792. *Adsorption on Oxide Gels from Binary Liquid Mixtures:*
Some Activity Coefficients of Materials at Surfaces.

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Activity coefficients are presented for adsorption at surfaces from binary liquid mixtures on alumina, silica, and titania gels respectively. Two of the three types of behaviour observed with carbon adsorbents are again observed with oxide gels. The nature of adsorption is controlled mainly by the polar nature of the adsorbents, the gels being very similar to one another. As compared with carbon adsorbents they show a much greater discrimination between polar and non-polar liquids.

IN the study of adsorption by solids from liquids, the evaluation of surface activity coefficients for the adsorbates provides one way in which the adsorptive characteristics of the solids can be compared irrespective of their specific surface areas. If, moreover, these coefficients are compared with the activity coefficients for the same components in the bulk liquid, a qualitative indication is obtained of the importance of the forces acting between solid and liquid compared with those between liquid and liquid.

Elton [1] discussed pairs of completely miscible liquids. Subsequently, data were presented for adsorption from a range of liquid mixtures on carbon adsorbents.[2] Three types of behaviour were found, as shown by the curves of surface activity coefficient against composition of the surface phase: Type I, in which the curves showed no inflexion; Type II, in which an inflexion was shown; Type III, in which the curves were clearly shown to cross. The relationship between these curves and the other adsorption data (isotherms of concentration change and individual adsorption isotherms) was pointed out.

We now record the corresponding results for adsorption on the more polar surfaces of alumina, silica gel, and titania gel. As previously,[2] $f_1 = a_1/x_1$ 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 surface phases respectively, a_1 and $a_1{}^s$ are the corresponding activities, and x_1 and $x_1{}^s$ are the corresponding mole fractions. The adsorption measurements which lead to values of x_1 and x_2 have been published.[3-5] Values for a_1 and a_2 are obtained from vapour-pressure data; those which have not been published previously are incorporated in the Tables. With the convention used previously, $a_1 = a_1{}^s$, and values for $f_1{}^s$ and $f_2{}^s$ can therefore readily be calculated.

[1] Elton, *J.*, 1954, 3813.
[2] Blackburn, Kipling, and Tester, *J.*, 1957, 2373.
[3] Kipling and Peakall, *J.*, 1956, 4828; 1957, 4054; 1958, 184.
[4] *Idem, J.*, 1957, 834.
[5] Allen, Lingo, and Felsing, *J. Phys. Chem.*, 1939, **43**, 425.

Benzene–cyclohexane–boehmite (Type II)

x_1 (C_6H_6)	x_1^s	f_1^s	f_2^s
0·10	0·457	0·363	1·66
0·20	0·605	0·471	2·05
0·30	0·713	0·555	2·52
0·40	0·795	0·620	3·12
0·50	0·846	0·689	3·65
0·60	0·878	0·763	3·88
0·70	0·902	0·829	3·90
0·80	0·925	0·887	3·72
0·90	0·949	0·950	3·10

Ethylene dichloride–benzene–boehmite (Type I)

x_1 ($C_2H_4Cl_2$)	x_1^s	f_1^s	f_2^s
0·10	0·252	0·397	1·20
0·20	0·433	0·462	1·41
0·30	0·578	0·519	1·66
0·40	0·681	0·587	1·88
0·50	0·768	0·651	2·16
0·60	0·832	0·721	2·38
0·70	0·892	0·785	2·78
0·80	0·929	0·861	2·82
0·90	0·968	0·930	3·13

Methyl acetate–benzene–boehmite (Type I)

x_1 (MeOAc)	x_1^s	f_1^s	f_2^s
0·10	0·529	0·268	2·04
0·20	0·665	0·430	2·72
0·30	0·760	0·534	3·67
0·40	0·828	0·612	4·40
0·50	0·878	0·682	5·39
0·60	0·913	0·742	6·33
0·70	0·942	0·805	7·26
0·80	0·966	0·871	8·38
0·90	0·982	0·939	9·94

