

944. *Adsorption from Binary Liquid Mixtures on Activated Alumina.*

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Data for physical adsorption from binary mixtures of completely miscible liquids by different types of alumina are analysed to give the isotherms for the individual components. For a group of relatively non-polar organic liquids these can most reasonably be interpreted in terms of unimolecular adsorption. From mixtures of benzene and an aliphatic alcohol, however, the alcohol is slowly chemisorbed at 20° by the surface oxide groups to give an "alkylated" surface. Subsequent physical adsorption on this surface can be analysed and interpreted in the same way as that of the non-polar substances on the original surface of the alumina.

THEORIES of physical adsorption from solution have been developed largely with reference to carbon adsorbents, which have also been widely used in the practical applications of this type of adsorption. The growing importance of activated alumina, especially in chromatographic techniques, suggested that the application of current theories of adsorption to such oxide adsorbents should be considered.

Elton¹ has suggested on theoretical grounds that *selective* adsorption in this type of system is unimolecular, *i.e.*, that the adsorbed layer at the solid-liquid interface, which has a different composition from that of the bulk liquid phase, is only one molecule thick. This concept can be expressed in the equation :

$$n_1^s/(n_1)_m + n_2^s/(n_2)_m = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n_1^s and n_2^s are the numbers of moles of components 1 and 2, respectively, adsorbed per g. of solid, and $(n_1)_m$ and $(n_2)_m$ are the monolayer values obtained for their separate vapour isotherms. The equation is valid only if the same area of surface is available to both components.

Equation (1) has been confirmed experimentally for a carbon adsorbent by comparing

¹ Elton, *J.*, 1951, 2598

the adsorption isotherms which it gives for the individual components with those obtained from the corresponding saturated vapours.^{2,3} We have now used it for analysing data obtained with alumina as the adsorbent, with a view to comparing the individual isotherms for adsorption on alumina with those for adsorption on carbon. In particular, these isotherms would be expected to throw further light on the opposite affinities shown by oxide adsorbents as compared with charcoals. Thus Bartell and his collaborators have shown that silica gel adsorbs ethyl alcohol preferentially from mixtures with benzene,⁴ whereas charcoals adsorb benzene preferentially from these mixtures.⁵ This follows from the shape of the isotherms of concentration change, and, for adsorption by charcoal, even more clearly from the individual adsorption isotherms.² In attempting to obtain the corresponding individual isotherms for adsorption on alumina, we discovered that adsorption is more complex for this system than had previously been recognised.

We may point out that the term "alumina" is used loosely to cover a range of materials of composition between Al_2O_3 and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Our use of this range of materials is important not only for its possible practical implications, but also because there are phases of well-defined composition which can be recognised crystallographically. Most of the present work has been done with boehmite, the so-called monohydrate, $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\gamma\text{-AlO} \cdot \text{OH}$.^{*} We have also used (a) the anhydrous oxide, $\gamma\text{-Al}_2\text{O}_3$, to provide information about the behaviour of a surface containing oxide but no hydroxide groups, (b) a material (referred to below as "gibbsite-type material") with a surface similar to that of gibbsite, $\gamma\text{-Al}(\text{OH})_3$, containing hydroxide but no oxide groups,[†] and (c) samples of boehmite and $\gamma\text{-Al}_2\text{O}_3$ treated with alcohols so as to modify their surfaces.

DISCUSSION

Boehmite.—Fig. 1 shows the isotherms of concentration change for some of the systems investigated. They were analysed in terms of equation (1). For a group of relatively non-polar adsorbates, it gives individual isotherms of the general shape familiar for carbon adsorbents. The data are given in Table 1, with typical curves illustrated in Fig. 2.

Equation (1) expresses the concept of unimolecular adsorption for this type of system, but could also give a reasonable analysis into individual isotherms in some cases of multilayer adsorption. In the work on charcoal, the results were interpreted in terms of unimolecular adsorption. Indeed, the pores of the charcoal were so fine that, in most cases, the adsorbed layer could not greatly exceed a monolayer. In spite of this, Hansen and Hansen⁶ proposed a "pore-filling" mechanism as an alternative interpretation of the data. From the theoretical point of view it had the drawback of giving a less specific explanation of the nature of adsorption, and, in practical terms, failed when applied in a critical case.³

Activated alumina has much wider pores than this charcoal, and its adsorption of single vapours involves multilayer formation and probably capillary condensation. Consequently, equilibrium adsorption from mixed saturated vapours would not readily lend itself to interpretation of liquid-phase data for such an adsorbent. The question arises, however, whether selective adsorption (as the term is used above) in adsorption from liquid mixtures is still confined, as with charcoal, to one molecular layer, or can spread to more than one layer in the wider pores of alumina.

Equation (1) is most easily interpreted in terms of filling of a specified *area* rather than a (possibly) unspecified *volume* with two types of adsorbed molecule. There are, however, three lines of experimental evidence which support the unimolecular interpretation for

* In designating the phases of alumina there is some variation between British, American, and German practice.

† Gibbsite itself has not been prepared with a high surface area, and we have therefore worked on a material which approximates to a layer of gibbsite supported on boehmite.

² Kipling and Tester, *J.*, 1952, 4123.

³ Blackburn and Kipling, *J.*, 1954, 3819.

⁴ Bartell, Scheffler, and Sloan, *J. Amer. Chem. Soc.*, 1931, 53, 2501.

⁵ Bartell and Sloan, *ibid.*, 1929, 51, 1643.

⁶ Hansen and Hansen, *J. Colloid Sci.*, 1954, 9, 1.

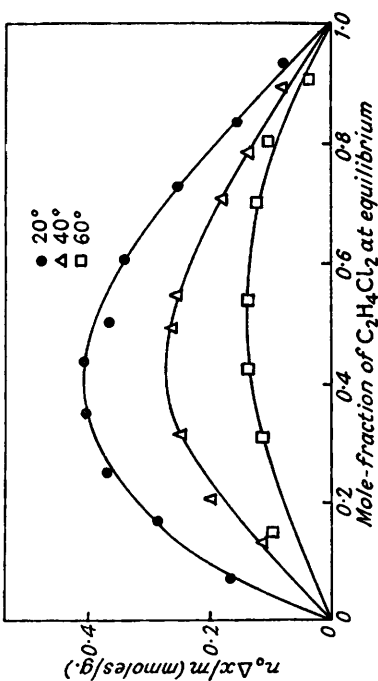


FIG. 1(a).
Fig. 1(b).

