

**Hydrogen Bonding Interactions of
Para-Substituted Phenols in Solution
and at a Solid-Solution Interface**

by

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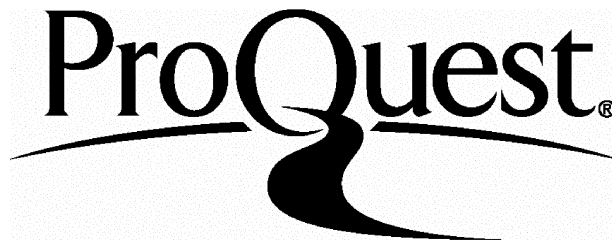
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I N T R O D U C T I O N

In the introduction to this thesis, the adsorption process at the solid-solution interface is discussed in terms of:-

- A. The Adsorption Isotherm
- B. The Nature of the Interactions at the Solid-Solution Interface
- C. The Nature of the Interactions in Solution
- D. Thermodynamic Considerations.

Throughout this introduction, proposals for the experimental study are outlined.

A. THE ADSORPTION ISOTHERM

(1) THE COMPOSITE ISOTHERM

Experimental adsorption data appropriate to the solid-solution interface is usually presented in the form of an adsorption isotherm, in which the change in mole fraction on adsorption of one of the components in a binary solution is plotted against the equilibrium mole fraction of that component in the liquid phase.

An equation expressing the change in mole fraction of component 1 in the mobile phase, on adsorption, in terms of the adsorption of both components is derived as follows:-

Consider a system of two components 1 and 2, the total number of moles being n_0 . When placed in contact with m grams of solid adsorbent, the mole fraction of component 1 decreases by Δx_1^l . This change in concentration is a result of the transfer of n_1^s moles of component 1 and n_2^s moles of component 2 from the solution to the surface of one gram of adsorbent. At equilibrium, there remain in solution n_1^l moles of component 1 and n_2^l of component 2, giving mole fractions x_1^l and x_2^l respectively, initial mole fractions being represented by $(x_1^l)_0$ and $(x_2^l)_0$. By simple algebra, it can be shown that

$$\frac{n_0 \Delta x_1^l}{m} = n_1^s \cdot x_2^l - n_2^s \cdot x_1^l \quad (1)$$

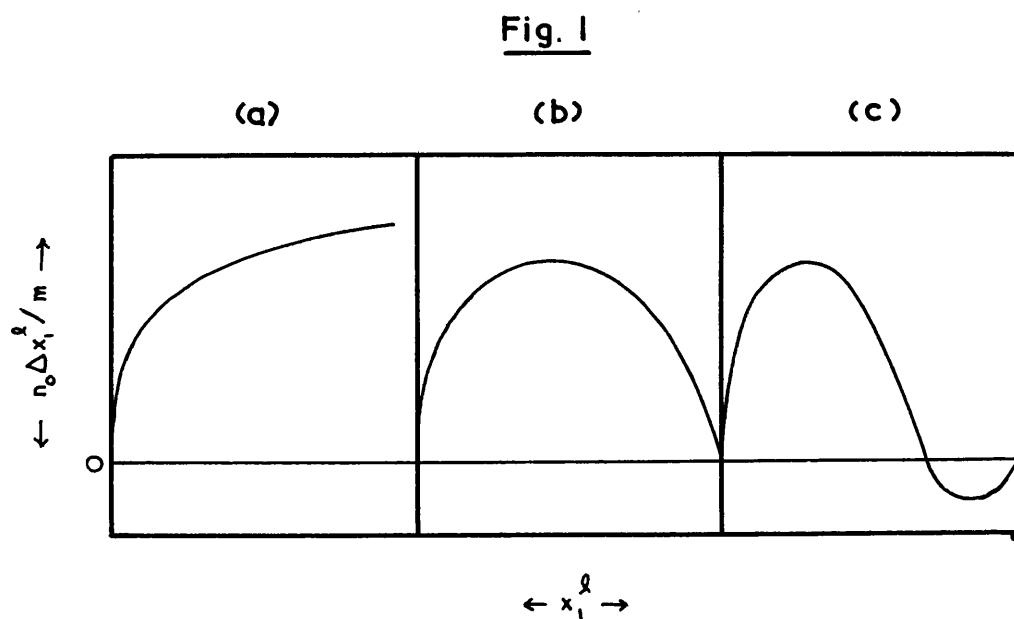
The composite isotherm representing adsorption of both components 1 and 2 is obtained by plotting $n_0 \Delta x_1^l / m$ against x_1^l . Sometimes the

isotherm is expressed in terms of $(x_1^S - x_1^L)$ where x_1^S is the mole fraction of component 1 in the adsorbed layer. This form emphasises the preferential adsorption of one component and it can be readily shown that

$$x_1^S - x_1^L = \frac{1}{n^S} \cdot \frac{n_0 \Delta x_1^L}{m} \quad (2)$$

where n^S is the total number of molecules in the adsorbed layer on unit weight of solid.

The main types of isotherm experimentally realised are shown in Fig. 1¹, isotherm (a) representing adsorption from dilute solution.



In the case of adsorption from a dilute solution of component 1 in component 2 or when component 1 has limited solubility in component 2, then

$$x_1^L \ll x_2^L \sim 1$$

Both n_1^S and n_2^S are small and thus $n_2^S x_1^L$ is small and equation (1) reduces to

$$\frac{n_1^0 \Delta x_1^L}{m} \sim n_1^S \quad (3)$$

indicating that the composite isotherm is almost identical with the isotherm representing adsorption of component 1 alone.

(2) THE INDIVIDUAL ISOTHERMS

As equation (1) contains two unknowns n_1^S and n_2^S , a further independent relationship between these two quantities is required before the composite isotherm can be resolved into its individual components.

If it is assumed that the solid surface is completely covered by the adsorbed layer whatever the composition of the liquid phase and that the layer is unimolecular², then

$$n_1^S A_1 + n_2^S A_2 = A \quad (4)$$

where A_1 , A_2 are the partial molar areas occupied at the surface by the two components, 1 and 2 respectively, and A is the surface area of unit weight of solid.

Kipling and Tester³ suggested the alternative form of this expression

$$\frac{n_1^S}{(n_1^S)_m} + \frac{n_2^S}{(n_2^S)_m} = 1 \quad (5)$$

$(n_1^S)_m$ and $(n_2^S)_m$ being the number of moles of the individual components

required to cover the surface area of unit weight of adsorbent completely with a monolayer. These latter quantities can be determined by vapour phase adsorption of the individual components.

If adsorption at the solid-solution interface is multi-molecular, then

$$\frac{n_1^S}{(n_1^S)_m} + \frac{n_2^S}{(n_2^S)_m} > 1$$

Application of equation (5) to adsorption on rutile from solutions of long chain alcohols and hydrocarbons led Day and Parfitt⁴ to conclude that multilayer adsorption of the parallel-orientated hydrocarbon molecules occurred in the spaces between the perpendicularly-orientated adsorbed alcohol molecules to an extent dependent upon the length of the alcohol molecule. Use of a $(n_2^S)_m$ value representing the number of moles of hydrocarbon occupying the same volume as that of a monolayer of alcohol molecules in a perpendicular orientation gave a value of 0.96 in equation (5) for the n-octanol/n-heptane system. This work emphasises the need to consider each system individually in order to decide whether the assumption of monolayer coverage of the adsorbent surface is justified.

B. INTERACTIONS AT THE SOLID-SOLUTION INTERFACE

The forces of attraction associated with a solid adsorbent may be of two kinds, physical and chemical, thus giving rise to physical adsorption and chemisorption respectively.

As the systems studied in the experimental part of this thesis relate specifically to physical adsorption, only this type of process will be considered. The experimental isotherms obtained are often characterised by the preferential adsorption of one component or the other over part or all of the concentration range studied and in general, the adsorption can be explained in terms of the polarity of the surface and that of the adsorbates.

Restricting the discussion to metal oxide surfaces we note, first of all that alcohols are adsorbed in preference to benzene over the whole of the concentration range,^{5,6,7} the interaction between the lower alcohols and the surface being most probably hydrogen bonding. Similarly methyl acetate is preferentially adsorbed from benzene by silica and alumina surfaces⁸, and this can be attributed to specific interaction of the polar centre of the ester molecule with the polar groups which cover the solid surface. The preferential adsorption of one component over the whole of the concentration range in the above examples suggests that the surface adsorption sites are homogeneously polar. However, some heterogeneity of oxide surfaces generally arises from the presence of both oxide and hydroxyl groups and as these are both highly polar, their different discriminations between pairs of adsorbates is not always easy to detect.

The type of orientation that the adsorbed molecule assumes at the adsorbent surface can provide information about the nature of the interaction between the adsorbate and the metal oxide surface. Monocarboxylic acids are adsorbed from organic solvents onto silica⁹ with their major axes parallel to the solid surface. Adsorption on alumina however occurs with the major axis of the adsorbed acid molecule perpendicular to the surface. On alumina, the adsorbed molecules do not form a close packed monolayer, implying adsorption on to specific sites such as oxygen atoms or ions. Thus while the adsorbate-adsorbent interaction in the case of silica is insufficient to cause rupture of the hydrogen bonds in the dimeric acid molecule, the stronger interaction on alumina results in bond breakage and adsorption of monomeric acid molecules on to specific sites on the surface.

Specific adsorption of silica is thought to be due mainly to hydrogen bonding between the surface hydroxyl groups of the adsorbent and the electron donor groups of the adsorbate^{10,11}. In this connection, Cusamo and Low¹² have recently studied the adsorption of a variety of substituted benzenes on to porous glass. They concluded that the π -OH interaction could be explained in terms of the charge transfer model developed by Mulliken¹³ and later modified by Puranik¹⁴. For a π -OH interaction, the model involved the formation of an asymmetrically bonded surface complex, an electron entering the antibonding orbital of the surface hydroxyl, interaction occurring between that orbital and the aromatic π -system along one of the C-C directions. Application of the charge transfer theory led to relationships between the shift of the hydroxyl absorption frequency $\Delta\nu_{OH}$, and the ionisation potential

of the adsorbate, and also between $\Delta\nu_{OH}$ and the change in the hydroxyl absorption intensity brought about by the adsorbate-OH interaction.

Various workers have studied the adsorptive properties of alumina and have concluded that the process of adsorption is brought about by:-

- (i) conventional electrostatic processes¹⁵
- (ii) hydrogen bonding with the alumina surface acting either as a proton donor¹⁶ or proton acceptor¹⁷
- (iii) charge transfer complexation with the alumina surface acting as either an electron donor or acceptor¹⁸
- (iv) ionisation of the adsorbate upon adsorption¹⁹.

Possible surface sites for adsorption on γ -alumina include hydroxyl groups, oxide ions or exposed aluminium ions.

The surface of the alumina used in this investigation is known to be completely hydroxylated implying the absence of oxide sites or exposed aluminium ions. Previous work carried out on this alumina has shown hydrogen bonding to be the essential mechanism of adsorption for a variety of adsorbates. Ibbitson, Jackson, McCarthy and Stone²⁰ studied the adsorption of substituted azo compounds from benzene by alumina and found that replacement of the hydrogen of the hydroxyl group in 4-hydroxyl-azobenzene resulted in negligible adsorption of 4-methoxy-azobenzene. Replacement of both hydrogen atoms in 4-amino-azobenzene by methyl groups produced a similar result. For the adsorption of phenols from cyclohexane, Eric, Goode and Ibbitson²¹ showed that phenol molecules were adsorbed perpendicularly to the

surface, the most probable mechanism of adsorption being hydrogen bonding of the phenolic hydroxyl group to the hydroxyl groups present on the alumina surface.

More recently, Vallance²² has studied the adsorption of p-substituted anilines from cyclohexane at the alumina interface, and has concluded that hydrogen bonding is the predominant interaction. Defining an arbitrary 'index of adsorption' Vallance was able to show that the adsorption tendency of the p-substituted anilines for the alumina surface was reflected in the changes in the electrical character of the OH group due to the presence of the para substituent.

One aspect of the present investigation is to study the adsorption tendencies of a series of p-substituted phenols in order to assess the effect of substitution on the adsorption affinity of the O-H group for both silica and alumina surfaces.

(C) INTERACTIONS IN THE LIQUID STATE

Interactions occurring in the liquid state will be between adsorptive molecules, and between adsorptive and solvent molecules and in nature will be electrostatic, dispersion, charge transfer or hydrogen bonding.

(1) THE SOLVENT EFFECT

One of the most satisfactory parameters representing solvent reactivity is the E_T value of Dimroch, Reichardt, Siepmann and Bohlmann²³. This parameter is determined experimentally from the position of the absorption band of solutions of pyridinium N-phenolbetaine in the visible region of the spectrum and is given by

$$E_T \text{ (kJ mol}^{-1}\text{)} = 1.195 \times 10^5 / \lambda_{\text{MAX}}$$

where λ_{MAX} = wavelength of maximum absorption in nm.

The stronger the stabilising effect of the solvent on the ionic ground state of the standard dye compared with that of the less polar excited state, the higher the energy of the electron transition and the lower the wavelength of the absorption band. Thus increasing E_T value represents increasing interaction between the solvent and the standard compound, pyridinium N-phenolbetaine and so provides a measure of solvent reactivity.

Other spectroscopic measures of solvent reactivity reported recently are the $\Delta\nu_D$ and $\Delta\nu_A$ values. Kagiya et al²⁴ have measured the infrared frequency of the O-D or C=O vibrational bands of monodeuteromethanol or acetophenone respectively, in various solvents.

Taking benzene as a standard, they have used the frequency shift as a measure of electron-donating power $\Delta\nu_D$ and electron-accepting power $\Delta\nu_A$, respectively, of a given solvent. For a homologous series, Kagiya found that the electron donating power as measured by $\Delta\nu_D$ decreased with an increase in the ionisation potential in the gaseous phase or with an increase in the pK_b value in the liquid phase. Similar correlations were obtained when considering $\Delta\nu_A$.

(2) HYDROGEN BONDING TYPE ASSOCIATION IN SOLUTION

Since the initial work of Benesi and Hildebrand²⁵ on donor-acceptor interactions in solution, there has been a great deal of theoretical and experimental interest in the nature of these and other non-ionic complexes. Mulliken¹³ considered that such complexes arise from a Lewis acid-base type of interaction, the bond between the components of the complex resulting from partial transfer of a π electron from the base to an orbital of the acid. He termed the compounds formed from this type of transfer 'charge transfer complexes'.

A more specific case occurs as a result of hydrogen bonding between the donor and acceptor molecules and it is this type of interaction with which we are concerned in the experimental work described in this thesis.

If a complex AD is formed by interaction of an electron acceptor A (e.g. phenol) with an electron donor (e.g. dioxan) which specifically involves the formation of a hydrogen bond, the association constant K is a measure of the tendency for the formation of the hydrogen bond

and is related to the standard free energy change ($\Delta G^\ominus$) of the process by $\Delta G^\ominus = -RT \ln K$. This standard free energy of association will represent a balance between the tendency to minimise the enthalpy change and to maximise the probability or disorder of the system, expressed thermodynamically by

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

where $\Delta H^\ominus$, $\Delta S^\ominus$ are the standard enthalpy and entropy changes, respectively, on association at constant pressure.

The standard enthalpy change $\Delta H^\ominus$ can be calculated from the temperature coefficient of the logarithm of the association constant K and is a direct measure of the strength of the hydrogen bond.

Although infrared spectroscopy has been widely used to investigate the properties of hydrogen bonded systems, ultra-violet spectroscopy has also provided useful information concerning the strength of hydrogen bonding in these systems. Changes in the ultra-violet spectrum of a molecule occurring as a result of hydrogen bond formation enable calculation of the complex present at equilibrium and hence determination of the association constant.

The ultra-violet spectrum of a molecule is altered by the formation of a hydrogen bond if the chromophoric portion of the molecule is perturbed by the bond. Changes in electronic transitions of acidic or basic substances on hydrogen bonding in solution are associated with shifts in the frequency of the band maximum. The shifts may be either to lower frequency (longer wavelength - red shift) or to higher frequency (shorter wavelength - blue shift) and usually there

is no pronounced change of the absorption coefficient.

It is commonly accepted²⁶ that $n \rightarrow \pi^*$ transitions which involve the excitation of non-bonding electrons into the lowest unoccupied π state in a molecule, always cause a frequency shift towards shorter wavelengths on hydrogen bond formation. The $\pi \rightarrow \pi^*$ transitions which correspond to the excitation of π -bonding electrons to the lowest antibonding π orbital, usually cause a frequency shift towards longer wavelengths.

Pimentel²⁷ has suggested that in general, the effect of hydrogen bonding on the ultra-violet spectrum overrides the effects of solvent polarisation, dipole-dipole interactions and dipole polarisation forces which have been discussed by Bayliss and McRae²⁸.

Brealey and Kasha²⁹ investigated the change in position of the $n \rightarrow \pi^*$ ultra-violet absorption band of a number of bases such as pyridine N oxide and benzophenone on changing from a hydrocarbon to a hydroxylic solvent. The large blue shift observed was shown to be due to hydrogen bonding of the n-electrons of the base by the hydroxylic solvent causing stabilisation of the ground state compared to the excited state of the molecule.

Nagakura and Baba³⁰ studied the ultra-violet absorption spectra of aniline, phenol and anisole in various hydrocarbon and ether-type solvents. The frequency shift was found to be anomalously large for aniline and phenol dissolved in the ether-type solvents and they concluded that hydrogen bonding occurred between the solute and solvent molecules.

Hawley³¹ investigated the effect of p-substitution on the hydrogen bonding tendency to dioxan of a series of p-substituted phenols in cyclohexane solution. The association constants K were calculated from ultra-violet spectroscopic data obtained at two temperatures and the results are recorded in Table 1.

TABLE 1

Phenols

<u>Substituent</u>	<u>K</u>		<u>pK</u>		<u>σ^+</u>
	<u>25°C</u>	<u>35°C</u>	<u>25°C</u>	<u>35°C</u>	
p-C(CH ₃) ₃	10.42	8.50	-1.02	-0.93	-0.20
p-CH ₃	10.94	8.81	-1.04	-0.95	-0.17
-H	15.21	10.79	-1.18	-1.03	0
p-Cl	24.43	18.28	-1.39	-1.26	0.23
p-CN	50.20	37.22	-1.70	-1.57	0.63
p-NO ₂	66.83	49.00	-1.83	-1.69	0.78

⁺Hammett's substituent parameter³²

At both temperatures a linear relationship was found to exist between pK and the Hammett substituent parameter σ , suggesting that the latter reflects the effect of the p-substituent on the hydrogen bonding tendency of the OH group.

A similar investigation has been carried out by Vallance²² for a series of p-substituted anilines and the calculated association constants are recorded in Table 2.

TABLE 2

Anilines

<u>Substituent</u>	<u>K</u>		<u>pK</u>		<u>σ^+</u>
	<u>25°C</u>	<u>35°C</u>	<u>25°C</u>	<u>35°C</u>	
p-OCH ₃	0.45	0.36	0.35	0.44	-0.27
p-CH ₃	0.51	0.44	0.29	0.36	-0.17
-H	0.59	0.53	0.23	0.28	0
p-Cl	0.84	0.66	0.08	0.18	0.23
p-Br	0.86	0.64	0.07	0.19	0.23
p-CH ₃ CO	1.09	0.88	-0.04	0.06	0.52
p-CN	1.20	1.00	-0.08	0.00	0.63

⁺Hammett's substituent parameter³²

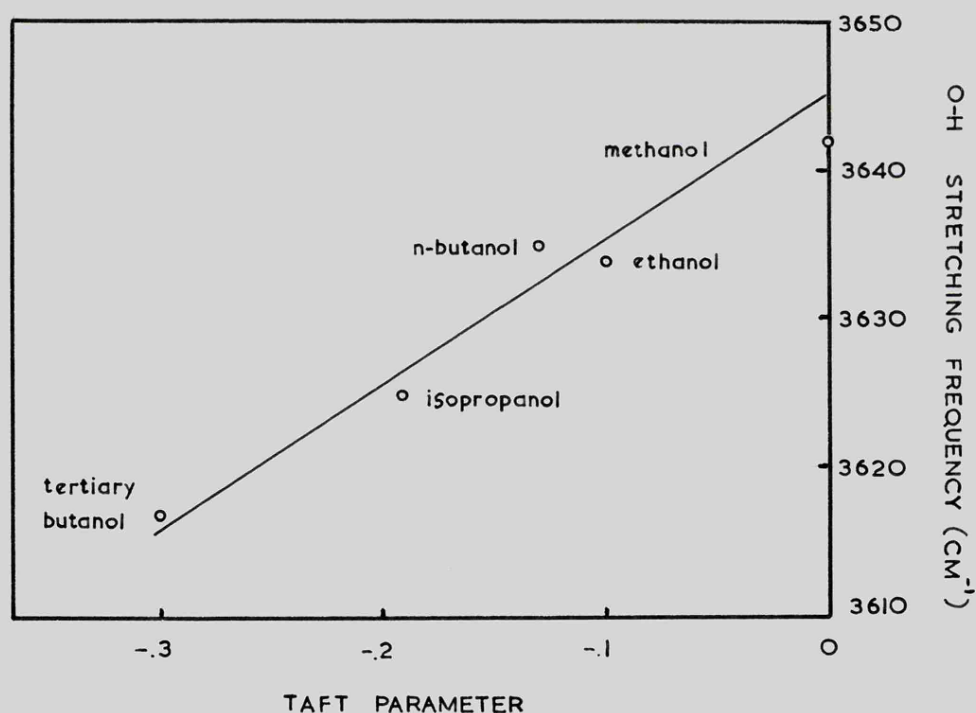
A linear correlation was again obtained between pK and the Hammett substituent constant σ and comparison with the results found for phenols, indicated a greater hydrogen bonding affinity of phenols than anilines for dioxan.

(3) CHANGES IN THE INFRARED SPECTRA ON ASSOCIATION

In the study of donor-acceptor type reactions in solution, infrared spectroscopy has provided useful information especially in those types of reactions involving hydrogen bond formation. As this thesis is mainly concerned with the properties of the O-H group, it is of interest to consider the effect of hydrogen bonding on the prominent O-H absorption bands in the region 3590-3650 cm⁻¹ of the infrared. The position of this band for a related series of compounds varies

significantly with substitution in the molecule, the shift being due to the electrical effect of the substituents³³. Thus for the alcohols studied in this thesis, the O-H stretching frequency is found to correlate with the Taft parameter³⁴ for the alkyl group of the alcohol (Fig. 2), and this parameter provides a quantitative measure of the inductive effect of a group when attached to a saturated carbon atom.

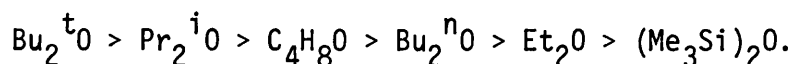
Fig. 2



Ingraham, Corse, Bailey and Stitt³⁵ examined the frequency of maximum adsorption of a series of p-substituted phenols in carbon tetrachloride solution and obtained a linear relationship between

the O-H stretching frequency and the Hammett σ value of the substituent.

Previous studies by Bellamy and Williams³⁶ have also shown that the O-H stretching frequencies in phenols vary systematically with basicity of the solvent. Bellamy, Eglinton and Morman³⁷ have compared the association constants for the interaction between o-substituted phenols and ethers with the frequency shift $\Delta\nu$ of the O-H stretching band, $\Delta\nu$ being defined by $\Delta\nu = \nu_{\text{OH}}^{\text{hexane}} - \nu_{\text{OH}}^{\text{ether/CCl}_4}$. For the unhindered phenols studied, the $\Delta\nu$ values were found to vary systematically with the basicity of the ethers, the order being as follows:-



Experimentally, absorption bands due to X-H stretching vibrations in linear hydrogen bonds are progressively lowered in frequency, broadened, and enhanced in integrated intensity, with increasing strength of hydrogen bonding³⁸. Thus in solutions of increasing concentration, association of phenol molecules by hydrogen bonding results in the sharp absorption peak at 3620 cm^{-1} being replaced by a broad absorption band at about 3330 cm^{-1} ³⁹. Similarly, self association in alcohols results in the monomer peak in the region of 3600 cm^{-1} being replaced by broad and complex bands at lower frequencies which have been attributed to the formation of dimer and polymer molecules⁴⁰.

Relationships between the frequency shift $\Delta\nu$ occurring on association with various physical properties of hydrogen bonded systems have been found. For a system represented as X-H...Y, the frequency shift is

seen to be directly related to the enthalpy of hydrogen bond formation $\Delta H^{\ominus}$, the X-H distance and the two infrared spectral properties (half-width and band intensity) but inversely related to the X...Y distance.

An interesting and perhaps controversial relationship is that between the frequency shift and the enthalpy of bond formation. Such a relationship was first proposed by Badger and Bauer⁴¹ since when various investigators have considered the possibility of a linear correlation between these two parameters. Pimentel and Brown⁴² from data obtained for phenol interacting with a variety of bases concluded that there was no general correlation between $\Delta\nu$ and $\Delta H^{\ominus}$ except for the phenol-ester systems which gave a smooth curve. Jones and Watkinson⁴³ investigated intermolecular bonding between a series of substituted phenols and n-heptyl fluoride in tetrachloroethylene and found $\Delta\nu$ and $\Delta H^{\ominus}$ were related in a linear manner. They suggested that when the systems being compared have the same electron donor atom, the $\Delta\nu$ values may give a reliable indication of relative hydrogen bond strengths, a conclusion supported by Gramstad⁴⁴. However, Joesten and Drago⁴⁵ reported a single linear relationship between $\Delta\nu$ and $\Delta H^{\ominus}$ for the interaction in carbon tetrachloride solution, of phenol and some thirty bases in which the electron donor atom was not always the same.

Epley and Drago⁴⁶ have discussed the experimental problems associated with accurate determination of $\Delta H^{\ominus}$ by spectroscopic techniques and have concluded that these are responsible for any apparent lack of linear correlation between $\Delta\nu$ and $\Delta H^{\ominus}$. These authors determined the $\Delta H^{\ominus}$ values for a series of phenol-base

complexes by a calorimetric method and found the linear correlation:-

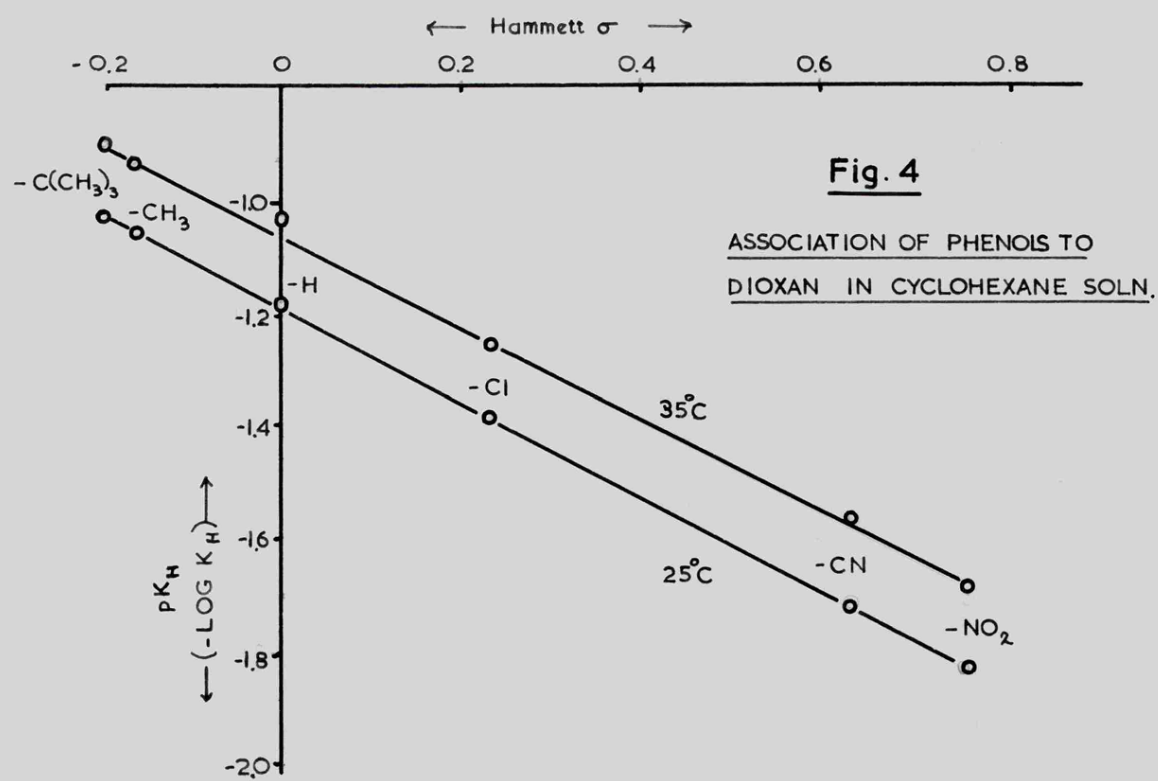
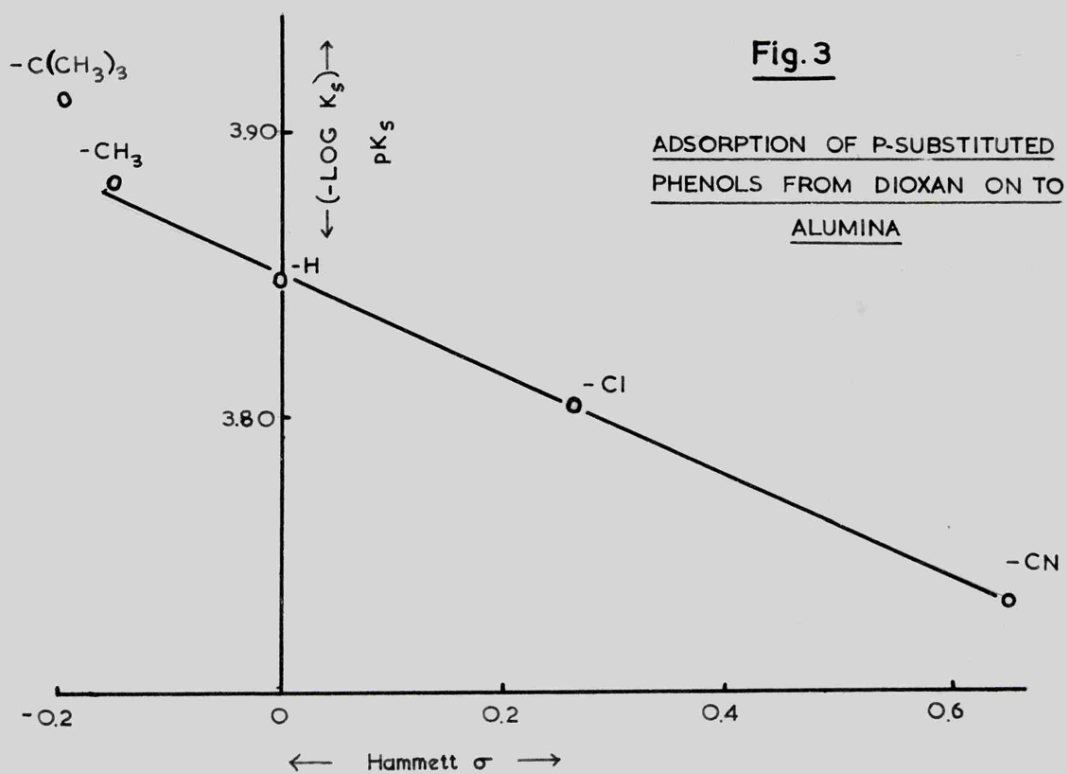
$$-\Delta H^{\ominus} \text{ (kJ mol}^{-1}\text{)} = [0.046\Delta\nu \text{ (cm}^{-1}\text{)} + 11.66] \pm 0.08 \quad (6)$$

Purcell and Drago⁴⁷ have provided a theoretical justification for this relationship by indicating that the change in frequency of the O-H bond is related to a change in force constant and, thus to the change in energy of the O-H bond.