Chloroform–benzene–boehmite ($p_1° = 159·6$; $p_2° = 74·1$) (Type I)

x_1 ($CHCl_3$)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·10	0·93	1·00	0·271	0·343	1·23
0·20	0·94	1·00	0·488	0·383	1·56
0·30	0·95	1·00	0·642	0·445	1·94
0·40	1·00	0·99	0·749	0·534	2·37
0·50	0·98	0·98	0·822	0·599	2·76
0·60	0·99	0·95	0·878	0·677	3·10
0·70	1·00	0·97	0·923	0·757	3·49
0·80	1·00	0·86	0·957	0·836	3·98
0·90	1·00	0·81	0·984	0·916	4·94

n-Butyl alcohol–benzene–boehmite (Type II)

x_1 (Bu^nOH)	f_1	f_2	x_1^s	x_2^s	f_1^s	f_2^s
0·10	3·57	1·06	0·707	0·293	0·505	3·25
0·20	3·11	1·13	0·720	0·280	0·862	3·23
0·30	2·59	1·23	0·730	0·270	1·06	3·19
0·40	2·02	1·35	0·730	0·270	1·11	3·01
0·50	1·71	1·53	0·740	0·260	1·15	2·95
0·60	1·42	1·75	0·750	0·250	1·14	2·80
0·70	1·24	2·02	0·773	0·227	1·13	2·67
0·80	1·12	2·42	0·773	0·227	1·17	2·13
0·90	1·04	2·88	0·804	0·196	1·16	1·47

Methyl acetate–ethylene dichloride–boehmite * ($p_1° = 168·4$; $p_2° = 61·0$) (Type I)

x_1 (MeOAc)	x_1^s	f_1^s	f_2^s
0·10	0·543	0·184	1·97
0·20	0·667	0·300	2·40
0·30	0·751	0·400	2·81
0·40	0·816	0·490	3·27
0·50	0·869	0·575	3·82
0·60	0·910	0·659	4·45
0·70	0·946	0·740	5·52
0·80	0·971	0·824	6·94
0·90	0·990	0·910	9·52

* $x_1 = a_1$; $f_1 = f_2 = 1$

n-Butylamine–benzene–boehmite (Type II)

x_1 (Bu^nNH_2)	x_1^s	f_1^s	f_2^s
0·10	0·536	0·218	1·97
0·20	0·636	0·365	2·27
0·30	0·694	0·493	2·39
0·40	0·740	0·608	2·44
0·50	0·776	0·728	2·39
0·60	0·810	0·820	2·34
0·70	0·827	0·924	2·04
0·80	0·843	1·02	1·60
0·90	0·868	1·09	1·08

Ethylene dichloride–benzene–γ-Al$_2$O$_3$ (Type I)

x_1 ($C_2H_4Cl_2$)	x_1^s	f_1^s	f_2^s
0·10	0·187	0·535	1·11
0·20	0·357	0·560	1·24
0·30	0·511	0·587	1·43
0·40	0·645	0·620	1·69
0·50	0·739	0·677	1·92
0·60	0·815	0·736	2·16
0·70	0·876	0·799	2·42
0·80	0·923	0·867	2·60
0·90	0·965	0·933	2·86

Ethyl alcohol–benzene–γ-Al$_2$O$_3$ (Type I)

x_1 (EtOH)	x_1^s	f_1^s	f_2^s
0·10	0·703	0·707	3·29
0·20	0·756	0·758	3·92
0·30	0·759	0·832	3·87
0·40	0·788	0·860	4·28
0·50	0·800	0·905	4·36
0·60	0·807	0·934	4·25
0·70	0·836	0·939	4·44
0·80	0·856	0·985	5·35
0·90	0·931	0·985	5·31

n-Butyl alcohol–benzene–γ-Al$_2$O$_3$ (Type I)

x_1 (Bu^nOH)	x_1^s	f_1^s	f_2^s
0·10	0·667	0·535	2·86
0·20	0·768	0·809	3·89
0·30	0·814	0·950	4·62
0·40	0·845	0·955	5·24
0·50	0·861	0·992	5·52
0·60	0·875	0·976	5·59
0·70	0·919	0·947	7·48
0·80	0·932	0·967	7·10
0·90	0·960	0·971	7·20

n-Butylamine–benzene–γ-Al$_2$O$_3$ (Type II)

