II) The curves do show a point of inflexion (Fig. 6). (III) The curves cross (Figs. 7 and 8).

Type I behaviour is shown by the systems which give a one-branch isotherm of concentration change and individual adsorption isotherms which show no point of inflexion. In such cases it is clear that one component of the mixture is more strongly adsorbed than the other at all concentrations. Figs. 1 and 2 each show both one- and two branched isotherms of concentration change. Fig. 4 shows examples of individual isotherms with and without points of inflexion.

Type II behaviour is shown by the majority of the systems studied. In these, the proportion of one component in the adsorbed phase is higher than in the liquid phase over part of the concentration range only, the position being reversed for the remainder of the concentration range. The pyridine–ethyl alcohol system has an isotherm of concentration change which shows only one branch, but this shows an anomalous point of inflexion and comes very close to showing a second branch. The individual isotherms do, in fact, show slight inflexions.

FIG. 5. *Surface activity coefficient curves for mixtures of benzene and* cyclo*hexane adsorbed on* (*A*) *charcoal and on* (*B*) *Spheron* 6. *Curves for the liquid phase shown broken.*

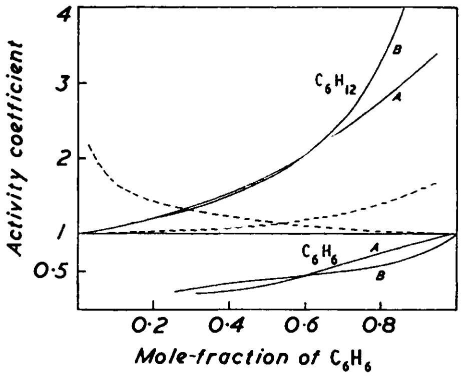


FIG. 6. *Surface activity coefficient curves for mixtures of benzene and* cyclo*hexane adsorbed on graphite.*

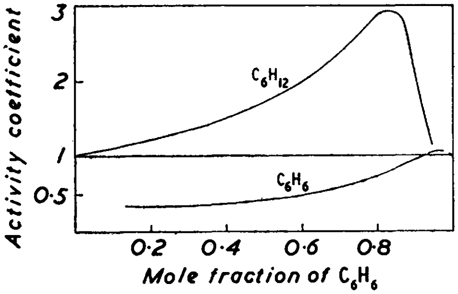


FIG. 7. *Surface activity coefficient curves for mixtures of chloroform and acetone adsorbed on charcoal. Curves for the liquid phase broken.*

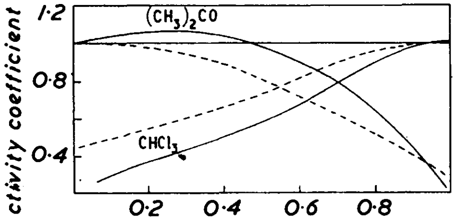
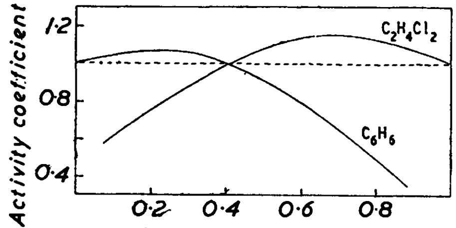


FIG. 8. *Surface activity coefficient curves for mixtures of ethylene dichloride and benzene adsorbed on charcoal. Curves for the liquid phase shown broken.*



Type III behaviour has been found in only two systems. The chloroform–acetone system is the only one of all the systems discussed in this paper in which the activity coefficient curves for the liquid phase cross at a value below 1. This behaviour in the liquid phase is attributed to strong intermolecular attraction amounting virtually to hydrogen-bond formation (see comments in ref. 4). It seems probable that the same phenomenon occurs in the adsorbed phase.