(4) MOBILE PHASE INTERACTIONS IN RELATION TO THE ADSORPTION PROCESS

Fundamentally the forces responsible for adsorption at a solid surface would be expected to be similar in nature to those acting in solution. Since the latter can be readily studied in a quantitative manner, for example by the measurement of association constants, it is interesting to compare such association constants with some experimentally determinable adsorption affinity.

Hawley³¹ has studied the adsorption of p-substituted phenols from dioxan solution onto an alumina surface. Defining an arbitrary 'index of adsorption K_s ' as the 'number of moles of phenol adsorbed at constant relative mole fraction of phenol in the mobile phase', Hawley found that the plot of $\log K_s$ against Hammett σ was almost linear (Fig. 3). As discussed previously, the association constants for a series of p-substituted phenols to dioxan in cyclohexane solution (Table 1) were found to correlate well with the Hammett σ constant (Fig. 4) suggesting that the nature of the interaction in both cases is essentially the same, namely hydrogen bonding.



Vallance²² when considering the adsorption of p-substituted anilines from cyclohexane solution onto an alumina surface found a similar relationship between the association of the anilines to dioxan in solution and the association to the adsorbent surface.

Thus in these instances, the process of adsorption at the solid-solution interface is analogous to that of association in solution in that a defined index of adsorption is related to the Hammett structural parameter in a similar manner to the association constant of the hydrogen bonding process to dioxan.

An aspect of the present investigation is a study of the interactions in the liquid phase between phenol and a series of alcohol and ether molecules whose functional groups can be considered similar to those present on silica and alumina surfaces. A further aspect concerns the adsorption of phenol from various solvents onto silica and alumina surfaces.

D. THERMODYNAMICS OF THE ADSORPTION PROCESS

The thermodynamic treatment of adsorption from solution is complex as it involves a study of the solution itself as well as that of the interfacial phenomena. In interpreting the thermodynamic properties of real systems it is therefore convenient to first establish an 'ideal' or 'perfect' reference system and then consider deviations from ideality in terms of activity coefficients.

A simple treatment which shows how the nature of the solution determines the form of the isotherm in adsorption on to a solid surface has been developed by Schay⁴⁸. This author assumes that a change in the chemical potential of the pure component occurs on adsorption and denotes this change by $\Delta\mu^0$.

$$\text{Thus } (\mu_1^s)^0 = (\mu_1^l)^0 + \Delta\mu_1^0 \quad (7)$$

where $(\mu_1^s)^0$, $(\mu_1^l)^0$ are the chemical potentials of the pure components in the adsorbed and mobile phases, respectively.

Conditions of equilibrium for a binary solution in contact with a solid surface are

$$\mu_1^{0,l} + RT \ln a_1^l = \mu_1^{0,s} + RT \ln a_1^s \quad (8)$$

and

$$\mu_2^{0,l} + RT \ln a_2^l = \mu_2^{0,s} + RT \ln a_2^s \quad (9)$$

Combining (7) and (8) gives:-

$$\underline{-\Delta\mu_1^0 = RT \ln \frac{a_1^s}{a_1^l}}$$

Elton⁴⁹ has suggested that the term $\mu_1^{0,l} - \mu_1^{0,s} = -\Delta\mu_1^0$ should be

referred to as the adsorption potential of component 1.

For an ideal liquid solution, activities can be replaced by mole fractions and it follows from equations (7), (8) and (9) that

$$\frac{x_1^S}{x_1^L} = \frac{x_2^S}{x_2^L} \cdot e^{(\Delta\mu_2^0 - \Delta\mu_1^0)/RT} \quad (10)$$

where $x_1^S, x_2^S; x_1^L, x_2^L$ are the mole fractions of components 1 and 2 in the adsorbed and mobile phases respectively.

Thus if the adsorption potential of component 1 is greater than component 2 then $e^{(\Delta\mu_2^0 - \Delta\mu_1^0)/RT} > 1$ and $x_1^S > x_1^L$

i.e. preferential adsorption of one component must occur over the whole concentration range and a U-shaped isotherm (Fig. 1b) will be observed.

Replacing $e^{(\Delta\mu_2^0 - \Delta\mu_1^0)/RT}$ by K in equation (10) gives

$$x_1^S = \frac{Kx_1^L}{Kx_1^L + x_2^L} \quad (11)$$

which is the individual isotherm for component 1, expressed in terms of its mole fraction in the adsorbed layer ($x_1^S = n_1^S/n^S$) and is of the Langmuir type.

Combination of equation (11) with that for the composite isotherm expressed in the form (equation 2) which emphasises the preferential adsorption of one component, leads to

$$\frac{n^0 \Delta x_1^L}{m} = n^S \left(\frac{Kx_1^L}{Kx_1^L + x_2^L} - x_1^L \right)$$

the linear form of which is

$$\frac{n^0 \Delta x_1^\ell}{x_2^\ell \cdot m} = n^s \left(\frac{K-1}{K} \right) - \frac{n^0 \Delta x_1^\ell}{m} \cdot \frac{1}{K \cdot x_1^\ell} \quad (12)$$

Siskova and Erdos⁵⁰ have found that equation (12) is valid over a wide range of concentrations for adsorption from a number of mixtures by silica gel (e.g. carbon tetrachloride-benzene) but does not apply to all systems and tends to be less satisfactory for adsorption by activated charcoal.

A more comprehensive thermodynamic treatment has been proposed by Everett⁵¹ who uses a simple molecular model as a basis for an ideal system which provides a reference state from which the behaviour of real systems can be studied.

According to Everett, adsorption occurs from a perfect solution consisting of two components 1 and 2 of different molar energies and entropies but of approximately similar surface area requirement on to a perfect adsorbing surface. This surface consists of a number of exactly equivalent adsorption sites and adsorption is assumed to be monomolecular. The molecules when adsorbed occupy one adsorption site each and are assumed to have no interaction with each other. The liquid phase is described as an assembly of plane lattices stacked together with their planes parallel to the surface of the adsorbent. Each plane, except the one adjacent to the adsorbent surface, is of the same composition with respect to components 1 and 2, the adsorbed phase being of different composition because of the selective adsorption of one or more components of the solution.

The free energy F of the system is defined as:-

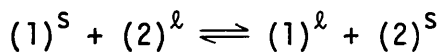
$$F = U - T(S_{\text{CONFIG.}} + S_{\text{THERM.}}) \quad (13)$$

where U is the energy of the system

$S_{\text{CONFIG.}}$, S_{THERM} are the configurational and thermal entropies respectively.

Consideration of the total number of ways of arranging the molecules on the surface and in the solution enables the configurational entropy to be expressed in terms of the number of the moles in each phase. The total entropy is computed by addition of the molar thermal entropies of the molecules in both phases, assuming independence of the composition of both surface and solution. Similarly the energy of the system can be expressed in terms of the molar energies of the two kinds of molecules.

The adsorption equilibrium is described as



where s and l superscripts represent the adsorbed and mobile phases respectively.

On considering a perturbation of the system at equilibrium such that dn moles of component 1 are replaced on the surface by the same number of molecules of component 2 from the solution, then the corresponding change in free energy dF can be found from expression (13).

Introducing the condition of equilibrium,

$$\left(\frac{dF}{dn} \right)_{T,V} = 0$$

Everett showed that:-

$$\frac{x_1^s \cdot x_2^l}{x_1^l \cdot x_2^s} = K_1 \quad (14)$$

where $x_1^s, x_2^s; x_1^l, x_2^l$ are the mole fractions of components 1 and 2 in the adsorbed and mobile phases respectively, and K_1 replaces an exponential factor which contains terms relating to the changes of entropy and energy occurring on adsorption.

Since $x_2^l = (1-x_1^l)$ and $x_2^s = (1-x_1^s)$, equation (14) becomes

$$x_1^s = \frac{K_1 x_1^l}{1 + (K_1 - 1) x_1^l} \quad (15)$$

If the two components have the same molecular area, then at all equilibrium concentrations:-

$$n_1^s + n_2^s = n^s$$

where n^s is the total number of moles which can be accommodated in the adsorbed phase by unit weight of solid.

$$\text{Also } x_1^s = \frac{n_1^s}{n^s} \quad (16)$$

Combining (15) and (16) gives

$$n_1^s = \frac{K_1 n^s x_1^l}{1 + (K_1 - 1) x_1^l} \quad (17)$$

$$\text{Similarly } n_2^s = \frac{n^s x_2^l}{K_1 - x_2^l (K_1 - 1)} \quad (18)$$

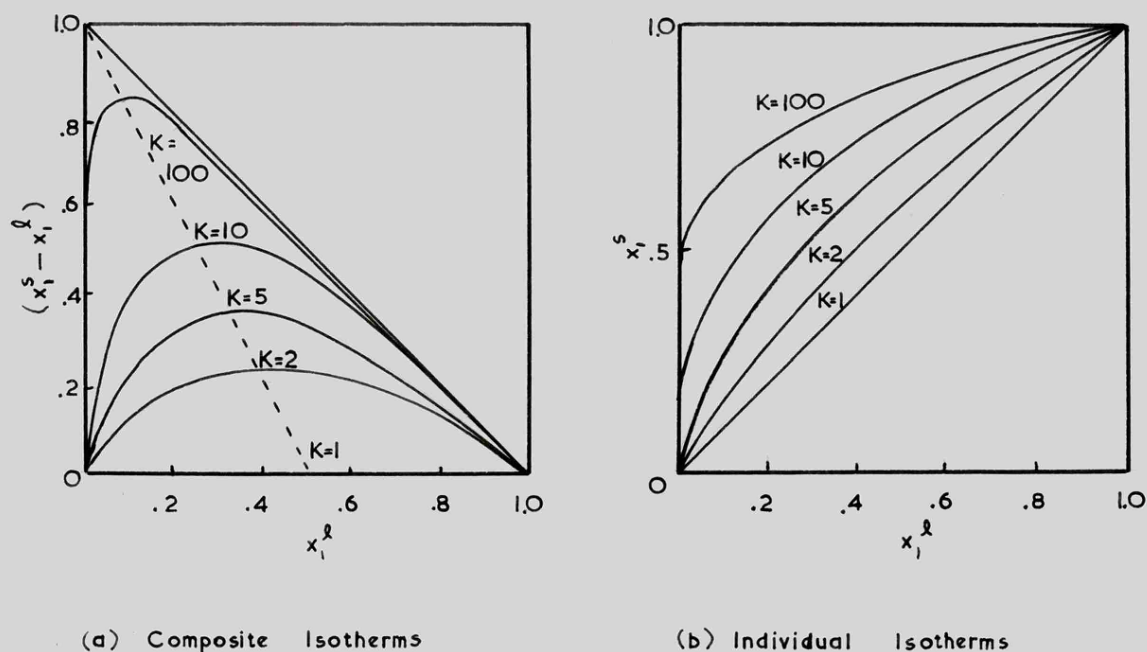
Combining (1), (17) and (18) gives

$$\frac{mx_1^l x_2^l}{n^0 \Delta x_1^l} = \frac{1}{n^s} \left(x_1^l + \frac{1}{(K-1)} \right) \quad (19)$$

A plot of the left hand side of this equation against x_1^l should give a linear graph of slope $1/n^s$ and of intercept $1/n^s(K-1)$, so allowing n^s and K to be determined. If the assumptions of the model are correct, and if the areas occupied by the two kinds of molecule do not differ significantly, then by assuming an area per molecule, the surface area per gram of solid can be calculated.

Theoretical composite and individual isotherms for different values of K are shown in Fig. 5. As with Schay's treatment the composite isotherms are seen to be U-shaped while the individual isotherms are of the Langmuir type.

Fig. 5



Wright⁵² has applied Everett's equation to adsorption from mixtures of benzene-ethylene dichloride and bromobenzene-chlorobenzene on to Graphon, a homogeneous surface and Spheron 6, a heterogeneous surface. The composite isotherms appropriate to the benzene-ethylene dichloride systems are shown in Fig. 6. Preferential adsorption of benzene over the whole concentration range is seen to occur on Graphon whereas with Spheron 6 as adsorbent the negative section of the composite isotherm at high benzene concentrations reveals preferential adsorption of ethylene dichloride in that region.

Application of equation (19) gives the plots shown in Figs. 7 and 8. Whereas the plot for Graphon is found to be linear, that for Spheron 6 is seen to be only linear at low concentrations. By determining the area requirement of each adsorbate from vapour phase adsorption, Wright calculated the surface area of Graphon from the slope of the Everett plot as $119.4 \text{ m}^2\text{g}^{-1}$ in reasonable agreement with that determined by low temperature nitrogen adsorption, $89.4 \text{ m}^2\text{g}^{-1}$. Wright considered that the results obtained on Spheron 6 have no significance due to lack of linearity of the Everett plot and concluded that the deviations observed with Spheron 6 were due to the nature of the adsorbent surface and the absence of any significant preferential adsorption of any one component over the whole concentration range.

More recently, Kagiya et al⁵³ have applied equation (19) to the adsorption from binary solutions of cyclohexane-aromatic compounds on to silica gel. Good linear plots were obtained and the values of $\log K$ (referred to as the separation factor α by the authors) were found to correlate well with the electron donating properties of these compounds as measured by their ionisation potentials or, in the case

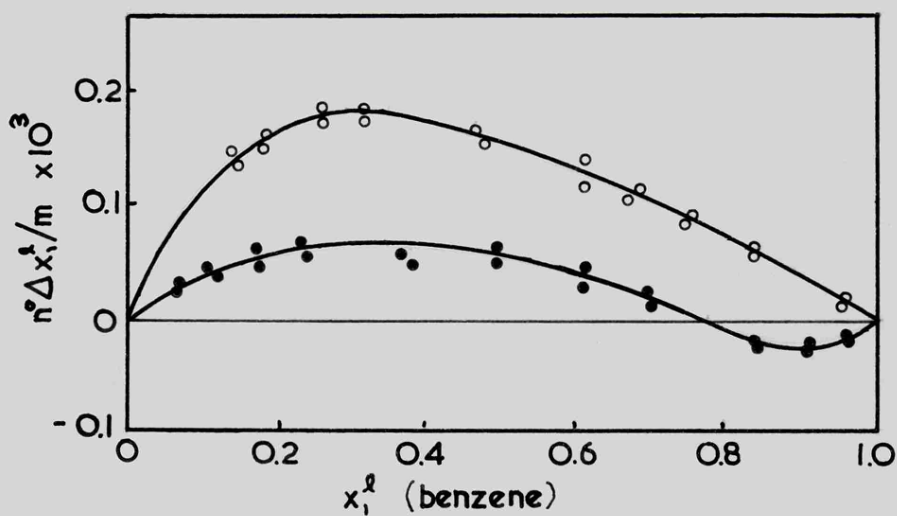


Fig.6

Adsorption from benzene and ethylene dichloride
solutions at 30°C o Graphon ● Spheron 6

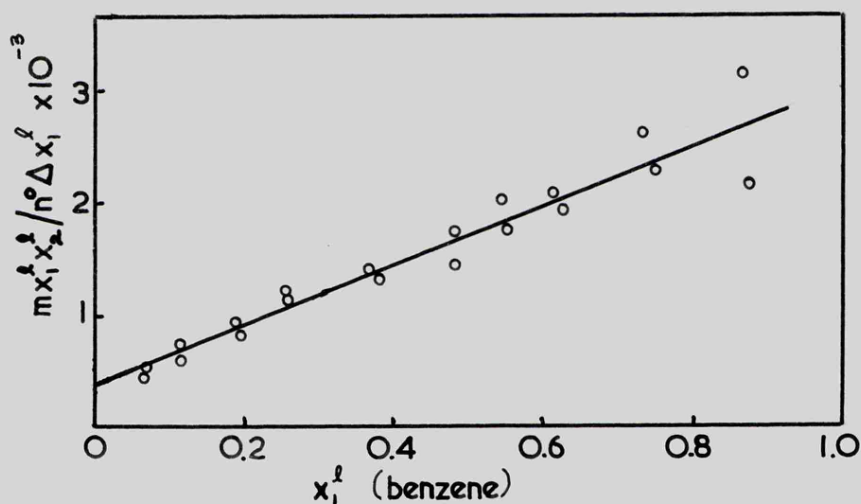


Fig.7

Graphon

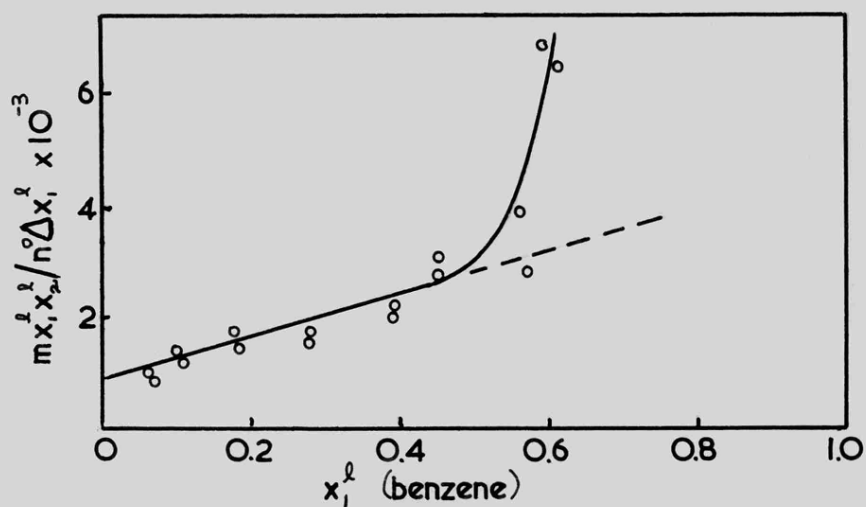


Fig.8

Spheron 6

of substituted aromatics, their Hammett sigma values. The authors concluded that the adsorption of the aromatic compounds was mainly due to the π -electrons of the benzene nuclei, except for anisole whose deviation from the observed correlations suggested adsorption via its oxygen atom.

The isotherms calculated theoretically for perfect monolayer adsorption from a perfect solution are seen to be either positive or negative over the whole concentration range. It is found experimentally, however, that in many instances the isotherms pass through zero, (i.e. S-shape) and from equation (2) it can be seen that at this point where $x_1^S = x_1^L$, the surface and bulk phases have the same composition. This point is analogous to an azeotropic point in liquid-vapour equilibrium. The simplest theoretical model showing this behaviour is that of a regular solution adsorbed as a regular monolayer on a homogeneous solid surface.

For regular solutions, Schay⁴⁸ uses activity coefficients defined by:-

$$\ln f_1 = q(1-x_1^L)^2; \quad \ln f_2 = q(x_1^L)^2$$

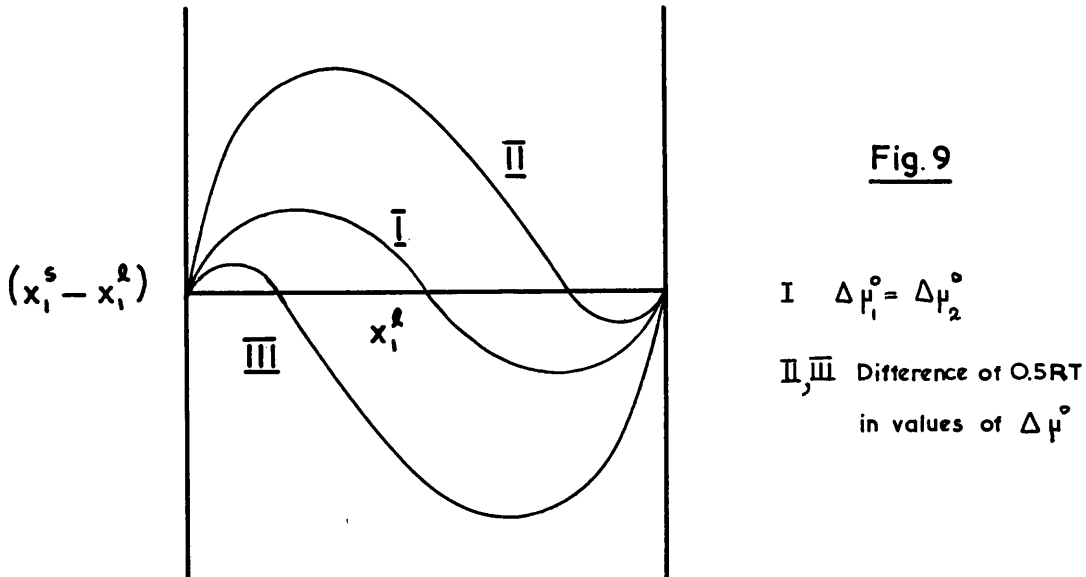
where q is a measure of the interaction between the two components at a given temperature. A different term q' is required for the adsorbed layer and Schay relates q' to q by assuming the adsorbed layer is a monolayer and that the molecules can be regarded as cubes, of the same size for the two components. Then each molecule in the bulk phase has 26 nearest neighbours, whereas each molecule in the surface layer has only 17.

$$\text{Hence } q' = \frac{17q}{26} = 0.654q$$

Application of the above definitions leads to the adsorption isotherm equation:-

$$\ln \frac{x_1^s}{1-x_1^s} - 1.308qx_1^s = \ln \frac{x_1^l}{1-x_1^l} + \frac{\Delta\mu_2^0 - \Delta\mu_1^0}{RT} + 0.346q - 2qx_1^l \quad (20)$$

and, a reversal of the sign of preferential adsorption is possible between $x_1^l = 0$ and $x_1^l = 1$ giving rise to a S-shaped composite isotherm. Thus for mixtures of benzene and ethanol, using a value of q derived from vapour pressure data, Schay calculated the isotherms shown in Fig. 9 for a small difference between $\Delta\mu_1^0$ and $\Delta\mu_2^0$. Large differences lead to U-shaped isotherms.



The treatment is not absolutely precise as the molecules of benzene and ethanol are unlikely to occupy equal areas on the surface as required by the theory. To allow for this, the thermodynamic

treatment by Butler⁵⁴ for adsorption at the liquid-vapour interface has shown that an extra term is required, namely

$$\sigma(A_1 - A_2)/RT$$

where σ is the interfacial tension,

A_1, A_2 are the respective partial molar surface areas.

As data for the interfacial (liquid/solid) tensions are not readily available, systems are usually chosen where $A_1 = A_2$.

The form of the isotherm equation for regular solutions, analogous to that for ideal solutions (equation 10) has been derived by Schay as:-

$$x_1^S = \frac{x_1^L}{x_1^L + \frac{x_2^L f_2^S f_1^S}{f_1 f_2^S} \cdot e^{\sigma(A_2 - A_1)/RT} \cdot e^{(\sigma_1^0 A_1 - \sigma_2^0 A_2)/RT}} \quad (21)$$

where σ is the interfacial tension and σ^0 that of the pure component in contact with the surface.

$f_1^S, f_2^S; f_1, f_2$ are the activity coefficients in the adsorbed and mobile phases respectively.

For non-ideal mixtures, Schay^{55,56} concluded that the shape of the composite isotherm depended on four factors:-

- (i) the difference in the adsorption potentials of the two components, $e^{(\sigma_1^0 A_1 - \sigma_2^0 A_2)/RT}$
- (ii) the nature of the bulk phase as given by f_2/f_1
- (iii) the interaction of the adsorbed species, as given by f_1^S/f_2^S
- (iv) the variation of the surface free energy with composition of the bulk phase, as given by $e^{\sigma(A_2 - A_1)/RT}$.

The importance of the second factor is often considerable⁵⁶.

Everett⁵⁷ has developed a rigorous thermodynamic treatment for adsorption from real systems by considering how non-ideality of the surface and bulk phases cause deviations from his previously defined 'perfect system' model.

Thus equation (14) can be rewritten as

$$\frac{x_1^S f_1^S x_2^L f_2^L}{x_1^L f_1^L x_2^S f_2^S} = K \quad (22)$$

where $f_1^S, f_2^S; f_1^L, f_2^L$ are the activity coefficients for components 1 and 2 in the adsorbed and mobile phases respectively.

Substitution in equation (22) of

$$p_1 = p_1^0 x_1^L f_1^L \quad \text{and} \quad p_2 = p_2^0 x_2^L f_2^L$$

and equation (2) leads to:-

$$\frac{f_2^S}{f_1^S} \cdot K = \frac{x_1^S \cdot x_2^L \cdot f_2^L}{x_2^S \cdot x_1^L \cdot f_1^L} = \frac{p_2 \cdot p_1^0}{p_1 \cdot p_2^0} \left[\frac{x_1^L + (n^0/n^S) \Delta x_1^L}{x_2^L - (n^0/n^S) \Delta x_1^L} \right] \quad (23)$$

where p_1 and p_2 are the partial vapour pressures of components 1 and 2 over the bulk solution at the equilibrium composition and p_1^0, p_2^0 are the vapour pressures of the pure components at the same temperature.

The value of n^S can be found from a knowledge of the surface area of the solid, and the individual values of K, f_1^S and f_2^S by the application of the Gibbs adsorption equation which Everett showed leads to:-

$$\int_0^1 \ln \left(\frac{x_1^s x_2^{\ell} \cdot f_2^{\ell}}{x_2^s \cdot x_1^{\ell} \cdot f_1^{\ell}} \right) dx_1^s = \ln K \quad (24)$$

and

$$\ln f_2^s = x_1^s \cdot \ln \left(\frac{x_1^s x_2^{\ell} f_2^{\ell}}{x_2^s x_1^{\ell} f_1^{\ell}} \right) - \int_0^{x_1^s} \ln \left(\frac{x_1^s x_2^{\ell} f_2^{\ell}}{x_2^s x_1^{\ell} f_1^{\ell}} \right) dx_1^s \quad (25)$$

Thus the equilibrium constant K can be evaluated for an imperfect system without knowledge of the surface activity coefficients.

Calculation of the surface activity coefficients from adsorption experiments using equation (25) enables a comparison to be made with those predicted by theoretical models of imperfect surface phases assuming that accurate data on the vapour pressures of the bulk solution are known.

For a theoretical model of the 'imperfect system', Everett considered adsorption from regular solutions, the properties of which can be discussed in terms of the quantity

$$\alpha = Nz [\epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22})]$$

where ϵ_{ij} ($i, j = 1, 2$) is the energy of interaction between a pair of molecules i, j on adjacent lattice sites,

N is Avogadro's number, and

z the number of nearest neighbours to a given lattice site.

For adsorption at a solid surface, Everett used the model defined previously for perfect systems⁵¹ and assumed that of the z nearest neighbours, a fraction ℓ were in the same lattice plane as the molecule considered and fractions m in each of the adjacent planes such that $\ell + 2m = 1$. By using the same procedure as Guggenheim⁵⁸

for the discussion of the liquid-vapour interface but including interactions between surface molecules and the adsorbing solid, Everett derived the following equation for the adsorption equilibrium:-

$$\ln \left(\frac{x_1^S x_2^L}{x_1^L x_2^S} \right) = \ln K + \frac{(\ell+m)}{RT} \alpha (x_2^L - x_1^L) + \frac{\ell \alpha}{RT} (x_1^S - x_2^S) \quad (26)$$

Equation (26) can be solved graphically or by an iterative procedure to obtain x_1^S as a function of x_1^L corresponding to chosen values of K and α . For a close-packed cubic lattice arrangement ($\ell = \frac{1}{2}$, $m = \frac{1}{4}$), Everett obtained S-shaped curves (Figs. 10,11).

In order to test the conformity of a system to regular surface behaviour Everett proposed the use of equation (23) to calculate $f_2^S K / f_1^S$ which is related to the bulk and surface concentrations by the expression:-

$$\ln(f_2^S K / f_1^S) = \ln K + (\alpha/RT) [\ell(1-2x_2^S) + m(1-2x_2^L)] \quad (27)$$

A plot of this equation enables values for K and α to be calculated for comparison with the K obtained from equation (24) experimentally and α derived from properties of the bulk solution.

Wright⁵⁹ has applied Everett's theory to adsorption data for the systems benzene-cyclohexane, benzene-carbon tetrachloride and carbon tetrachloride-cyclohexane using the adsorbents coconut shell charcoal and decolorising charcoal. Although the systems were found not to follow strictly the requirements of equation (19) for perfect surface

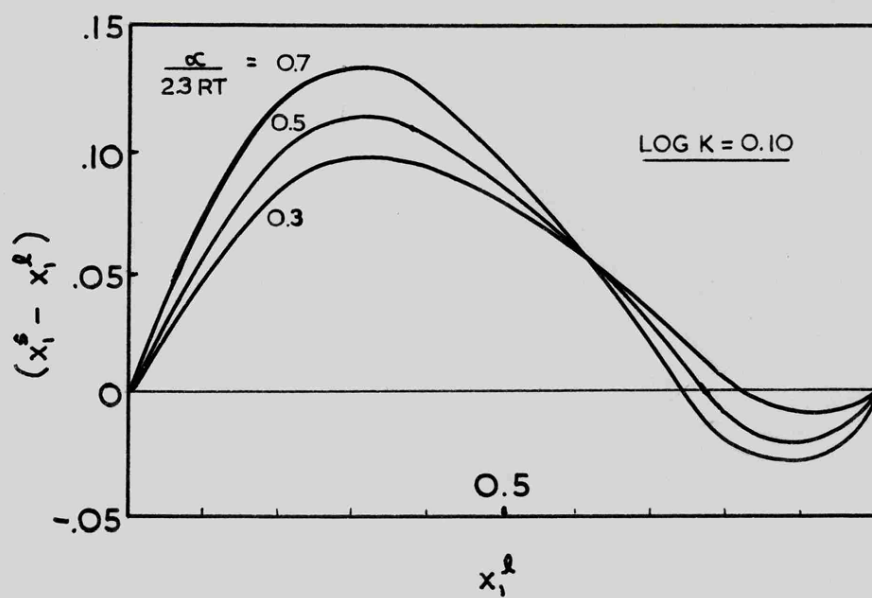


Fig. 10

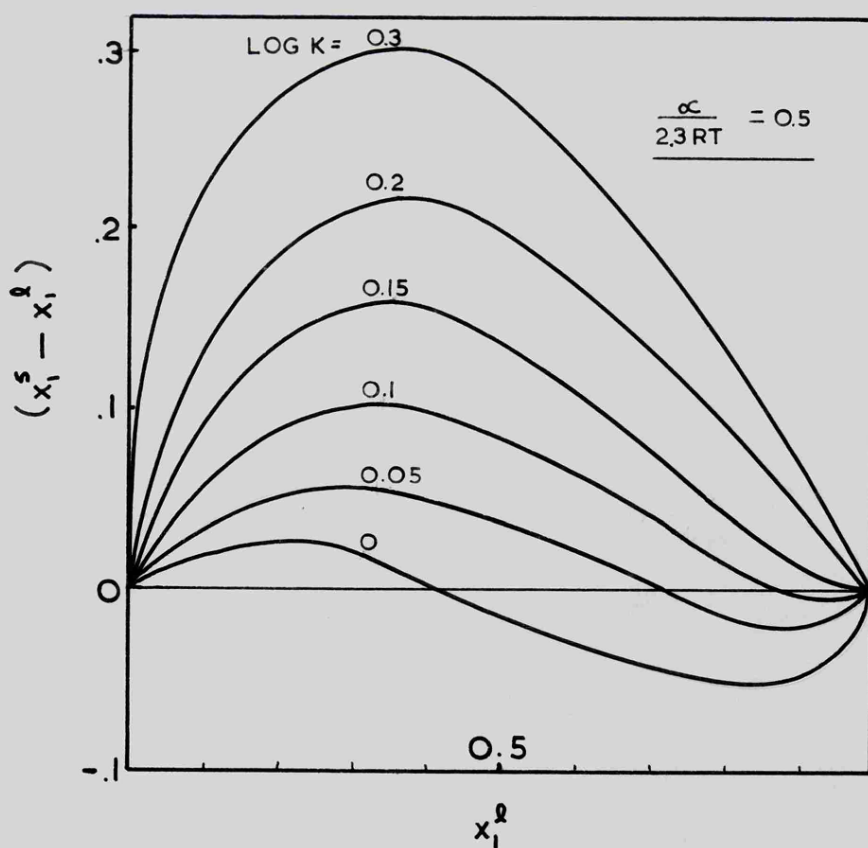


Fig. 11

behaviour, close correlations were obtained despite the non-ideality of the solutions and the non-Langmuir surfaces of the adsorbents. Application of equation (27) for regular surface behaviour gave plots (Figs. 12, 13 and 14) from which values of K were obtained which showed good agreement with those found experimentally (equation 24), Table 3.