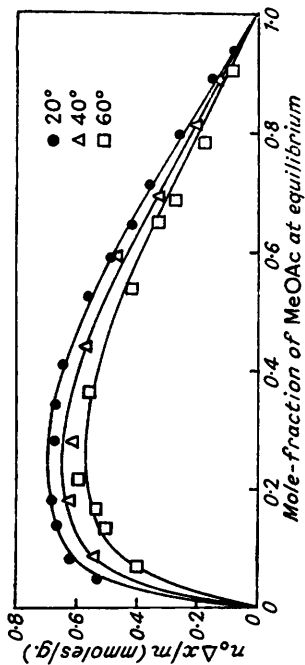


FIG. 1(c).
Fig. 1(d).

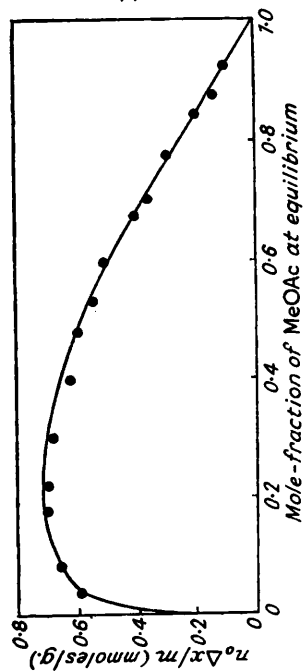
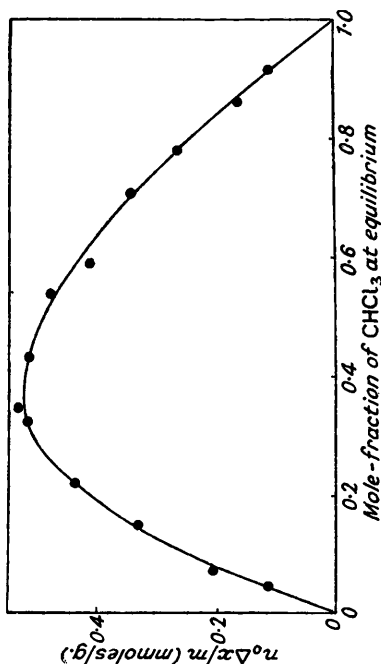
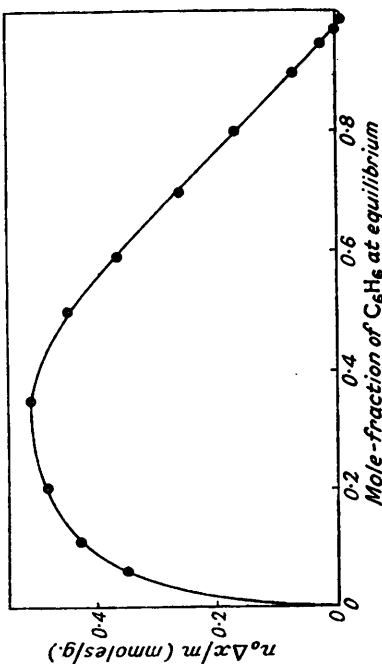


FIG. 1(e).

FIG. 1. Isotherms of concentration change for adsorption on boehmite from: (a) benzene-cyclohexane, (b) ethylene dichloride-benzene, (c) chloroform-benzene, (d) methyl acetate-benzene, (e) methyl acetate-ethylene dichloride.

this first group of adsorbates. In the simplest theory of multilayer adsorption of *single* vapours,⁷ it is assumed that the second and subsequent molecular layers are held by forces substantially equivalent to those operating in the bulk liquid (homogeneous or adsorbate-adsorbate forces), and significantly different from those holding the first layer (heterogeneous or adsorbent-adsorbate forces). This concept is now thought to be somewhat over-simplified, though as a first approximation it has been confirmed experimentally.

TABLE I. *Individual isotherms for adsorption on boehmite from various systems.**

(a) cycloHexane-benzene								
x (C_6H_6)	Adsorption (mmoles/g.) of :		x (C_6H_6)	Adsorption (mmoles/g.) of :		x (C_6H_6)	Adsorption (mmoles/g.) of :	
	C_6H_{12}	C_6H_6		C_6H_{12}	C_6H_6		C_6H_{12}	C_6H_6
0.0	0.99	0.00	0.4	0.26	1.01	0.8	0.10	1.24
0.1	0.62	0.52	0.5	0.20	1.10	0.9	0.07	1.30
0.2	0.47	0.72	0.6	0.16	1.15	1.0	0.00	1.37
0.3	0.35	0.88	0.7	0.13	1.20			
(b) Ethylene dichloride-benzene								
x ($C_2H_4Cl_2$)	Adsorption (mmoles/g.) of :		x ($C_2H_4Cl_2$)	Adsorption (mmoles/g.) of :		x ($C_2H_4Cl_2$)	Adsorption (mmoles/g.) of :	
	$C_2H_4Cl_2$	C_6H_6		$C_2H_4Cl_2$	C_6H_6		$C_2H_4Cl_2$	C_6H_6
0.0	0.00	1.37	0.4	0.98	0.46	0.8	1.37	0.11
0.1	0.35	1.04	0.5	1.12	0.34	0.9	1.43	0.05
0.2	0.61	0.90	0.6	1.22	0.25	1.0	1.48	0.00
0.3	0.83	0.60	0.7	1.31	0.16			
(c) Chloroform-benzene								
x ($CHCl_3$)	Adsorption (mmoles/g.) of :		x ($CHCl_3$)	Adsorption (mmoles/g.) of :		x ($CHCl_3$)	Adsorption (mmoles/g.) of :	
	$CHCl_3$	C_6H_6		$CHCl_3$	C_6H_6		$CHCl_3$	C_6H_6
0.0	0.00	1.37	0.4	1.11	0.37	0.8	1.46	0.07
0.1	0.38	1.03	0.5	1.23	0.27	0.9	1.50	0.03
0.2	0.70	0.74	0.6	1.33	0.18	1.0	1.53	0.00
0.3	0.94	0.53	0.7	1.40	0.12			
(d) Methyl acetate-benzene								
x ($MeOAc$)	Adsorption (mmoles/g.) of :		x ($MeOAc$)	Adsorption (mmoles/g.) of :		x ($MeOAc$)	Adsorption (mmoles/g.) of :	
	$MeOAc$	C_6H_6		$MeOAc$	C_6H_6		$MeOAc$	C_6H_6
0.0	0.00	1.37	0.4	1.24	0.26	0.8	1.47	0.05
0.1	0.77	0.68	0.5	1.32	0.18	0.9	1.50	0.03
0.2	0.98	0.49	0.6	1.38	0.13	1.0	1.53	0.00
0.3	1.13	0.36	0.7	1.43	0.09			
(e) Methyl acetate-ethylene dichloride								
x ($MeOAc$)	Adsorption (mmoles/g.) of :		x ($MeOAc$)	Adsorption (mmoles/g.) of :		x ($MeOAc$)	Adsorption (mmoles/g.) of :	
	$MeOAc$	$C_2H_4Cl_2$		$MeOAc$	$C_2H_4Cl_2$		$MeOAc$	$C_2H_4Cl_2$
0.0	0.00	1.48	0.4	1.24	0.28	0.8	1.48	0.04
0.1	0.82	0.69	0.5	1.32	0.20	0.9	1.51	0.02
0.2	1.00	0.50	0.6	1.39	0.14	1.0	1.53	0.00
0.3	1.14	0.38	0.7	1.44	0.08			

