# The effect of aprotic solvents on the adsorption of phenol by alumina*

B. HIGGINS AND J. H. RICHARDS

The isotherms for the adsorption of phenol onto alumina from cyclohexane, benzene, nitrobenzene, ethyl acetate and 1,4-dioxan solutions have been determined at 25°. The change in solvent in the above order causes a successive decrease in the amount of phenol adsorbed at the 'saturation level' and possible explanations of the solvent effects are discussed.

THE adsorption of non-electrolytes from solution, which is of importance in the chromatographic separation of many materials, can be affected by solute-solvent and solvent-adsorbent interactions. In the event of solute-solvent interactions, e.g. molecular complex formation, the number of free solute molecules will be reduced and the amount of adsorption will therefore decrease. It is possible that the solute-solvent complex may also be adsorbed thus resulting in a mixed surface layer of solute and solvent molecules. This possibility will depend on the nature of the complex and the adsorbent. The solvent may itself be adsorbed either at the same sites as the solute molecules, thus being in direct competition with them, or at other sites, so providing the possibility of partial block of the solute sites by steric hindrance. In either instance there will be a reduction in the degree of solute adsorption. Often the solvent may show a combination of the above effects, which involve interaction with the solute and substrate respectively.

There has been little previous work discussing in detail the effects of solvents on a particular adsorption system. Although the results for the adsorption of solutes from different solvents have been reported, no attempts have been made to find any definite correlation between the solvent properties and the effects on adsorption. For example, Kipling & Wright (1962) have shown that the amount of stearic acid adsorbed onto "Spheron 6" decreases as the solvent changes through the series cyclohexane, ethanol, carbon tetrachloride and benzene. They state that it is possible that the orientation of the molecules at the surface may vary, depending on the solvent from which they are adsorbed, although they conclude that it is more likely that the adsorbed layer is a mixed layer containing solvent as well as solute molecules. In addition, Chatterji & Singhal (1960) have shown that the amounts of butyric, propionic and acetic acids adsorbed onto alumina, decreased with solvent in the order benzene, toluene, n-propanol and water. Where n-propanol and water were used as solvents the decrease in acid adsorption was attributed to adsorption of the solvent. A mention of the possible importance of solvent-solute association was made by Venturello & Ghe

(1959), who measured the adsorption of iodine onto magnesia from pentane, carbon tetrachloride, dioxan and benzene solutions. These authors found that the amount of iodine adsorbed from any solvent decreased in the above solvent order and suggested that this may be due to the formation of iodine-solvent complexes with benzene and dioxan.

In view of the small amount of available information about the effects of solvents on adsorption systems we decided to investigate a specific system in an attempt to clarify these effects.

Alumina was chosen as the adsorbent because it is a common chromatographic material and the main mechanism for the adsorption of organic non-electrolytes onto it has been reasonably well established. Phenol was chosen as the solute because its concentration in solution can be readily determined by several methods and because it is readily adsorbed by alumina (Crisp, 1956; Eric, Goode & Ibbitson, 1960). The mechanism of this adsorption has been shown to involve hydrogen bond formation between the phenolic OH group and the surface oxygen atoms of alumina (Giles, Mehta & others, 1954; Cummings, Garven & others, 1959). A series of aprotic solvents, showing a range of hydrogen-accepting ability, was chosen to provide a variation in the degree of solute-solvent interaction by intermolecular hydrogen bond formation while, at the same time, allowing the competition of the solvent for the adsorption sites of phenol to be neglected. The shifts in the hydroxyl stretching frequency ($\triangle v_{OH}$) of phenol in the various solvents were used as an approximate indication of the relative hydrogen accepting abilities of the solvents chosen for this investigation. These solvents were cyclohexane, benzene, nitrobenzene, ethyl acetate and 1,4-dioxan, for which the $\triangle v_{OH}$ values were 0, 63, 102, 161 and 307 cm$^{-1}$ respectively, relative to the stretching frequency of the hydroxyl group of phenol in cyclohexane solution (Tsuboi, 1952; Bellamy, Hallam & Williams, 1958).

# Experimental

## MATERIALS

Neutral chromatographic alumina of activity grade 1 (Woelm) was stored in bulk in a well-closed container. Periodic checks were made, by measurement of the adsorption isotherm of phenol from cyclohexane solution, to ensure that there was no loss in activity. Phenol (A.R.) was fractionally distilled at atmospheric pressure (b.p. 182°), and stored in a well-closed container.

Cyclohexane (A.R.) was dried over calcium chloride and then fractionally distilled from potassium metal through a 20-plate column. The product was stored in well-closed amber containers over sodium wire. It had b.p. 80·8° at 760 mm.