TABLE 3

Adsorbates \ Adsorbents	Coconut Shell Charcoal		Decolorising Charcoal	
	K		K	
	eqn. 27	eqn. 24	eqn. 27	eqn. 24
benzene-cyclohexane	15.8	16.6	14.9	15.2
benzene-carbon tetrachloride	4.8	4.3	5.3	5.5
carbon tetrachloride-cyclohexane	3.9	3.8	4.1	4.2

Wright concluded that either the equations were insensitive in distinguishing completely between perfect and regular surface behaviour, or that the systems chosen were intermediate in character and thus tended to satisfy some aspects of both situations.

Day, Eltekov, Parfitt and Thompson⁶⁰ have studied adsorption from binary liquid mixtures of p-xylene and n-heptane at 25°C on to characterised rutile surfaces containing various amounts of molecular water and hydroxyl groups. The composite isotherms obtained are shown in Fig. 15. Surface S1 was outgassed at 450°C and contained no molecular water on the surface, S4 had a water coverage approximating to one monolayer and S5 contained two to three monolayers of adsorbed water.

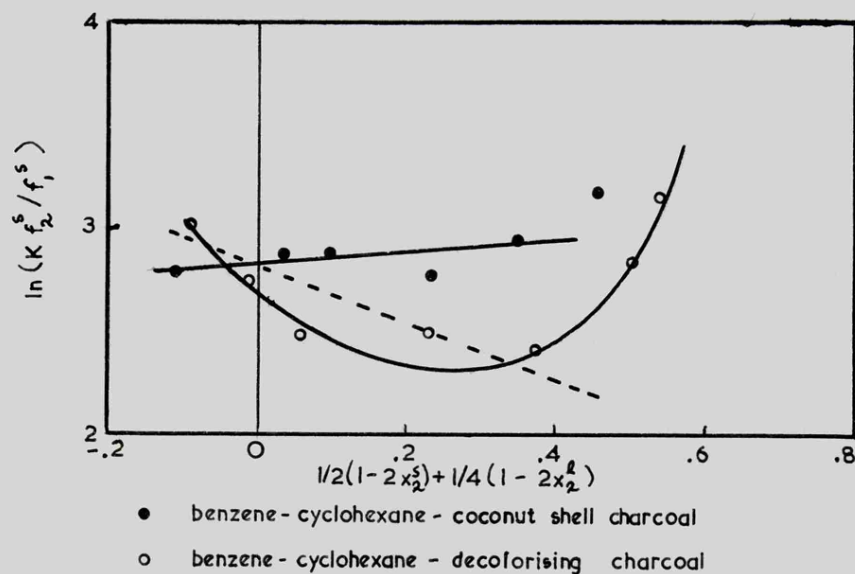


Fig.12

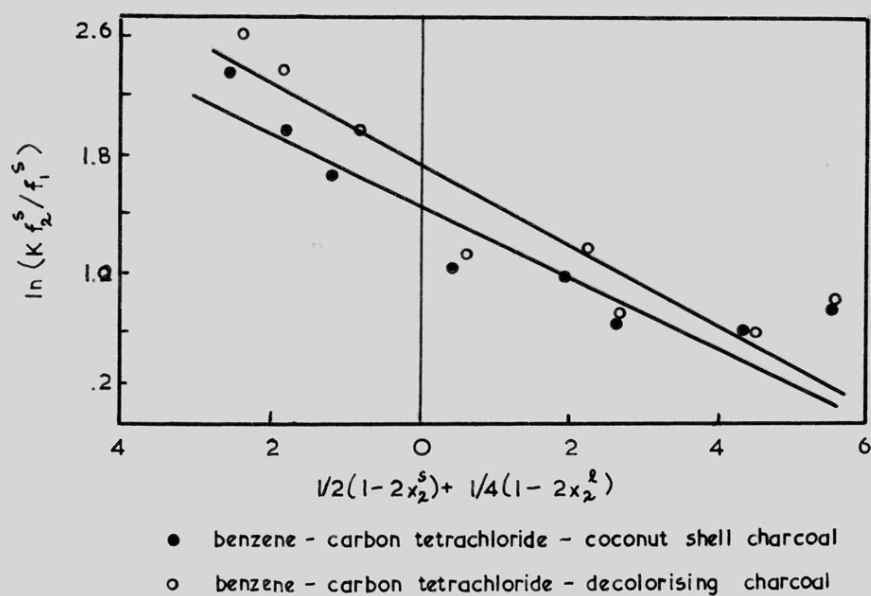


Fig.13

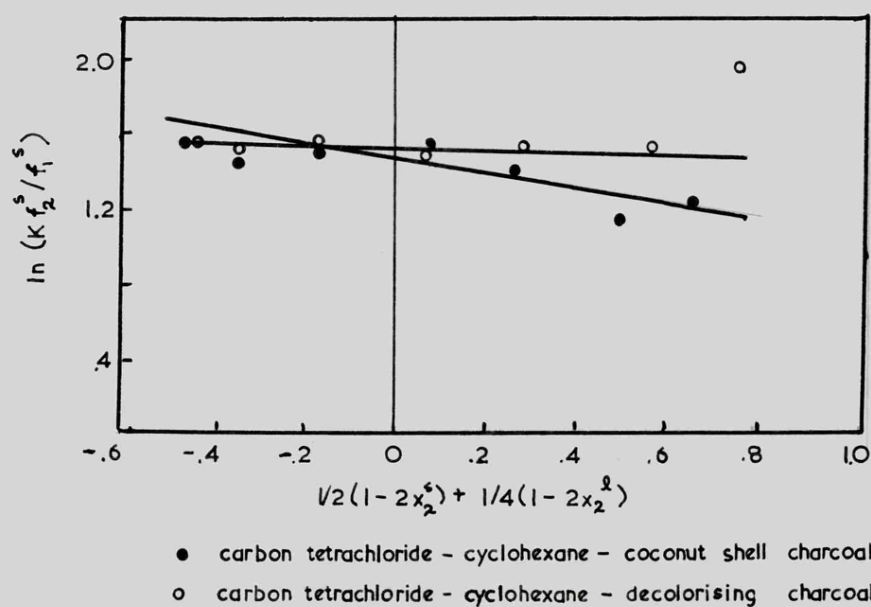
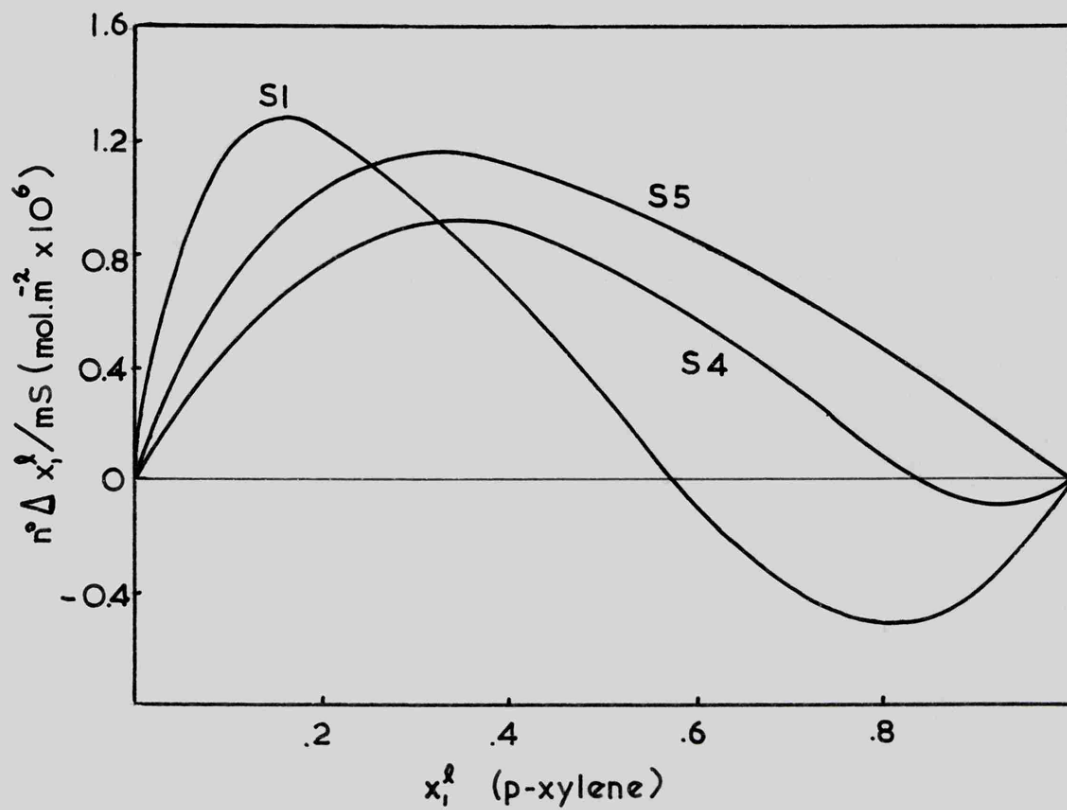


Fig.14

Values of the surface activity coefficients were calculated using the theories of Schay and Everett and are plotted against the surface mole fractions in Fig. 16. For the S1 surface, the surface activity coefficients for both components deviate markedly from unity and the authors attributed the non-ideality of the adsorbed phase to the presence on the surface of isolated hydroxyl groups and vacancy defects associated with strong dehydroxylation which provide adsorption centres capable of strong interaction with the p-xylene. For the surfaces S4 and S5 which contain increasing amounts of adsorbed water the surface activity coefficients are seen to approach unity indicating that removal of the specific influence of the hydroxyl groups with adsorbed water leads to a surface phase which is approximately ideal over the whole range of composition. The authors concluded that the adsorbed layers formed on the surfaces S4 and S5 were sufficiently ideal for a thermodynamic analysis using the theories of Schay and Everett.

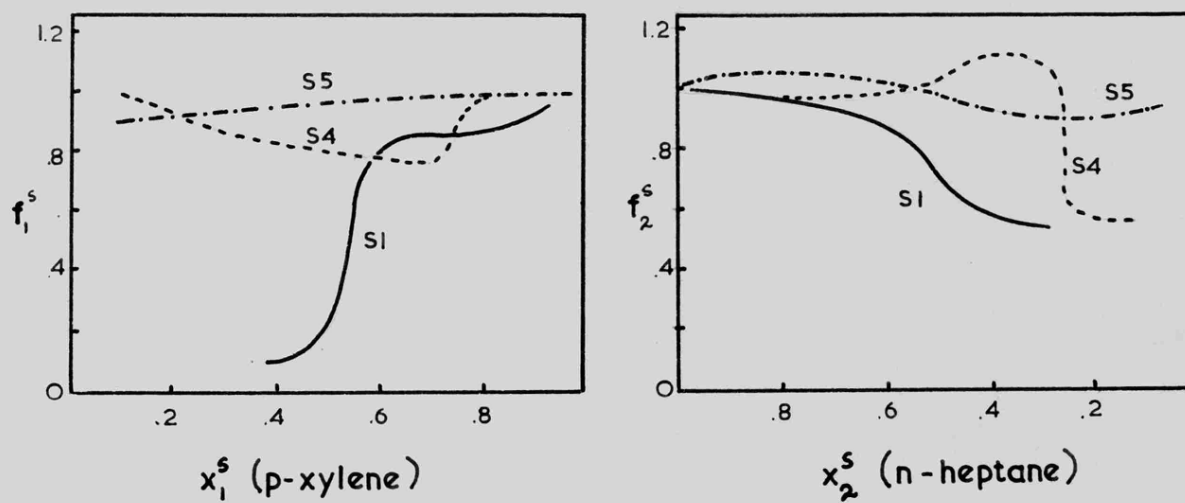
One aspect of this present investigation is to apply Everett's equations to the adsorption systems considered in this thesis and to assess closeness of approach to his 'ideal system' model. It is also proposed to consider whether the value of K obtained thermodynamically reasonably represents a measure of the adsorption affinity of the adsorbate for the adsorbent surfaces.

Fig.15



Adsorption of p-xylene from n-heptane on to rutile

Fig.16



EXPERIMENTAL

The experimental work contained in this thesis consists of a study of the influences of p-substitution and solvent interaction on the following properties of the O-H bond in phenols:

- A. Changes in the group stretching frequencies in the infrared occurring on association.
- B. The hydrogen bonding tendency in solution of the O-H group to a series of ether and alcohol type donors as reflected in the magnitude of the association constant.
- C. The hydrogen bonding affinity of the O-H group for alumina and silica surfaces from measurement of adsorption at the solution-solid interface.

A. GROUP STRETCHING FREQUENCY IN THE NEAR INFRARED

(1) MATERIALS AND APPARATUS

(a) The Solvents

Cyclohexane, Dioxan, Tetrahydrofuran, Dibutyl ether, Diethyl ether, Di-isopropyl ether and 1,2 Dimethoxyethane were allowed to stand in contact with fresh sodium wire for three days, refluxed over sodium for several hours and then fractionally distilled, the middle fraction being collected.

Carbon tetrachloride was dried over calcium chloride and fractionally distilled, the middle fraction being collected.

'Analar' grade Methanol, n-Butanol and 'Absolute' Ethanol were dried over calcium oxide and fractionally distilled.

'Analar' grade Isopropanol, Tertiary Butanol and 3 Methyl 1 Butanol were dried by forming the azeotrope with benzene, removal of the azeotrope and excess benzene by distillation followed by fractional distillation of the residue.

Dimethylformamide was purified by forming the azeotrope with benzene followed by its subsequent removal by distillation. The residue was allowed to stand over freshly heated barium oxide for one day and then distilled under reduced pressure.

All the solvents were checked for purity by gas-liquid chromatography.

(b) The Solute

'Analar' grade Phenol was fractionally distilled three times and dried in vacuo over phosphorus pentoxide.

Physical constants of the solvents and solute are recorded in Table 4.

TABLE 4

	Boiling/Melting Point ($^{\circ}\text{C}$ at atmos. press.)	
	<u>Experimental</u>	<u>Literature⁶¹</u>
Cyclohexane	81	81
Dioxan	101	101
Tetrahydrofuran	67	65
Dibutyl ether	142	142
Diethyl ether	35	35
1,2 Dimethoxyethane	86	85
Carbon Tetrachloride	77	77
Methanol	65	65
n-Butanol	118	118
Ethanol	78	79
Isopropanol	82	82
Tertiary Butanol	82	82
3 Methyl 1 Butanol	132	132
Dimethylformamide	152	153
Phenol	41	43 ⁶¹ , 41 ⁶²
Di-isopropyl ether	67	68

(c) The Apparatus

Spectroscopic measurements in the near infrared were made using a Unicam SP 700 recording spectrophotometer. The instrument was fitted

with an absorbance unit (Unicam) and aluminium cell housings which permits the control of cell temperature by circulation of water at $25 \pm 0.02^{\circ}\text{C}$ from a thermostatically controlled water bath.

In the region of interest, $4000\text{--}3000\text{ cm}^{-1}$, the radiation from a tungsten filament lamp is dispersed by a grating (Merton - N.P.L. replica, 7500 lines/in., blazed at 3333 cm^{-1}) disposed at an angle to the incident beam. The monochromatic radiation from the exit slit is divided into two parts and passed alternatively through the sample and reference cells. The two beams are then focused on a lead sulphide detector and the signal from the latter passes to a recorder which displays the transmittance or optical density of the sample cell with respect to the reference cell. The slit width is controlled automatically such that the energy detected in the reference beam is constant at a level determined by the resolution setting.

The spectrum is presented on the chart of a Honeywell recorder as a linear graph of percentage transmittance or absorbance against wavenumber (cm^{-1}), every 20 cm^{-1} being marked automatically by two pens at the edges of the chart.

The instrument has 5 scanning speeds and 4 chart speeds which allows optimum conditions to be selected for frequency measurement. A series of multipots are provided at 100 cm^{-1} intervals, to adjust the 100% transmittance line as a function of wavenumber and so compensate for differences in the transmission of the sample and reference cells or for differences in the optics of the two beams.

(d) Procedure

Solutions were prepared containing initial concentrations of phenol and donor molecules such that the complex formed in solution gave approximately 50% transmittance. At these concentrations, solute-solute interactions were found to be negligible. Flasks containing the solutions were stored in a thermostatically controlled water bath ($25 \pm 0.02^{\circ}\text{C}$) and water from the latter was circulated through the cell housings for about 2 hours before any measurements were made. The two cells were rinsed and filled with carbon tetrachloride and then mounted in the cell compartments. The multipots were adjusted at 100 cm^{-1} intervals over the range required and a solvent-solvent base line recorded. The sample cell was then refilled with the solution under investigation and the spectrum recorded after the cell had attained temperature equilibrium. After a series of measurements had been made the solvent-solvent base line was rechecked.

The stretching frequencies of the 'free' and 'bonded' hydroxyl group in phenol were measured and the shift occurring on association calculated. Calibration of the instrument in the $3700\text{-}3500\text{ cm}^{-1}$ range was achieved by recording the absorption bands of water vapour in the atmosphere at the end of each series of measurements. The peak frequencies were located with a vernier scale to the nearest 0.5 cm^{-1} and compared with the precise literature values⁶³. The indene peak⁶³ at $3297.0 \pm 1.5\text{ cm}^{-1}$ was used for frequency calibration in the vicinity of 3300 cm^{-1} .

(2) EXPERIMENTAL RESULTS

The experimental results are recorded in Table 5.

TABLE 5

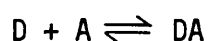
<u>Donor</u>	<u>Frequency of Max. Absorption (cm⁻¹)</u>		<u>Frequency Shift</u>
	<u>Free 'OH' (Phenolic)</u>	<u>Bonded 'OH'</u>	<u>$\Delta \nu$ cm⁻¹</u>
Dimethylformamide	3610	3317	293
1,2 Dimethoxyethane	3610	3366	244
Tetrahydrofuran	3610	3320	290
Dioxan	3610	3368	242
Diethyl ether	3610	3330	280
Dibutyl ether	3610	3325	285
Di-isopropyl ether	3610	3313	297
Methanol	3610	3396	214
Ethanol	3610	3381	229
n-Butanol	3610	3377	233
Isopropanol	3610	3374	236
3 Methyl 1 Butanol	3610	3374	236
Tertiary Butanol	3610	3357	253

B. ASSOCIATION IN SOLUTION

(1) INTRODUCTION

Ultra-violet spectroscopy has been used by many workers, notably, Benesi and Hildebrand²⁵, Ketelaar et al⁶⁴, Nagakura et al^{30,65,66}, and Keefer and Andrews^{67,68}, to determine the association constant of complex formation in solution.

Rose and Drago⁶⁹ devised a general method for rigorously treating spectrophotometric data for any donor-acceptor system. The general equation for the equilibrium involved is:-



where D is an electron pair donor

A is an electron pair acceptor.

The expression for the molar equilibrium constant K_c , is:-

$$K_c = \frac{e_c}{(c_D - e_c)(c_A - e_c)} \quad (28)$$

where c_D , c_A are the initial concentrations of D and A respectively

e_c is the equilibrium concentration of complex DA

If the donor molecule does not absorb in the region studied, and additivity of absorbances is assumed, then for a cell of unit path length and at constant wavelength

$$A = \epsilon_c \cdot e_c + \epsilon_A \cdot e_A \quad (29)$$

where A = absorbance of solution

ϵ_c = extinction coefficient of complex

ϵ_A = extinction coefficient of electron pair acceptor

e^c_A = equilibrium concentration of A.

$$\text{Also } c_A = e^c_c + e^c_A \quad (30)$$

Expanding equation (28) gives:-

$$K_c = e^c_c / (c_D \cdot c_A + e^c_c^2 - e^c_c \cdot c_D - e^c_c \cdot c_A) \quad (31)$$

Eliminating e^c_A between (29) and (30)

$$A = e^c_c(\epsilon_c - \epsilon_A) + \epsilon_A \cdot c_A$$

If A^0 corresponds to the absorbance of A alone at its initial concentration, c_A , at the same wavelength and in the absence of D, then:-

$$A^0 = \epsilon_A \cdot c_A$$

and

$$A = e^c_c(\epsilon_c - \epsilon_A) + A^0 \quad (32)$$

Rearranging (32) gives $e^c_c = (A - A^0) / (\epsilon_c - \epsilon_A)$

Substituting this value of e^c_c in equation (31) gives:-

$$K_c^{-1} = \frac{c_D c_A (\epsilon_c - \epsilon_A)}{A - A^0} - c_D + \frac{A - A^0}{\epsilon_c - \epsilon_A} - c_A \quad (33)$$

Equation (33) may be solved for the association constant K_c if a series of absorbances A corresponding to solutions containing different equilibrium amounts of complex and acceptor are known. Accordingly, the absorbances A are measured experimentally at a selected wavelength for a series of solutions in an inert solvent containing a constant initial amount of acceptor with varying amounts of donor.

If the experimental conditions are chosen such that $c_D \gg c_A$, then

$(A-A^0)/(\epsilon_C - \epsilon_A) - c_A$ may be neglected when compared to

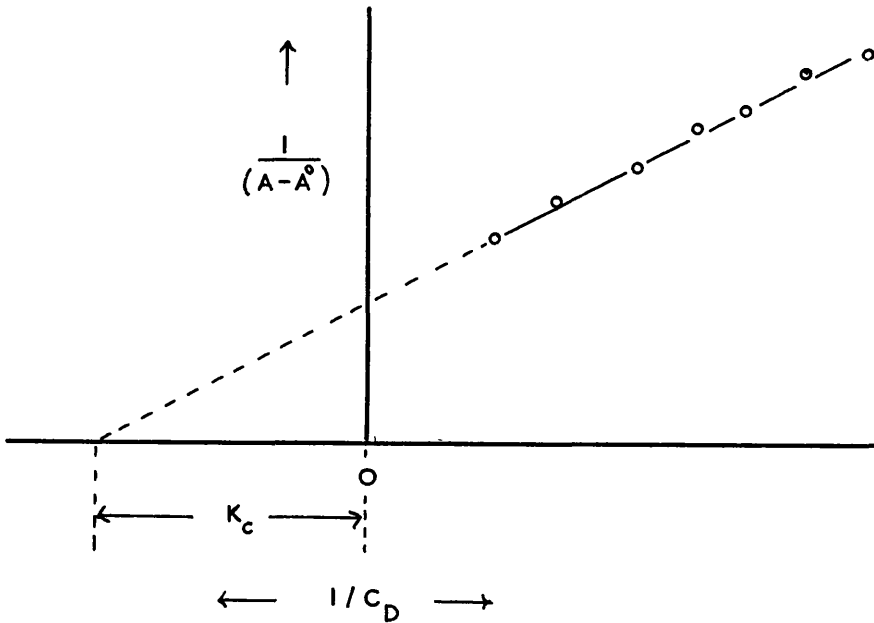
$c_D c_A (\epsilon_C - \epsilon_A)/(A-A^0) - c_D$ and equation (33) reduces to:-

$$K_C^{-1} = c_D c_A (\epsilon_C - \epsilon_A)/(A-A^0) - c_D$$

$$\text{or } \frac{c_A}{(A-A^0)} = \frac{1}{K_C (\epsilon_C - \epsilon_A)} \cdot \frac{1}{c_D} + \frac{1}{(\epsilon_C - \epsilon_A)} \quad (34)$$

Equation (34) has been used by Nagakura et al^{30,70,71} to evaluate association constants of complex formation, since a linear plot of $1/(A-A^0)$ against $1/c_D$, extrapolated to $1/(A-A^0) = 0$ gives the association constant as $K_C = -(1/c_D)_{\text{extrapolated}}$ (Fig. 17).

Fig. 17



(2) EXPERIMENTAL PROCEDURE

Association constants for the process



have been determined from absorbance measurements at a predetermined wavelength in the ultra-violet, for a series of solutions of phenol in cyclohexane-donor and carbon tetrachloride-donor mixtures of varying composition.

(a) Apparatus

A Unicam SP 500 Photoelectric Quartz Spectrophotometer fitted with an accurately thermostatted cell compartment was used to measure absorbances.

This instrument can be used to investigate the absorption characteristics of compounds in solution throughout the visible and ultra-violet regions (200-1000 nm) of the spectrum. A hydrogen discharge lamp, supplied with stabilised current of 300 mA is used for the ultra-violet region (200-320 nm), and a tungsten lamp for the visible region (320-1000 nm). The monochromator assembly consists of a quartz prism and collimating mirror with a slit aperture calibrated from 0.01 to 2.00 nm. Two photocells are employed, a red sensitive cell for use above 625 nm, and an ultra-violet sensitive cell for use below 625 nm. A Labgear Power Supply Unit 115D provides a supply of 6v at 6A .DC for the tungsten filament light source, and also 6v and 2v at 100 mA .DC for valve heating. The photo-cell current is fed to a

two-stage amplifier and passes to an indicating meter which is adjusted to zero current by a potentiometer calibrated in both absorbance and percentage transmission scales.

(b) Preparation of Solutions

An approximately 10^{-4} molar solution of phenol in the chosen solvent (cyclohexane or carbon tetrachloride) was prepared at 25°C (Solution A).

A solution of the donor in the same solvent of known weight fraction was prepared by weighing (Solution B).

Solutions for absorbance measurements were prepared by weighing suitable volumes of solution B (E.g. 0, 0.9, 1.2, 1.6, 2.0, 2.5, 5.0 and 10.0 cm³), adding 25 cm³ of solution A and diluting to 50 cm³ with the solvent at 25°C. As reference solutions, solvent mixtures of composition identical to the solutions under examination, were used.

(c) Determination of Optimum Wavelength for Absorbance Measurements

A preliminary examination was carried out of the absorption spectrum of phenol dissolved in the solvent alone and then in the donor alone, using solutions of equivalent concentration (approx. 10^{-4} M) in the range 260-320 nm. These absorption curves were obtained with the Unicam SP 800 spectrophotometer. On superimposing and inspecting, a wavelength was chosen at which the difference between the absorbances of the two solutions was a maximum. An optimum wavelength for each of

the donors studied, was determined in this manner.

(d) Procedure

Each sample solution was placed in the cell compartment together with the corresponding reference solution. After allowing sufficient time (10 mins) for thermal equilibrium to be attained at 25°C, the absorbance of the solution A was measured. The absorbance A^0 of the solution containing no donor was measured with the solvent as reference. The measurements were repeated at 30°C, 35°C and 40°C. The concentrations of donor (c_D mol dm⁻³) and phenol (c_A mol dm⁻³) at these temperatures were calculated from the ratios of the respective solution densities as follows:-

$$\left(\text{Concentration of component at } T_2 \right) = \left(\text{Concentration of component at } T_1 \right) \left(\frac{\text{Density of solution at } T_2}{\text{Density of solution at } T_1} \right)$$

The ratio $d_{\text{soln}}(T_2)/d_{\text{soln}}(T_1)$ was found to be essentially constant over the range of donor concentrations and temperatures studied, their values being recorded in Table 6.

TABLE 6

<u>Solvent</u>	<u>Ratio $d_{\text{soln}}(T_2)/d_{\text{soln}}(25^\circ\text{C})$</u>			
	$T_2 =$	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
Cyclohexane/Donor		0.994	0.988	0.982
Carbon Tetrachloride/Donor		0.994	0.988	0.982
Pure Cyclohexane		0.995	0.988	0.982
Pure Carbon Tetrachloride		0.994	0.988	0.982

Consideration of the values recorded in Table 6 show that the solution density ratios are within 0.001 of the pure solvent density ratios indicating that under the experimental conditions used, the former are independent of the donor considered.

(e) Experimental Results

The experimental results are recorded in Tables 7 to 19.