* In Tables 1-4, x is the mole-fraction of the constituent of the given formula in the liquid.

Thus the magnetic susceptibility of simple organic substances in the second and subsequent layers adsorbed on silica gel has been shown to be the same as that of the bulk liquid, though different from that of the first layer.⁸

If the same concept is applied to the adsorption of *mixtures* it would be expected that the first layer, held by heterogeneous forces, would have a different composition from that of the bulk liquid, whereas the second and subsequent layers, held by homogeneous forces, would have substantially the same composition as the bulk liquid. The second line of evidence confirms this. Cines and Ruehlen,⁹ in a study of the adsorption of mixed vapours

⁷ Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.

⁸ Milligan and Whitehurst, *J. Phys. Chem.*, 1952, **56**, 1073.

⁹ Cines and Ruehlen, *ibid.*, 1953, **57**, 710.

on silica gel, have shown that selective adsorption is vested almost entirely in the first molecular layer.

Thirdly, Bartell and Benner¹⁰ have calculated that the adsorbed layer at the interface between silica gel and mixtures of *isopentyl* alcohol and *isooctane* "need not be more than of unimolecular thickness."¹⁰ This study was accompanied by a study of the liquid-vapour interface, for which the same conclusion has long been held. By contrast, the only decisive evidence for multilayer formation at the liquid-solid interface is for adsorption from incompletely miscible substances, *e.g.*, adsorption on graphite from aqueous solutions of hexanoic and valeric acid.¹¹

For the first group of adsorbates, it seems reasonable to conclude that selective adsorption is, at least to a first approximation, confined to one molecular layer.

The isotherms of concentration change for a second group of adsorbates are shown in

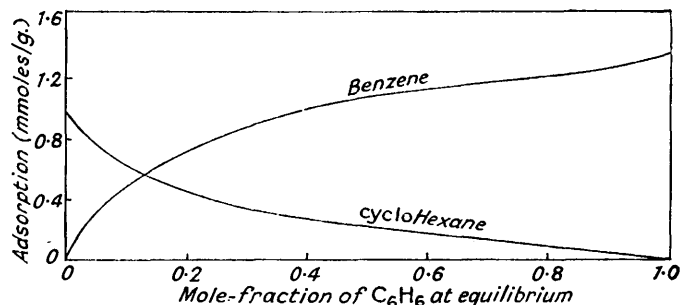


FIG. 2(a).

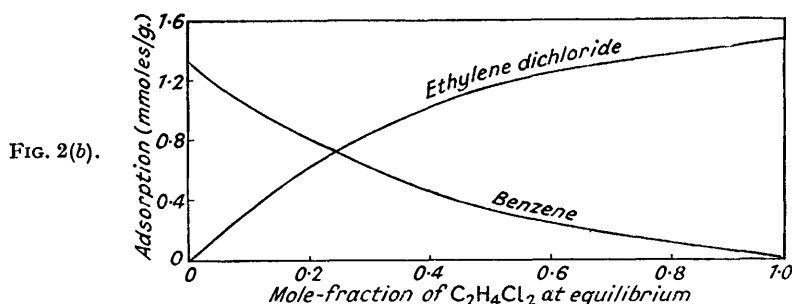


FIG. 2(b).

FIG. 2. Adsorption (individual isotherms) on boehmite from: (a) benzene-cyclohexane, (b) ethylene dichloride-benzene.

Fig. 3; each of these systems has an aliphatic alcohol as one component. These isotherms were obtained, as were those shown in Fig. 1, by shaking the adsorbent with the liquid mixtures for about 24 hours. Initially we assumed that monolayer values could be calculated from the vapour-phase isotherm for each component. It was found, however, that the maxima in the isotherms of concentration change corresponded, at the relevant concentrations, to adsorption of the respective alcohols greater than these "monolayer" values.

This is just the situation which would arise if the alcohol were adsorbed to a much greater extent than the benzene in each of several layers. It was therefore necessary to consider whether the results should be analysed in terms of the equations appropriate to multilayer formation or pore-filling.

Further experiments with boehmite, however, suggest a different explanation. In all previous experiments with this type of liquid system, adsorption equilibrium has been established well within 24 hours. For the systems containing an alcohol, however, a slow

¹⁰ Bartell and Benner, *J. Phys. Chem.*, 1942, **46**, 847.

¹¹ Hansen, Fu, and Bartell, *ibid.*, 1949, **53**, 769.

change continued over a much longer period (Fig. 4), and equilibrium could not be regarded as established until about 3 weeks had elapsed. This required a re-examination of the vapour-phase experiments, and it was found that the alcohols were slowly chemisorbed by boehmite at room temperature, and that the chemisorption appeared to take place at the oxide, but not at the hydroxide groups.¹² It therefore seems likely that chemisorption of alcohols similarly takes place in the liquid phase and that by the time equilibrium has been reached, the chemisorption has extended over the whole of the available surface to give an "alkylated" alumina surface. On this new surface physical adsorption of both benzene and alcohol can follow in the normal way and would be expected to extend for only one molecular layer beyond the chemisorbed material.