Benzene (A.R.) was washed with concentrated sulphuric acid (100 ml/litre of benzene) until no further discolouration of the acid occurred. The benzene was then washed with three lots of distilled water (100 ml/litre) and dried over two successive amounts of sodium hydroxide pellets.

The dried product was distilled from potassium metal through a 20-plate column and the distillate was stored in well-closed amber containers over sodium wire. It had b.p. 80·4 at 760 mm.

1,4-Dioxan (A.R.) was refluxed over sodium until the metal remained bright and then distilled from fresh sodium through a 20 plate column. The product was stored over sodium wire in well-closed amber containers. It had b.p. 101·3° at 760 mm.

Ethyl acetate (A.R.) was dried over anhydrous sodium carbonate and then fractionally distilled through a 20-plate column. The product was stored over molecular sieve type 4A in well-closed amber containers. It had b.p. 77·1° at 760 mm.

Nitrobenzene (A.R.) was dried over calcium chloride and then fractionally distilled under reduced pressure. The product was stored in well-closed amber containers over molecular sieve type 4A. It had b.p. 211° at 760 mm.

METHOD

The adsorption of phenol by 1 g quantities of alumina from 20 ml samples of solution was measured by a batch process in glass 60 ml ampoules. The sealed ampoules were submerged in a water-bath at 25·0° and rotated at 30 rev/min for 30 min. This time had been found, from preliminary experiments, to be sufficient to allow equilibrium to be attained. After careful drying the ampoules were opened and the supernatant solutions were decanted and analysed.

The above procedure was modified for the determination of desorption isotherms. After adsorption the ampoules were opened at the tip and the supernatant solutions were decanted. The maximum amount of liquid was removed carefully without the removal of any alumina. Pure solvent (20 ml) or phenol solution of a lower concentration than that removed, was then added. The ampoules were resealed and equilibrated for a further 30 min.

A Unicam S.P. 500 spectrophotometer was used in the analysis of the phenol in solutions except when it was in nitrobenzene solution where a procedure similar to the B.P. method of assay for phenol was used. A blank determination was made using pure nitrobenzene. The accuracy of the method was tested using several solutions of known phenol concentration in nitrobenzene, and the error was less than 1%.

## Results

The isotherms for the adsorption of phenol onto alumina from cyclohexane, benzene, nitrobenzene, ethyl acetate and 1,4-dioxan solutions at 25° are shown in Fig. 1.

The applicability of the Langmuir equation to these adsorption results was tested. This equation may be written as

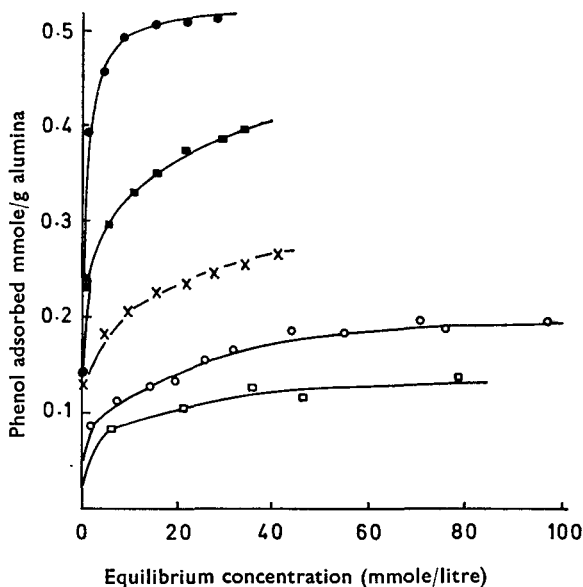$$\frac{c}{x_0} = \frac{1}{x_1 a} + \frac{c}{x_1} \qquad (1)$$

FIG. 1. Isotherms for the adsorption of phenol onto alumina from cyclohexane (●), benzene (■), nitrobenzene (×), ethyl acetate (○) and 1,4-dioxan (□) solutions at 25°.

where $c$ is the equilibrium concentration of phenol in solution, $x_0$ is the amount of solute adsorbed by unit weight of the adsorbent, $x_1$ is the corresponding amount adsorbed at the "saturation level", i.e. the mono-layer capacity of the solid, and a is constant for a particular system. Linear plots of $c/x_0$ against c were obtained in all cases, thus indicating the applicability of equation (1) to these results. The slopes and intercepts of these plots could be used to obtain the values of $1/x_1$ and $1/x_1a$, respectively.

Table 1 shows the values of $x_1$ and a obtained from a least squares treatment of the adsorption data, together with the values of the coverage factor ($\theta$), which represents the fraction of the surface covered with phenol molecules relative to an assumed complete coverage in the cyclohexane system.