TABLE 7. Dimethylformamide

Carbon Tetrachloride

$C_D / (\text{mol dm}^{-3})$ at 25°C	A (275 nm)	
	25°C	35°C
-	0.437	0.428
0.0570	0.590	0.567
0.0762	0.602	0.581
0.1017	0.612	0.593
0.1283	0.620	0.602
0.1599	0.625	0.609
0.3204	0.639	0.626

$$C_A = 2.890 \times 10^{-4}$$

TABLE 8. Diethyl Ether

<u>Cyclohexane</u>		<u>Carbon Tetrachloride</u>	
$C_D / (\text{mol dm}^{-3})$ at 25°C	A (280 nm) 25°C	$C_D / (\text{mol dm}^{-3})$ at 25°C	A (282.5 nm) 25°C
-	0.223	-	0.355
0.0298	0.308	0.0535	0.434
0.0455	0.337	0.0720	0.452
0.0606	0.357	0.0964	0.473
0.0919	0.395	0.1213	0.492
0.1289	0.423	0.1521	0.510
0.2590	0.475	0.3049	0.562
0.5195	0.505	0.6085	0.605

$$C_A = 2.890 \times 10^{-4}$$

$$C_A = 3.590 \times 10^{-4}$$

TABLE 9. 1,2 Dimethoxyethane

Cyclohexane

$C_D/(\text{mol dm}^{-3})$ at 25°C	A (281 nm)		$C_D/(\text{mol dm}^{-3})$ at 25°C	A (281 nm)	
	25°C	35°C		30°C	40°C
-	0.132	0.134	-	0.108	0.107
0.0267	0.316	0.272	0.0405	0.282	0.241
0.0403	0.359	0.312	0.0543	0.309	0.267
0.0542	0.391	0.343	0.0719	0.332	0.291
0.0811	0.433	0.384	0.0912	0.355	0.312
0.1140	0.464	0.418	0.1135	0.371	0.330
0.2280	0.515	0.475	0.2286	0.416	0.381
0.4571	0.540	0.510	0.4514	0.443	0.416

$$C_A = 3.230 \times 10^{-4}$$

$$C_A = 3.144 \times 10^{-4}$$

Carbon Tetrachloride

$C_D/(\text{mol dm}^{-3})$ at 25°C	A (282.5 nm)		$C_D/(\text{mol dm}^{-3})$ at 25°C	A (282.5 nm)	
	25°C	35°C		30°C	40°C
-	0.316	0.294	-	0.273	0.262
0.0280	0.400	0.362	0.0404	0.367	0.340
0.0420	0.427	0.386	0.0539	0.387	0.358
0.0559	0.447	0.406	0.0719	0.408	0.378
0.0741	0.468	0.427	0.0904	0.424	0.394
0.0934	0.485	0.445	0.1128	0.441	0.412
0.1167	0.502	0.463	0.2260	0.488	0.465
0.2340	0.545	0.512	0.4525	0.525	0.509

$$C_A = 3.592 \times 10^{-4}$$

$$C_A = 3.059 \times 10^{-4}$$

TABLE 10. Tetrahydrofuran

<u>Cyclohexane</u>			<u>Carbon Tetrachloride</u>		
$C_D/(\text{mol dm}^{-3})$ at 25°C	A (280.5 nm) 25°C	35°C	$C_D/(\text{mol dm}^{-3})$ at 25°C	A (282.5 nm) 25°C	35°C
-	0.133	0.133	-	0.265	0.256
0.0423	0.312	0.279	0.0647	0.417	0.379
0.0633	0.348	0.312	0.0854	0.439	0.401
0.0845	0.374	0.337	0.1152	0.464	0.425
0.1267	0.400	0.368	0.1448	0.481	0.443
0.1782	0.424	0.393	0.1810	0.497	0.462
0.3562	0.457	0.432	0.3624	0.537	0.508
0.7145	0.473	0.452	0.7256	0.562	0.539
$C_A = 2.657 \times 10^{-4}$			$C_A = 3.209 \times 10^{-4}$		

TABLE 11. Dioxan

<u>Cyclohexane</u>			<u>Carbon Tetrachloride</u>		
$C_D/(\text{mol dm}^{-3})$ at 25°C	A (280.5 nm) 25°C	35°C	$C_D/(\text{mol dm}^{-3})$ at 25°C	A (282.5 nm) 25°C	35°C
-	0.129	0.137	-	0.270	0.256
0.0330	0.257	0.236	0.0400	0.338	0.309
0.0500	0.295	0.268	0.0507	0.351	0.320
0.0662	0.322	0.292	0.0678	0.368	0.335
0.0884	0.350	0.318	0.0906	0.387	0.352
0.1113	0.371	0.338	0.1138	0.402	0.367
0.1390	0.391	0.358	0.1418	0.417	0.382
0.2785	0.441	0.412	0.2844	0.460	0.428
$C_A = 3.039 \times 10^{-4}$			$C_A = 3.272 \times 10^{-4}$		

TABLE 12. Dibutyl Ether

Cyclohexane

$C_D / (\text{mol dm}^{-3})$ at 25°C	A (280 nm)		$C_D / (\text{mol dm}^{-3})$ at 25°C	A (280 nm)	
	25°C	35°C		30°C	40°C
-	0.168	0.167	-	0.189	0.187
0.0203	0.213	0.200	0.0374	0.262	0.241
0.0406	0.248	0.226	0.0486	0.279	0.253
0.0543	0.268	0.242	0.0651	0.299	0.270
0.0682	0.284	0.256	0.0868	0.323	0.290
0.0849	0.300	0.270	0.1097	0.344	0.307
0.1703	0.357	0.322	0.1368	0.364	0.326
0.3412	0.408	0.373	0.2740	0.412	0.377

$$C_A = 2.699 \times 10^{-4}$$

$$C_A = 2.719 \times 10^{-4}$$

Carbon Tetrachloride

$C_D / (\text{mol dm}^{-3})$ at 25°C	A (282.5 nm)		$C_D / (\text{mol dm}^{-3})$ at 25°C	A (282.5 nm)	
	25°C	35°C		30°C	40°C
-	0.255	0.244	-	0.215	0.205
0.0517	0.315	0.288	0.0375	0.253	0.233
0.0684	0.330	0.300	0.0483	0.262	0.240
0.0913	0.347	0.314	0.0645	0.275	0.250
0.1146	0.362	0.327	0.0860	0.289	0.262
0.1432	0.377	0.340	0.1083	0.302	0.273
0.2860	0.425	0.387	0.1348	0.316	0.285
0.5730	0.467	0.433	0.2701	0.363	0.329

$$C_A = 3.166 \times 10^{-4}$$

$$C_A = 2.741 \times 10^{-4}$$

TABLE 13. Di-isopropyl Ether

<u>Cyclohexane</u>			<u>Carbon Tetrachloride</u>		
$C_D/(\text{mol dm}^{-3})$ at 25°C	A(280 nm) 25°C	35°C	$C_D/(\text{mol dm}^{-3})$ at 25°C	A (282.5 nm) 25°C	35°C
-	0.217	0.205	-	0.294	0.265
0.0459	0.336	0.295	0.0333	0.364	0.316
0.0613	0.357	0.315	0.0443	0.377	0.329
0.0817	0.380	0.337	0.0588	0.395	0.344
0.1029	0.400	0.352	0.0743	0.408	0.358
0.1286	0.417	0.371	0.0924	0.429	0.374
0.2576	0.462	0.422	0.1856	0.482	0.426
0.5150	0.495	0.465	0.3711	0.529	0.480

$$C_A = 3.081 \times 10^{-4}$$

$$C_A = 3.208 \times 10^{-4}$$

TABLE 14. Methanol

Carbon Tetrachloride

$C_D/(\text{mol dm}^{-3})$ at 25°C	A (276.5 nm)	
	25°C	35°C
-	0.423	0.419
0.0602	0.501	0.473
0.0732	0.510	0.480
0.0872	0.519	0.487
0.1009	0.526	0.493
0.1086	0.529	0.496
0.1286	0.538	0.506
0.1416	0.542	0.508

$$C_A = 3.081 \times 10^{-4}$$

TABLE 15. Ethanol

Cyclohexane

$C_D/(\text{mol dm}^{-3})$ at 25°C	A (275 nm)		$C_D/(\text{mol dm}^{-3})$ at 25°C	A (275 nm)	
	25°C	35°C		30°C	40°C
-	0.313	0.314	-	0.267	0.262
0.0646	0.496	0.470	0.0535	0.403	0.369
0.0804	0.511	0.485	0.0693	0.418	0.384
0.0976	0.521	0.496	0.0808	0.427	0.392
0.1140	0.531	0.506	0.0925	0.434	0.401
0.1314	0.538	0.513	0.1086	0.443	0.410
0.1473	0.543	0.520	0.1241	0.449	0.416
0.1644	0.547	0.525	0.1397	0.454	0.422

$$C_A = 3.379 \times 10^{-4}$$

$$C_A = 2.953 \times 10^{-4}$$

Carbon Tetrachloride

$C_D/(\text{mol dm}^{-3})$ at 25°C	A (276.5 nm)		$C_D/(\text{mol dm}^{-3})$ at 25°C	A (276.5 nm)	
	25°C	35°C		30°C	40°C
-	0.428	0.426	-	0.435	0.435
0.0652	0.517	0.495	0.0619	0.515	0.488
0.0811	0.531	0.507	0.0781	0.528	0.498
0.0976	0.540	0.516	0.0935	0.539	0.506
0.1137	0.549	0.526	0.1097	0.549	0.516
0.1305	0.557	0.534	0.1249	0.557	0.523
0.1464	0.565	0.541	0.1402	0.564	0.529
0.1635	0.570	0.547	0.1572	0.572	0.536

$$C_A = 2975 \times 10^{-4}$$

$$C_A = 3.208 \times 10^{-4}$$

TABLE 16. n-Butanol

<u>Cyclohexane</u>			<u>Carbon Tetrachloride</u>		
$C_D / (\text{mol dm}^{-3})$ at 25°C	A (275 nm)		$C_D / (\text{mol dm}^{-3})$ at 25°C	A (276.5 nm)	
	25°C	35°C		25°C	35°C
-	0.256	0.260	-	0.448	0.444
0.0439	0.401	0.362	0.0434	0.511	0.485
0.0564	0.418	0.376	0.0541	0.521	0.493
0.0689	0.431	0.387	0.0650	0.531	0.500
0.0879	0.446	0.400	0.0762	0.539	0.507
0.1077	0.457	0.411	0.0978	0.553	0.518
0.1261	0.465	0.418	0.1089	0.560	0.524

$$C_A = 3.026 \times 10^{-4}$$

$$C_A = 3.166 \times 10^{-4}$$

TABLE 17. Isopropanol

<u>Cyclohexane</u>			<u>Carbon Tetrachloride</u>		
$C_D / (\text{mol dm}^{-3})$ at 25°C	A (275 nm)		$C_D / (\text{mol dm}^{-3})$ at 25°C	A (276.5 nm)	
	25°C	35°C		25°C	35°C
-	0.283	0.290	-	0.402	0.400
0.0449	0.435	0.413	0.0469	0.472	0.456
0.0689	0.466	0.444	0.0602	0.486	0.468
0.0919	0.485	0.462	0.0668	0.492	0.474
0.1380	0.508	0.487	0.0800	0.503	0.485
0.1926	0.524	0.505	0.0938	0.513	0.495

$$C_A = 2.869 \times 10^{-4}$$

$$C_A = 2.889 \times 10^{-4}$$

TABLE 18. 3 Methyl 1 Butanol

Cyclohexane

$C_D/(\text{mol dm}^{-3})$ at 25°C	A (275 nm)		$C_D/(\text{mol dm}^{-3})$ at 25°C	A (275 nm)	
	25°C	35°C		30°C	40°C
-	0.267	0.270	-	0.258	0.258
0.0451	0.405	0.379	0.0356	0.360	0.330
0.0566	0.420	0.393	0.0415	0.370	0.337
0.0679	0.433	0.405	0.0517	0.384	0.348
0.0792	0.443	0.415	0.0626	0.395	0.358
0.0913	0.452	0.424	0.0730	0.405	0.366
0.1023	0.459	0.430	0.0832	0.413	0.373
0.1139	0.466	0.436	0.0939	0.420	0.379

$$C_A = 2.997 \times 10^{-4}$$

$$C_A = 2.804 \times 10^{-4}$$

Carbon Tetrachloride

$C_D/(\text{mol dm}^{-3})$ at 25°C	A (276.5 nm)		$C_D/(\text{mol dm}^{-3})$ at 25°C	A (276.5 nm)	
	25°C	35°C		30°C	40°C
-	0.431	0.427	-	0.410	0.408
0.0402	0.486	0.469	0.0352	0.453	0.436
0.0469	0.493	0.473	0.0439	0.462	0.442
0.0532	0.499	0.478	0.0530	0.470	0.448
0.0623	0.508	0.485	0.0621	0.478	0.452
0.0714	0.515	0.491	0.0709	0.485	0.459
0.0819	0.523	0.499	0.0795	0.491	0.464
0.0893	0.528	0.504	0.0891	0.498	0.469

$$C_A = 3.102 \times 10^{-4}$$

$$C_A = 2.996 \times 10^{-4}$$

TABLE 19. Tertiary Butanol

<u>Cyclohexane</u>			<u>Carbon Tetrachloride</u>		
$C_D / (\text{mol dm}^{-3})$ at 25°C	A (275 nm)		$C_D / (\text{mol dm}^{-3})$ at 25°C	A (276.5 nm)	
	25°C	35°C		25°C	35°C
-	0.317	0.318	-	0.482	0.472
0.0366	0.493	0.452	0.0415	0.565	0.536
0.0493	0.519	0.478	0.0477	0.573	0.543
0.0615	0.537	0.497	0.0591	0.587	0.556
0.0743	0.553	0.513	0.0712	0.600	0.568
0.0862	0.564	0.525	0.0835	0.610	0.579
0.0995	0.575	0.537	0.0952	0.620	0.588
0.1112	0.578	0.545	0.1075	0.628	0.598
$C_A = 3.399 \times 10^{-4}$			$C_A = 3.358 \times 10^{-4}$		

(f) Calculation of Association Constant

Association constants (K_C) were calculated by Rose and Drago's method⁶⁹, using an IBM 1130 computer. A copy of the Fortran program used is detailed in the appendix.

An approximate value of K_C was first calculated from equation (34) and used to calculate a series of values for ${}_e c_C$ (equilibrium concentration of complex) and ${}_e c_A$ (equilibrium concentration of acceptor) from the experimentally determined values of C_D and C_A by application of equations (28) and (30). Substituting those values in equation (29) enables the extinction coefficient of the complex ϵ_C to be evaluated at each donor concentration. An average extinction coefficient was calculated and values taken either side of the mean. Insertion of these values in equation (33) gives further K_C values and a plot of K_C^{-1} against ϵ_C can be constructed for each donor concentration. As the true value of K_C is constant, the straight lines corresponding to different values of donor concentration should intersect at one point. Experimentally the majority of the intersections occur in a small area (Fig. 18) indicating good experimental precision and strong support for the assumption that a 1:1 complex is formed in solution. Association constants for the complexes were determined for all intersections and an average K_C and standard deviation calculated. By eliminating those K_C values outside twice the standard deviation, until the latter changed by less than 20%, association constants were obtained with standard deviations of the order of 5%.

The method of calculation is illustrated in Table 20 for the association of phenol to tetrahydrofuran in carbon tetrachloride solution. Values

of the association constants with their respective standard deviations are given in Tables 21 and 22.

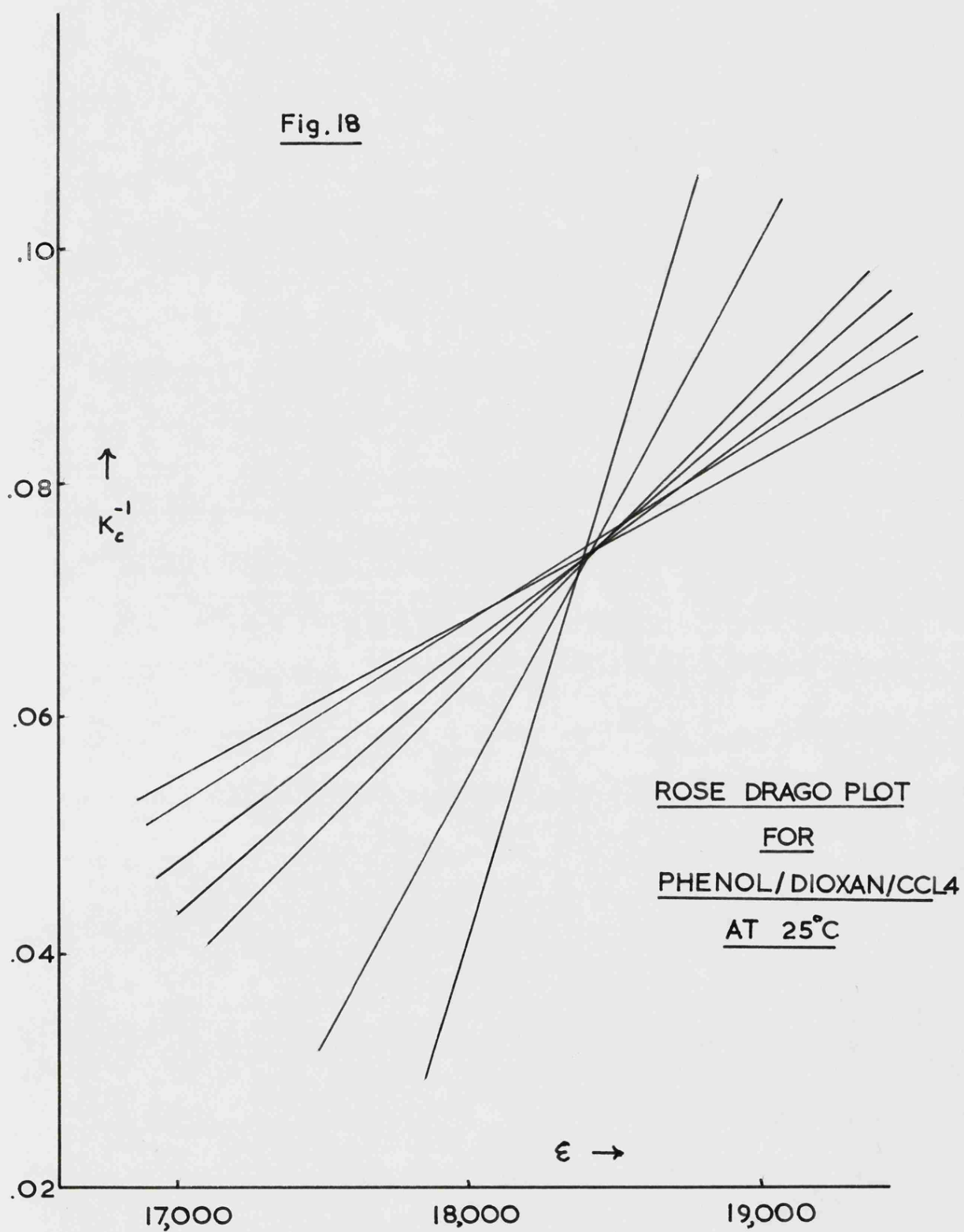


TABLE 20

Association Constant for Phenol-Tetrahydrofuran in
Carbon Tetrachloride Solution at 25°C

The experimental values of concentration and absorbances are given in Table 10. The mean extinction coefficient of the complex is calculated to be $18,500 \text{ dm}^2 \text{ mol}^{-1}$ for a path length of 0.1 dm.

Using values $18,500 \pm 1000$ for the extinction coefficient ϵ_c , two values of K_c are calculated from equation (33) and a series of plots for each donor concentration of K_c^{-1} against ϵ_c constructed (Fig. 18). The points of intersection of each line with each other representing values of K_c are given below:-

$\frac{K_c}{/(\text{dm}^3 \text{ mol}^{-1})}$	<u>Deviation</u>	$\frac{K_c}{/(\text{dm}^3 \text{ mol}^{-1})}$	<u>Deviation</u>	$\frac{K_c}{/(\text{dm}^3 \text{ mol}^{-1})}$	<u>Deviation</u>
14.182	+0.825*	13.033	-0.324	13.472	+0.115
13.266	-0.091	13.066	-0.291	13.152	-0.204
13.428	+0.071	13.165	-0.192	13.264	-0.093
13.373	+0.016	13.266	-0.090	13.387	+0.031
13.351	-0.006	13.875	+0.518	13.309	-0.048
13.405	+0.048	13.524	+0.168	13.445	+0.088
12.461	-0.896*	13.406	+0.049	13.663	+0.306

Mean K_c value = 13.36 Standard Deviation + 0.33

Values marked * rejected as outside twice the standard deviation giving

$K_c = \underline{13.36}$ Standard Deviation + 0.19

Further rejection gives a standard deviation of 0.16 which is a change of less than 20% on the previous value.

TABLE 21

Association Constants for Phenol-Donor Complexes
in Cyclohexane Solution

<u>Donor</u>	<u>Association Constant $K_c / (\text{dm}^3 \text{mol}^{-1})$ at</u>			
	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
1,2 Dimethoxyethane	26.3±1.1	22.1±0.3	18.5±0.5	15.4±0.2
Tetrahydrofuran	23.1±1.1	-	17.5±1.0	-
Dioxan	15.1±0.2	-	11.7±0.2	-
Diethyl ether	11.4±0.3	-	-	-
Di-isopropyl ether	12.9±0.4	-	8.8±0.5	-
Dibutyl ether	7.9±0.6	6.9±0.6	6.0±0.1	5.2±0.5
Ethanol	27.8±1.6	23.7±1.1	20.9±0.8	16.8±1.3
n-Butanol	25.8±0.3	-	19.6±1.3	-
Isopropanol	24.2±0.3	-	18.1±0.5	-
3 Methyl 1 Butanol	21.6±0.5	19.1±0.8	16.8±0.8	15.1±0.7
Tertiary Butanol	27.3±1.0	-	18.0±0.5	-

TABLE 22

Association Constants for Phenol-Donor Complexes
in Carbon Tetrachloride Solution

<u>Donor</u>	<u>Association Constant $K_c / (\text{dm}^3 \text{mol}^{-1})$ at</u>			
	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
Dimethylformamide	42.5 $\pm$ 1.2	-	31.4 $\pm$ 0.6	-
1,2 Dimethoxyethane	14.0 $\pm$ 0.3	11.5 $\pm$ 0.4	10.0 $\pm$ 0.2	8.4 $\pm$ 0.3
Tetrahydrofuran	13.4 $\pm$ 0.2	-	9.5 $\pm$ 0.2	-
Dioxan	8.5 $\pm$ 0.1	-	6.1 $\pm$ 0.1	-
Diethyl ether	6.1 $\pm$ 0.3	-	-	-
Di-isopropyl ether	8.2 $\pm$ 0.5	-	6.0 $\pm$ 0.6	-
Dibutyl ether	5.2 $\pm$ 0.2	4.3 $\pm$ 0.2	3.7 $\pm$ 0.1	3.0 $\pm$ 0.1
Methanol	11.0 $\pm$ 0.4	-	7.7 $\pm$ 0.5	-
Ethanol	9.5 $\pm$ 0.3	7.6 $\pm$ 0.3	6.2 $\pm$ 0.4	4.5 $\pm$ 0.4
n-Butanol	8.6 $\pm$ 0.4	-	5.6 $\pm$ 0.4	-
Isopropanol	7.5 $\pm$ 0.4	-	4.7 $\pm$ 0.4	-
3 Methyl 1 Butanol	6.8 $\pm$ 0.5	5.2 $\pm$ 0.4	3.9 $\pm$ 0.4	3.4 $\pm$ 0.1
Tertiary Butanol	10.2 $\pm$ 0.5	-	6.2 $\pm$ 0.2	-

C. ADSORPTION AT THE SOLID-SOLUTION INTERFACE

(1) CHARACTERISATION OF THE ADSORBENT

For an understanding of the mechanism of adsorption process at the solid-solution interface, a knowledge of the character of the adsorbent surface is essential. The characterisation undertaken involves:-

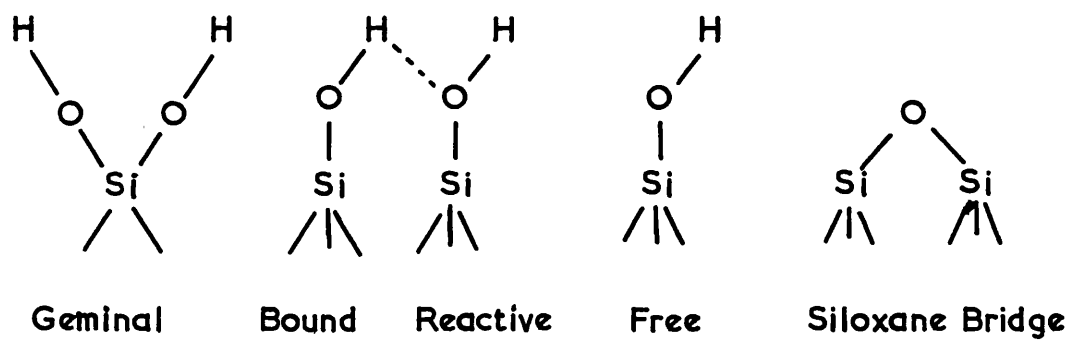
- (a) the nature and distribution of surface adsorption sites on the polar adsorbents considered.
- (b) a determination of the specific surface area available to the adsorptive molecules.
- (c) the extent of porosity of the surface obtained from a pore size distribution analysis assuming a pore shape for the adsorbent.

(a) Nature of the Adsorbent Surfaces

(i) Silica

Electron microscopy and X-ray examination have shown that silicas in general are non crystalline and are composed of small elementary particles possessing hydroxylated surfaces aggregated into larger spheroidal particles of the order of 10 nm diameter. An elementary particle is considered to consist of an irregular three dimensional network of SiO_4 tetrahedra, each silicon atom being linked together by Si-O-Si bridges. The pore system within this aggregate is formed by open spaces between the elementary particles and thus its characteristics depend on the size and packing of these particles⁷².

The hydroxyl groups on the silica surface may be classified into the following types⁷³:-



A major role has been accorded to the 'free' and 'reactive' hydroxyl groups in adsorption on the silica surface^{74,75}; the 'reactive' hydroxyls constituting the strongest adsorption sites for polar and unsaturated molecules. Surface siloxane groups are regarded as being inactive as preferential adsorption of polar and unsaturated molecules from solution

on to silica disappears on a severely dehydrated silica where the surface has been predominantly converted to siloxane groups⁷⁶.

Under normal atmospheric conditions, the silica surface also contains adsorbed water and Vleeskens⁷⁷ has shown that it is extremely difficult to define precisely the temperature at which all physisorbed and no chemisorbed water has been removed. The term 'chemisorbed' refers to hydroxyl groups chemically bound to a surface silicon atom.

Infrared studies⁷⁸ have shown that the surface silanols exhibit absorption in quite separate regions of the spectrum; at about 3750 cm^{-1} , 3650 cm^{-1} , 3500 cm^{-1} and 1640 cm^{-1} . If physisorbed water is present a very broad band is obtained at 3400 cm^{-1} and the absorption at 1640 cm^{-1} is also increased. It is generally agreed^{79,80,81,82} that the absorption bands in $3650\text{--}3750\text{ cm}^{-1}$ region are due to single surface hydroxyls and that those appearing at 3400 cm^{-1} and 1640 cm^{-1} when molecular water is present are due to physisorbed water held on the surface by hydrogen bonding. The band at 3500 cm^{-1} and the associated band at 1640 cm^{-1} have been attributed either to the presence of strongly physisorbed water^{82,83} or to surface arrangements involving geminal hydroxyls⁸¹. This uncertainty makes any distinction between chemisorbed and physisorbed water based on the presence or absence of a band at 3500 cm^{-1} very unreliable. Also the absorption band at 1640 cm^{-1} , apart from inferring the presence of physisorbed water, could be due to a harmonic of an SiO vibration⁸² or to geminal surface hydroxyls⁷⁸.

The indecisiveness of the infrared and thermogravimetric studies has thus led to a difference of opinion as to the relative concentrations

of physisorbed water remaining on silicas heated to above 115°C. Fripiat and Uytterhoeven⁸² conclude that a temperature of 300°C is needed to remove all physisorbed water while Davydov et al⁸⁴ state that the drying temperature in vacuo must not exceed 150-200°C or appreciable dehydroxylation of the surface will occur. De Boer and Vleeskens⁸⁵ consider a silica dried at 120°C under atmospheric conditions has lost all physisorbed water but still contains all surface hydroxyls. For the silica under investigation a drying temperature of 120°C was chosen as only a small loss of water occurred in the range 120-200°C. A drying temperature above 200°C was not considered due to the possibility of loss of surface hydroxyl groups.

Several workers have investigated the effect of temperature on the concentration of surface hydroxyls on silica. Using thermogravimetric methods, De Boer and Vleeskens⁸⁵ found that silicas approached a limiting surface coverage or concentration of 4.6 hydroxyl groups per nm² of surface after they had been repeatedly rehydroxylated and annealed at 450°C. They assumed that the constant value of 4.6 surface hydroxyls per nm² corresponded to a state in which all the silicon atoms in the surface carried one hydroxyl group and extra hydroxyl groups on virgin silicas were attributed to surface irregularities. Davydov et al⁸⁴ have shown that some silicas contain substantial amounts of bulk hydroxyls located within the solid and conclude that the true surface concentration of hydroxyls for a wide range of silicas was 4.8 per nm². For a fully hydrated surface in which two hydroxyl groups are bound to a single silicon atom, Iher⁸⁶ found a surface concentration of about 8 hydroxyls per nm². Peri and

Hensley⁸⁷ considered such a surface resembled a 100 face of β -cristobalite and random partial dehydration by a 'Monte Carlo' statistical method yielded a relatively stable surface holding 4.56 hydroxyls per nm². Of this total, Armistead⁸⁸ suggested that 1.4 groups existed as single non hydrogen bonded species while the remaining 3.2 hydroxyl groups were present as pairs. Further dehydration was seen to result in complete removal of the paired hydroxyl groups at a temperature of about 500°C. Armistead concluded that the silica surface corresponded to an array of different crystal planes, some of which contain hydroxyl groups at relatively large interhydroxyl spacings and others containing hydroxyl groups held in such a way as to promote interhydroxyl hydrogen bonding.

Thermogravimetric data on the silica under investigation are given in Table 23.

TABLE 23

<u>Temperature °C</u>	<u>Loss on Ignition %</u>	<u>Hydroxyl Groups per nm² of surface</u>
120	2.7	5.6
200	2.9	5.2
300	3.9	3.6
500	5.6	1.0
1,000	6.3	-

The number of hydroxyl groups per nm² or surface has been calculated assuming that the loss on ignition at 1,000°C represents the total water content present as hydroxyl groups and molecularly adsorbed water. The results are in reasonable agreement with those of Armistead and show that after drying at 120°C the silica surface is fully hydroxylated and contains a small amount of physically adsorbed water.

A drying temperature between 200 and 300°C is indicated in order to remove all physisorbed water but in this temperature range loss of surface hydroxyl groups is also possible.

(ii) Alumina

Activated alumina is produced by the controlled heating of the hydrate which exists in four different modifications, i.e. hydrargillite, bayerite, diasporite and boehmite. X-ray diffraction examination^{89,90,91} has shown the existence of seven nearly anhydrous forms of alumina intermediate between the hydrate and the final decomposition product, α -alumina obtained at 1,000°C. The alumina used in this investigation was heated to 800°C during manufacture and the suppliers (Camag) classify the material as ' γ -alumina'. The sample of alumina was submitted to a detailed X-ray diffraction examination at the laboratories of the B.P. refinery at Southampton who report that the sample consists mainly of γ -alumina admixed with approximately 10% boehmite (α -monohydrate). Electron micrographs of the alumina revealed the presence of slit and wedge-shaped pores²².

Thermogravimetric experiments on the alumina under investigation²² have shown that after drying at 120°C, the surface contains approximately 5.8 water molecules per nm² present as hydroxyl groups. According to Peri⁹², monolayer coverage corresponds to 6.25 molecules of water per nm² and thus at the drying temperature employed, the surface of the alumina can be considered fully hydroxylated.

(b) Specific Surface Area of the Adsorbents

The most reliable and widely used method available for the determination of the surface area of solid adsorbents is the low temperature adsorption of nitrogen. In addition, the adsorption of other molecules of known physical dimensions, can provide information on the available surface area of the adsorbent when considering adsorption from solution. As the experimental work concerns the adsorption of p-substituted phenols from benzene, the adsorption isotherm for benzene vapour was determined.

The method of calculating the specific surface area from the gas adsorption isotherms is first considered before describing the experimental technique involved in their determination.

(i) Calculation of Specific Surface Area

Brunauer, Emmett and Teller^{93,94} derived the following equation (35) for multimolecular adsorption on a non porous surface.

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \cdot \frac{p}{p_0} \quad (35)$$

where v = volume of gas adsorbed (cm^3 at N.T.P.) on the surface at equilibrium pressure p

v_m = volume of gas adsorbed (cm^3 at N.T.P.) corresponding to monolayer coverage of the surface

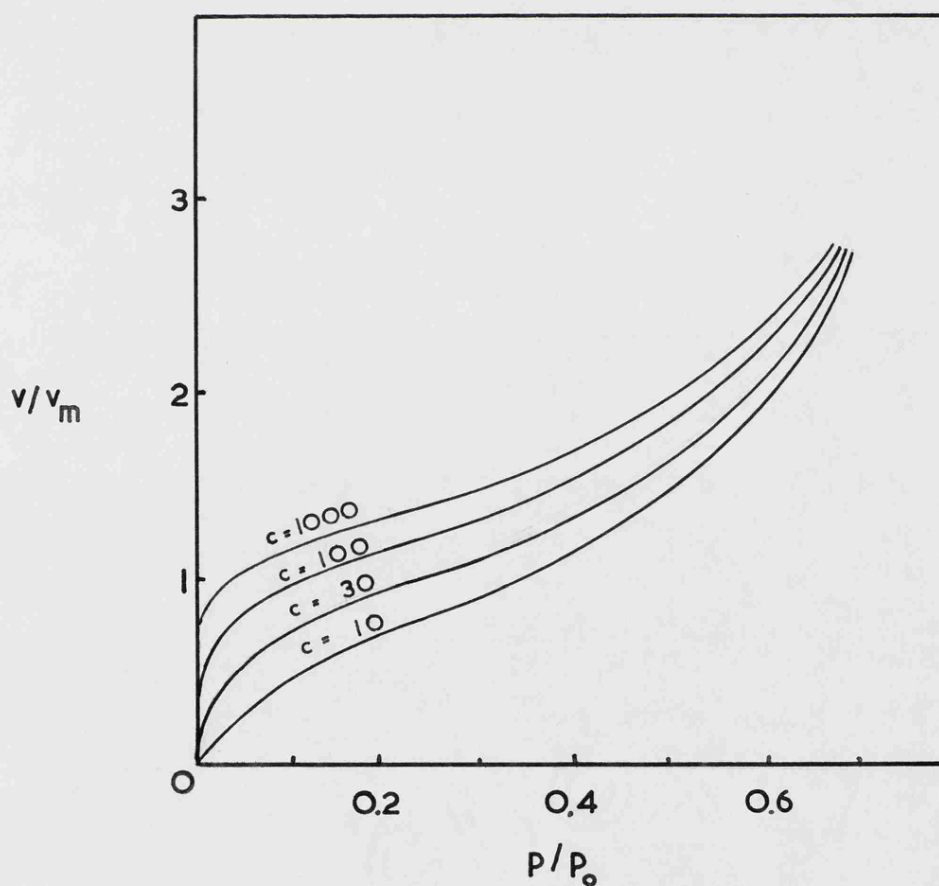
p_0 = saturation pressure of the gas

c = a constant related to the heat of adsorption in the first layer.