The ethylene dichloride–benzene system shows almost ideal behaviour in the liquid phase,[7] but it is generally believed that this is due to the partial cancellation of opposing

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[7] Sieg, Crutzen, and Jost, *Z. phys. Chem.*, 1951, **198**, *A*, 263.

factors.[8] In particular, there is evidence of weak association between the two substances.[9, 10] Comparison of the surface activity coefficient curves with those for the system chloroform–acetone suggests that such association may persist in the adsorbed layer.

It is possible that Type II and Type III curves are extreme forms of the same type of behaviour, for there are indications that the curves of Type II might cross if they were continued to higher mole-fractions. In this region, however, it becomes increasingly difficult to obtain results of the necessary accuracy, whether in adsorption or partial-pressure determinations. With this reservation, therefore, it is probably desirable to separate Type II and Type III behaviour. If the curves of Type II do cross, they do so only at one extreme of the concentration range. Curves of Type III, on the other hand, cross nearer the middle of the concentration range where the experimental data are much more accurate.

Two specific points may be made on the series in which close comparison is possible. The systems containing carbon tetrachloride and/or derivatives in which a methyl group replaces a chlorine atom have almost identical molecular size in each of the components, as the chlorine atom and the methyl group occupy almost the same volume. The results can be interpreted in terms of a greater affinity of the charcoal surface for the less polar methyl group (or even the hydrogen atom in the case of chloroform) than for the more polar chlorine atom (methylchloroform and chloroform are more strongly adsorbed than carbon tetrachloride), but this factor is clearly secondary in importance to that of volatility (*tert.*-butyl chloride is less strongly adsorbed than either carbon tetrachloride or methylchloroform, and is by far the most volatile of the three). This accords with the general experience that, other things being equal, the less volatile component of a mixture is usually the more strongly adsorbed at a charcoal surface. The same point has been made differently by Hirschler and Amon, who studied adsorption from mixed hydrocarbons on activated carbon and silica gel.[11] For a homologous series, increase in molecular weight was accompanied by increased ease of adsorption on carbon, but the reverse was found for silica gel. Increasing molecular weight in such a series brings about decreasing volatility, and we believe that the conclusion can be applied more widely in terms of the latter function. We hope to consider adsorption at oxide surfaces in a later paper.

The second comparison is the adsorption of benzene–*cyclo*hexane mixtures at the three solid surfaces. If allowance is made for the difference in surface area between the charcoal and the carbon black (as is done by considering surface mole-fractions and surface activity coefficients) their behaviour is almost identical (Fig. 5; cf. also Figs. 1 and 4 of this paper with Figs. 1 and 5 of ref. 4). We can conclude, therefore, that the porous nature of the charcoal does not modify adsorption for this system by comparison with that at a free surface. In this respect, it is interesting to compare the chemical nature of the surfaces. From the analyses (charcoal: C, 89·8; H, 1·3; ash, 3·1; O, 5·8%; carbon black: C, 95·2; H, 2·77; O, 1·09% [12]) it can be seen that the surfaces, allowance again being made for the fact that the hydrogen and oxygen are spread over a specific surface area about five times greater for the charcoal than for the carbon black, are comparable, though not identical. Both have appreciable quantities of hydrogen and oxygen chemisorbed on the surface, possibly covering a large fraction of the "carbon" surface.[13]

The sample of graphite shows very similar adsorption over most of the concentration range for this mixture, but departs from the other two adsorbents in showing slight preferential adsorption of *cyclo*hexane when it is present at low mole-fractions (Figs. 1

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[8] Glasstone, *Trans. Faraday Soc.*, 1937, **33**, 158.
[9] Staveley, Hart, and Tupman, *Discuss. Faraday Soc.*, 1953, **15**, 130.
[10] Stearn and Smyth, *J. Amer. Chem. Soc.*, 1934, **56**, 1667.
[11] Hirschler and Amon, *Ind. Eng. Chem.*, 1947, **39**, 1583.
[12] Smith and Schaeffer, *Proc. 2nd Rubber Techn. Conf.*, London, 1948.
[13] Kipling, *Quart. Reviews*, 1956, **10**, 1.