The application of the composite isotherm treatment advocated by Kipling and his co-workers (Kipling, 1951, Kipling & Peakall, 1956; Kipling & Wright, 1962, 1964) to the adsorption data obtained for the

TABLE 1. THE LANGMUIR CONSTANTS ($a$ AND $x_1$) AND COVERAGE FACTORS ($\theta$) FOR THE ADSORPTION OF PHENOL ONTO ALUMINA FROM SOLUTION AT 25°

| Solvent | | $a$ | $x_1$ moles/g | $\theta$ |
|---|---|---|---|---|
| Cyclohexane | .. | 4·87 | 0·513 | 1·00 |
| Benzene | .. | 0·76 | 0·398 | 0·78 |
| Nitrobenzene | .. | 0·47 | 0·267 | 0·52 |
| Ethyl acetate | .. | 0·12 | 0·214 | 0·42 |
| 1.4-Dioxan | . | 0·09 | 0·154 | 0·30 |

cyclohexane and 1,4-dioxan systems produced little change in the adsorption isotherms shown in Fig. 1. This is as expected (Kipling & Wright, 1962) since only dilute solutions were involved and therefore such treatment was not used further in this investigation.

It was found that the desorption isotherms for the phenol–alumina–cyclohexane and phenol–alumina–benzene systems were identical to the corresponding adsorption isotherms.

## Discussion

The identical shapes of the adsorption and desorption isotherms for the phenol–alumina–cyclohexane and phenol–alumina–benzene systems indicate that the adsorption of phenol onto alumina is completely reversible and the model of a dynamic equilibrium can therefore be envisaged. This is a factor in support of the application of the Langmuir equation to these systems. It is realized that care must be taken in the application of the Langmuir equation to solution adsorption data. However, the equation is used mainly in this investigation for the calculation of $x_1$, values. These calculated results show good agreement with the values obtained by extrapolation of the isotherms.

The adsorption isotherm for the phenol-alumina-cyclohexane system is similar to the 'L2' isotherm in the classification of isotherms for adsorption from solution suggested by Giles, MacEwan & others (1960). The steep slope of the first part of the adsorption isotherm indicates ease of adsorption of phenol molecules because of a large proportion of adsorption sites being initially available to the molecules. In a strictly Langmuirian system this slope decreases as the surface becomes filled with adsorbed molecules. However, the initial slope of the isotherm in Fig. 1 does not decrease as adsorption takes place, in fact the isotherm is almost coincident with the $x_0$ axis, and the phenol molecules are almost quantitatively adsorbed from solution giving equilibrium concentrations close to zero. This as a slight deviation from the Langmuir shape, which is not reflected in the plot of $c/x_0$ against $c$ due to the low values of $c$ and $/cx_0$. Although the adsorption isotherm is considered to be an "L2" isotherm, it is very close to the "H" type isotherm in the classification of Giles & others (1960). However, the equilibrium concentration of phenol is in fact finite in all cases and not zero, as with the "H"-type isotherm. The distinction between "H" and "L" isotherms may be somewhat artificial, since it depends on the sensitivity of the method used for the determination of equilibrium concentration.

The amount of solute adsorbed at the "saturation level" may represent the formation of a complete monolayer of adsorbate but, as pointed out by Giles & others (1960), this does not necessarily imply that there is a close-packed layer of a single species. The layer may contain solvent molecules as well as solute molecules, or it may consist of isolated clusters of solute molecules adsorbed at active sites.

Phenol molecules are believed to be adsorbed onto alumina in an end-on orientation with their hydroxyl groups directed towards the alumina

surface. Such orientation is also suggested by the "L" type of adsorption isotherms obtained in this investigation since this shape is claimed to be a characteristic of systems involving the end-on adsorption of a polar solute onto a polar substrate from a non-polar liquid (Giles & others, 1960). In addition, Giles and his co-workers (1960) state that the adsorption of a polar solute onto a polar substrate from a polar liquid usually gives an "S" type of isotherm since the solute meets with strong competition from the solvent for the adsorbent surface. Although cyclohexane, benzene and 1,4-dioxan are all non-polar, ethyl acetate and nitrobenzene are not and the isotherms for the systems involving the latter two solvents might therefore be expected to differ from those for the other systems. However the isotherms obtained for all of the systems appear to be of the "L2" type. This suggests that ethyl acetate and nitrobenzene do not compete strongly with phenol for sites on the alumina surface, and thus do not give rise to "S" type isotherms. It would appear, therefore, that interpretations of isotherms for adsorption from solution as suggested by Giles & others (1960) are of a general nature and that additional factors must sometimes be taken into account when interpreting the shape of a particular isotherm.

