# 803. *Adsorption from Binary Liquid Mixtures on Silica and Titania Gels.*

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Data for physical adsorption at 20° from binary liquid mixtures on silica gel and on titania gel have been analysed to give individual adsorption isotherms. For systems containing an alcohol, allowance is made for the slow chemisorption which takes place, and individual isotherms for the residual physical adsorption are then calculated.

Recently[1] we discussed adsorption from binary liquid mixtures on various forms of alumina at room temperature, analysing the results to give individual adsorption isotherms for each component. For mixtures containing an alcohol the analysis was complicated by its chemisorption in addition to physical adsorption of both components. This paper is concerned with adsorption from similar systems by silica and titania gels.

(a) *Systems involving Physical Adsorption only.*—For alumina, arguments[1] were adduced that physical adsorption from mixtures of completely miscible liquids is normally confined effectively to a monolayer. The experimental data were analysed on this assumption to give individual isotherms for the adsorption of each component. The same analysis has been applied to data for adsorption from benzene–ethylene dichloride by silica gel and by titania gel, and from benzene–methyl acetate by silica gel. The significance of the data and the method of analysis have been discussed previously.[1,2] Both the isotherms of concentration change (Fig. 1 and Table 1) and the individual isotherms (Fig. 2 and Table 2) are very similar to those obtained for adsorption by alumina.

Table 1. *Adsorption by silica gel from mixtures of methyl acetate and benzene.*

| 20° | | | | 60° | | | |
|---|---|---|---|---|---|---|---|
| Equilibrium mole fraction of MeOAc | $\frac{n_0\Delta x}{m}$ (mmoles/g.) | Equilibrium mole fraction of MeOAc | $\frac{n_0\Delta x}{m}$ (mmoles/g.) | Equilibrium mole fraction of MeOAc | $\frac{n_0\Delta x}{m}$ (mmoles/g.) | Equilibrium mole fraction of MeOAc | $\frac{n_0\Delta x}{m}$ (mmoles/g.) |
| 0·03 | 1·27 | 0·53 | 1·19 | 0·04 | 1·08 | 0·53 | 1·03 |
| 0·07 | 1·42 | 0·57 | 1·17 | 0·07 | 1·22 | 0·62 | 0·86 |
| 0·11 | 1·48 | 0·62 | 0·99 | 0·12 | 1·34 | 0·66 | 0·88 |
| 0·17 | 1·50 | 0·66 | 0·88 | 0·17 | 1·41 | 0·75 | 0·53 |
| 0·22 | 1·49 | 0·75 | 0·66 | 0·22 | 1·43 | 0·78 | 0·48 |
| 0·27 | 1·48 | 0·78 | 0·58 | 0·28 | 1·43 | 0·83 | 0·38 |
| 0·32 | 1·48 | 0·83 | 0·47 | 0·32 | 1·38 | 0·88 | 0·27 |
| 0·38 | 1·45 | 0·88 | 0·37 | 0·38 | 1·34 | 0·95 | 0·11 |
| 0·42 | 1·37 | 0·95 | 0·17 | 0·42 | 1·31 | | |
| 0·46 | 1·35 | | | 0·46 | 1·25 | | |

Table 2. *Adsorption by titania gel from mixtures of ethylene dichloride and benzene at 20°.*

| Mole fraction of $C_2H_4Cl_2$ at equilibrium | Adsorption (mmoles/g.) of $C_2H_4Cl_2$ | $C_6H_6$ |
|---|---|---|
| 0·00 | 0·00 | 0·92 |
| 0·10 | 0·19 | 0·72 |
| 0·20 | 0·34 | 0·57 |
| 0·30 | 0·46 | 0·43 |
| 0·40 | 0·58 | 0·31 |
| 0·50 | 0·68 | 0·21 |
| 0·60 | 0·75 | 0·13 |
| 0·70 | 0·81 | 0·08 |
| 0·80 | 0·84 | 0·04 |
| 0·90 | 0·86 | 0·02 |
| 1·00 | 0·88 | 0·00 |