The dip in the curve of $n_0\Delta x/m$ against time before the final slow rise (Fig. 4)

FIG. 3. Isotherms of concentration change (after 1 day) for adsorption on boehmite from alcohol-benzene systems.

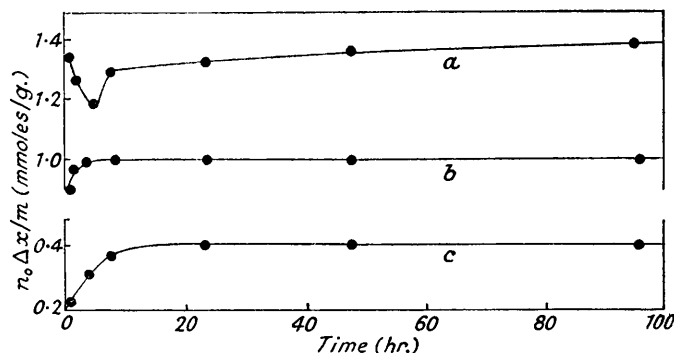
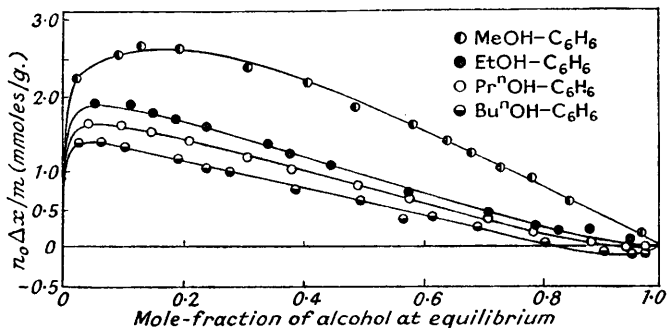


FIG. 4. Variation of concentration change with time: (a) ethyl alcohol-benzene on boehmite, at 0.318 mole-fraction of ethyl alcohol, (b) ethyl alcohol-benzene on gibbsite-type surface, at 0.322 mole-fraction of ethyl alcohol, (c) ethylene dichloride-benzene on boehmite, at 0.331 mole-fraction of ethylene dichloride.

is anomalous. It may result from displacement of some alcohol, initially physically adsorbed, as chemisorption proceeds; the ethyl alcohol molecule occupies a greater area when chemisorbed than when physically adsorbed.¹³

Three further observations, relating to periods shorter than are required for equilibrium with the liquid mixture to be established, support the assumption that the alcohol is in part chemisorbed. The concentration change is reduced by cooling the adsorbent during the addition of the liquid mixture, and thereby counteracting the rise in temperature due to liberation of the initial heat of adsorption. Such a rise in temperature would increase the rate of chemisorption as compared with that obtaining at the temperature of the thermostat bath (20°).

This effect of temperature has been confirmed by examining adsorption after 1 day at 20°, 40°, and 60°. For a system in which physical adsorption only takes place, there is, at the higher temperatures, an overall decrease in the preferential adsorption of the more

¹² Kipling and Peakall, *Research*, 1955, 8, S 31.

¹³ *Idem*, *J.*, in the press.

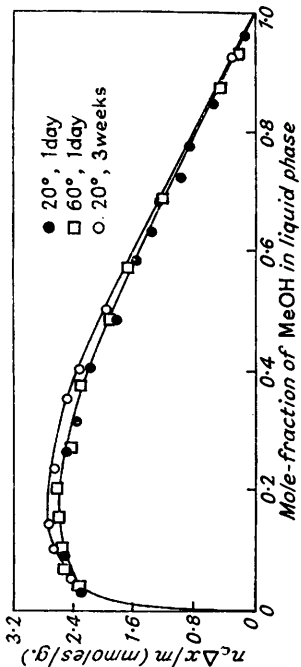


FIG. 5(a).
FIG. 5(b).

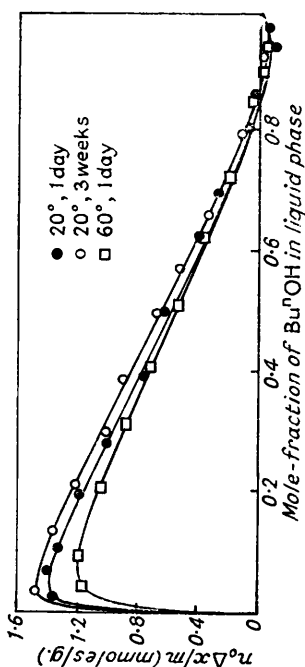


FIG. 5(d).

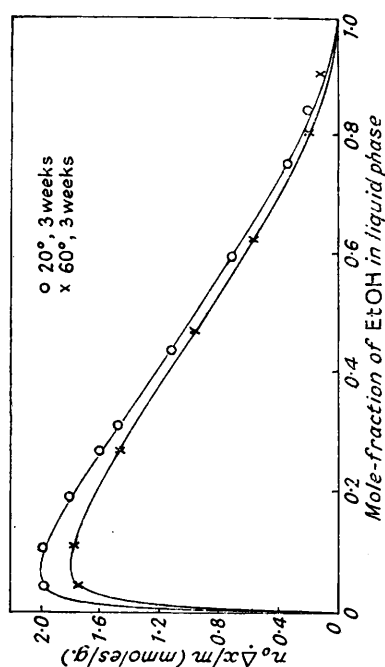


FIG. 5(e).

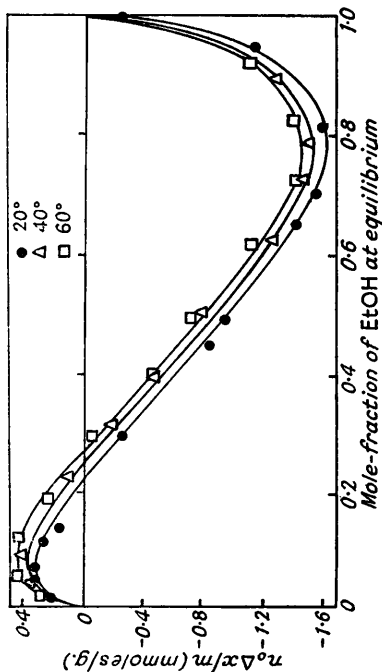


FIG. 5(c).