Benzene–cyclo*hexane–charcoal* (p_1° = 74·3; p_2° = 78·0).

x_1 (C_6H_6)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 (C_6H_6)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·025	2·20	1·00	0·254	0·217	1·31	0·60	1·12	1·18	0·837	0·800	2·90
0·05	1·94	1·00	0·411	0·235	1·61	0·70	1·07	1·27	0·876	0·854	3·08
0·10	1·66	1·00	0·503	0·330	1·81	0·80	1·03	1·39	0·916	0·896	3·32
0·20	1·42	1·01	0·620	0·460	2·14	0·90	1·00	1·58	0·953	0·946	3·36
0·30	1·32	1·03	0·690	0·574	2·33	0·95	1·00	1·69	0·976	0·973	3·54
0·40	1·23	1·07	0·752	0·655	2·58	0·975	1·00	1·79	—	—	—
0·50	1·17	1·12	0·795	0·733	2·74						

Monolayer values : benzene, 3·41 millimoles/g.; *cyclo*hexane, 2·64 millimoles/g.

Benzene–cyclo*hexane–Spheron* 6 (p_1° = 74·3; p_2° = 78·0).

x_1 (C_6H_6)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 (C_6H_6)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·025	2·20	1·00	0·248	0·222	1·30	0·50	1·17	1·12	0·869	0·671	4·29
0·05	1·94	1·00	0·328	0·296	1·41	0·60	1·12	1·18	0·908	0·738	5·14
0·10	1·66	1·00	0·482	0·344	1·74	0·70	1·07	1·27	0·940	0·796	6·36
0·20	1·42	1·01	0·630	0·452	2·18	0·80	1·03	1·39	0·962	0·853	7·34
0·30	1·32	1·03	0·736	0·538	2·73	0·90	1·00	1·58	0·982	0·918	8·78
0·40	1·23	1·07	0·816	0·604	3·48	0·95	1·00	1·69	0·991	0·959	9·44

Monolayer values : benzene, 0·45 millimole/g.; *cyclo*hexane, 0·40 millimole/g.

Benzene–cyclo*hexane–graphite* (p_1° = 74·3; p_2° = 78·0).

x_1 (C_6H_6)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 (C_6H_6)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·025	2·20	1·00	0·165	0·333	1·17	0·60	1·12	1·18	0·835	0·802	2·87
0·05	1·94	1·00	0·282	0·344	1·32	0·70	1·07	1·27	0·865	0·865	2·83
0·10	1·66	1·00	0·432	0·384	1·58	0·80	1·03	1·39	0·889	0·924	2·51
0·20	1·42	1·01	0·587	0·485	1·95	0·90	1·00	1·58	0·912	0·989	1·80
0·30	1·32	1·03	0·689	0·575	2·32	0·95	1·00	1·69	0·940	1·01	1·41
0·40	1·23	1·07	0·757	0·651	2·63	0·975	1·00	1·79	0·953	1·02	0·93
0·50	1·17	1·12	0·804	0·725	2·87						

Monolayer values : benzene, 0·49 millimole/g.; *cyclo*hexane, 0·41 millimole/g.

Chloroform–carbon tetrachloride–charcoal (p_1° = 160·3; p_2° = 91·0).

x_1 ($CHCl_3$)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 ($CHCl_3$)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·05	1·07	1·00	0·199	0·268	1·19	0·50	1·05	1·02	0·660	0·794	1·50
0·10	1·08	1·00	0·296	0·365	1·28	0·60	1·03	1·05	0·731	0·850	1·56
0·20	1·08	1·01	0·410	0·524	1·36	0·70	1·02	1·07	0·800	0·894	1·61
0·30	1·06	1·02	0·502	0·631	1·43	0·80	1·01	1·11	0·868	0·931	1·68
0·40	1·05	1·02	0·583	0·719	1·47	0·90	1·01	1·12	0·935	0·968	1·72

Monolayer values : chloroform, 3·85 millimoles/g.; carbon tetrachloride, 2·93 millimoles/g.