Table 3. *Adsorption by titania gel from mixtures of ethyl alcohol and benzene (one day).*

| 20° | | 60° | |
|---|---|---|---|
| Equilibrium mole fraction of EtOH | $\frac{n_0\Delta x}{m}$ (mmoles/g.) | Equilibrium mole fraction of EtOH | $\frac{n_0\Delta x}{m}$ (mmoles/g.) |
| 0·04 | 1·08 | 0·03 | 0·88 |
| 0·10 | 1·05 | 0·06 | 0·91 |
| 0·20 | 0·98 | 0·12 | 0·84 |
| 0·21 | 0·81 | 0·31 | 0·74 |
| 0·31 | 0·79 | 0·43 | 0·55 |
| 0·50 | 0·62 | 0·50 | 0·53 |
| 0·60 | 0·48 | 0·61 | 0·42 |
| 0·69 | 0·38 | 0·71 | 0·34 |
| 0·80 | 0·20 | 0·80 | 0·25 |
| 0·90 | 0·11 | 0·90 | 0·10 |

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[1] Kipling and Peakall, *J.*, 1956, 4828.

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

The effect of changing the temperature of adsorption from 20° to 60° has also been examined. In each case the effect is similar to that found with alumina, and is consistent with the behaviour of a system showing physical adsorption only (Fig. 1).

(b) *Systems involving both Chemisorption and Physical Adsorption.*—Our previous work has shown that the lower alcohols can be chemisorbed, at room temperature, by forms of alumina which have free oxide ions at the surface. This chemisorption takes place both from solutions in benzene[1] and from the pure alcohol vapour.[3] Chemisorption takes place from the vapour phase on silica gel and titania gel giving " alkylated " surfaces.[3] It thus remains to examine adsorption from solutions of the alcohols by these gels.

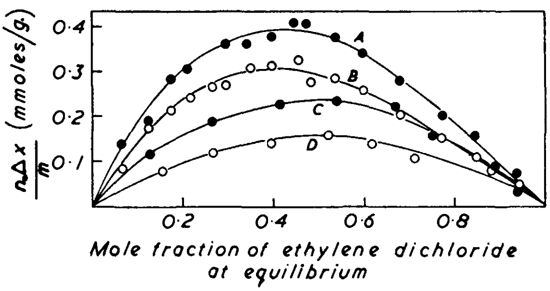

FIG. 1. *Isotherms of concentration change for adsorption from ethylene dichloride–benzene on (A) silica gel at 20°, (B) silica gel at 60°, (C) titania gel at 20°, (D) titania gel at 60°.* The decrease in mole fraction of ethylene dichloride ($\Delta x$) due to adsorption is expressed in relation to the total number of millimoles of liquid ($n_0$) brought into contact with *m* g. of adsorbent.[2]

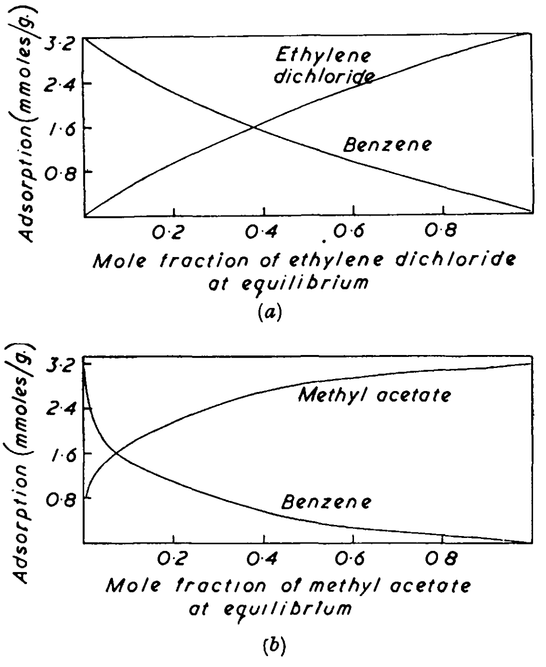

FIG. 2. *Adsorption (individual isotherms) at 20° by silica gel from mixtures with benzene of*

(*a*) *Ethylene dichloride.*
(*b*) *Methyl acetate.*

Adsorption by silica gel from liquid mixtures of ethyl alcohol and benzene has previously been studied by Bartell, Scheffler, and Sloan.[4] In the light of our results for adsorption from this system by alumina, the maximum point in their isotherm of concentration change seemed remarkably high for a system showing physical adsorption only, due allowance having been made for the probability that the silica gel had a higher specific surface area. This system was therefore studied with a sample of silica gel which had