x_1 (Bu^nNH_2)	x_1^s	f_1^s	f_2^s
0·10	0·500	0·234	1·83
0·20	0·600	0·387	2·06
0·30	0·637	0·537	2·01
0·40	0·662	0·680	1·88
0·50	0·675	0·833	1·65
0·60	0·700	0·949	1·48
0·70	0·725	1·10	1·28
0·80	0·753	1·14	1·02
0·90	0·787	1·20	1·18

n-Butyl alcohol–benzene–γ-Al(OH)$_3$ (Type I)

x_1 (Bu^nOH)	x_1^s	f_1^s	f_2^s
0·10	0·741	0·482	3·68
0·20	0·756	0·821	3·70
0·30	0·771	1·01	3·75
0·40	0·780	1·03	3·69
0·50	0·803	1·06	3·89
0·60	0·832	1·03	4·16
0·70	0·875	0·99	4·85
0·80	0·925	0·97	6·44
0·90	0·966	0·96	8·32

Ethylene dichloride–benzene–silica gel (Type I)

x_1 ($C_2H_4Cl_2$)	x_1^s	f_1^s	f_2^s
0·10	0·158	0·633	1·07
0·20	0·295	0·678	1·13
0·30	0·417	0·719	1·20
0·40	0·524	0·763	1·26
0·50	0·621	0·805	1·32
0·60	0·707	0·849	1·37
0·70	0·786	0·891	1·40
0·80	0·861	0·929	1·44
0·90	0·934	0·964	1·50

Methyl acetate–benzene–silica gel (Type I)

x_1 (MeOAc)	x_1^s	f_1^s	f_2^s
0·10	0·548	0·259	2·12
0·20	0·662	0·432	2·70
0·30	0·762	0·533	3·54
0·40	0·835	0·607	4·58
0·50	0·886	0·676	5·76
0·60	0·920	0·736	6·89
0·70	0·945	0·802	7·63
0·80	0·962	0·874	7·60
0·90	0·982	0·939	8·02

n-*Butylamine–benzene–silica gel*
(*Type I*)   **Pyridine–cyclohexane–silica gel (*Type I*)**

x_1 (Bu^nNH_2)	x_1^s	f_1^s	f_2^s	x_1 (C_5H_5N)	f_1	f_2	x_1^s	f_1^s	f_2^s
0·10	0·635	0·184	2·51	0·10	3·29	1·01	0·824	0·399	5·16
0·20	0·701	0·331	2·76	0·20	2·63	1·07	0·892	0·589	7·90
0·30	0·743	0·460	2·84	0·30	2·09	1·18	0·920	0·682	10·3
0·40	0·781	0·576	2·89	0·40	1·76	1·32	0·931	0·755	11·5
0·50	0·818	0·687	2·94	0·50	1·54	1·53	0·939	0·822	12·5
0·60	0·854	0·778	3·05	0·60	1·32	1·79	0·944	0·838	12·8
0·70	0·885	0·863	3·06	0·70	1·18	2·14	0·959	0·858	15·7
0·80	0·919	0·936	3·10	0·80	1·07	2·56	0·970	0·882	17·0
0·90	0·956	0·987	3·23	0·90	1·01	3·17	0·979	0·924	15·1

Ethylene dichloride–benzene–titania gel (*Type I*)

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
0·10	0·208	0·481	1·14	0·40	0·648	0·617	1·70	0·70	0·914	0·766	3·49
0·20	0·357	0·560	1·24	0·50	0·765	0·654	2·13	0·80	0·957	0·836	4·65
0·30	0·517	0·580	1·45	0·60	0·852	0·704	2·70	0·90	0·983	0·916	5·88

DISCUSSION

Representative data are shown in the Figures, in which surface activity coefficients are plotted against *surface* mole fractions; further data are tabulated. The data fall into two of the three types which were noted previously. For systems which are free from chemisorption, Type I is the commonest, whereas for carbon surfaces Type II was the commonest. The extent to which the two types of surface have been compared is limited, in part, by reaction of some substances with or at the gel surface. Nevertheless, the results reflect the ability of the more polar surfaces of the gels to interact more strongly with polar liquids than can carbon, whereas both types of solid will interact relatively weakly with the less polar liquids. Usually the oxide gels adsorb one liquid preferentially at all concentrations, whereas the carbons show opposite preferences at the two ends of the concentration range. The greater discriminating power of the gels is further shown by the higher values to which they give rise for the surface activity coefficients of the less strongly adsorbed component than for adsorption on carbons.