1 : 1 : 1-*Trichloroethane* (*methylchloroform*)–tert.-*butyl chloride–charcoal*
(p_1° = 97·3; p_2° = 243·2).

x_1 ($CMeCl_3$)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 ($CMeCl_3$)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·10	1·25	1·00	0·265	0·472	1·22	0·60	1·05	1·02	0·817	0·770	2·24
0·20	1·13	1·01	0·464	0·487	1·50	0·70	1·03	1·03	0·876	0·826	2·51
0·30	1·11	1·01	0·584	0·572	1·70	0·80	1·02	1·04	0·917	0·891	2·51
0·40	1·09	1·01	0·671	0·647	1·85	0·90	1·01	1·05	0·958	0·952	2·50
0·50	1·07	1·01	0·748	0·714	2·01						

Monolayer values : methyl chloroform, 2·88 millimoles/g.; *tert.*-butyl chloride, 2·65 millimoles/g.

1 : 1 : 1-*Trichloroethane* (*methylchloroform*)–*carbon tetrachloride–charcoal*
(p_1° = 97·3; p_2° = 91·0).

x_1 ($CMeCl_3$)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 ($CMeCl_3$)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·10	1·11	1·00	0·162	0·685	1·08	0·60	1·01	1·05	0·617	0·985	1·09
0·20	1·07	1·01	0·277	0·773	1·12	0·70	1·00	1·06	0·700	1·00	1·06
0·30	1·04	1·02	0·369	0·845	1·13	0·80	1·00	1·07	0·790	1·01	1·02
0·40	1·03	1·03	0·453	0·907	1·13	0·90	1·00	1·10	0·890	1·01	1·00
0·50	1·02	1·04	0·534	0·957	1·12						

Monolayer values : methylchloroform, 2·88 millimoles/g.; carbon tetrachloride, 2·93 millimoles/g.

tert.-Butyl chloride–carbon tetrachloride–charcoal ($p_1^\circ = 243·2$; $p_2^\circ = 91·0$).

x_1 (Bu^{t}Cl)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 (Bu^{t}Cl)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·025	1·596	1·00	0·041	0·973	1·02	0·50	1·07	1·22	0·295	1·81	0·865
0·05	1·316	1·01	0·062	1·06	1·02	0·60	1·05	1·28	0·361	1·74	0·803
0·075	1·288	1·01	0·099	0·977	1·03	0·70	1·04	1·29	0·455	1·60	0·708
0·10	1·25	1·02	0·103	1·21	1·02	0·80	1·02	1·33	0·570	1·44	0·621
0·20	1·19	1·04	0·145	1·64	0·977	0·90	1·01	1·41	0·736	1·24	0·534
0·30	1·14	1·08	0·191	1·80	0·937	0·95	1·00	1·582	0·853	1·11	0·538
0·40	1·10	1·14	0·241	1·83	0·904						

Monolayer values: *tert.*-butyl chloride, 2·65 millimoles/g.; carbon tetrachloride, 2·93 millimoles/g.

Chloroform–acetone–charcoal ($p_1^\circ = 160·3$; $p_2^\circ = 185·5$).

x_1 ($CHCl_3$)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 ($CHCl_3$)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·05	0·460	0·996	0·084	0·274	1·03	0·60	0·818	0·708	0·660	0·744	0·83
0·10	0·490	0·992	0·148	0·331	1·05	0·70	0·894	0·610	0·747	0·838	0·72
0·20	0·545	0·973	0·267	0·408	1·06	0·80	0·959	0·510	0·827	0·927	0·59
0·30	0·593	0·940	0·369	0·482	1·04	0·90	0·989	0·400	0·9065	0·982	0·43
0·40	0·655	0·885	0·470	0·557	1·00	0·975	0·998	0·300	0·971	1·002	0·26
0·50	0·728	0·806	0·567	0·642	0·93						

Monolayer values: chloroform, 3·85 millimoles/g.; acetone, 4·18 millimoles/g.