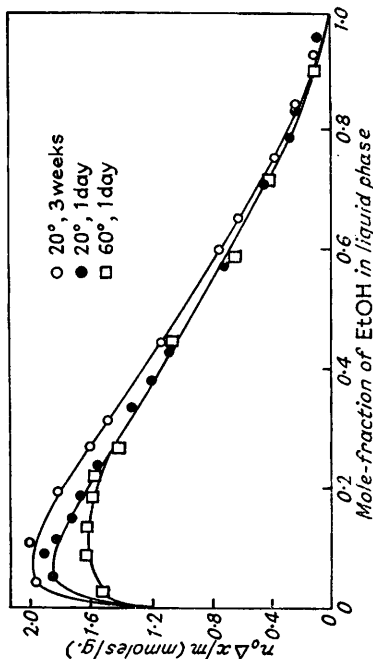


FIG. 5. Effects of time and temperature on isotherms of concentration change for adsorption from: (a) ethyl alcohol-benzene on charcoal, (b) methyl alcohol-benzene on boehmite, (c) ethyl alcohol-benzene on boehmite, (d) n-butyl alcohol-benzene on boehmite, (e) ethyl alcohol-benzene on boehmite.

strongly adsorbed component. Fig. 1(b) shows this for the system ethylene dichloride-benzene with boehmite; Fig. 5(a) shows the same effect for benzene-ethyl alcohol with charcoal. For the benzene-alcohol systems with boehmite, however, this effect is found over only part of the concentration range after 1 day's contact [Fig. 5(b)—(d)]. For the remainder, it seems that the decrease in the preferential physical adsorption has been offset by increased chemisorption. On the other hand, at equilibrium (3 weeks), the chemisorption should be the same at 20° and 60°, any difference in the isotherms at the two temperatures being due to change in physical adsorption alone and therefore extending over the whole of the concentration range. This is found in practice [Fig. 5(e)].

Similarly, if the system ethylene dichloride-benzene-boehmite is held for successive periods of a day at 20°, 60°, and 20°, the final position of equilibrium at 20° is the same as the original position at this temperature. With the system alcohol-benzene-boehmite, however, the effect of temperature is not reversible in this way as it should be for purely physical adsorption.

FIG. 6. Isotherms of concentration change for physical adsorption on "alkylated" boehmites.

Points = experimental results on "alkylated" samples; curves = calculated from results on untreated boehmite.

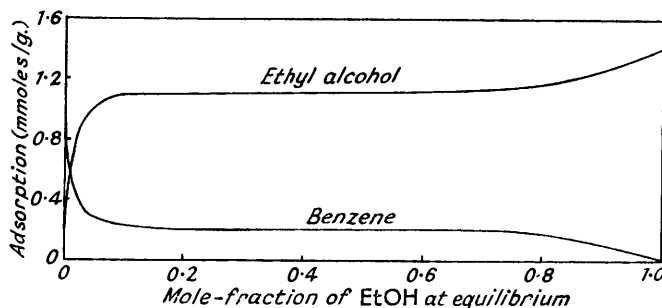
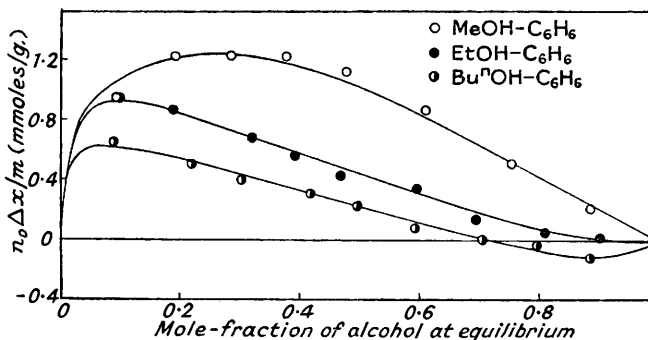


FIG. 7. Physical adsorption (individual isotherms) on "alkylated" boehmite from ethyl alcohol-benzene.

Any analysis of the isotherms of concentration change can only be attempted after both physical and chemical adsorption have been completed. The isotherms for this purpose were therefore determined after 3 weeks' contact between the adsorbent and the liquid mixtures (Fig. 5). The extent of chemisorption of the alcohols is known from the vapour-phase studies.¹² The effect of chemisorption on the liquid-phase adsorption can therefore be calculated and subtracted from the isotherms of concentration change to give the concentration changes due to physical adsorption only (Fig. 6).

The same separation into two stages has also been achieved experimentally. Boehmite was allowed to stand under pure ethyl alcohol for 3–4 weeks, so that the surface should become completely "ethylated" by chemisorption. The "ethylated" material, freed from excess of alcohol by evacuation, was then shaken with benzene-ethyl alcohol mixtures. Equilibrium was established in the time appropriate for physical adsorption, and the isotherm of concentration change for this stage was in agreement with that calculated by the above procedure (Fig. 6). Similar results were obtained with the other alcohols.

The curves in Fig. 6 can be analysed to show the physical adsorption of each component by using equation (1). For this purpose, it would be incorrect to use the "monolayer

values" derived from adsorption results on the untreated boehmite, as this adsorption was in part chemisorption. Instead, the adsorption of benzene vapour and of the appropriate alcohol vapour on each of the "alkylated" samples was measured and used to give monolayer values for physical adsorption. From these values, the individual isotherms for the liquid-phase adsorption were calculated (Table 2 and Fig. 7). These are of the normal

TABLE 2. Individual isotherms for physical adsorption on boehmite from various systems.

(a) Methyl alcohol-benzene								
x (MeOH)	Adsorption (mmoles/g.) of:		x (MeOH)	Adsorption (mmoles/g.) of:		x (MeOH)	Adsorption (mmoles/g.) of:	
	MeOH	C_6H_6		MeOH	C_6H_6		MeOH	C_6H_6
0.0	0.00	1.08	0.4	1.99	0.07	0.8	2.13	0.005
0.1	1.14	0.50	0.5	2.05	0.05	0.9	2.13	0.004
0.2	1.59	0.28	0.6	2.09	0.03	1.0	2.14	0.00
0.3	1.78	0.18	0.7	2.12	0.01			

(b) Ethyl alcohol-benzene								
x (EtOH)	Adsorption (mmoles/g.) of:		x (EtOH)	Adsorption (mmoles/g.) of:		x (EtOH)	Adsorption (mmoles/g.) of:	
	EtOH	C_6H_6		EtOH	C_6H_6		EtOH	C_6H_6
0.0	0.00	0.97	0.4	1.10	0.21	0.8	1.16	0.17
0.1	1.09	0.22	0.5	1.11	0.20	0.9	1.26	0.10
0.2	1.10	0.21	0.6	1.12	0.20	1.0	1.40	0.00
0.3	1.10	0.21	0.7	1.12	0.19			