It is assumed that the forces responsible for adsorption are the same as those involved in the process of liquefaction. The theory retains the concept of fixed, energetically uniform, adsorption sites as proposed by Langmuir, but allows for the formation of an adsorbed layer more than one molecule thick. The lateral interactions between molecules in the adsorbed phase are neglected and the molecules in all layers after the first are assumed to be subject to forces of similar magnitude.

The shape of the isotherm obtained by plotting (v/v_m) against (p/p_0) varies according to the magnitude of 'c' as shown in Fig. 19.

Fig.19



Isotherms of these shapes are widely realised on the plotting of experimental data. Equation (35) can be used to calculate the monolayer capacity v_m by plotting $p/v(p_0-p)$ against p/p_0 when values for the intercept and slope of the linear plot are given by $1/v_m c$ and $(c-1)/v_m c$ respectively.

In practice, reliable v_m values are only obtained when the isotherm has a well defined 'knee' or plateau, implying a high value for the constant 'c'. In such a case, the isotherm is found to have a linear section and Brunauer and Emmett⁹⁵ concluded that the beginning of this section (designated point B) corresponds to coverage of the adsorbent surface by a complete monolayer of adsorbed gas.

Having obtained the value of v_m from the experimental data, the area occupied by each molecule of the gas on the surface must be known before the surface area of the adsorbent can be determined. The average cross-sectional area of the adsorbed molecules is assumed to be the same as that obtained from the normal packing of the molecules in the liquefied gas⁹⁵, giving:-

$$A_m = f \left(\frac{M}{\rho N} \right)^{2/3} \times 10^{14} \text{ nm}^2 \quad (36)$$

where A_m = cross-sectional area of the molecule (nm^2) in the adsorbed phase

M = molecular weight of the adsorbate

N = Avogadro's number

ρ = density (g/cm^3) of the liquefied gas

f = packing factor for the gas molecules on the surface of the adsorbent.

For nitrogen, the packing of the molecules on the surface is assumed to be hexagonal with each molecule having twelve nearest neighbours, giving a value of 1.091 for the packing factor 'f'.

The specific surface area S of the adsorbent is then calculated from equation (37).

$$S = \frac{V_m}{22400} \cdot N \cdot A_m \times 10^{-18} \text{ m}^2 \quad (37)$$

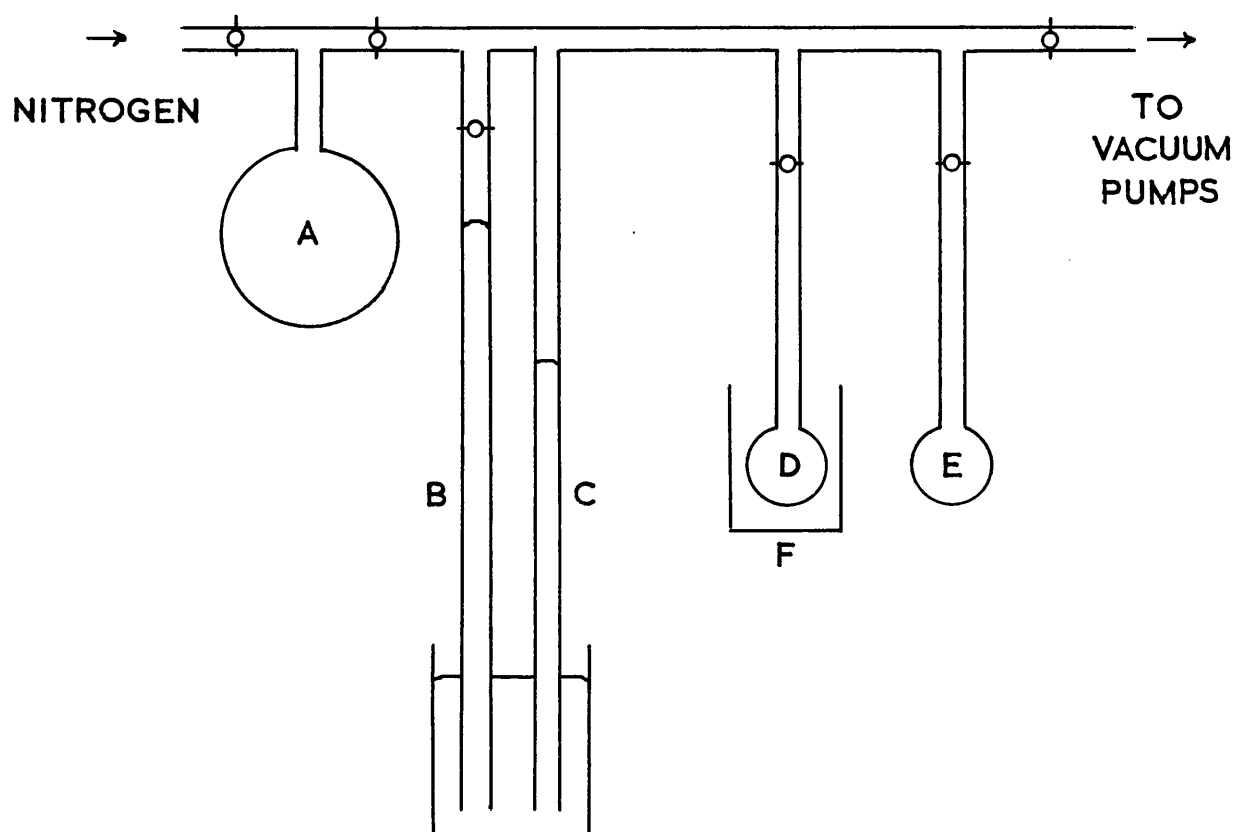
(ii) Adsorption of Nitrogen at -196°C

The gas adsorption experiments were carried out using a conventional type apparatus (shown schematically in Fig. 20). Nitrogen, from a gas cylinder, was purified by passing through alkaline pyrogallol and then through a column of molecular sieves designed to remove water vapour. The apparatus was evacuated by means of a Tower mercury diffusion pump working on conjunction with a Speedivac oil vacuum pump. A Macleod pressure gauge was incorporated in the system to check the 'hardness' of the vacuum obtained. The apparatus was calibrated from p - v relationships using known volumes of nitrogen gas. The 'dead space' in the adsorption bulb due to the adsorbent was obtained from measurement of the density of the solid.

The silica was dried at 120°C for 24 hours and outgassed at room temperature 2 hours prior to the adsorption experiment. The volumes of nitrogen adsorbed by a sample of the silica (1g) were measured for a series of different equilibrium pressures at liquid nitrogen temperature (-196°C). Adsorption and desorption measurements were carried out and the results obtained recorded in Table 24.

Fig. 20

SCHEMATIC DIAGRAM OF THE GAS ADSORPTION APPARATUS



- A storage flask containing nitrogen at atmospheric pressure
- B reference barometer
- C measuring barometer
- D adsorption bulb containing adsorbent
- E adsorption bulb for use in the adsorption of organic liquids as vapours
- F thermos flask containing liquid nitrogen

TABLE 24

<u>Adsorption</u>			<u>Desorption</u>		
Equilibrium Pressure	Relative Pressure	Volume of N ₂ adsorbed at N.T.P.	Equilibrium Pressure	Relative Pressure	Volume of N ₂ adsorbed at N.T.P.
$p/(\text{kNm}^{-2})$	p/p_0	$v/(\text{cm}^3)$	$p/(\text{kNm}^{-2})$	p/p_0	$v/(\text{cm}^3)$
0.00	0.000	8.7	94.31	0.931	282.5
0.00	0.000	18.2	82.43	0.814	278.1
0.04	0.000	35.2	78.34	0.773	274.6
0.43	0.004	54.0	73.32	0.724	267.6
1.77	0.017	69.0	69.55	0.687	259.9
4.45	0.044	81.9	65.33	0.645	250.4
7.48	0.074	90.9	60.16	0.594	238.6
10.80	0.107	98.7	54.88	0.542	226.1
15.55	0.154	108.4	50.01	0.494	211.2
19.90	0.196	116.6	47.02	0.464	187.1
24.80	0.245	124.5	43.37	0.428	165.8
30.52	0.301	134.0	38.25	0.377	152.6
36.03	0.356	145.9	32.95	0.325	141.6
42.86	0.423	160.8	27.67	0.273	131.1
47.81	0.472	175.5	23.88	0.236	124.1
52.93	0.523	190.5	21.76	0.215	119.9
58.07	0.573	205.0	18.91	0.187	114.5
63.17	0.624	220.2	14.30	0.141	106.0
71.13	0.702	244.0	11.06	0.109	99.4
77.13	0.761	260.4	7.52	0.074	91.0
80.91	0.799	267.4			
82.71	0.817	271.0			
94.35	0.931	282.1			
98.95	0.977	283.4			

$$p_0 = 101.29 \text{ kNm}^{-2}$$

The combined adsorption and desorption isotherms obtained by plotting the volume of gas (at N.T.P.) adsorbed against the relative pressure is shown in Fig. 21.

From the linear plot of $p/v(p_0-p)$ against p/p_0 (Fig. 22) over the relative pressure range 0.05 to 0.35,

$$\text{Intercept} = \frac{1}{v_m c} = 0.141 \times 10^{-3}$$

$$\text{Slope} = \frac{c-1}{v_m c} = 0.999 \times 10^{-2}$$

$$\text{giving } \underline{v_m = 98.7 \text{ cm}^3}$$

(compare point B from Fig. 21; $v_m = 100 \text{ cm}^3$)

From equation (36), the area requirement per molecule of nitrogen

$$\underline{A_m = 0.162 \text{ nm}^2}^{96,97,98}$$

Using equation (37), the specific surface area S of the silica is calculated as $432 \text{ m}^2 \text{g}^{-1}$.

Previous work²² has shown the specific surface area of the alumina as assessed by nitrogen adsorption to be $132 \text{ m}^2 \text{g}^{-1}$.

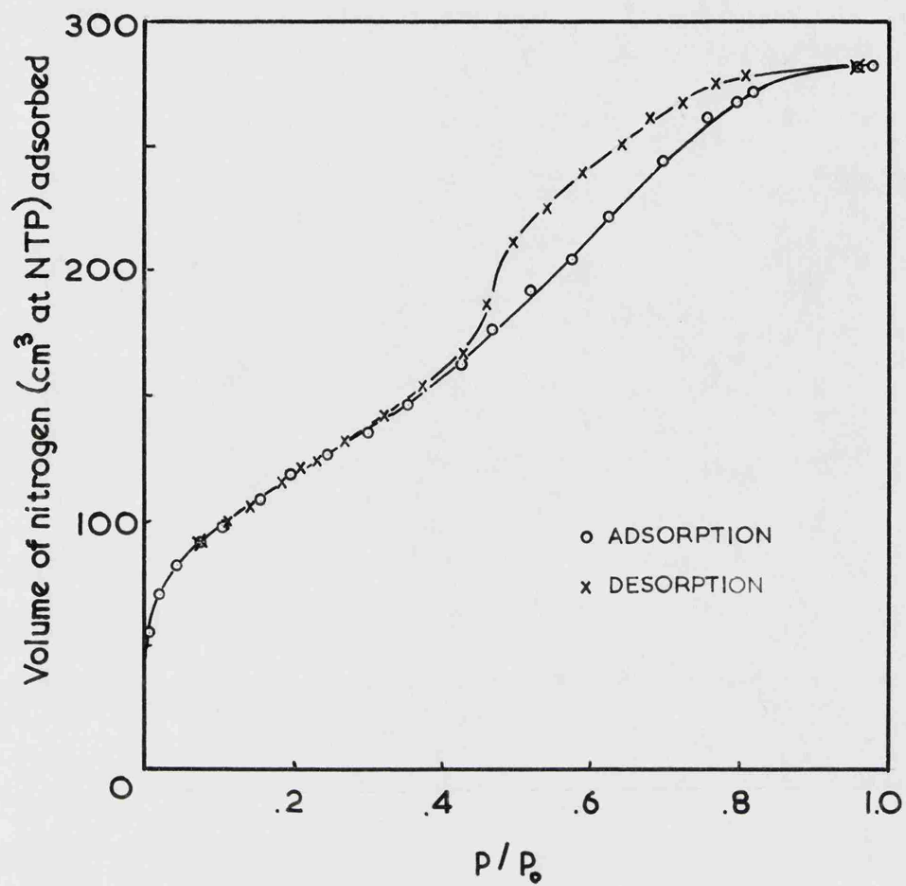


Fig.21

Adsorption of nitrogen on to silica

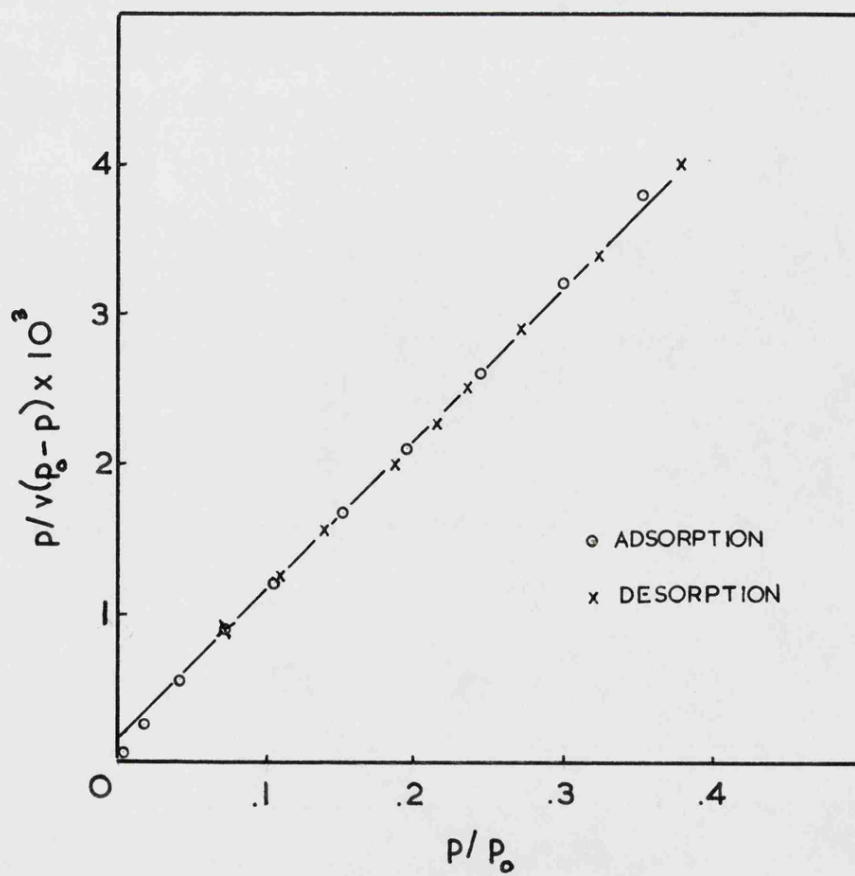


Fig.22

(iii) Adsorption of Benzene Vapour at Room Temperature

The adsorption experiment was repeated using benzene vapour at room temperature. Measurements were made up to a relative pressure of 0.45 and the results obtained recorded in Table 25.

TABLE 25

Equilibrium Pressure $p/(\text{kNm}^{-2})$	Relative Pressure p/p_0	Volume adsorbed at N.T.P. $v/(\text{cm}^3)$
0.00	0.000	1.4
0.00	0.000	5.0
0.04	0.004	8.4
0.27	0.025	14.3
0.60	0.056	20.5
1.03	0.095	26.1
1.63	0.151	33.7
2.23	0.207	40.1
2.87	0.266	47.7
3.41	0.317	54.1
4.25	0.317	61.9
4.69	0.436	69.8

$$\underline{p_0 = 10.76 \text{ kNm}^{-2} \text{ at } 21.7^\circ\text{C}}$$

The adsorption isotherm is shown in Fig. 23 and from the plot of $p/v(p_0-p)$ against p/p_0 (Fig. 24)

$$\text{Intercept} = 0.185 \times 10^{-2}$$

$$\text{Slope} = 0.0219$$

$$\text{giving } \underline{v_m = 42.2 \text{ cm}^3}$$

The specific surface area S of the silica was calculated from equation (37) as $\underline{454 \text{ m}^2\text{g}^{-1}}$, assuming that the surface area requirement (A_m) of a benzene molecule is 0.40 nm^2 99,100.

Previous work²² has shown the specific surface area of the alumina to be $102 \text{ m}^2\text{g}^{-1}$ as assessed by vapour phase adsorption of benzene.

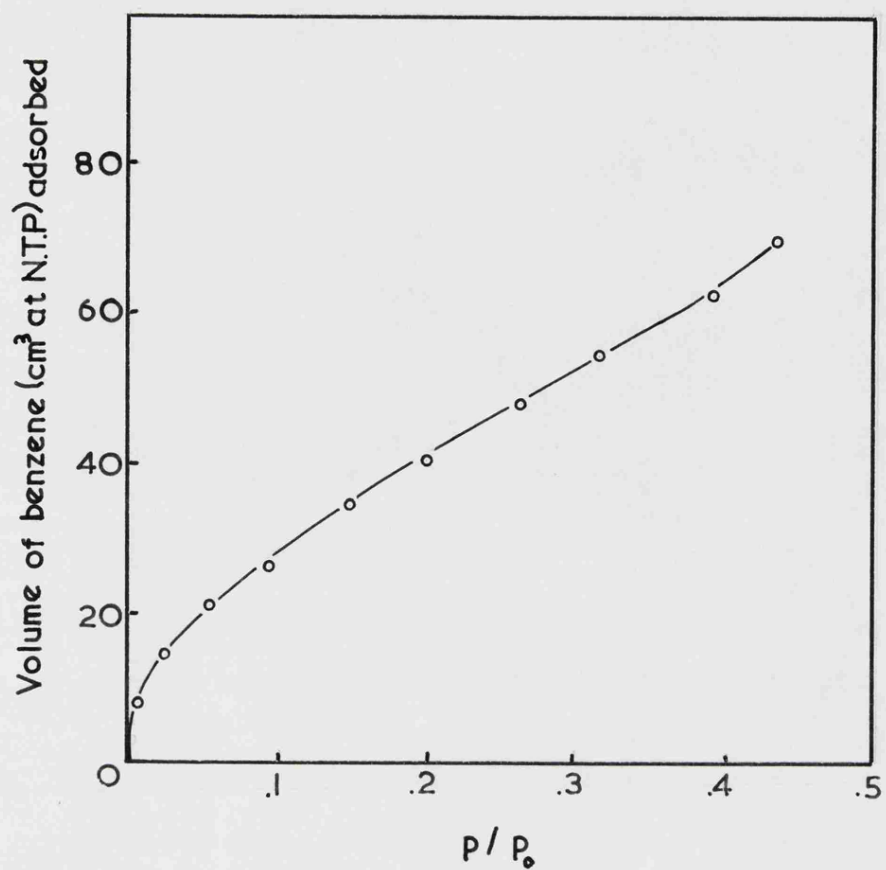


Fig.23

Adsorption of benzene on to silica

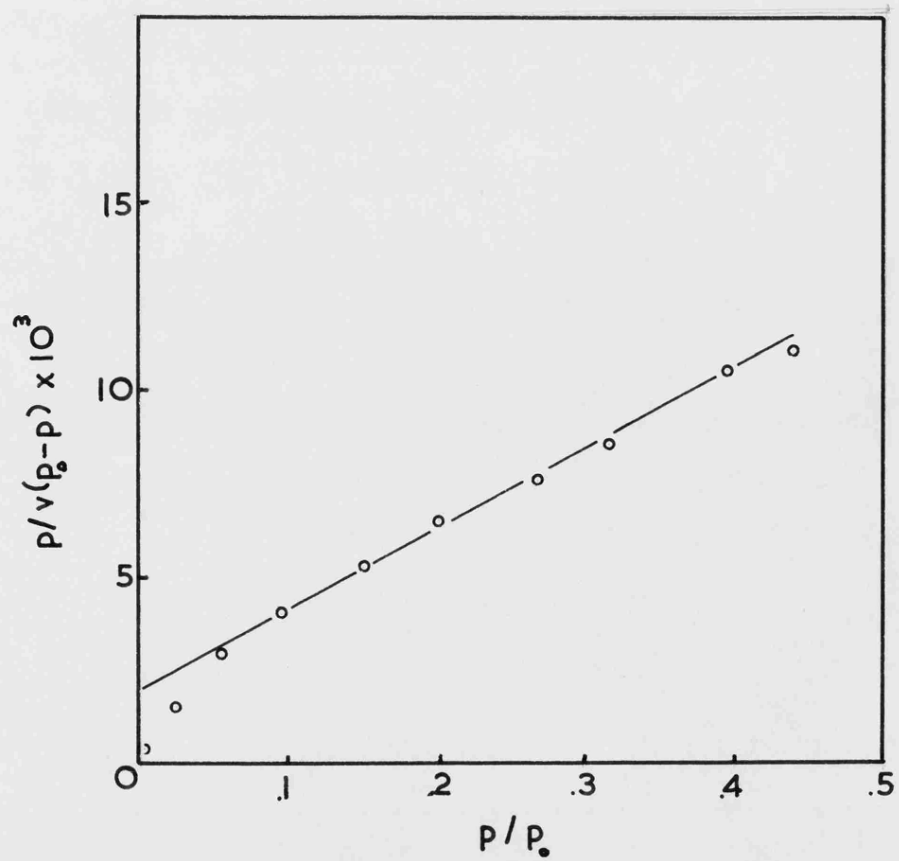


Fig.24

(c) Assessment of Surface Porosity

(i) The 't' and 'v_s' curves

Lippens and De Boer¹⁰¹ have developed a graphical procedure which enables interpretation to be made of nitrogen adsorption isotherms in terms of porosity of the solid adsorbent. The method involves plotting the volume of nitrogen adsorbed on the adsorbent under investigation against the corresponding statistical thickness 't' of the adsorbed layer of nitrogen on a non-porous reference solid.

The statistical thickness 't' of the adsorbed layer is given by

$$t = \left(\frac{v}{v_m} \right)_l 0.354 = \left(\frac{v}{v_m} \right)_g 0.354 \quad (38)$$

where v = volume adsorbed corresponding to a thickness 't'

v_m = volume adsorbed corresponding to a monolayer

subscripts 'l' and 'g' refer to volumes of liquid and gas respectively (cm³ at N.T.P.).

The factor 0.354 represents a monolayer thickness in nm and is equal to the volume of nitrogen which occupies 1 nm² of surface. This volume is calculated simply from the density of liquid nitrogen (0.81 g cm⁻³), the area requirement of a nitrogen molecule (0.162 nm²) and the molecular weight of nitrogen (28).

Several workers^{102,103,104} have noted that nitrogen adsorption isotherms for many non-porous substances are almost superimposable when plotted in a reduced form (v/v_m against p/p₀) and that deviations from this

standard isotherm may be analysed in terms of micropore filling and capillary condensation. De Boer, Linsen and Osinga¹⁰⁵ suggested that the adsorption data of Lippens, Linsen and De Boer¹⁰⁶ obtained by using several well selected samples of non-porous aluminas and aluminium hydroxides was suitable for the construction of an 'experimental master curve' up to a relative pressure of 0.98. The thickness of the adsorbed layer 't' is calculated from equation (38) and tabulated as a function of relative equilibrium pressure p/p_0 in Table 26.

TABLE 26

p/p_0	$t/(\text{nm})$	p/p_0	$t/(\text{nm})$	p/p_0	$t/(\text{nm})$
0.08	0.351	0.40	0.571	0.72	0.891
0.10	0.368	0.42	0.586	0.74	0.927
0.12	0.383	0.44	0.602	0.76	0.965
0.14	0.397	0.46	0.618	0.78	1.007
0.16	0.410	0.48	0.634	0.80	1.057
0.18	0.423	0.50	0.650	0.82	1.117
0.20	0.436	0.52	0.666	0.84	1.189
0.22	0.449	0.54	0.682	0.86	1.275
0.24	0.462	0.56	0.699	0.88	1.382
0.26	0.475	0.58	0.717	0.90	1.494
0.28	0.488	0.60	0.736	0.92	1.60*
0.30	0.501	0.62	0.756	0.94	1.75*
0.32	0.514	0.64	0.777	0.96	1.98*
0.34	0.527	0.66	0.802	0.98	2.29*
0.36	0.541	0.68	0.826		
0.38	0.556	0.70	0.857		

* extrapolated values

The thickness of the adsorbed layer 't' can be related to the surface area of the adsorbent as follows:-

$$t = \frac{v_l}{S} \times 10^{-6} \times 10^9 \text{ nm} \quad (39)$$

where v_l = volume of liquid nitrogen adsorbed (cm^3)
 S = specific surface area of adsorbent (m^2g^{-1})

Volume of nitrogen gas adsorbed at N.T.P. (v)

$$= \frac{v_l \cdot 22400}{V_{\text{Sp}} \cdot M} \text{ cm}^3 \quad (40)$$

where V_{Sp} = specific volume of liquid nitrogen (cm^3g^{-1})
 M = molecular weight of nitrogen.

Substituting (40) in (39) gives

$$\begin{aligned} t &= \frac{v \cdot M \cdot V_{\text{Sp}}}{22400 S} \times 10^3 \text{ nm} \\ &= 1.55 \left(\frac{v}{S} \right) \text{ nm} \end{aligned} \quad (41)$$

Rearranging equation (41) gives

$$v = \frac{S}{1.55} \cdot t \quad (42)$$

Thus a plot of 'v' against 't' for non-porous solids should be linear, should pass through the origin and have a slope related to the surface area of the solid (Fig. 25 curve A). No deviation from this linear plot should be observed unless the adsorbent considered is porous when capillary condensation or closing of pores may occur. If at some value of 't', a positive deviation is observed then more nitrogen is being taken up than corresponds to multimolecular adsorption and the onset of capillary condensation is suggested (Fig. 25 curve B).

When the pores are full, the plot should become linear and almost parallel to the 't' axis, the slope indicating the outer surface area. In the case of curve C in Fig. 25, capillary condensation occurs in very narrow pores and the initial slope is indicative of the surface area of these pores.

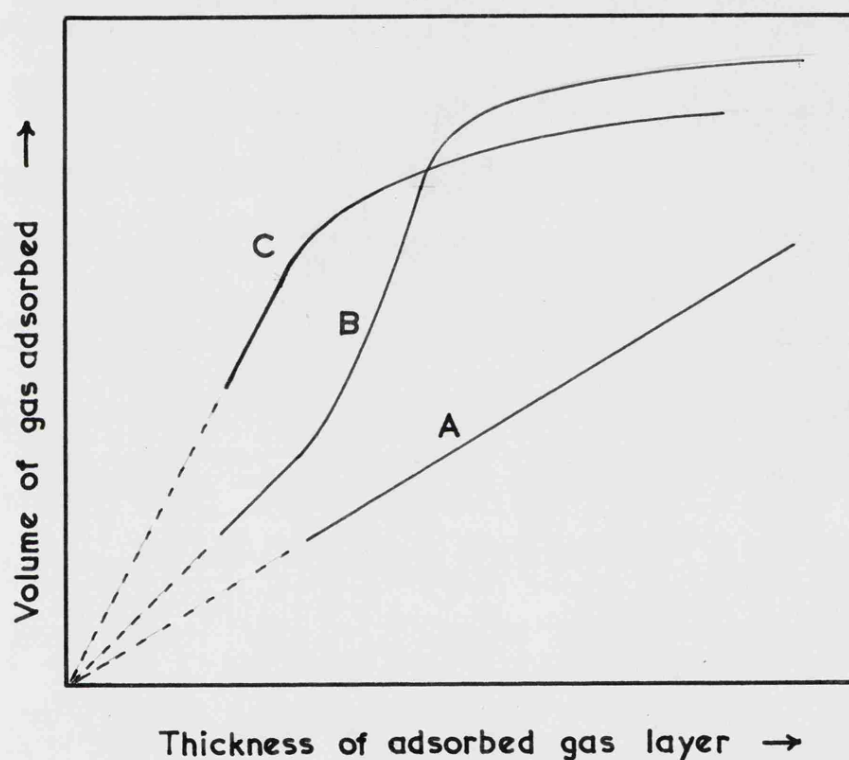


Fig. 25

Sing¹⁰⁷ has developed a method similar to that of Lippens and De Boer¹⁰¹ but which is independent of the B.E.T. analysis of the adsorption isotherm. The method consists of plotting the amount of nitrogen adsorbed on the adsorbent under investigation ' v ' against ' v_s ' (instead of t), where ' v_s ' is the ratio of the amount of nitrogen adsorbed on a non-porous reference solid at the given relative pressure (p/p_0) to

that adsorbed at a selected relative pressure $(p/p_0)_x$. The value of $(p/p_0)_x$ is chosen as 0.4 since monolayer coverage and micropore filling usually occur at $(p/p_0) < 0.4$ whereas capillary condensation in association with hysteresis takes place at $(p/p_0) > 0.4$. Deviation of the ' v_s ' curve from linearity at $(p/p_0) < 0.4$ suggests micropore filling while at $(p/p_0) > 0.4$ capillary condensation may accompany multilayer formation. When micropore filling is absent, the surface area of the adsorbent under investigation can be calculated from the initial slope of the ' v_s ' curve by using a normalising factor, obtained from the standard isotherm on a non-porous reference solid of known surface area.

For alumina,

$$\text{Surface area} = 2.87 (\text{initial slope of } 'v_s' \text{ curve}) \text{ m}^2\text{g}^{-1}.$$

The factor 2.87 is obtained by calibration against the surface area of Degussa Aluminiumoxid C, the standard reference solid, determined by electron microscopy.

For silica,

$$\text{Surface area} = 2.89 (\text{initial slope of } 'v_s' \text{ curve}) \text{ m}^2\text{g}^{-1}.$$

The factor 2.89 is obtained by calibration against the surface area of Fransil EL, the standard reference solid, determined by electron microscopy.

The values of (p/p_0) , ' t ' and ' v_s ' obtained by Carruthers et al¹⁰⁸ for adsorption on Fransil EL are recorded in Table 27.

TABLE 27

p/p_0	$t/(nm)$	v_s	p/p_0	$t/(nm)$	v_s
0.09	0.353	0.66	0.38	0.524	0.98
0.10	0.364	0.68	0.40	0.535	1.00
0.12	0.375	0.70	0.42	0.540	1.01
0.14	0.391	0.73	0.44	0.556	1.04
0.16	0.401	0.75	0.46	0.567	1.06
0.18	0.412	0.77	0.50	0.589	1.10
0.20	0.428	0.80	0.55	0.615	1.14
0.22	0.439	0.82	0.60	0.653	1.22
0.24	0.449	0.84	0.65	0.690	1.29
0.26	0.460	0.86	0.70	0.738	1.38
0.28	0.471	0.88	0.75	0.787	1.47
0.30	0.482	0.90	0.80	0.867	1.62
0.32	0.492	0.92	0.85	0.967	1.81
0.34	0.503	0.94	0.90	1.28	2.4
0.36	0.514	0.96	0.95	1.98	3.7

Using the data in Tables 26 and 27, the 't' and ' v_s ' curves were constructed for the silica under investigation and are shown in Figs. 26 and 27 respectively. The surface area values calculated from the initial slopes of these plots are given in Table 28 and are seen to be in good agreement with the B.E.T. values.