Ethylene dichloride–benzene–charcoal * ($p_1^\circ = 61·0$; $p_2^\circ = 74·3$).

x_1 ($C_2H_4Cl_2$)	x_1^s	f_1^s	f_2^s	x_1 ($C_2H_4Cl_2$)	x_1^s	f_1^s	f_2^s	x_1 ($C_2H_4Cl_2$)	x_1^s	f_1^s	f_2^s
0·05	0·086	0·581	1·039	0·40	0·402	0·995	1·003	0·80	0·693	1·151	0·656
0·10	0·145	0·690	1·053	0·50	0·471	1·062	0·945	0·90	0·797	1·129	0·493
0·20	0·245	0·816	1·060	0·60	0·540	1·111	0·870	0·95	0·867	1·096	0·376
0·30	0·329	0·912	1·043	0·70	0·613	1·142	0·775				

* $x_1 = a_1$; $f_1 = f_2 = 1$.
Monolayer values: ethylene dichloride, 3·91 millimoles/g.; benzene, 3·41 millimoles/g.

Methyl acetate–benzene–charcoal ($p_1^\circ = 168·4$; $p_2^\circ = 74·3$).

x_1 (MeOAc)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 (MeOAc)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·10	1·42	1·07	0·124	1·15	1·09	0·60	1·13	1·38	0·418	1·62	0·95
0·20	1·43	1·14	0·173	1·65	1·10	0·70	1·08	1·40	0·498	1·52	0·84
0·30	1·35	1·20	0·225	1·80	1·09	0·80	1·05	1·42	0·597	1·41	0·71
0·40	1·27	1·26	0·281	1·80	1·05	0·90	1·02	1·46	0·735	1·25	0·55
0·50	1·20	1·31	0·348	1·72	1·01	0·95	1·01	1·56	0·846	1·14	0·51

Monolayer values: methyl acetate, 3·98 millimoles/g.; benzene, 3·41 millimoles/g.

Ethyl alcohol–benzene–charcoal ($p_1^\circ = 44·7$; $p_2^\circ = 74·3$).

x_1 (EtOH)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 (EtOH)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·025	11·4	—	0·103	2·76	—	0·60	1·26	2·05	0·263	2·87	1·11
0·05	8·28	1·04	0·138	3·00	1·15	0·70	1·12	2·43	0·301	2·61	1·04
0·10	4·97	1·08	0·178	2·79	1·19	0·80	1·05	2·85	0·379	2·22	0·919
0·20	2·87	1·20	0·203	2·82	1·21	0·90	1·02	3·66	0·534	1·72	0·785
0·30	2·10	1·33	0·219	2·88	1·19	0·95	1·01	4·18	0·701	1·37	0·699
0·40	1·69	1·51	0·230	2·95	1·18	0·975	1·00	4·48	0·840	1·17	0·700
0·50	1·45	1·74	0·241	3·01	1·15						

Monolayer values: ethyl alcohol, 5·34 millimoles/g.; benzene, 3·41 millimoles/g.

Butylamine–benzene–charcoal ($p_1^\circ = 68·2$; $p_2^\circ = 74·1$).

x_1 (Bu^{n}NH$_2$)	f_1	f_2	x_1^s	f_1^s	f_2^s	x_1 (Bu^{n}NH$_2$)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·05	1·23	1·01	0·362	0·170	1·49	0·50	1·12	1·07	0·717	0·784	1·89
0·10	1·17	1·02	0·465	0·252	1·72	0·60	1·11	1·11	0·775	0·857	1·98
0·20	1·16	1·03	0·547	0·425	1·82	0·70	1·09	1·17	0·832	0·919	2·10
0·30	1·14	1·04	0·602	0·568	1·84	0·80	1·08	1·25	0·888	0·969	2·24
0·40	1·12	1·06	0·658	0·684	1·85	0·90	1·05	1·42	0·947	0·997	2·54

Monolayer values: *n*-butylamine, 3·39 millimoles/g.; benzene, 3·41 millimoles/g.