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[3] Kipling and Peakall, *J.*, 1957, 834.
[4] Bartell, Scheffler, and Sloan, *J. Amer. Chem. Soc.*, 1931, **53**, 2501.

been used in our vapour-phase experiments; our results are shown in Fig. 3. The isotherms have a very high maximum, comparable with that obtained by Bartell, Scheffler, and Sloan. It is also comparable with Rao's results for this system, which were expressed in terms of his " selectivity " units.[5] The maximum in Fig. 3 is greater than that in Fig. 1 by an order of magnitude.

Two further results were found which had previously been observed with alumina. The system does not reach equilibrium within the short period normally sufficient for physical adsorption. This recalls Lambert and Foster's observation that a period of up to a month was required for silica gel to " settle down " to reproducible behaviour after initial contact with ethyl alcohol vapour.[6] Further, adsorption at 60° for one day gives an isotherm which is not completely separate from the 20° isotherm. The significance of these results has been discussed.[1] Together with the results for adsorption of ethyl alcohol vapour, they show that chemisorption of ethyl alcohol takes place on this silica gel. A similar conclusion can be drawn from the results obtained with titania gel (Table 3).

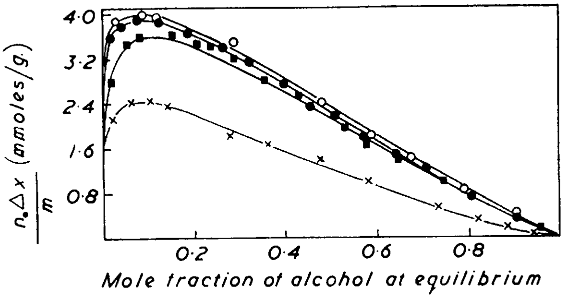
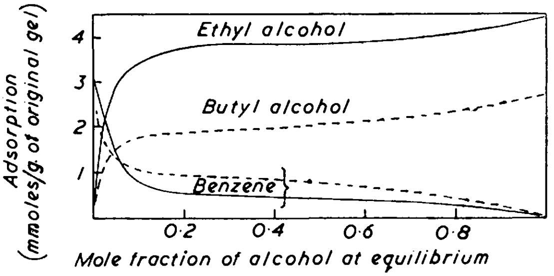


FIG. 3. *Isotherms of concentration change for adsorption on silica gel from mixtures of benzene with ethyl alcohol and with* n-*butyl alcohol.*

○ Ethyl alcohol, 20°, 3 weeks.
● Ethyl alcohol, 20°, 1 day.
■ Ethyl alcohol, 60°, 1 day.
× Butyl alcohol, 20°, 3 weeks.

FIG. 4. *Physical adsorption (individual isotherms) on " alkylated " silica gel from mixtures of benzene with ethyl alcohol and with* n-*butyl alcohol.*



Data have also been obtained for adsorption by silica gel from *n*-butyl alcohol—benzene. This system has been examined by Jones and Outridge,[7] and our isotherm of concentration change resembles theirs closely. They pointed out the important distinction between adsorbate held by forces emanating from the solid surface and liquid mechanically held in the pores, the latter being merely an extension of the equilibrium bulk liquid into the pores of the solid. This distinction is important whether one regards the adsorbate as being confined essentially to a monolayer [2] or not.[8] By allowing for mechanically held liquid, they were able to calculate individual isotherms for the adsorption of each component, assuming that these obeyed Freundlich equations. In more recent work Jones and Mill [8] calculated the individual isotherms by assuming that the two adsorbates jointly occupy a constant volume in the pores of the adsorbent (cf. Hansen and Hansen [9]

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[5] B. S. Rao, *J. Phys. Chem.*, 1932, **36**, 615.
[6] Lambert and Foster, *Proc. Roy. Soc.*, 1931, *A*, **134**, 246.
[7] Jones and Outridge, *J.*, 1930, 1574.
[8] Jones and Mill, *J.*, 1957, 213.
[9] Hansen and Hansen, *J. Colloid Sci.*, 1954, **9**, 1.

and Blackburn and Kipling[10]). In our work, results similar to those obtained with the system ethyl alcohol–benzene showed the necessity to allow for chemisorption of the butyl alcohol. This would be more serious than in Jones and Outridge's experiments, as our gel had a lower water content than theirs (4·0% compared with 5·2%) and hence, presumably, a higher concentration of oxide ions at the surface.