The initial parts of the isotherms for adsorption from cyclohexane, benzene and nitrobenzene are identical and are almost coincident with the $x_0$ axis. The difference between these isotherms arises at the point of breakaway from the $x_0$ axis these points being at 0·38, 0·23 and 0·12 mmole/ g on the $x_0$ axis, for cyclohexane, benzene and nitrobenzene respectively. The points for the isotherms for adsorption from ethyl acetate and 1,4-dioxan solutions indicate that these isotherms may not be coincident with the $x_0$ axis at all and it is difficult to estimate a point of breakaway from the axis. The effect of the solvent on the initial parts of the isotherms is similar to that expected from theoretical considerations, since the varying degrees of competition of the solvents for phenol would cause a gradual increase in the equilibrium concentration of phenol required to produce a constant level of adsorption. However, it is difficult to observe a definite relationship between a constant amount of phenol adsorbed and the equilibrium concentration required to produce it in each solvent, because of the different "saturation levels" of the five isotherms. This variation in "saturation level," which is the main difference between the isotherms, is unexpected since previous work had suggested that the chosen solvents would not be adsorbed by alumina to any appreciable extent (Cummings & others, 1959; Giles & McKay, 1961). Thus, it was expected that a similar "saturation level" of phenol on alumina would be obtained in all the solvents and the equilibrium concentration at which this level would be reached would depend on the degree of phenol-solvent interaction. Although high equilibrium concentrations were used in the more active solvents no significant increases were observed in the amounts of phenol adsorbed.

The reduction of the amount of phenol adsorbed at "saturation level" from benzene, nitrobenzene, ethyl acetate and 1,4-dioxan may be due to any one of the following factors, or a combination of two or more:

(i) *Change in orientation of the adsorbed phenol molecules with change of solvent.* This may explain two levels of adsorption in a system where the molecules are adsorbed either flat or end-on at the surface. However, it is very unlikely that a change in orientation of phenol molecules could explain the five different adsorption levels observed here.

(ii) *Adsorption of a mixed monolayer of phenol and solvent molecules.* Although, as previously emphasized, the solvents should not be strongly adsorbed onto alumina, it is possible that they may be sufficiently adsorbed to affect the "saturation level" of the phenol.

(iii) *Adsorption of the phenol-solvent complex.* Phenol associates with each of the solvent species, benzene, nitrobenzene, ethyl acetate and 1, 4-dioxan, by the formation of an intermolecular hydrogen bond. It is unlikely that the phenol-solvent complex would be adsorbed, because it has no free hydrogen atom capable of bonding with oxygen atoms on the alumina surface. Adsorption will only occur if the complex hydrogen bond is broken, or if the complex is adsorbed at the surface by mechanisms other than hydrogen bonding.

(iv) *Phenol-solvent interaction.* The strength of the phenol-solvent interaction as indicated by $\triangle v_{OH}$ values (Tsuboi, 1952; Bellamy & others, 1958) increases in the inverse order to the $x_1$ values of the phenol-alumina-solvent systems. If the adsorbent sites on the alumina surface have a range of activity, then only those sites with a high activity are capable of adsorbing phenol molecules from a solvent such as 1,4-dioxan, in which the phenol-solvent interaction is relatively strong, since such adsorption involves the initial rupture of solute-solvent bonds. The weaker surface sites would only be of importance when the strength of the phenol-solvent bonds is reduced, as in the other solvents used in this investigation.

A consideration of the structure of alumina indicates that there will be some variation in the electronegativity of the surface oxygen atoms, depending on their position in the surface and the nature of adjacent atoms. In addition, the presence of some aluminium atoms and hydroxy groups on the alumina surface will lead to a variation in site activity, which is implicit in the proposition of different mechanisms of adsorption by alumina. Evidence for surface heterogeneity was obtained by Clark & Holm (1963), who investigated the adsorption of ammonia onto alumina and concluded that there was a broad distribution of adsorbent site energies. They stated that on adsorption the most active sites were filled first, followed by those of a lesser activity and so on. Further evidence in support of the concept of heterogeneity of the surface forces on alumina is obtained from the correlation of results for the adsorption of phenol from cyclohexane with the work of Graham (1953). This author classified adsorption systems on the basis of plots of an equilbrium function, given by $\theta/(1-\theta)c$, versus $\theta$, which is the coverage factor, and suggested that surface heterogeneity is shown by an immediate tendency for the equilibrium function to decrease with increase in $\theta$ in these plots. A similar

treatment of the results obtained for the phenol-alumina-cyclohexane system produced this decrease in the equilibrium function.

The above evidence indicates that the adsorbing sites on the surface of alumina show a variation in activity. It would therefore seem possible to explain the difference in the "saturation levels" obtained in the various solvents on the basis of the change in the strength of the phenol-solvent interaction and the variation in the activity of the surface of alumina.

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