These features are well illustrated by the system methyl acetate–benzene (Fig. 1). With charcoal the system gives Type II curves, the more volatile methyl acetate having a higher surface activity coefficient over most of the concentration range. Methyl acetate thus does not interact with the charcoal surface sufficiently strongly to overcome the effect of its greater volatility with respect to benzene. Boehmite, however, can interact with the polar centre in the methyl acetate molecule strongly enough to adsorb it preferentially from all mixtures with benzene, as it can with methyl acetate–ethylene dichloride. Ethylene dichloride is itself more strongly held than benzene (presumably owing to polarisation of the chlorine atoms) but boehmite still discriminates very sharply between methyl acetate and ethylene dichloride when it is brought into contact with mixtures of the two.

The system ethylene dichloride–benzene has been examined with nearly all of the adsorbents we have studied. With charcoal it gives the rather rare Type III behaviour. With all the gels it gives Type I behaviour, ethylene dichloride being the more strongly adsorbed component. The behaviour of this system is very similar with all the gels, which are differentiated only by the values of the surface-activity coefficients; boehmite and γ-alumina appear as more " active " solids than silica and titania gels.

For the system benzene–*cyclo*hexane, in which the difference in polar character between the two liquids is less, the differences in behaviour between the two types of solid are much less. Although Type I behaviour is found with charcoal, Type II behaviour is found with both graphite [2] and boehmite (Fig. 2).

The chemical reactions which take place at the surface of the gels with a number of the most polar liquids include the catalysed decomposition of some potential adsorbates (*e.g.*,

FIG. 1. *Surface-activity coefficient curves for mixtures of methyl acetate and benzene adsorbed on (a) charcoal and (b) boehmite.*
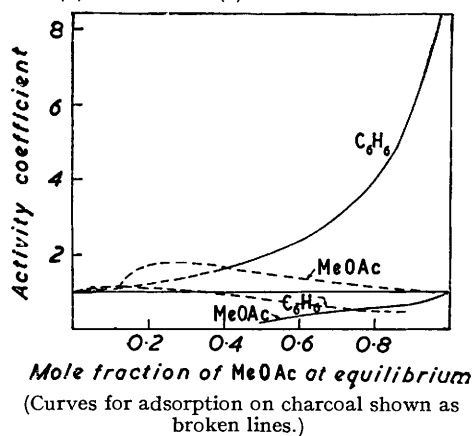
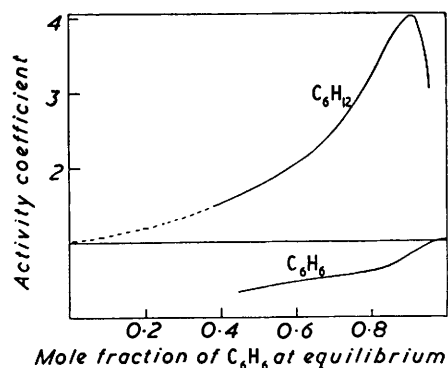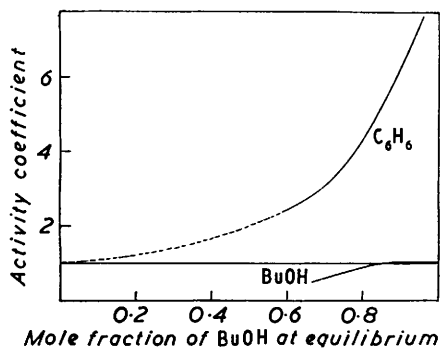FIG. 2. *Surface-activity coefficient curves for mixtures of benzene and* cyclo*hexane adsorbed on boehmite.*

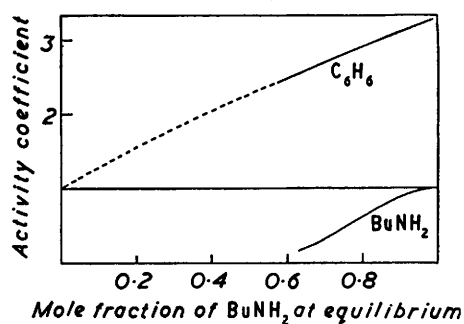(Curves for adsorption on charcoal shown as broken lines.)