The vapour-phase studies give the total extent of chemisorption of each alcohol. From the isotherm of concentration change it is thus possible to subtract the change due to chemisorption, leaving a composite isotherm representing physical adsorption only. As we have previously shown[2] that the Freundlich equation cannot describe the individual isotherms over the whole concentration range, we have obtained these isotherms by assuming that they refer to monolayer adsorption occurring on the " alkylated " surfaces. The results are shown in Fig. 4 for silica gel. This analysis seems more satisfactory, for this type of system, than one based on complex formation, as suggested by Rao and Jatkar.[11]

The method which we have used for the separate determination of chemisorption and physical adsorption had hitherto been employed for systems at equilibrium. It may also be used for systems which have not reached equilibrium, a procedure which may be of value in the practical application of adsorbents. This is illustrated for one day's adsorption at 20° by titania gel from the system ethyl alcohol–benzene. The isotherm of concentration change is given in Table 3. The change in concentration due to the chemisorption occurring after one day's contact[3] is then subtracted, and the resulting isotherm, which relates to physical adsorption only, is analysed to give individual isotherms. For the last stage of this calculation, monolayer values are derived from isotherms for adsorption of the relevant vapours on samples of the gel which had been in contact with ethyl alcohol for one day. The individual isotherms (Fig. 5) are very similar in shape to those obtained at equilibrium for silica gel. Bearing in mind the relatively small change in concentration which occurs after one day for such systems, we may conclude that analysis of the one-day isotherm gives a good approximation to equilibrium conditions, provided that the very substantial concentration change due to chemisorption is allowed for.

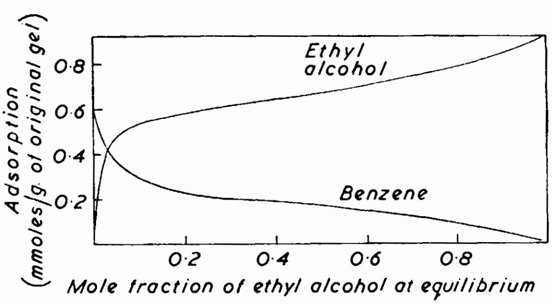

FIG. 5. *Physical adsorption (individual isotherms) on partially " ethylated " titania gel from mixtures of ethyl alcohol and benzene.*

The analysis of experimental data which we presented for adsorption from binary liquid mixtures on alumina is equally valuable when applied to data for adsorption on silica gel and on titania gel. The three adsorbents are essentially similar in the preferences shown in systems for which physical adsorption only is observed, in their slow chemisorption of the lower aliphatic alcohols, and in the type of physical adsorption which takes place on the " alkylated " surfaces.

## EXPERIMENTAL

The adsorbents were the silica gel (I) and the titania gel described in a previous paper.[3] The adsorbates and procedure have also been described previously.

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

[11] N. S. Rao and Jatkar, *Quart. J. Indian Institute*, **1943**, **5**, 65.

Monolayer values, obtained by applying the B.E.T. equation to the 20° adsorption isotherms for the individual vapours, are summarised in Table 4.

TABLE 4. *Monolayer values from B.E.T. equation (mmoles/g.)*

| | $C_6H_6$ | $C_2H_4Cl_2$ | MeOAc | EtOH | $Bu^nOH$ |
|---|---|---|---|---|---|
| Silica gel | 3·22 | 3·20 | 3·21 | — | — |
| Silica gel, " ethylated " * | 3·11 | — | — | 4·49 | — |
| Silica gel, " butylated " * | 2·87 | — | — | — | 2·73 |
| Titania gel | 0·92 | 0·88 | — | — | — |
| Titania gel, " ethylated " * | 0·61 | — | — | 0·92 | — |

* Referred to 1 g. of original gel.

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