(c) n-Butyl alcohol-benzene								
x (BuOH)	Adsorption (mmoles/g.) of:		x (BuOH)	Adsorption (mmoles/g.) of:		x (BuOH)	Adsorption (mmoles/g.) of:	
	BuOH	C_6H_6		BuOH	C_6H_6		BuOH	C_6H_6
0.0	0.00	0.82	0.4	0.73	0.27	0.8	0.78	0.23
0.1	0.70	0.29	0.5	0.74	0.26	0.9	0.82	0.20
0.2	0.72	0.28	0.6	0.75	0.25	0.95	0.95	0.10
0.3	0.73	0.27	0.7	0.78	0.23	1.0	1.08	0.00

type, and show that the alcohol is preferentially adsorbed on to the alkylated surface. This might well be expected, as the surface still contains accessible hydroxide groups, which inevitably show preference for adsorption of ethyl alcohol (see below), while the chemisorbed alkyl groups may well show a slight preference for aliphatic over aromatic compounds.

γ -Alumina. As chemisorption of alcohol vapours also occurs with anhydrous alumina,¹² the liquid-phase adsorption would be expected to be essentially similar to that described for boehmite. This is borne out by experiment. Adsorption from the less polar substances follows the normal pattern for physical adsorption (Fig. 8a). On the other hand, adsorption from systems containing an alcohol involves chemisorption. The same effects of time and temperature are observed [Fig. 8(b)—(d)], and again only physical adsorption appears to occur on alkylated surfaces. Individual isotherms of physical adsorption for these systems are of the normal type (Table 3).

Gibbsite-type material. Chemisorption of alcohols from the vapour phase does not occur on an alumina with a purely hydroxylic ("gibbsite") surface. Adsorption from liquid mixtures containing an alcohol was therefore studied and was found to show the characteristics of physical adsorption only. Equilibrium was rapidly established (Fig. 4), the effect of temperature was that expected for physical adsorption (Fig. 9), and the isotherms of concentration change could be analysed directly in terms of unimolecular selectivity. The individual isotherms thus obtained show that the surface has a strong preference for alcohol as compared with benzene (Table 4).

General.—Our results on physical adsorption have not proved that adsorption from the systems we have studied is unimolecular. In view of the existing evidence for this type of system, the successful analysis of our data in terms of equation (1) makes it highly likely that this is so. It is particularly significant that, even in the cases of simple physical

FIG. 8(a).

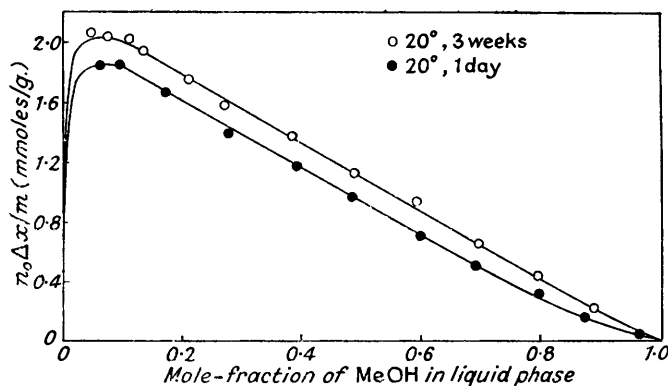
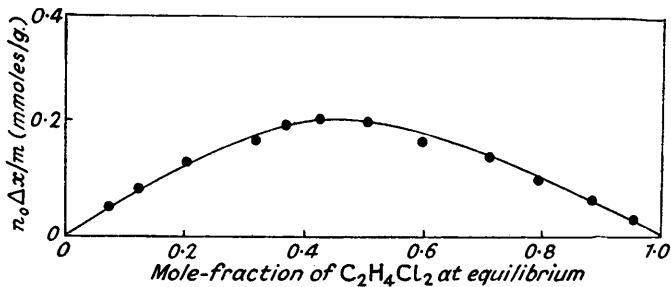


FIG. 8(b).

FIG. 8(c).

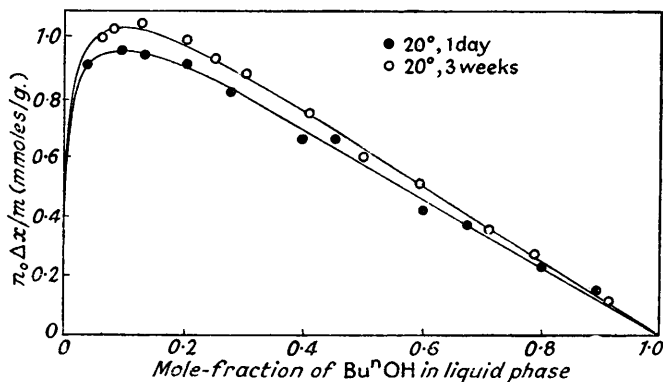
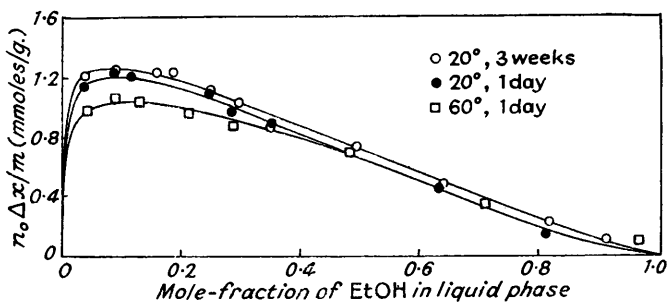


FIG. 8(d).

FIG. 8. Isotherms of concentration change for adsorption on $\gamma-Al_2O_3$ from : (a) ethylene dichloride-benzene, (b) methyl alcohol-benzene, (c) ethyl alcohol-benzene, (d) n-butyl alcohol-benzene.

TABLE 3. Individual isotherms for physical adsorption on γ -alumina from various systems.