Pyridine–ethyl alcohol–charcoal * ($p_1^\circ = 15·9$; $p_2^\circ = 44·2$).

x_1 (C_5H_5N) $= a_1$	x_1^s	f_1^s	f_2^s	x_1 (C_5H_5N) $= a_1$	x_1^s	f_1^s	f_2^s	x_1 (C_5H_5N) $= a_1$	x_1^s	f_1^s	f_2^s
0·05	0·231	0·216	1·24	0·40	0·614	0·651	1·55	0·80	0·858	0·932	1·41
0·10	0·320	0·313	1·32	0·50	0·683	0·732	1·58	0·90	0·919	0·979	1·23
0·20	0·443	0·451	1·44	0·60	0·745	0·805	1·57	0·95	0·956	0·994	1·14
0·30	0·538	0·558	1·51	0·70	0·802	0·873	1·51				

* $f_1 = f_2 = 1$.
Monolayer values: pyridine, 4·10 millimoles/g.; ethyl alcohol, 5·26 millimoles/g.

and 4). In this case, the solid surface is much more nearly pure carbon (C, 97·1; H, 0·53; ash, 1·75; O, 0·61% *).

Two general points may be made. In a theoretical study, Elton [14] predicted that few cases of U-shaped isotherms of concentration change ("complete preferential adsorption") would be found, most being S-shaped. Until a more representative set of data has been collected, it is too early to say how valid this generalisation is. Nevertheless, the U-shaped isotherm is claimed to be generally observed in adsorption on active carbon from mixtures of hydrocarbons,[11, 15] and we have found it for about one-third of the mixtures used in the present study. It would be valuable to have an explanation of this phenomenon in terms of the specific forces responsible for adsorption.

Comparison of the "escaping tendencies" from the surface and from the liquid phase shows no obvious correlations, except in the two cases mentioned above in which intermolecular attractive forces are thought to be predominant in the liquid phase. For the remaining systems, absolute volatility seems to be more important than relative volatility when other factors do not intervene; this has been found previously when mixtures of paraffins are adsorbed on charcoal.[16] For most systems, however, the forces acting between the surface and the adsorbate seem to over-ride all other considerations.

EXPERIMENTAL

The charcoal was the steam-activated coconut-shell charcoal, washed with water as described previously.[4] The carbon black was a sample of Spheron 6 provided by Godfrey L. Cabot, Inc. The graphite was a sample of synthetic graphite of surface area 120 m.^{2}/g., provided by Acheson Colloids Ltd.

Methods of measuring adsorption, in all cases at 20°, have already been described.[3–6] The interferometer was used for a number of the systems. Partial pressures were determined at 20° as before,[3] with the exception that taps were lubricated with a heavy "Fluorolube" fraction during work on the chlorinated compounds.

Adsorbates not previously discussed [3–6, 17] were purified as follows: Carbon tetrachloride was fractionally distilled; the sample used had n_D^{20} 1·4602, in agreement with figures quoted by Timmermans.[18] Methylchloroform was fractionally distilled; the fraction used had n_D^{20} 1·4380 (cf. 1·4379 given by Turkevich and Smyth [19]). *tert.*-Butyl chloride was washed with water, dried, and fractionally distilled; the sample used had n_D^{20} 1·3853 (cf. 1·3850 given by Hart and Simons,[20] 1·3856 by Vogel,[21] and 1·3859 by Kuschner, Crowe, and Smyth [22]). *n*-Butylamine was dried over sodium wire and fractionally distilled; the fraction used had n_D^{20} 1·4007 (cf. 1·4009 given by Vogel [23]).

Monolayer values for Spheron 6 and for graphite have been obtained from B.E.T. plots for the respective vapours. The monolayer values for benzene and *cyclo*hexane are in about the same ratio for these two adsorbents, the absolute values for graphite being slightly higher in accordance with its slightly higher surface area. These values are not, however, in accordance with the molecular areas given by Smith, Pierce, and Cordes,[24] which would require a higher adsorption of *cyclo*hexane than of benzene.

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