TABLE 28

<u>Adsorbent</u>	<u>Surface Area/(m²g⁻¹)</u>		
	<u>The 't' curve</u>	<u>The 'v_s' curve</u>	<u>B.E.T.</u>
Silica	414	434	432
Alumina ²²	126	-	132

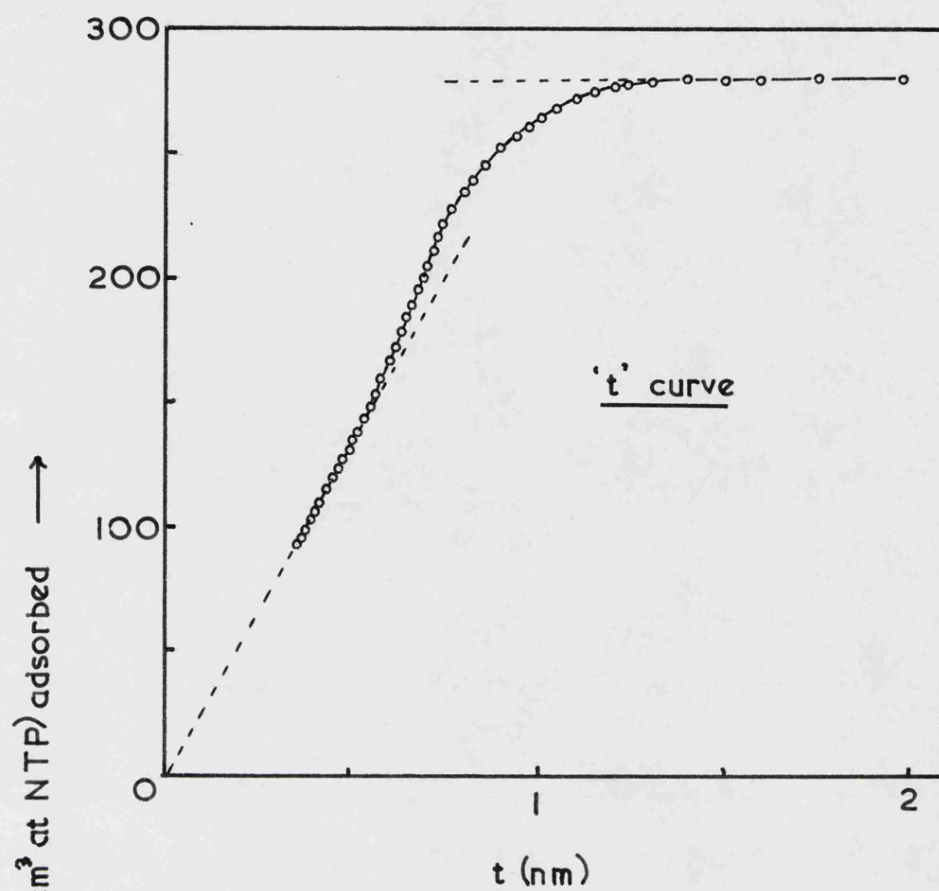


Fig.26

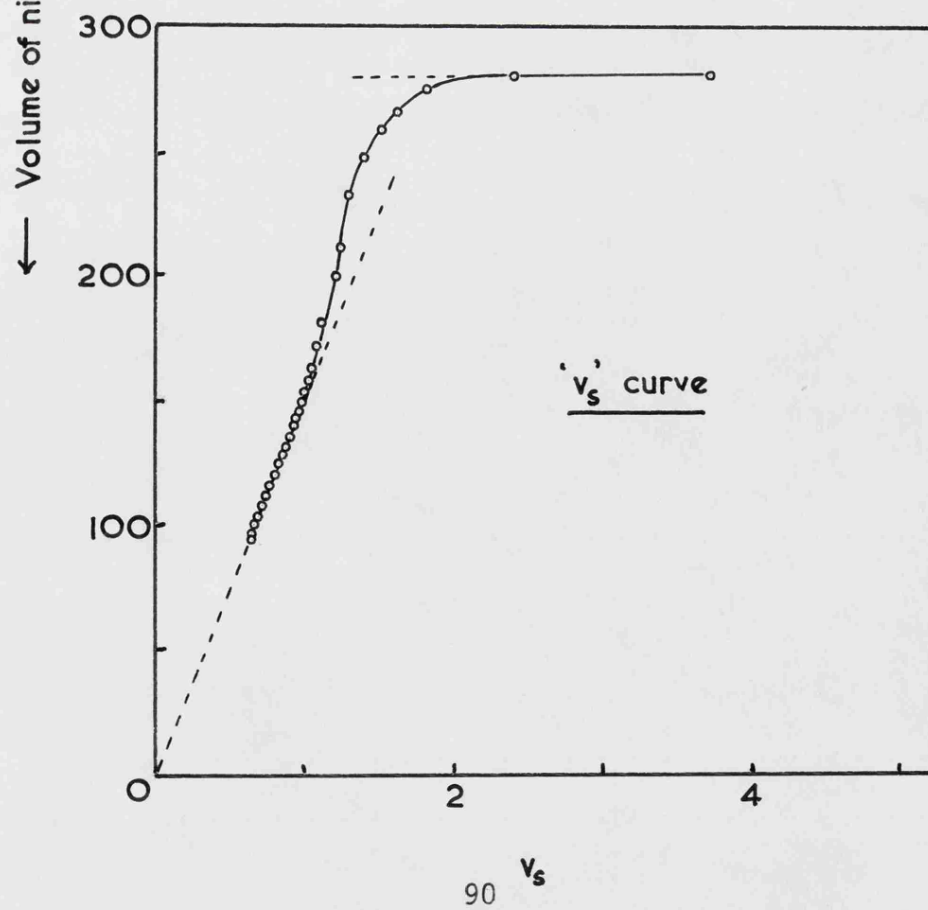


Fig.27

Both the 't' and 'v_s' curves show the absence of micropores in the silica under investigation and suggest that capillary condensation commences at a relative pressure of 0.3.

The Kelvin equation is,

$$\log \left(\frac{p}{p_0} \right) = - \frac{2\gamma V \cos \theta}{r_k RT} \quad (43)$$

where γ = surface tension of liquid nitrogen ($8.72 \times 10^{-3} \text{ Nm}^{-1}$)

V = molar volume of the adsorbed and/or capillary condensed nitrogen ($34.68 \text{ cm}^3 \text{ mol}^{-1}$)

T = absolute temperature of boiling liquid nitrogen (78K)

and r_k is the Kelvin radius.

which reduces to

$$r_k = -0.405 / \log(p/p_0) \text{ nm} \quad (44)$$

if the contact angle θ between the surface of the adsorbed liquid nitrogen and the wall of the capillary is taken to be zero.

Thus the Kelvin radius corresponding to a relative pressure of 0.3 is calculated as 0.8 nm from equation (44). The relation between the Kelvin radius r_k and the pore radius r_p , assuming cylindrical pores to be present in the silica under investigation (see 'pore size distribution analysis'), is given by

$$r_p = r_k + t \quad \text{where } t = \text{thickness of adsorbed layer.}$$

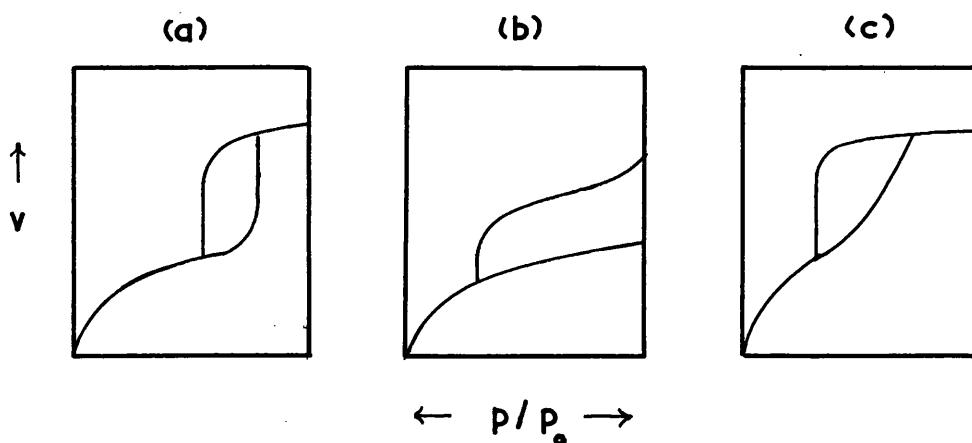
Thus, the onset of capillary condensation occurs in pores of radius 1.3 nm.

For the alumina under investigation, the corresponding 't' curve²² indicates the absence of micropores while capillary condensation commences in pores of width 1.8 nm assuming the pores to be slit-shaped²².

(ii) Pore Size Distribution Analysis

In the adsorption of a gas by a porous solid, it is found that the experimental desorption isotherm differs from the adsorption isotherm over a range of relative pressures such that the combined isotherm exhibits a hysteresis loop (Fig. 21). The occurrence of the hysteresis loop has been attributed to the different mechanisms by which the pores of the adsorbent fill and empty. According to De Boer¹⁰⁹, five fundamentally different types of hysteresis loops may be observed and of these types A, B and E are frequently encountered in practice (Fig. 28).

Fig. 28



Classification of hysteresis loops (a) A-type (b) B-type (c) E-type

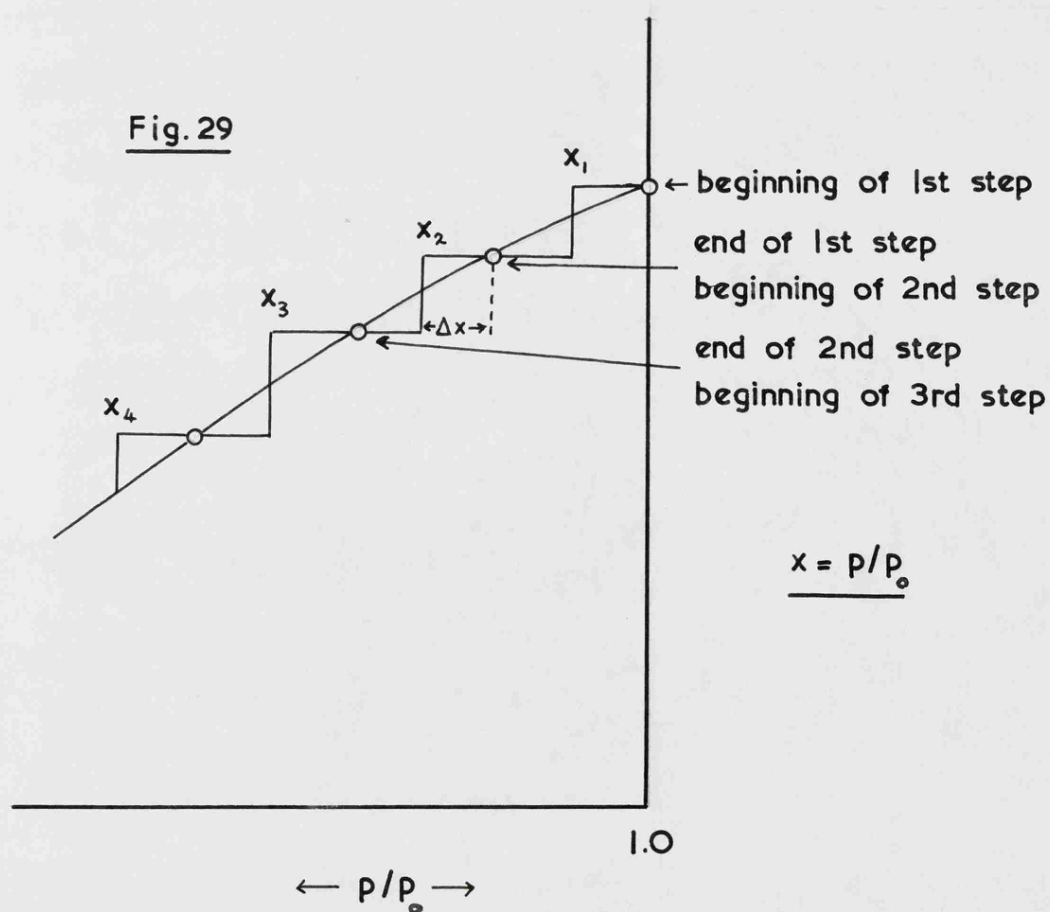
The variety of pore shapes which give rise to A and E type hysteresis loops can be represented approximately by the model of cylindrical pores while B type hysteresis loops are associated with the occurrence of slit-shaped pores¹⁰⁹.

The method of pore size analysis based on nitrogen isotherms was introduced by Wheeler¹¹⁰ in 1945 since when, numerous modifications have been made. The analysis is performed on the desorption or adsorption branch of the hysteresis loop and it is assumed that all pores in the adsorbent are either cylindrical or slit-shaped. The Kelvin equation is used to calculate the radius at each relative pressure considered and the pore radius ' r ' calculated from this parameter by allowing for the thickness of the adsorbed layer ' t '. Values of the latter are obtained from a suitable ' t ' curve and a variety of these are available in the literature. The ' t ' curves of different investigators^{102,103,105} differ from each other, depending on the group of adsorbents used for their determination and a ' t ' curve is selected which corresponds to the type of adsorbent under investigation. However, the choice of ' t ' curve is not critical, partly because such curves do not differ greatly from each other, and partly because the t -values constitute only a part of the pore radius. The cumulative pore volume and surface area are then determined by summing the pore volumes and surfaces of groups of pores that have radii between $(r+\Delta r)$ and $(r-\Delta r)$ over the range of the hysteresis loop.

For the silica under investigation, the pore size analysis, based on the method of Barrett et al¹¹¹, has been carried out on the desorption branch of the isotherm using the model of cylindrical pores as the shape of the hysteresis loop (Type A with some E type characteristics)

indicates this pore shape to be the most probable. The data of Carruthers et al¹⁰⁸ for the adsorption of nitrogen on a non-porous silica has been used for calculating the thickness of the adsorbed layer at various relative pressures.

In this analysis, it is assumed that at a relative pressure $x = 1$, all pores (including a portion of intergranular space) are filled with liquid nitrogen. The branch of the isotherm to be analysed is divided into steps corresponding to equal relative pressure increments of $2\Delta x$ (Fig. 29).



At the beginning of the i^{th} step, the relative pressure is $(x_i + \Delta x)$, the volume adsorbed (expressed in cm^3 liquid nitrogen) $X_{(x_i + \Delta x)}$, and the thickness of the layers of nitrogen adsorbed on the surface $t_{(x_i + \Delta x)}$.

If the relative pressure is lowered to $(x_i - \Delta x)$, those pores having a Kelvin radius between $(r_k)_{(x_i + \Delta x)}$ and $(r_k)_{(x_i - \Delta x)}$ are emptied. If Δx is sufficiently small, this group of pores can be assigned a mean Kelvin radius $(r_k)_{x_i}$, the actual radius of the pore being r_{x_i} .

The mean thickness of the adsorbed layer t_{x_i} at the relative pressure x_i is given by

$$r_{x_i} = (r_k)_{x_i} + t_{x_i}$$

At the end of the i^{th} step, the relative pressure is $(x_i - \Delta x)$, the adsorbed volume of nitrogen, $X_{(x_i - \Delta x)}$, and the thickness of the adsorbed layer, $t_{(x_i - \Delta x)}$. The surface area and volume of this group of pores can be represented by ΔS_{x_i} and ΔV_{x_i} respectively.

Thus during the i^{th} step, the desorbed volume ΔX_i is given by

$$\Delta X_i = X_{(x_i + \Delta x)} - X_{(x_i - \Delta x)}$$

This desorbed volume is formed by:-

- (a) the volume originating from the capillary evaporation from the i^{th} group of pores at the relative pressure x_i and the decrease of the thickness of the adsorbed layer of this group of pores by

lowering the relative pressure from x_i to $(x_i - \Delta x)$

$$\dots\dots V_1$$

$$\text{where } V_1 = \frac{\pi(r_{x_i} - t_{(x_i - \Delta x)})^2 \cdot L_i}{}$$

and L_i = the total length of the pores with a radius of r_{x_i} .

(b) the decrease of the thickness of the adsorbed layer in the pores which were already emptied at the relative pressure $(x_i + \Delta x)$ during the lowering of the pressure to $(x_i - \Delta x)$

$$\dots\dots V_2$$

$$\begin{aligned} \text{where } V_2 &= \sum_{i=1}^{i-1} \left[\pi(r_{x_i} - t_{(x_i - \Delta x)})^2 L_i - \pi(r_{x_i} - t_{(x_i + \Delta x)})^2 L_i \right] \\ &= (t_{(x_i + \Delta x)} - t_{(x_i - \Delta x)}) \sum_{i=1}^{i-1} 2\pi L_i \cdot (r_k)_{x_i} \end{aligned}$$

Now $2\pi L_i (r_k)_{x_i} = \Delta(S_k)_{x_i}$ the area of the inner surface formed by the adsorbed layer, thickness t_{x_i} for the group having a mean Kelvin radius $(r_k)_{x_i}$

$$\text{and } \Delta S_{x_i} = 2\pi L_i \cdot r_{x_i}$$

$$\therefore \Delta(S_k)_{x_i} = \frac{(r_{x_i} - t_{x_i})}{r_{x_i}} \cdot \Delta S_{x_i}$$

$$\text{Thus } V_2 = \frac{(t_{(x_i + \Delta x)} - t_{(x_i - \Delta x)}) \sum_{i=1}^{i-1} \Delta S_{x_i} (r_{x_i} - t_{x_i}) / r_{x_i}}{}$$

Hence during the i^{th} step,

$$\text{desorbed volume } \Delta X_i = V_1 + V_2$$

$$= \pi(r_{x_i} - t_{(x_i - \Delta x)})^2 L_i + (t_{(x_i + \Delta x)} - t_{(x_i - \Delta x)}) \sum_{i=1}^{i-1} c_i \Delta S_{x_i}$$

$$\text{where } c_i = (r_{x_i} - t_{x_i}) / r_{x_i}.$$

$$\text{Now } \Delta V_{x_i} = \pi (r_{x_i})^2 L_i$$

where ΔV_{x_i} = volume of pores with radius r_{x_i} .

$$\text{Thus } \Delta X_i = \Delta V_{x_i} (r_{x_i} - t_{(x_i - \Delta x)})^2 / (r_{x_i})^2 + (t_{(x_i + \Delta x)} - t_{(x_i - \Delta x)}) \sum_{i=1}^{i-1} c_i \Delta S_{x_i}$$

$$\text{Putting } R_{x_i} = (r_{x_i})^2 / (r_{x_i} - t_{(x_i - \Delta x)})^2$$

$$\Delta V_{x_i} = (R_{x_i} \Delta X_i) - (R_{x_i} \Delta t_{x_i} \sum_{i=1}^{i-1} \Delta S_{x_{i-1}}) \quad (45)$$

Summing up all contributions of ΔS_{x_i} gives the cumulative quantity S_{cum} representing the total surface area of pores having a width greater than r_{x_i} . The computation was carried out using an IBM 1130 computer and the results obtained for the silica under investigation given in Table 29. The analysis was concluded at a relative pressure of 0.3 which the 't' and 'v_s' curves (Figs. 26 and 27) indicate is the pressure below which capillary condensation does not occur. A copy of the Fortran program used is given in the Appendix.

The results are also expressed graphically in Figs. 30 and 31 where cumulative surface area (S_{cum}) is plotted against pore radius (r) (Fig. 30) and the pore surface area distribution as a function of pore radius (r) (Fig. 31).

TABLE 29

x	v	t	r_{x_i}	$\Delta X_i \times 10^3$	$\Delta V_{x_i} \times 10^3$	ΔS_{x_i}	S_{cum}
	/cm ³ (gas)	/nm	/nm	/cm ³ (liquid)	/cm ³	/m ² g ⁻¹	/m ² g ⁻¹
0.94	282.6	1.815					
			14.52	0.31	0.39	0.05	0.05
0.92	282.4	1.510					
			11.28	0.62	0.77	0.14	0.19
0.90	282.0	1.280					
			9.20	0.93	1.16	0.25	0.44
0.88	281.4	1.105					
			7.75	1.39	1.79	0.46	0.90
0.86	280.5	1.005					
			6.71	1.24	1.61	0.48	1.38
0.84	279.7	0.943					
			5.93	2.17	2.93	0.99	2.37
0.82	278.3	0.897					
			5.31	2.17	3.01	1.13	3.51
0.80	276.9	0.867					
			4.80	2.94	4.13	1.72	5.23
0.78	275.0	0.829					
			4.38	3.72	5.40	2.46	7.69
0.76	272.6	0.803					
			4.03	4.03	5.94	2.94	10.64
0.74	270.0	0.778					
			3.73	4.64	7.03	3.77	14.41
0.72	267.0	0.757					
			3.47	5.73	8.89	5.12	19.53
0.70	263.3	0.738					
			3.24	6.66	10.45	6.45	25.97
0.68	259.0	0.717					
			3.04	6.81	10.92	7.19	33.17
0.66	254.6	0.700					
			2.86	7.28	11.82	8.28	41.44
0.64	249.9	0.683					
			2.69	7.28	11.97	8.88	50.33
0.62	245.2	0.667					
			2.55	7.28	12.20	9.58	59.91
0.60	240.5	0.653					

TABLE 29 (cont.)

x	v	t	r_{x_i}	$\Delta X_i \times 10^3$	$\Delta V_{x_i} \times 10^3$	ΔS_{x_i}	S_{cum}
	/cm ³ (gas)	/nm	/nm	/cm ³ (liquid)	/cm ³	/m ² g ⁻¹	/m ² g ⁻¹
0.60	240.5	0.653					
			2.41	7.59	12.98	10.75	70.66
0.58	235.6	0.640	2.29	6.97	11.70	10.21	80.88
0.56	231.1	0.625	2.18	7.59	13.20	12.12	92.99
0.54	226.2	0.612	2.08	8.98	16.19	15.60	108.60
0.52	220.4	0.600	1.98	11.15	20.88	21.09	129.69
0.50	213.2	0.589	1.89	15.95	31.01	32.79	162.48
0.48	202.9	0.578	1.81	29.73	60.48	66.90	229.38
0.46	183.7	0.567	1.73	19.51	38.63	44.66	274.05
0.44	171.1	0.556	1.65	11.61	19.08	23.08	297.13
0.42	163.6	0.540	1.58	9.13	18.57	23.45	320.58
0.40	157.7	0.535	1.52	7.74	12.60	16.58	337.16
0.38	152.7	0.524	1.46	7.43	12.49	17.15	354.31
0.36	147.9	0.514	1.40	6.50	9.75	13.96	368.27
0.34	143.7	0.503	1.34	6.50	9.81	14.66	382.93
0.32	139.5	0.492	1.28	6.35	10.11	15.75	398.69
0.30	135.4	0.482	1.23	6.35	9.52	15.49	414.17
0.28	131.3	0.471					

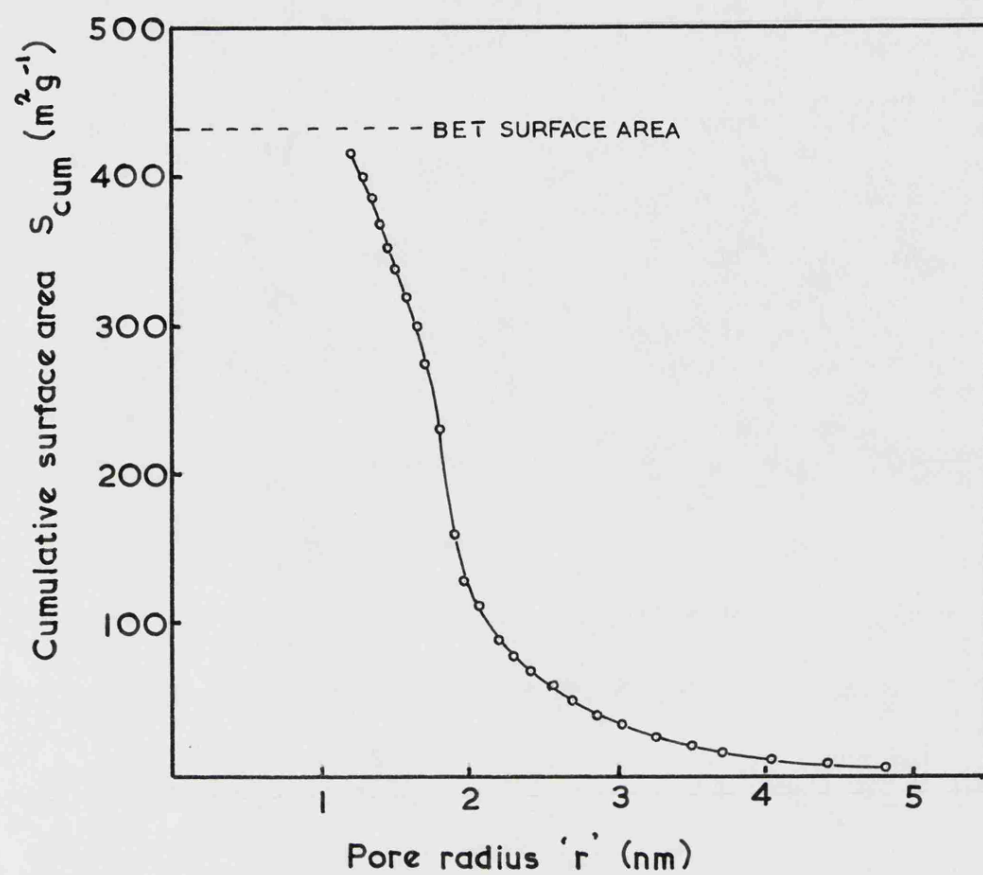


Fig.30

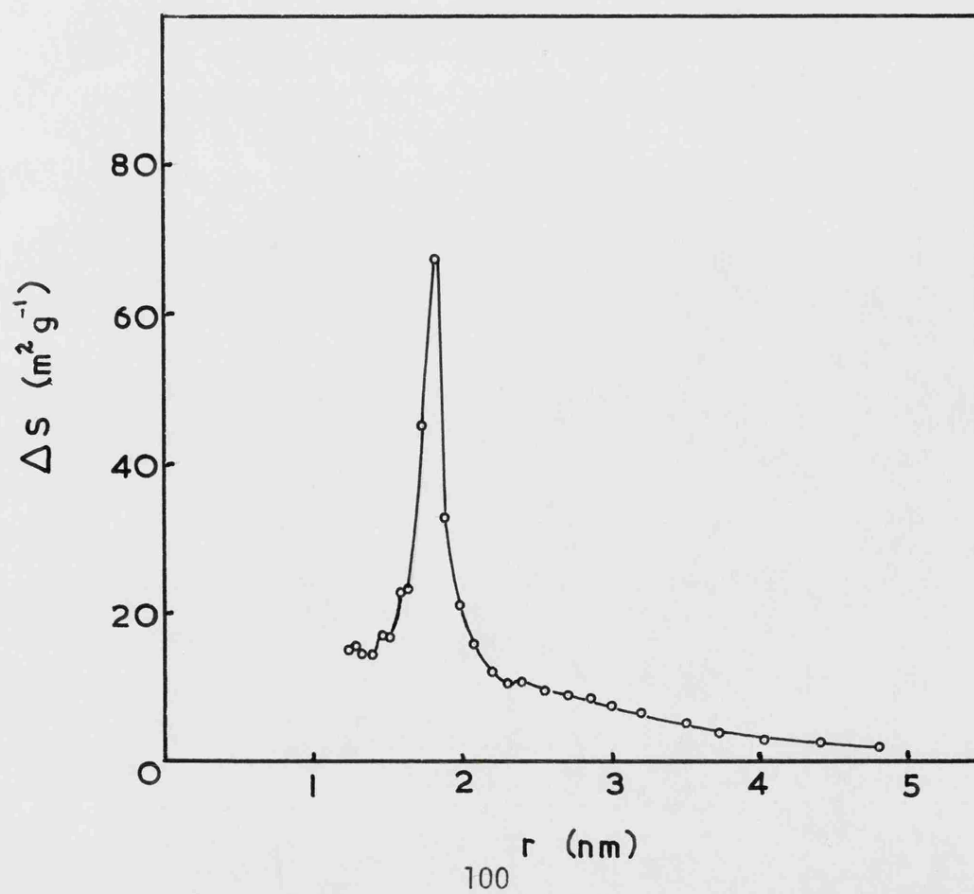


Fig.31

From the pore size distribution analysis, it can be seen that good agreement is obtained between the cumulative surface area ($414 \text{ m}^2\text{g}^{-1}$) and the B.E.T. value ($432 \text{ m}^2\text{g}^{-1}$) and that the largest part of the surface area of the silica arises from pores having a radius between 1.7-2.0 nm.

An analysis using the adsorption branch of the nitrogen isotherm gives a cumulative surface area of $347 \text{ m}^2\text{g}^{-1}$ and a pore size distribution indicating the majority of the pores to have radii between 1.5-2.0 nm.

For the alumina, previous work²² has shown that about 90% of the surface area is accounted for by slit-shaped pores having a width greater than 2 nm, the majority of the pores having diameters between 2.7-3.2 nm.

(2) ADSORPTION OF p-SUBSTITUTED PHENOLS FROM SOLUTION ON TO ALUMINA AND SILICA

(a) The Adsorbents

Alumina, 100-200 mesh, manufactured by 'Camag' M.F.C. was dried at 120°C for 48 hours.

Silica, 100-200 mesh, manufactured by Joseph Crosfield and Sons Ltd. under the trade name "Sorbsil" was dried at 120°C for 24 hours.

(b) The Solvents

Benzene, Toluene and n-Hexane were allowed to stand in contact with fresh sodium wire for three days, refluxed over sodium for several hours and then fractionally distilled, the middle fraction being collected.

Carbon Tetrachloride and Cyclohexane were purified as previously described.

(c) The Adsorptives

Phenol, p-methyl phenol, p-t-butyl phenol, and p-chloro phenol were fractionally distilled three times and dried in vacuo over phosphorus pentoxide.

p-Methoxy phenol and p-bromo phenol were recrystallised three times

from a mixture of benzene and petroleum ether and dried in vacuo over phosphorus pentoxide.

Ethyl p-hydroxy benzoate, p-hydroxy benzaldehyde, p-cyano phenol, p-nitro phenol and p-hydroxy acetophenone were recrystallised three times from benzene and dried in vacuo over phosphorus pentoxide.

Physical constants of the solvents and solutes are recorded in Table 30.

TABLE 30

	<u>Boiling/Melting Point ($^{\circ}\text{C}$ at atmos. press.)</u>	
	<u>Experimental</u>	<u>Literature</u> ⁶¹
Benzene	80	80
Toluene	111	111
n-Hexane	69	68
Phenol	41	41 ⁶² , 43 ⁶¹
p-Methyl Phenol	34	35
p-t-Butyl Phenol	99	99
p-Chloro Phenol	43	43
p-Methoxy Phenol	53	53
p-Bromo Phenol	64	66
Ethyl p-Hydroxy Phenol	115	116
p-Hydroxy Benzaldehyde	117	116
p-Cyano Phenol	113	113
p-Nitro Phenol	114	114
p-Hydroxy Acetophenone	109	109

(d) Adsorption Procedure

A stock solution of the phenol in the appropriate solvent was prepared at 25⁰C. Suitable volumes of the solution were measured into a series of drawn-out tubes and then made up to 15.0 cm³ by addition of an appropriate volume of solvent. Solutions of each concentration were prepared in triplicate.

A weighed (wet-weight) quantity of the adsorbent dried at 120⁰C, was transferred directly from the drying oven to each solution, the tubes blown out with nitrogen and sealed in a flame. The tubes were then agitated at 35.0 ± 0.1⁰C for a period of four days. Preliminary experiments showed that equilibrium was attained after a period of three days at this temperature.

After equilibrium, the tubes were taken from the bath, the solutions decanted from the adsorbent and the absorbances determined at a suitable but arbitrary wavelength using a Unicam SP 500 Spectrophotometer. Solutions of known concentration were prepared from the original stock solution and a calibration graph constructed at the wavelength chosen.

Mean equilibrium concentrations of phenol in the liquid phase were determined from the calibration graph and the amounts of phenol adsorbed per gram of adsorbent calculated.

Saturated solutions of the phenol in the organic solvents were prepared at 35⁰C. A weighed quantity of the solution was transferred to a volumetric flask and diluted with a known weight of solvent. The absorbance of the solution was measured by an SP 500 spectrophotometer which had been previously calibrated at a suitable wavelength. From

the concentration of the phenol in the diluted solution, the saturation mole fraction of the phenol in the organic solvent at 35°C was calculated.