(a) Ethylene dichloride-benzene								
x ($C_2H_4Cl_2$)	Adsorption (mmoles/g.) of:		x ($C_2H_4Cl_2$)	Adsorption (mmoles/g.) of:		x ($C_2H_4Cl_2$)	Adsorption (mmoles/g.) of:	
	$C_2H_4Cl_2$	C_6H_6		$C_2H_4Cl_2$	C_6H_6		$C_2H_4Cl_2$	C_6H_6
0.0	0.00	0.77	0.4	0.51	0.28	0.8	0.75	0.06
0.1	0.15	0.63	0.5	0.59	0.21	0.9	0.78	0.03
0.2	0.28	0.50	0.6	0.66	0.15	1.0	0.81	0.00
0.3	0.40	0.39	0.7	0.71	0.10			
(b) Methyl alcohol-benzene								
x (MeOH)	Adsorption (mmoles/g.) of:		x (MeOH)	Adsorption (mmoles/g.) of:		x (MeOH)	Adsorption (mmoles/g.) of:	
	MeOH	C_6H_6		MeOH	C_6H_6		MeOH	C_6H_6
0.0	0.00	0.71	0.4	0.89	0.29	0.8	1.19	0.15
0.1	0.80	0.33	0.5	0.92	0.27	0.9	1.30	0.09
0.2	0.82	0.32	0.6	1.00	0.22	1.0	1.49	0.00
0.3	0.86	0.30	0.7	1.09	0.19			
(c) Ethyl alcohol-benzene								
x (EtOH)	Adsorption (mmoles/g.) of:		x (EtOH)	Adsorption (mmoles/g.) of:		x (EtOH)	Adsorption (mmoles/g.) of:	
	EtOH	C_6H_6		EtOH	C_6H_6		EtOH	C_6H_6
0.0	0.00	0.57	0.4	0.68	0.16	0.8	0.74	0.12
0.1	0.63	0.19	0.5	0.69	0.15	0.9	0.83	0.07
0.2	0.63	0.19	0.6	0.71	0.14	1.0	0.95	0.00
0.3	0.67	0.16	0.7	0.72	0.14			
(d) n-Butyl alcohol-benzene								
x (BuOH)	Adsorption (mmoles/g.) of:		x (BuOH)	Adsorption (mmoles/g.) of:		x (BuOH)	Adsorption (mmoles/g.) of:	
	BuOH	C_6H_6		BuOH	C_6H_6		BuOH	C_6H_6
0.0	0.00	0.52	0.4	0.60	0.11	0.8	0.69	0.05
0.1	0.44	0.22	0.5	0.62	0.10	0.9	0.72	0.03
0.2	0.53	0.16	0.6	0.63	0.09	1.0	0.75	0.00
0.3	0.57	0.13	0.7	0.68	0.06			

TABLE 4. Individual isotherms for adsorption on "gibbsite" from various systems.

(a) Methyl alcohol-benzene								
x (MeOH)	Adsorption (mmoles/g.) of:		x (MeOH)	Adsorption (mmoles/g.) of:		x (MeOH)	Adsorption (mmoles/g.) of:	
	MeOH	C_6H_6		MeOH	C_6H_6		MeOH	C_6H_6
0.0	0.00	1.17	0.4	2.15	0.07	0.8	2.23	0.02
0.1	1.96	0.16	0.5	2.17	0.05	0.9	2.26	0.01
0.2	2.06	0.11	0.6	2.20	0.04	1.0	2.27	0.00
0.3	2.11	0.08	0.7	2.21	0.03			
(b) Ethyl alcohol-benzene								
x (EtOH)	Adsorption (mmoles/g.) of:		x (EtOH)	Adsorption (mmoles/g.) of:		x (EtOH)	Adsorption (mmoles/g.) of:	
	EtOH	C_6H_6		EtOH	C_6H_6		EtOH	C_6H_6
0.0	0.00	1.17	0.4	1.54	0.16	0.8	1.60	0.11
0.1	1.45	0.22	0.5	1.55	0.15	0.9	1.65	0.08
0.2	1.51	0.18	0.6	1.56	0.14	1.0	1.77	0.00
0.3	1.53	0.16	0.7	1.58	0.13			
(c) n-Butyl alcohol-benzene								
x (BuOH)	Adsorption (mmoles/g.) of:		x (BuOH)	Adsorption (mmoles/g.) of:		x (BuOH)	Adsorption (mmoles/g.) of:	
	BuOH	C_6H_6		BuOH	C_6H_6		BuOH	C_6H_6
0.0	0.00	1.17	0.4	1.10	0.31	0.8	1.35	0.11
0.1	1.03	0.36	0.5	1.14	0.28	0.9	1.43	0.05
0.2	1.05	0.34	0.6	1.19	0.24	1.0	1.49	0.00
0.3	1.08	0.32	0.7	1.26	0.18			

adsorption in which the adsorbent showed the greatest preference for one adsorbate (alcohol-benzene systems with "gibbsite"), equation (1) could still be applied. This is a very severe test, for the first layer could be predicted to be very largely composed of alcohol at most concentrations, owing to hydrogen-bonding between the hydroxyl groups of the alcohol and the surface. Thus the only cases in which equation (1) could not be applied directly were those for which evidence of chemisorption was found. The more complex adsorption taking place in these cases can be interpreted in terms of chemisorption of the alcohol, followed by unimolecular physical adsorption on to the new surface so formed.

It is valuable to compare the mole-fraction of ethyl alcohol which is *physically* adsorbed from mixtures with benzene on each of the three solids. The curves are in the order

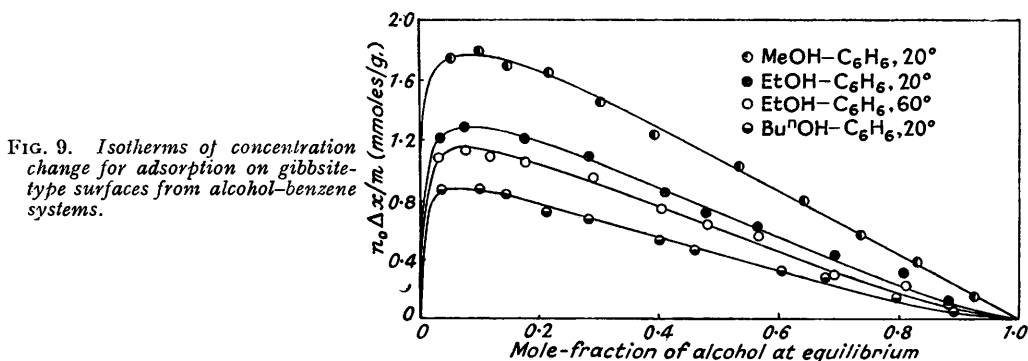


FIG. 9. Isotherms of concentration change for adsorption on gibbsite-type surfaces from alcohol-benzene systems.