FIG. 3a.

FIG. 3b.

FIG. 3. *Surface activity coefficient curves for (a) mixtures of* n-butyl alcohol and benzene adsorbed on γ-Al_2O_3, *(b) mixtures of* n-butylamine and benzene adsorbed on silica gel.
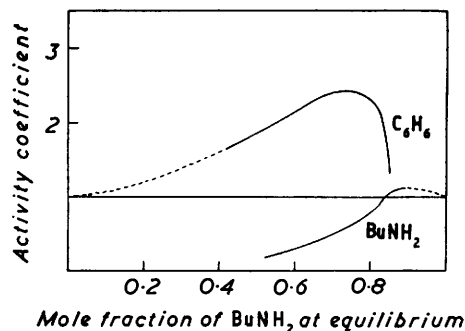
FIG. 4a.
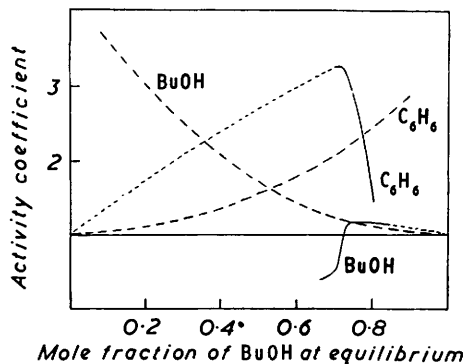
FIG. 4b.

FIG. 4. *Surface activity coefficient curves for (a) mixtures of* n-butyl alcohol and benzene adsorbed on boehmite *(curves for activity coefficients for the liquid phase against liquid phase composition are shown as broken lines), (b) mixtures of* n-butylamine and benzene adsorbed on boehmite.

acetone and *tert.*-butyl chloride in contact with boehmite), the dissolution of boehmite by the lower fatty acids, and the chemisorption of the lower alcohols by oxide groups at the surface.[4] In the last case, physical adsorption of the alcohols from mixtures with benzene may occur on the surface which has been modified by chemisorption. Even on the modified surface the adsorption of the alcohols is so strong that it is difficult to evaluate surface activity coefficients over any considerable range of surface mole fraction, and in the small range available the accuracy is not high. To a less extent, the same applies to adsorption from mixture of nitrogenous bases with hydrocarbons. Nevertheless, from the systems most favourable for calculations, there are indications that both Type I (ethyl alcohol–benzene–γ-Al_2O_3, Fig. 3*a*; *n*-butylamine–benzene–silica gel, Fig. 3*b*) and Type II (*n*-butyl alcohol–benzene–boehmite, Fig. 4*a*; *n*-butylamine–benzene–boehmite, Fig. 4*b*) curves are found.

Two general conclusions may be drawn. When there is no chemisorption, physical adsorption from a given mixture is very similar on all the gels. Furthermore, absolute volatility, which was found in some cases to be important in determining the nature of preferential adsorption on carbon surfaces, has not been found to be important in adsorption on the gels. In all cases the polar nature of the adsorbates is of greater importance, and leads to Type I behaviour in most cases. When the surface is modified by chemisorption, so that it becomes somewhat less polar (chemisorption of alcohols leaves a number of free hydroxyl groups [4]), Type II behaviour is more often observed. This may reflect the dual nature of the surface, part of which is still polar and the remainder non-polar where alkyl groups are bonded to it. Type III behaviour, in which the interaction at the surface is so non-specific that it is of less consequence than interaction between the two components of the liquid, has not yet been observed with these gels.

EXPERIMENTAL

The adsorption [3] and most of the activity data for the bulk liquids have been published.[2] The remainder have been determined from our vapour-pressure data, with the exception of those for the system *n*-butyl alcohol–benzene; for this system we used data [5] for 25°, which therefore apply only approximately to the adsorption data, which were obtained at 20°.