The results obtained are recorded in Tables 31 to 47. Adsorption isotherms were constructed by plotting the moles of phenol adsorbed ($n^0 \Delta x_1^l / m$) against the equilibrium mole fraction of phenol in the liquid phase (x_1^l) and the curves obtained shown in Figs. 32, 33, 34 and 35.

(e) Experimental Results

In the tables of results given below, the symbols used have the following significance:-

x_1^0	mole fraction of the phenol in liquid phase before adsorption.
x_1^l	mole fraction of the phenol in liquid phase after adsorption.
Δx_1^l	change in mole fraction of the phenol during adsorption $= x_1^0 - x_1^l$
x_2^l	mole fraction of solvent after adsorption $= 1 - x_1^l$
n^0	total number of moles in 15 cm ³ of solution before adsorption.
$(x_1^l)_s$	mole fraction of the phenol in a saturated solution at 35°C.

TABLE 31. Phenol in Cyclohexane

$$\underline{(x_1^{\ell})_s = 0.872}$$

x_1^o $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
<u>Alumina</u>				
0.372	0.068	0.1384	0.421	1.61
0.619	0.215	0.1388	0.561	3.82
0.865	0.425	0.1391	0.612	6.95
1.109	0.653	0.1395	0.636	10.26
1.473	1.011	0.1400	0.647	15.63
1.835	1.361	0.1405	0.665	20.47
<u>Silica</u>				
1.259	0.292	0.1399	1.352	2.16
1.753	0.617	0.1406	1.600	3.86
2.243	1.000	0.1413	1.757	5.69
2.728	1.422	0.1420	1.854	7.67
3.208	1.871	0.1427	1.907	9.81
3.683	2.334	0.1434	1.934	12.07

TABLE 32. Phenol in Carbon Tetrachloride

$$\underline{(x_1^{\ell})_S = 0.939}$$

x_1^0 $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^0	$n^0 \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^0 \Delta x_1^{\ell}$
<u>Alumina</u>				
0.289	0.048	0.1548	0.372	1.29
0.480	0.171	0.1551	0.479	3.56
0.671	0.297	0.1554	0.581	5.10
0.861	0.470	0.1557	0.608	7.72
1.144	0.754	0.1561	0.609	12.38
1.426	1.035	0.1566	0.612	16.91
<u>Silica</u>				
0.747	0.164	0.1557	0.907	1.80
1.238	0.439	0.1564	1.250	3.51
1.725	0.774	0.1572	1.495	5.18
2.207	1.167	0.1580	1.643	7.10
2.921	1.835	0.1592	1.728	10.62
3.625	2.532	0.1603	1.751	14.46

TABLE 33. Phenol in Dioxan

$$\underline{(x_1^{\ell})_s = 0.938}$$

Alumina

x_1^o $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
0.108	0.050	0.1752	0.101	5.04
0.179	0.106	0.1753	0.129	8.16
0.251	0.165	0.1755	0.151	10.97
0.322	0.231	0.1756	0.160	14.40
0.429	0.335	0.1758	0.166	20.11
0.536	0.439	0.1760	0.171	25.63

TABLE 34. Phenol in Tetrahydrofuran

$$\underline{(x_1^{\ell})_s = 0.945}$$

Alumina

x_1^o $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
0.104	0.043	0.1841	0.112	3.88
0.174	0.088	0.1842	0.157	5.61
0.243	0.145	0.1844	0.181	7.98
0.312	0.204	0.1845	0.200	10.20
0.416	0.300	0.1847	0.215	13.96
0.520	0.402	0.1849	0.217	18.50

TABLE 35. Phenol in Toluene

$$\underline{(x_1^{\ell})_s = 0.938}$$

Silica

x_1^o $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
0.837	0.428	0.1418	0.580	7.39
1.388	0.849	0.1426	0.769	11.04
1.932	1.292	0.1434	0.918	14.08
2.470	1.767	0.1442	1.013	17.45
3.267	2.498	0.1454	1.117	22.37
4.050	3.271	0.1466	1.143	28.63

TABLE 36. Phenol in n-Hexane

$$\underline{(x_1^{\ell})_s = 0.879}$$

Silica

x_1^o $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
0.813	0.120	0.1176	0.816	1.47
1.348	0.233	0.1183	1.319	1.77
1.877	0.477	0.1189	1.665	2.86
2.400	0.854	0.1196	1.848	4.62
3.175	1.537	0.1205	1.974	7.79
3.937	2.242	0.1215	2.059	10.89

TABLE 37. Phenol in Benzene

$$\underline{(x_1^{\ell})_s = 0.909}$$

x_1^o $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
<u>Alumina</u>				
0.343	0.123	0.1684	0.370	3.33
0.570	0.287	0.1687	0.478	5.99
0.798	0.480	0.1691	0.538	8.92
1.022	0.697	0.1695	0.567	12.30
1.357	1.016	0.1701	0.581	17.47
1.691	1.345	0.1707	0.590	22.78
<u>Silica</u>				
0.531	0.345	0.1687	0.314	11.00
0.882	0.607	0.1692	0.465	13.05
1.230	0.883	0.1698	0.589	15.00
1.576	1.177	0.1704	0.677	17.40
2.090	1.612	0.1713	0.819	19.70
2.599	2.097	0.1722	0.866	24.22

TABLE 38. p-Methoxy Phenol in Benzene

$$\underline{(x_1^{\ell})_s = 0.461}$$

x_1^o $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
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Alumina

0.245	0.056	0.1682	0.317	1.77
0.407	0.160	0.1685	0.417	3.83
0.570	0.287	0.1687	0.476	6.04
0.731	0.429	0.1690	0.510	8.42
0.972	0.647	0.1694	0.551	11.73
1.212	0.883	0.1698	0.560	15.76

Silica

0.657	0.331	0.1689	0.552	5.99
1.091	0.631	0.1696	0.781	8.08
1.521	0.977	0.1704	0.937	10.43
1.947	1.361	0.1711	1.002	13.58
2.579	1.959	0.1722	1.068	18.35
3.203	2.577	0.1733	1.085	23.75

TABLE 39. p-Methyl Phenol in Benzene

$$\underline{(x_1^{\ell})_S = 0.850}$$

x_1^0 $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^0	$n^0 \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^0 \Delta x_1^{\ell}$
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Alumina

0.301	0.085	0.1683	0.364	2.33
0.501	0.229	0.1686	0.459	4.99
0.700	0.403	0.1690	0.502	8.04
0.898	0.583	0.1693	0.534	10.90
1.194	0.869	0.1698	0.551	15.78
1.482	1.153	0.1704	0.561	20.56

Silica

0.638	0.403	0.1685	0.397	10.16
1.059	0.737	0.1690	0.546	13.51
1.476	1.073	0.1696	0.688	15.60
1.890	1.413	0.1702	0.816	17.31
2.505	1.973	0.1712	0.915	21.56
3.111	2.551	0.1722	0.970	26.30

TABLE 40. p-t-Butyl Phenol in Benzene

$$\underline{(x_1^l)_s = 0.337}$$

x_1^o $\times 10^2$	x_1^l $\times 10^2$	n^o	$n^o \Delta x_1^l / m$ $\times 10^3$	$m x_1^l x_2^l / n^o \Delta x_1^l$
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Alumina

0.238	0.066	0.1682	0.288	2.30
0.396	0.186	0.1685	0.352	5.29
0.553	0.328	0.1687	0.380	8.61
0.710	0.473	0.1690	0.400	11.81
0.944	0.702	0.1694	0.411	17.08
1.177	0.935	0.1698	0.411	22.76

Silica

0.581	0.386	0.1688	0.329	11.74
0.964	0.685	0.1694	0.474	14.46
1.345	1.001	0.1701	0.584	17.16
1.722	1.332	0.1707	0.666	20.00
2.283	1.865	0.1717	0.718	26.00
2.852	2.424	0.1727	0.739	32.80

TABLE 41. p-Chloro Phenol in Benzene

$$\underline{(x_1^{\ell})_s = 0.846}$$

x_1^o $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
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Alumina

0.268	0.081	0.1682	0.309	2.61
0.445	0.214	0.1685	0.390	5.48
0.622	0.368	0.1688	0.429	8.57
0.799	0.523	0.1691	0.466	11.22
1.062	0.770	0.1696	0.495	15.58
1.324	1.020	0.1700	0.516	19.77

Silica

0.666	0.488	0.1689	0.301	16.21
1.105	0.822	0.1697	0.480	17.13
1.540	1.189	0.1704	0.598	19.88
1.972	1.550	0.1712	0.722	21.47
2.612	2.122	0.1723	0.843	25.16
3.243	2.725	0.1734	0.898	30.34

TABLE 42. p-Bromo Phenol in Benzene

$$\underline{(x_1^{\ell})_s = 0.474}$$

x_1^o $\times 10^2$	x_1^{ℓ} $\times 10^2$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
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Alumina

0.204	0.053	0.1681	0.253	2.09
0.339	0.131	0.1684	0.350	3.74
0.474	0.242	0.1686	0.390	6.23
0.609	0.358	0.1688	0.423	8.48
0.810	0.543	0.1692	0.451	12.05
1.010	0.733	0.1695	0.471	15.57

Silica

0.678	0.485	0.1689	0.327	14.84
1.126	0.834	0.1697	0.495	16.86
1.569	1.219	0.1705	0.596	20.48
2.008	1.598	0.1712	0.701	22.79
2.660	2.175	0.1724	0.836	26.02
3.302	2.792	0.1735	0.885	31.56

TABLE 43. Ethyl p-Hydroxy Benzoate in Benzene

$$\underline{(x_1^{\ell})_s = 0.013}$$

x_1^o $\times 10^3$	x_1^{ℓ} $\times 10^3$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
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Alumina

0.647	0.098	0.1679	0.184	0.53
1.078	0.273	0.1680	0.270	1.01
1.508	0.490	0.1680	0.342	1.43
1.938	0.786	0.1681	0.402	1.95
2.583	1.268	0.1682	0.442	2.87
3.227	1.821	0.1683	0.473	3.85

Silica

0.652	0.277	0.1679	0.252	1.09
1.087	0.542	0.1680	0.366	1.48
1.521	0.831	0.1680	0.464	1.79
1.954	1.152	0.1681	0.540	2.13
2.604	1.735	0.1682	0.585	2.97
3.253	2.266	0.1683	0.665	3.41

TABLE 44. p-Hydroxy Acetophenone in Benzene

$$\underline{(x_1^{\ell})_s = 0.0025}$$

x_1^o $\times 10^3$	x_1^{ℓ} $\times 10^3$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
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Alumina

0.359	0.005	0.1678	0.119	0.045
0.599	0.039	0.1679	0.188	0.206
0.839	0.090	0.1679	0.251	0.358
1.078	0.169	0.1680	0.305	0.555
1.436	0.291	0.1680	0.385	0.757
1.795	0.436	0.1681	0.457	0.955

Silica

0.350	0.069	0.1678	0.189	0.365
0.583	0.139	0.1679	0.298	0.464
0.816	0.226	0.1679	0.396	0.571
1.049	0.319	0.1680	0.490	0.651
1.398	0.483	0.1680	0.616	0.783
1.747	0.665	0.1681	0.728	0.913

TABLE 45. p-Hydroxy Benzaldehyde in Benzene

$$\underline{(x_1^{\ell})_s = 0.0032}$$

x_1^o $\times 10^3$	x_1^{ℓ} $\times 10^3$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
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Alumina

0.355	0.016	0.1678	0.114	0.138
0.591	0.021	0.1679	0.192	0.108
0.828	0.078	0.1679	0.252	0.311
1.064	0.133	0.1680	0.313	0.425
1.418	0.262	0.1680	0.389	0.673
1.772	0.435	0.1681	0.449	0.968

Silica

0.360	0.114	0.1678	0.165	0.689
0.600	0.184	0.1679	0.280	0.657
0.839	0.288	0.1679	0.371	0.777
1.079	0.407	0.1680	0.452	0.901
1.438	0.600	0.1680	0.563	1.066
1.797	0.795	0.1681	0.673	1.180

TABLE 46. p-Cyano Phenol in Benzene

$$\underline{(x_1^{\ell})_s = 0.016}$$

x_1^o $\times 10^3$	x_1^{ℓ} $\times 10^3$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
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Alumina

0.892	0.051	0.1679	0.283	0.18
1.487	0.267	0.1680	0.410	0.65
2.080	0.585	0.1681	0.503	1.16
2.673	0.953	0.1682	0.579	1.65
3.560	1.591	0.1684	0.663	2.40
4.446	2.279	0.1685	0.728	3.13

Silica

0.901	0.450	0.1679	0.303	1.48
1.501	0.777	0.1680	0.487	1.60
2.100	1.142	0.1681	0.644	1.77
2.700	1.556	0.1682	0.769	2.03
3.595	2.221	0.1684	0.925	2.40
4.489	2.959	0.1685	1.032	2.87

TABLE 47. p-Nitro Phenol in Benzene

$$\underline{(x_1^{\ell})_s = 0.014}$$

x_1^o $\times 10^3$	x_1^{ℓ} $\times 10^3$	n^o	$n^o \Delta x_1^{\ell} / m$ $\times 10^3$	$m x_1^{\ell} x_2^{\ell} / n^o \Delta x_1^{\ell}$
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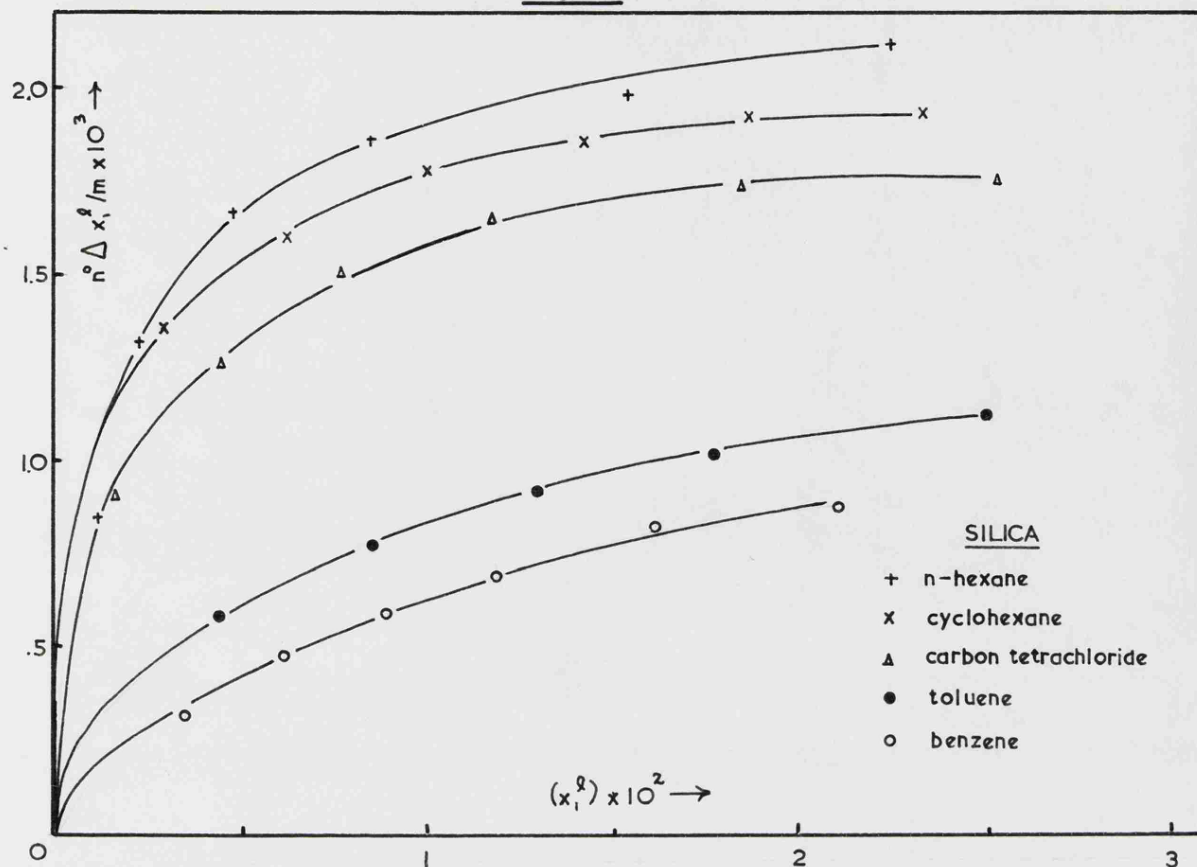
Alumina

1.297	0.405	0.1680	0.300	1.35
2.160	0.828	0.1681	0.448	1.85
3.021	1.357	0.1683	0.560	2.42
3.881	1.985	0.1684	0.639	3.11
5.168	3.027	0.1687	0.723	4.19
6.452	4.185	0.1689	0.766	5.46

Silica

1.339	0.968	0.1680	0.250	3.88
2.231	1.659	0.1682	0.385	4.31
3.120	2.386	0.1683	0.494	4.83
4.008	3.097	0.1685	0.613	5.05
5.336	4.237	0.1687	0.742	5.71
6.662	5.366	0.1689	0.876	6.13

Fig. 32



Adsorption of phenol from different solvents

Fig. 33

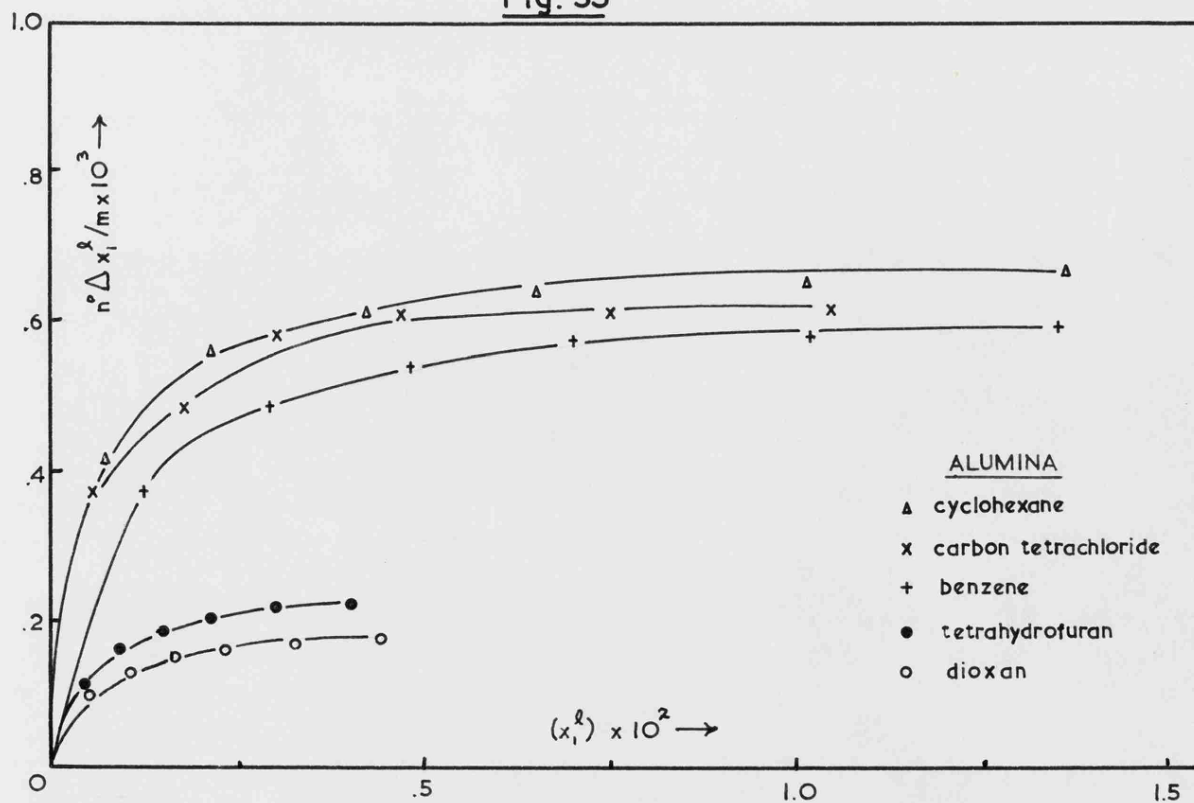
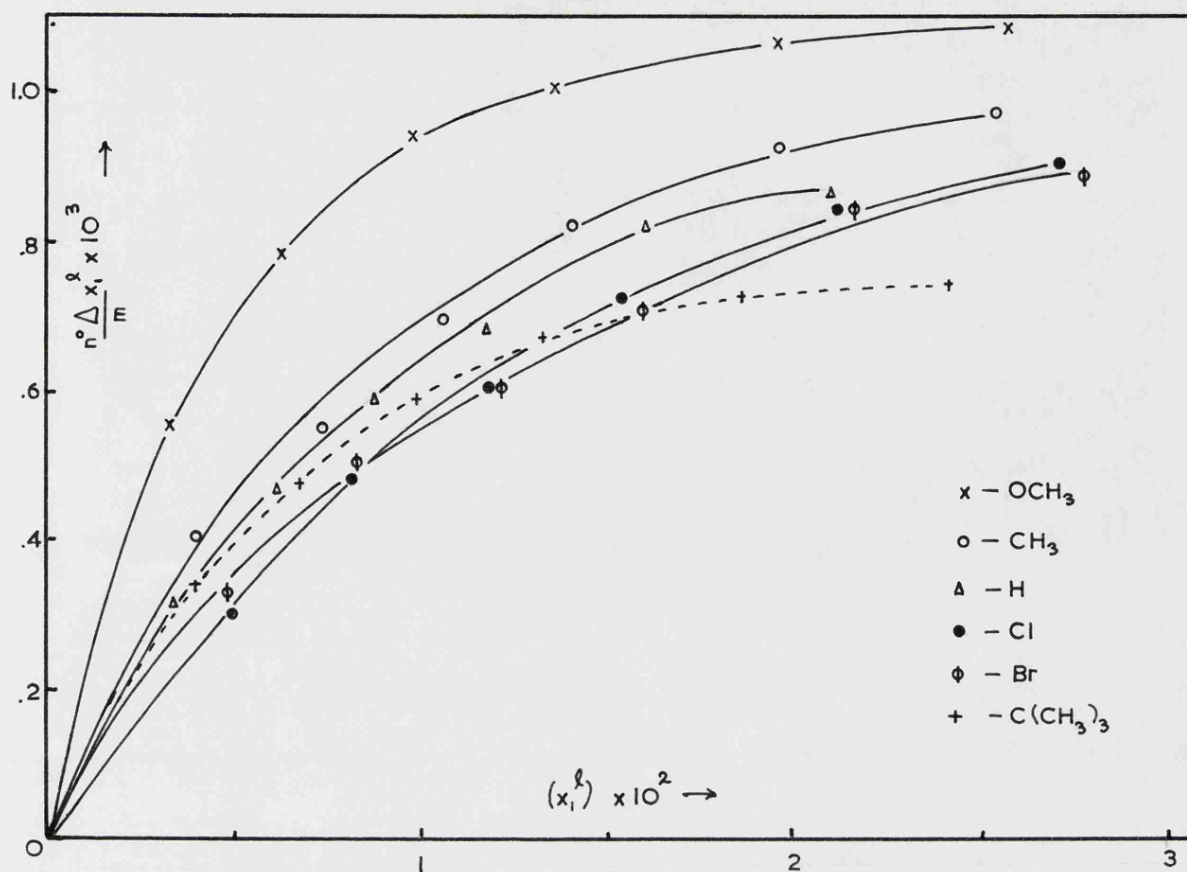


Fig. 34



Adsorption of p-substituted phenols from benzene on to silica

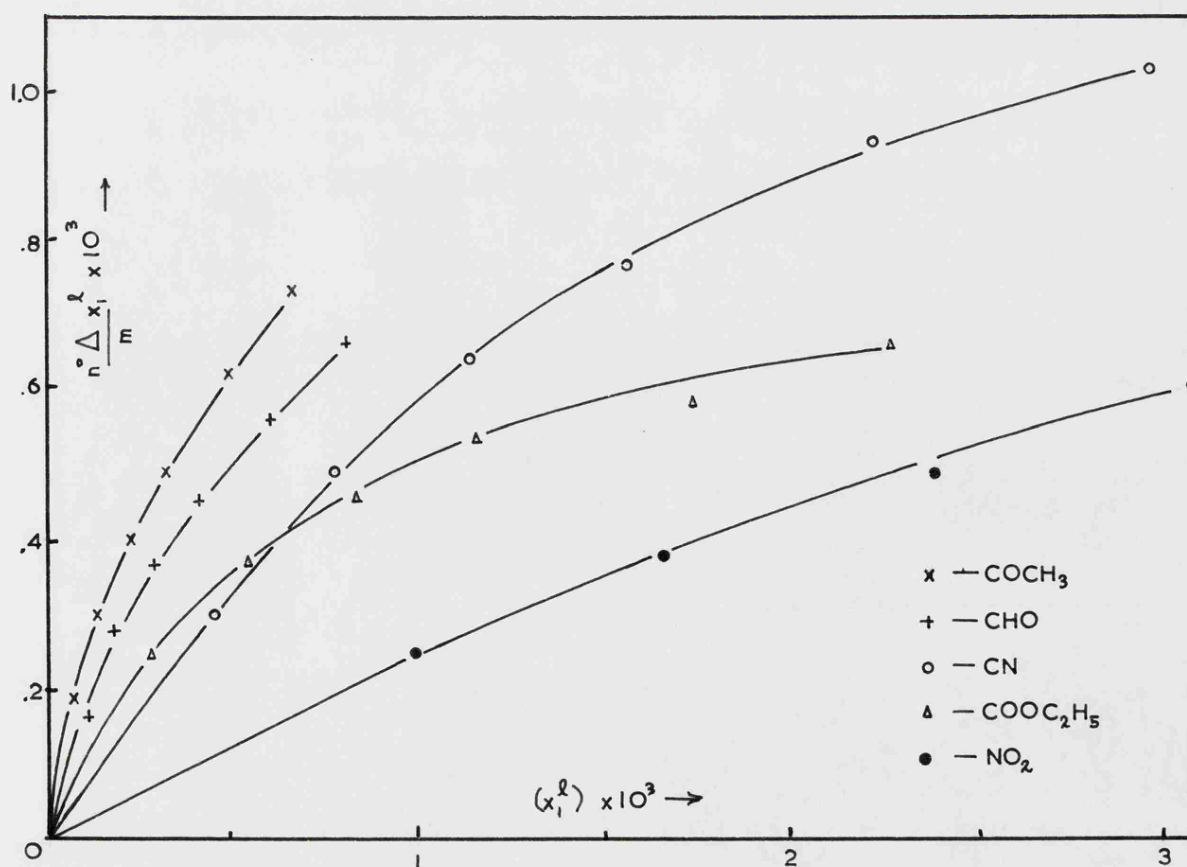
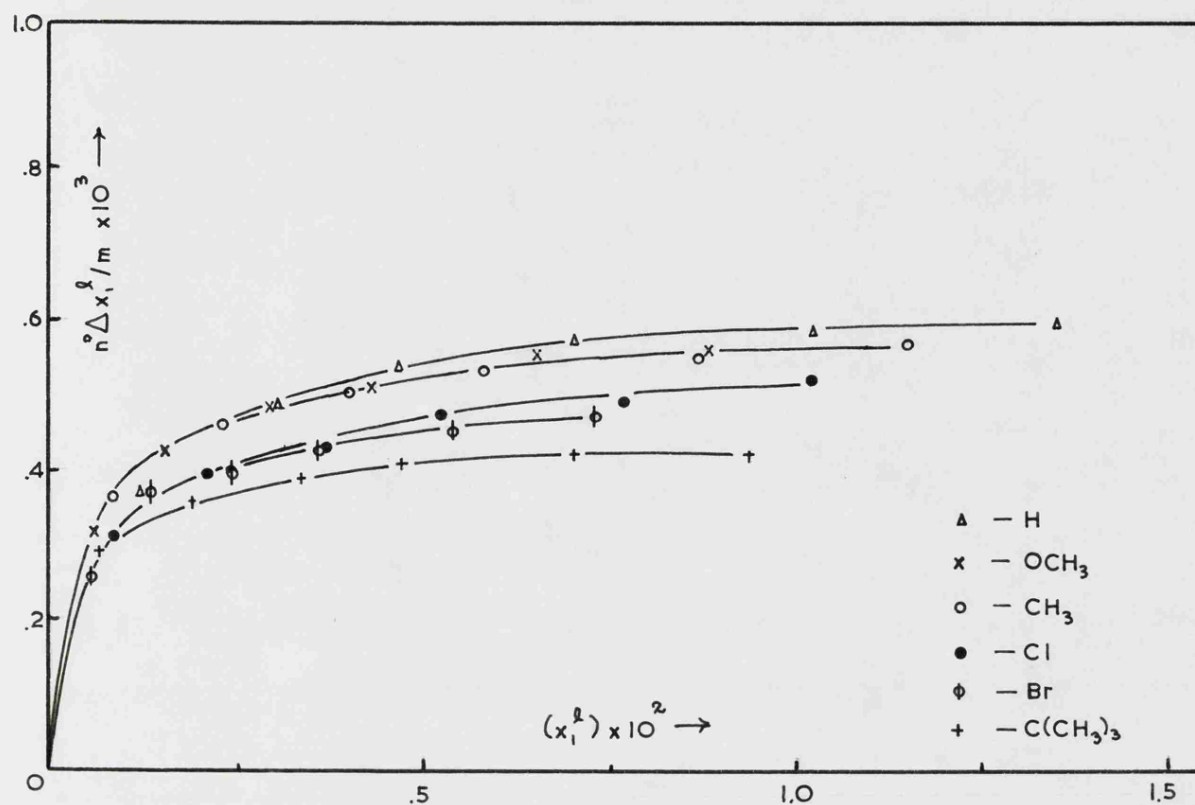
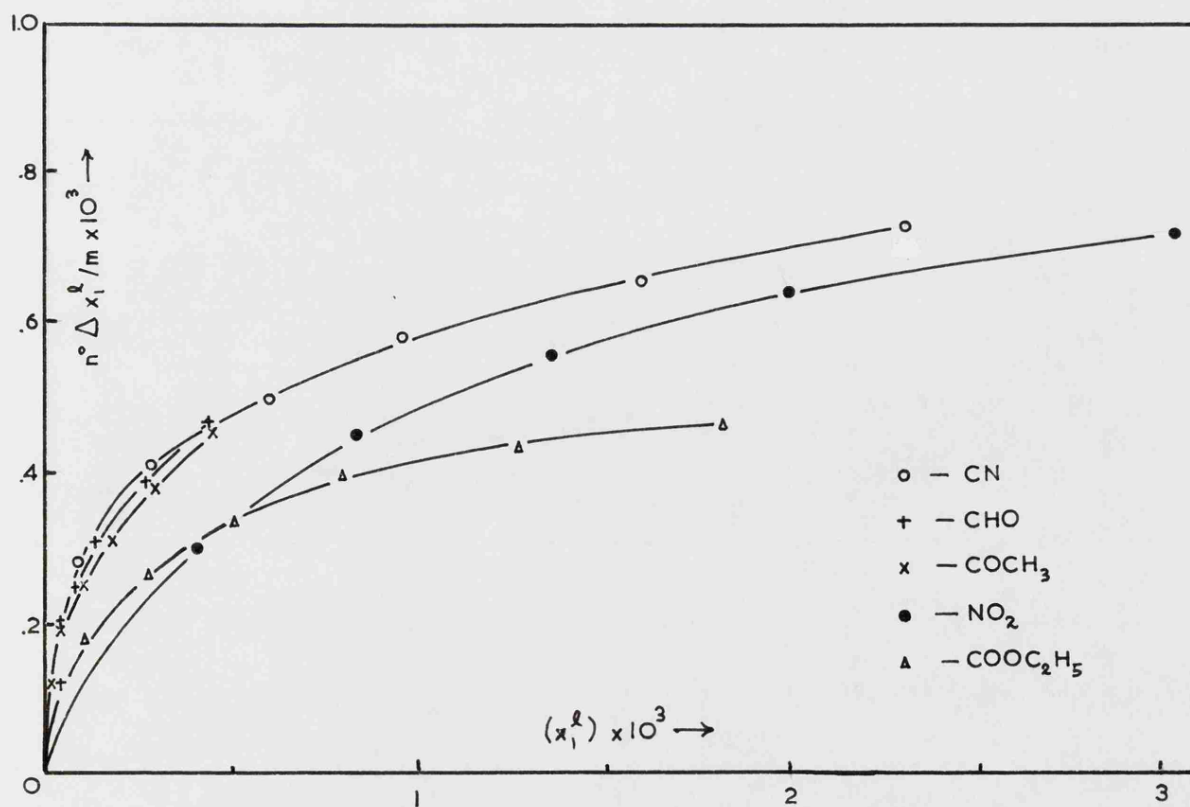


Fig. 35



Adsorption of p-substituted phenols from benzene on to alumina



DISCUSSION

In the discussion to this thesis, the experimental results are considered in terms of:-

1. association in solution
2. adsorption at the solid-solution interface and comparison made between the two processes.