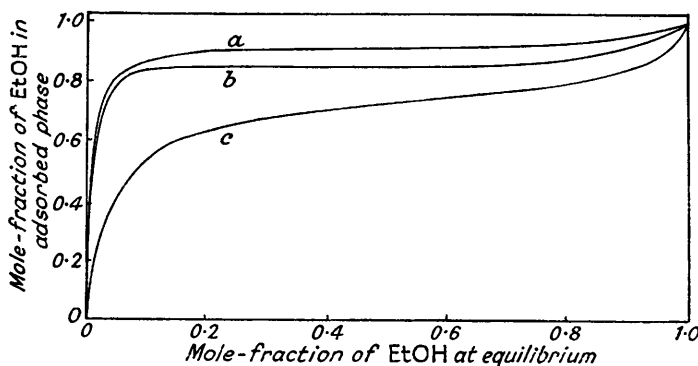


FIG. 10. Mole-fraction of ethyl alcohol adsorbed from mixtures with benzene on different surfaces: (a) gibbsite-type surface, (b) "ethylated" boehmite, (c) "ethylated" γ - Al_2O_3 (Sample 2).

required by the above discussion (Fig. 10). The alcohol is most strongly held (relative to benzene) by the completely hydroxylic surface, less strongly by the modified boehmite surface which presents a mixture of hydroxide and alkyl groups, and less strongly still by the modified γ - Al_2O_3 surface, which has a considerably lower proportion of accessible hydroxide groups.

In terms of both physical adsorption and chemisorption, these results suggest that, when an alcohol is being used in chromatography with an alumina column, some thought should be given to the "degree of hydration" of the alumina. This has already been appreciated empirically,¹⁴ but the present studies give a detailed explanation.

Finally we note that Bartell, Scheffler, and Sloan's work on silica gel⁴ gave very high maxima in the isotherms of concentration change for systems containing an alcohol, suggesting that chemisorption takes place similarly on this surface. We hope to report on this in a later paper.

¹⁴ Lederer and Lederer, "Chromatography," Elsevier, Amsterdam, 1954.

EXPERIMENTAL

Adsorbents.—The boehmite was Messrs. Peter Spence's "Type A" activated alumina, which the manufacturers state to be essentially sub-crystalline γ -AlO·OH; it was used in B.S.S. grading 6—20. Two samples of anhydrous alumina, γ -Al₂O₃, were made by heating this boehmite (i) to 500° for 5 hr., (ii) to 700° for 24 hr.; the surface areas differed accordingly. The material with the gibbsite-type surface was made by keeping the boehmite under water for 4 weeks at room temperature, and then drying it at about 80°. This procedure was followed because gibbsite cannot be made in bulk with a large surface area. Alkylated aluminas were made by similar treatment of boehmite and anhydrous alumina respectively with the appropriate alcohols; excess of alcohol was removed under vacuum at room temperature.

The charcoal sample was that used by Blackburn and Kipling.³

Adsorbates.—The alcohols were treated with magnesium activated by iodine,¹⁵ and fractionated. The fractions used had the following values for n_D^{20} : methyl alcohol, 1.3289 (cf. 1.3291¹⁶); ethyl alcohol, 1.3613 (in agreement with Smith and Bonner's value¹⁷); *n*-propyl alcohol, 1.3854 (in agreement with Carley and Bertelsen's value¹⁸); *n*-butyl alcohol, 1.3993 (cf. 1.3992¹⁹).

Methyl acetate was refluxed over phosphoric oxide and fractionated. The fraction used had n_D^{20} 1.3612 (cf. 1.3619²⁰).

The purification of the other adsorbates used has been described previously.^{2,3}

Procedure.—Monolayer values were obtained by applying the B.E.T. equation to the 20° adsorption isotherms for each vapour. The isotherms were of Type IV in Brunauer's classification.²¹ The monolayer values calculated from them are summarised in Table 5.

TABLE 5. *Monolayer values from B.E.T. equation (in millimoles per g.)*

	CHCl ₃	C ₂ H ₄ Cl ₂	MeOAc	C ₆ H ₆
Boehmite	1.531	1.481	1.528	1.369
γ -Alumina (1)	—	0.813	—	0.765
	C ₆ H ₆	MeOH	EtOH	Bu ⁿ OH
Boehmite	1.369	—	—	—
"Gibbsite"	1.174	2.274	1.773	1.492
"Methylated" boehmite	1.083	2.124	—	—
"Ethylated" boehmite	0.971	—	1.400	—
"Butylated" boehmite	0.833	—	—	1.081
γ -Alumina (2)	0.854	—	—	—
"Methylated" γ -alumina (2)	0.708	1.494	—	—
"Ethylated" γ -alumina (2)	0.567	—	0.947	—
"Butylated" γ -alumina (2)	0.525	—	—	0.754

Adsorption from the liquid phase has been described previously,^{2,3} and took place at 20° except where another temperature is recorded.

In connection with vapour-phase adsorption, we have noted that activated alumina can catalyse the decomposition of ethyl alcohol at low temperatures. Although the recorded rates of decomposition²² are only small, it seemed desirable to make sure that such decomposition was not responsible for the long time apparently required for equilibrium to be reached in the liquid-phase experiments, the refractive index of the mixture being taken as the criterion. Accordingly, ethyl alcohol was shaken with boehmite for periods up to two weeks and was examined for a change in refractive index. No change was found greater than the experimental error. Although we believe that some catalytic decomposition does take place, we think that it is on too small a scale to modify the conclusions reached above.

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¹⁵ Weissberger, Proskauer, Riddick, and Toops, "Organic Solvents," Interscience, New York and London, 2nd edn., 1955.

¹⁶ Edwards, *Trans. Faraday Soc.*, 1937, **33**, 1294.

¹⁷ Smith and Bonner, *Analyt. Chem.*, 1952, **24**, 517.

¹⁸ Carley and Bertelsen, *Ind. Eng. Chem.*, 1949, **41**, 2806.

¹⁹ Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312.

²⁰ Vogel, *J.*, 1948, 624.

²¹ Brunauer, "Physical Adsorption of Gases and Vapours," Oxford Univ. Press, 1944.

²² Heinemann, Wert, and McCarter, *Ind. Eng. Chem.*, 1949, **41**, 2928.