For interactions occurring in solution, a quantitative measure is provided by the association constant, the temperature dependence of which enables the strength of bonding in the complexes formed to be determined.

For adsorption at the solid-solution interface, the adsorption affinity of the molecule for the surface is considered on a quantitative basis using Everett's thermodynamic theory of adsorption while changes in adsorptive structure due to p-substitution are represented by the Hammett substituent parameter.

In both cases the E_T parameter is used as a measure of solvent reactivity towards the phenol

1. ASSOCIATION IN SOLUTION

(a) THE ASSOCIATION CONSTANT

(i) Concentration Scale Dependence

In the determination of the association constant by the Benesi-Hildebrand equation, different values for the spectroscopic parameters (extinction coefficients in ultra violet measurements, limiting chemical shifts in N.M.R. measurements) of various charge transfer complexes have been observed depending on which of the three concentration scales is used. Trotter and Hanna¹¹² consider that the above variation arises when the concentration of donor is so high that the concentrations on the three scales are no longer proportional to each other and conclude that solution ideality only exists on one concentration scale. Kuntz et al¹¹³ suggest how the concentration scale most appropriate to a given system can be determined experimentally and conclude that the molar scale seems to give the most consistent results for such as those under discussion. It is proposed to consider the concentration scale dependence in the Benesi-Hildebrand equation as applied to the acid-base type reactions studied in this thesis before discussing the association constants obtained experimentally.

The Benesi-Hildebrand equation for the molar scale is:-

$$\frac{c_A \cdot \ell}{(A-A^0)} = \frac{1}{K_C} \cdot \frac{1}{(\epsilon_C - \epsilon_A)} \cdot \frac{1}{c_D} + \frac{1}{(\epsilon_C - \epsilon_A)} \quad (46)$$

where ℓ = path length

ϵ_A, ϵ_C = extinction coefficients of acceptor and complex, respectively

A^0, A = absorbances of acceptor alone and acceptor plus complex,
respectively

c_A, c_D = initial concentrations of acceptor and donor, respectively.

It is usual in spectroscopic measurements to express concentrations in mol dm^{-3} , consistent units for path length and extinction coefficient being dm and $\text{dm}^2 \text{mol}^{-1}$ respectively.

If there are n_D moles of donor, molecular weight M_D , in n_S moles of solvent, molecular weight M_S , giving a solution of density ρ , then the following relationships exist:-

$$\frac{x_D}{c_D} = \frac{(n_S M_S + n_D M_D)}{\rho (n_D + n_S)} \quad (47)$$

$$\frac{m_D}{c_D} = \frac{(n_S M_S + n_D M_D)}{n_S M_S \rho} \quad (48)$$

where x_D, m_D are concentrations on the mole fraction and molality scales respectively.

From the thermodynamic definition of the chemical potential of a component of an ideal solution, it follows that $\frac{e^x_c}{e^{x_A} \cdot e^{x_D}}$ is constant.

This quotient is symbolised by K_x , subscript 'e' to the x values implying equilibrium mole fractions.

Combining with (47) gives

$$K_x = \frac{e^{c_c}}{e^{c_A} \cdot e^{c_D}} \cdot \frac{\rho (n_D + n_S)}{(n_S M_S + n_D M_D)}$$

$$= \frac{K_c \rho (n_D + n_S)}{(n_S M_S + n_D M_D)} \quad (49)$$

the assumptions being made that acceptor and complex concentrations are sufficiently small for proportionality to exist between 'c' and 'x' in each case.

If the solution is thermodynamically ideal and so dilute that $n_S \gg n_D$, expressions (47), (48) and (49) reduce to

$$\frac{x_D}{c_D} = \frac{M_S}{\rho} ; \quad \frac{m_D}{c_D} = \frac{1}{\rho} ; \quad K_x = K_c \frac{\rho}{M_S}$$

Substituting these expressions in equation (46) gives:-

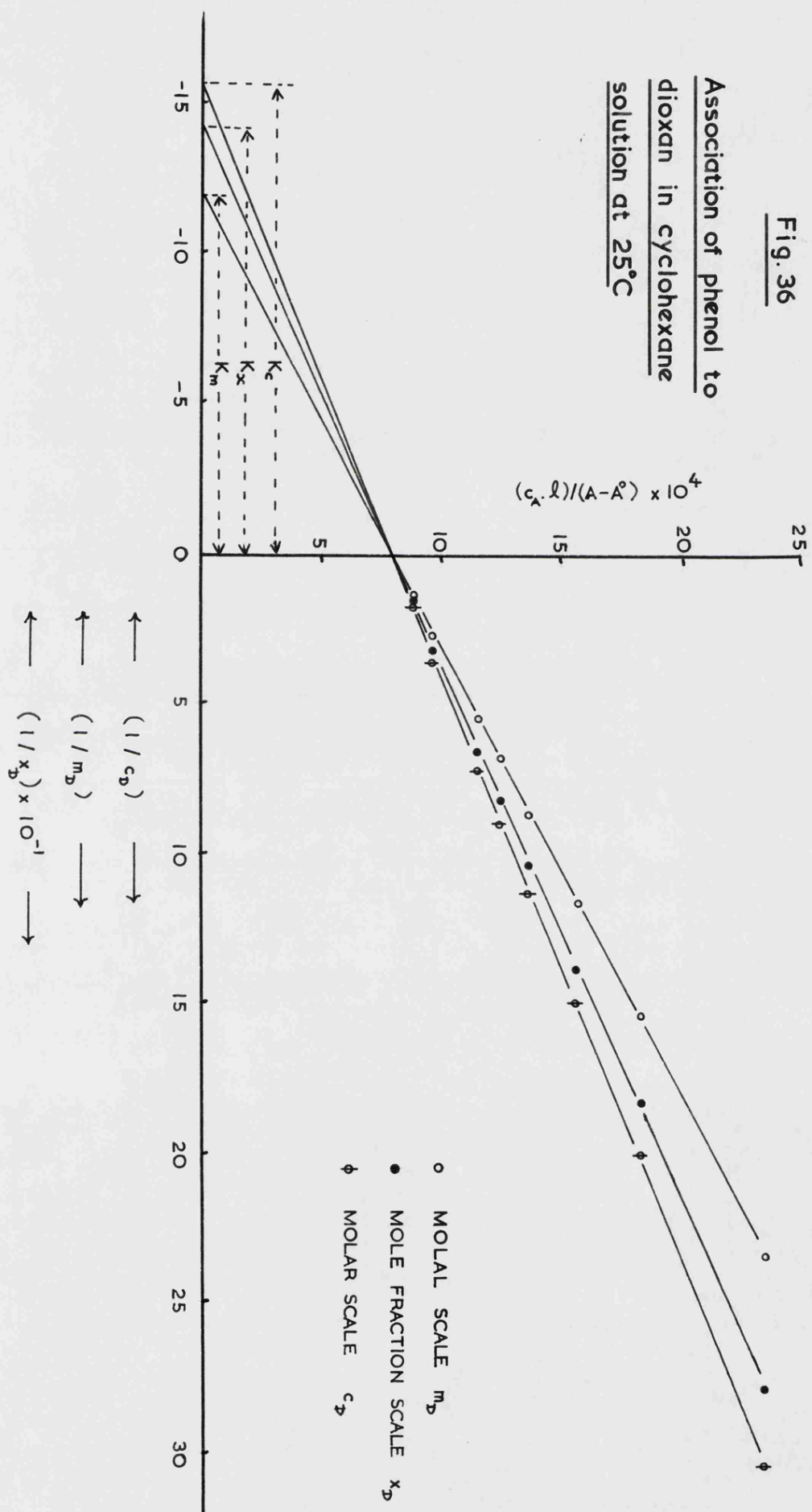
$$\frac{c_A \cdot \ell}{(A - A^0)} = \frac{\rho}{M_S K_x (\epsilon_c - \epsilon_A)} \cdot \frac{1}{c_D} + \frac{1}{(\epsilon_c - \epsilon_A)} \quad (50)$$

$$\frac{c_A \cdot \ell}{(A - A^0)} = \frac{1}{M_S K_x (\epsilon_c - \epsilon_A)} \cdot \frac{1}{m_D} + \frac{1}{(\epsilon_c - \epsilon_A)} \quad (51)$$

$$\frac{c_A \cdot \ell}{(A - A^0)} = \frac{1}{K_x (\epsilon_c - \epsilon_A)} \cdot \frac{1}{x_D} + \frac{1}{(\epsilon_c - \epsilon_A)} \quad (52)$$

Thus when $n_S \gg n_D$ and the solutions are ideal, the three concentration scales are directly proportional to each other and equations (50), (51) and (52) will be linear having a common intercept of $1/(\epsilon_c - \epsilon_A)$. The experimental results obtained for the association of phenol to dioxan in cyclohexane solution (Table 11, p.56) have been assessed on the three concentration scales (Fig. 36) and the extinction

Fig. 36
Association of phenol to
dioxan in cyclohexane
solution at 25°C



coefficient ϵ_c and association constant K_x calculated from equations (50), (51) and (52) are given in Table 48.

TABLE 48

Association of Phenol to Dioxan in Cyclohexane at 25°C

<u>Concentration Scale</u>	<u>$\epsilon_c / (\text{dm}^2 \text{ mol}^{-1})$</u>	<u>K_x</u>
Mole Fraction	16,980	137.8
Molar	16,970	138.2
Molal	16,890	138.9

Thus for the systems studied in this thesis, it is concluded that the solutions used are ideal and sufficiently dilute ($n_S \gg n_D$) that the choice of concentration scale is not critical.

When the solutions are ideal but not so dilute ($n_S \approx n_D$), expressions (47) and (48) show that the three concentration scales are no longer proportional to each other and equations (50) and (51) are no longer applicable and must be replaced by equations (53) and (54) respectively,

$$\frac{c_{A \cdot l}}{(A-A^0)} = \frac{\rho}{K_X M_S (\epsilon_c - \epsilon_A)} \cdot \frac{1}{c_D} + \frac{1}{(\epsilon_c - \epsilon_A)} \left[1 - \frac{(M_D - M_S)}{M_S} \cdot \frac{1}{K_X} \right] \quad (53)$$

$$\frac{c_{A \cdot l}}{(A-A^0)} = \frac{1}{K_X M_S (\epsilon_c - \epsilon_A)} \cdot \frac{1}{m_D} + \frac{1}{(\epsilon_c - \epsilon_A)} \left[1 + \frac{1}{K_X} \right] \quad (54)$$

These equations are obtained by substituting expressions (47), (48) and (49) in equation (46). It is noted that under these conditions, linear plots of differing slopes and intercepts will be obtained.

(ii) Correlation with the Solvent Parameter E_T

The association constants for phenol bonding to a series of ether and alcohol type donors in cyclohexane and carbon tetrachloride solution at various temperatures are recorded in Tables 21 and 22, (p. 66 , 67) The values obtained show that the temperature coefficient of the association constant is as expected, K_c decreasing with increasing temperature. Increasing the polarity of the solvent from cyclohexane to carbon tetrachloride is seen to decrease the K_c values for the ethers by about one half while the K_c values for the alcohols are reduced to about one third. This suggests that the solvation energy of carbon tetrachloride for the alcohols is greater than that for the ethers resulting in a greater reduction in the magnitude of the interaction with phenol.

On plotting $\log K_c$ against the solvent parameter E_T from the data in Table 49, good correlations are observed for both types of donor molecules (Fig. 37) showing that the decrease in standard free energy of association ($-\Delta G^\ominus$) increases with increasing donor reactivity.

TABLE 49

<u>Donor</u>	E_T^{114} /kJ mol ⁻¹	$\log K_c$			
		<u>Cyclohexane</u>		<u>Carbon Tetrachloride</u>	
		25°C	35°C	25°C	35°C
Dimethylformamide	183.3	-	-	1.63	1.50
1,2 Dimethoxyethane	159.8	1.42	1.27	1.15	1.00
Tetrahydrofuran	156.5	1.36	1.24	1.13	0.98
Dioxan	150.6	1.18	1.07	0.93	0.79
Diethyl ether	144.8	1.06	-	0.79	-
Di-isopropyl ether	142.3	1.11	0.94	0.91	0.78
Dibutyl ether	139.7	0.90	0.78	0.72	0.57
Methanol	232.2	-	-	1.04	0.89
Ethanol	217.2	1.44	1.32	0.98	0.79
n-Butanol	210.0	1.41	1.29	0.93	0.75
Isopropanol	203.3	1.38	1.26	0.88	0.67
3 Methyl 1 Butanol	196.6	1.33	1.23	0.83	0.59
Tertiary Butanol	191.2	1.43	1.25	1.01	0.79
		30°C	40°C	30°C	40°C
1,2 Dimethoxyethane		1.34	1.19	1.06	0.92
Dibutyl ether		0.84	0.72	0.63	0.48
Ethanol		1.37	1.23	0.88	0.65
3 Methyl 1 Butanol		1.28	1.18	0.71	0.53

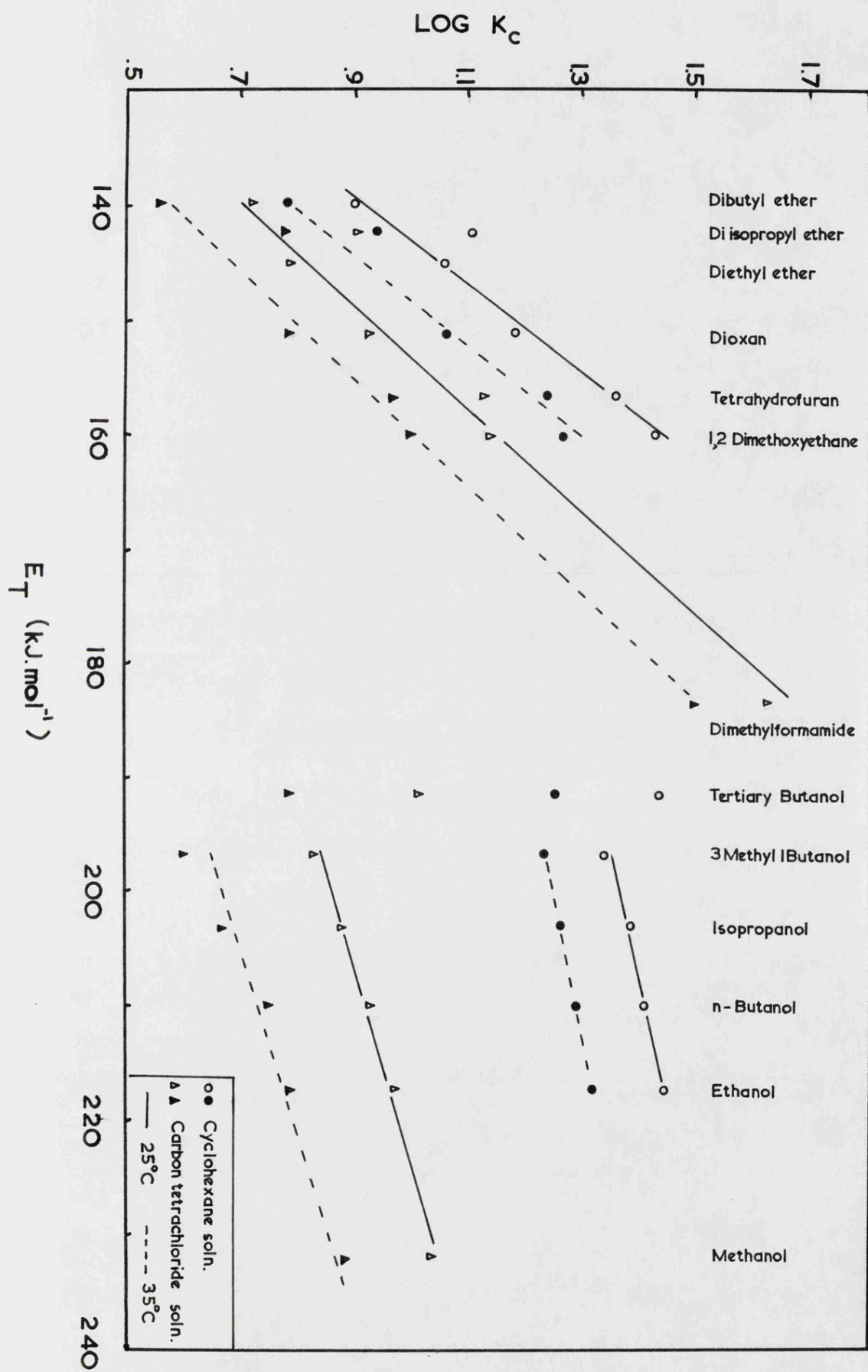


Fig. 37

As the E_T parameter is derived from the charge transfer transition in the visible region of the spectrum occurring in a compound with an ionic ground state (pyridinium N- phenol betaine), the above correlation suggests that the association between phenol and donor in solution can be considered to result in the formation of a charge transfer complex with a ground state possessing some degree of ionic character. This is in agreement with the expectation of operation of hydrogen bonding in the formation of these complexes. Charge transfer structures contribute to hydrogen bonded complexes as illustrated by the five structures shown below:

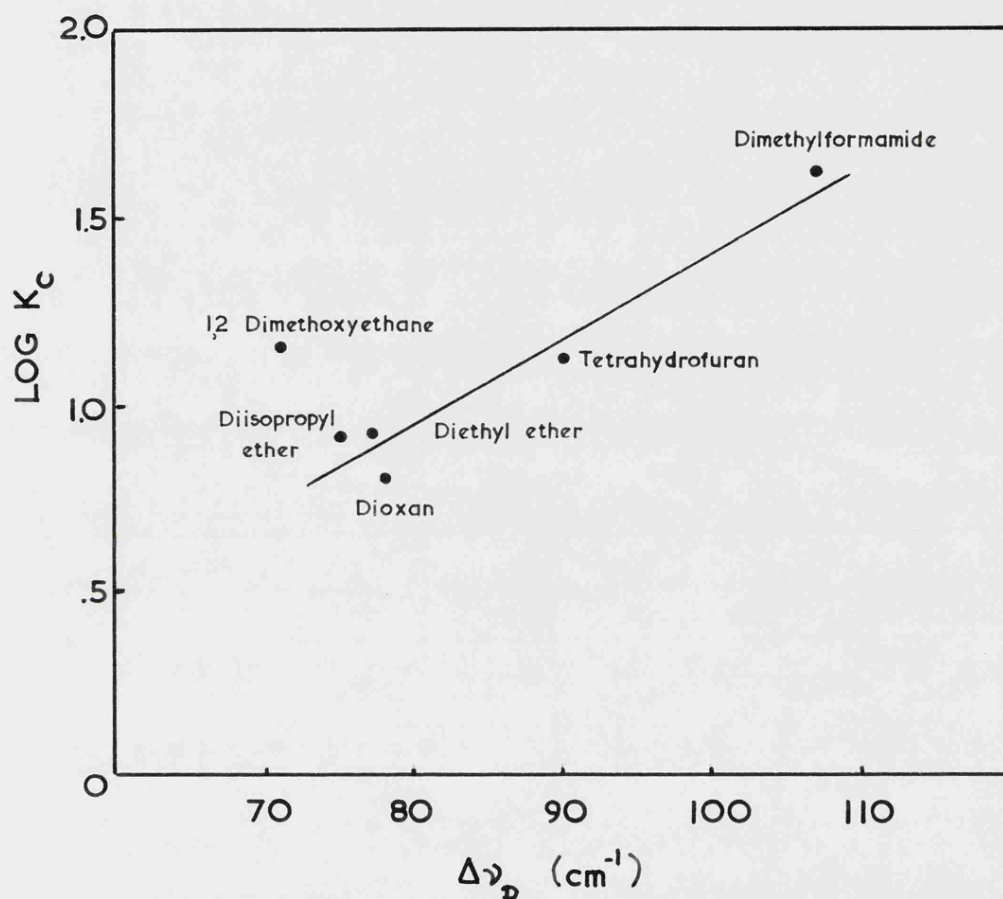
- (i) $A-H \quad B$ covalent A-H bond
- (ii) $A^- \quad H^+ \dots B$ ionic (no charge transfer)
- (iii) $A^- \quad H-H^+ B$ covalent H-B bond (with charge transfer)
- (iv) $A^+ \quad H^- \quad B$ ionic (no charge transfer)
- (v) $A \quad H^- \quad B^+$ covalent A-B bond (with charge transfer)

(iii) Correlation with the Solvent Parameter $\Delta\nu_D$

The shift in the O-D stretching frequency ($\Delta\nu_D$) of methanol-d, defined as $\Delta\nu_D = \nu_D (\text{benzene}) - \nu_D (\text{solvent})$, has been used to provide a measure of the electron donating power of the ethers used in this study. As these ethers will hydrogen bond to phenol by the lone pair electrons on the oxygen atom, the association constant would be expected to reflect the electron donating properties of these compounds. A reasonable correlation is found between $\Delta\nu_D$

and the association constants for phenol bonding to the ethers and dimethylformamide in carbon tetrachloride solution at 25°C (Fig. 38).

Fig. 38



(b) ENTHALPY CHANGE ON ASSOCIATION, $\Delta H^\ominus$

The strength of the hydrogen bonds $\Delta H^\ominus$ in the phenol-donor complexes can be determined from values of the association constant at two temperatures by application of equation (55),

$$\log \left(\frac{K_2}{K_1} \right) = \frac{\Delta H^\ominus}{2.303R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \quad (55)$$

where K_1 , K_2 are the association constants at $T_1^{\circ}\text{C}$ and $T_2^{\circ}\text{C}$ or, more reliably, from a plot of the integrated form of expression (56) for several temperatures,

$$\frac{d\ln K}{dt} = \frac{\Delta H^{\ominus}}{RT^2} \quad (56)$$

It is assumed that $\Delta H^{\ominus}$ remains constant over the range of temperature considered.

The results obtained are given in Table 50 and the plots of $\log K_c$ against $1/T$ are shown in Fig. 39. An independent assessment of the enthalpy change on association $\Delta H^{\ominus}$ can be obtained from the frequency shift values recorded in Table 5 (p.46) by use of the Epley-Drago relationship

$$-\Delta H^{\ominus} \text{ (kJ mol}^{-1}\text{)} = [0.046 \Delta \nu (\text{cm}^{-1}) + 11.66] \pm 0.08$$

and the results are also recorded in Table 50.

Fig. 39

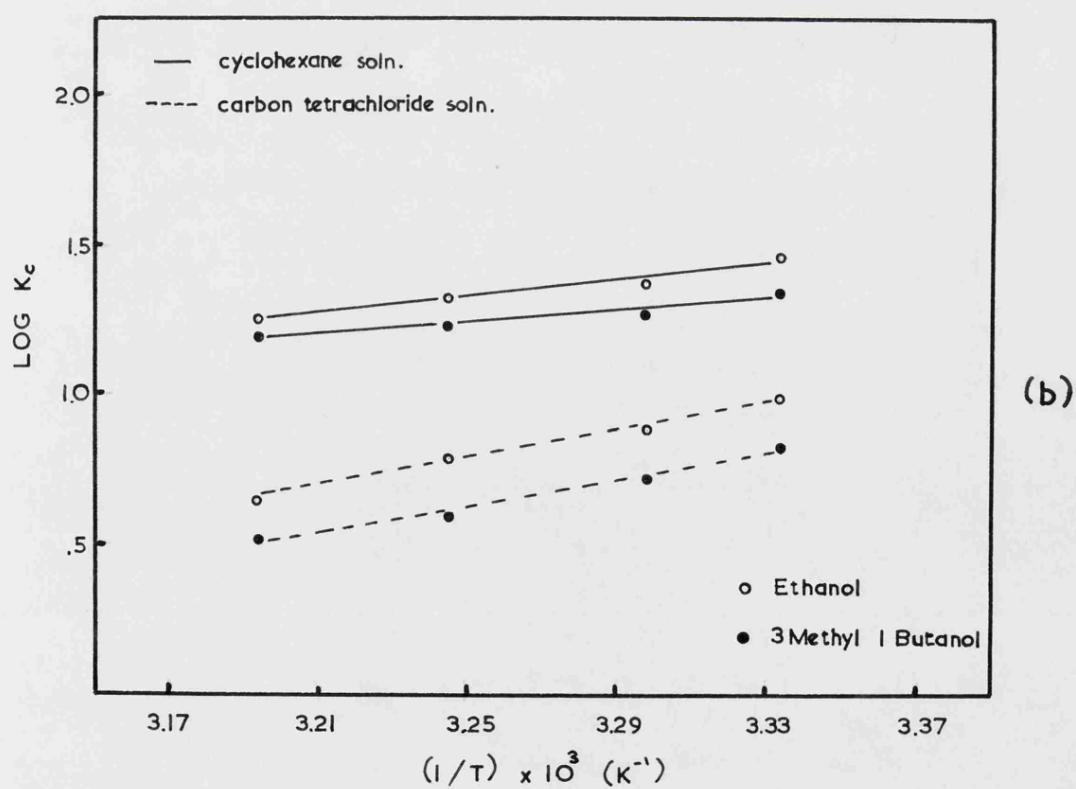
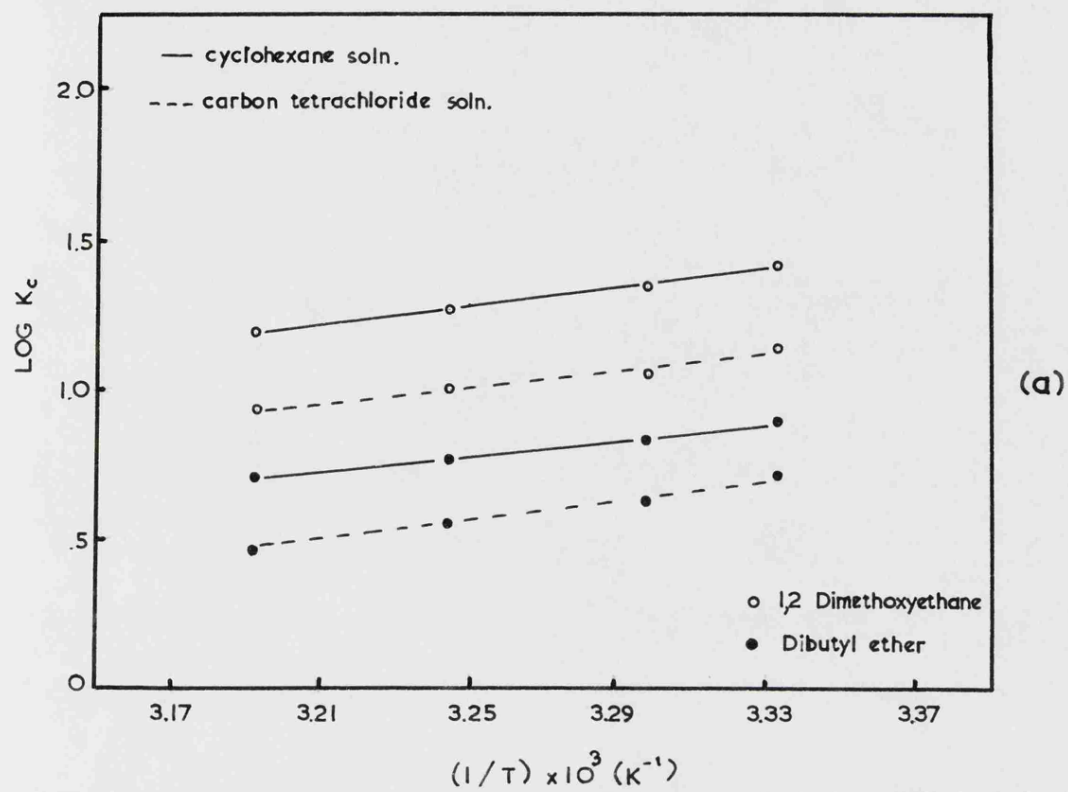


TABLE 50

Donor \ Solvent	$-\Delta H^\ominus / (\text{kJ mol}^{-1})$				
	<u>Cyclohexane</u>		<u>Carbon Tetrachloride</u>		
	eqn. (55)	eqn.(56)	eqn.(55)	eqn.(56)	ex. Δv_{OH}
Dimethylformamide	-	-	23.2	-	25.1
1,2 Dimethoxyethane	26.4	26.2	25.9	25.3	23.0
Tetrahydrofuran	22.3	-	25.9	-	25.0
Dioxan	19.9	-	25.1	-	22.8
Diethyl ether	-	-	-	-	24.5
Di-isopropyl ether	29.3	-	23.1	-	25.3
Dibutyl ether	21.0	23.0	21.0	27.5	24.8
Methanol	-	-	27.6	-	21.5
Ethanol	21.6	25.5	32.1	37.4	22.2
n-Butanol	21.2	-	31.9	-	22.4
Isopropanol	21.8	-	36.0	-	22.5
3-Methyl 1 Butanol	19.1	17.7	41.9	35.9	22.5
Tertiary Butanol	31.3	-	38.7	-	23.3

The $\Delta H^\ominus$ values calculated from these equations are seen to be in reasonable agreement with each other except for the systems, phenol-alcohols in carbon tetrachloride solution. No significant trend in $\Delta H^\ominus$ with changing donor is apparent from the data in Table 50 and it is concluded that the use of the temperature coefficient of the association constant in determining the enthalpy change on association is not sufficiently sensitive or accurate to detect the small variations in the strength of hydrogen bonding in these systems. The $\Delta H^\ominus$ values obtained from the frequency shift $\Delta \nu_{OH}$ show a maximum variation of only 2 kJ mol^{-1} for both the phenol-ether and phenol-alcohol systems studied.

(c) ENTROPY OF ASSOCIATION $\Delta S^\ominus$

As the standard enthalpy change on association can be considered virtually constant for the systems studied, the variation in association constant and hence the standard free energy of association $\Delta G^\ominus$ could arise principally from changes in the standard entropy of association $\Delta S^\ominus$.

Since for the systems considered, $\Delta S^\ominus$ will always be negative and since the standard enthalpy change $\Delta H^\ominus$, is also negative, increasing K values (for $K \geq 1$) will be associated with decreasing $-\Delta S^\ominus$ values. Theoretically, the change in standard entropy occurring on association will be largely a result of a decrease in the number of degrees of freedom leading to an increase in the 'order' of the system. As the number of degrees of freedom of a molecule increases with its steric

complexity, then the negative standard entropy change on association would be expected to increase as the reacting molecules become more complex.

The values of the standard entropy change on association have been calculated using the $\Delta H^\ominus$ values obtained from Δv_{OH} (Table 50) and are given in Table 51.

TABLE 51

Donor	<u>Cyclohexane</u>		<u>Carbon Tetrachloride</u>	
	$-\Delta G^\ominus$	$-\Delta S^\ominus$	$-\Delta G^\ominus$	$-\Delta S^\ominus$
	/kJ mol ⁻¹ (25°C)	/J mol ⁻¹ K ⁻¹	/kJ mol ⁻¹ (25°C)	/J mol ⁻¹ K ⁻¹
Dimethylformamide	-	-	9.3	53.0
1,2 Dimethoxyethane	8.1	50.0	6.5	55.3
Dioxan	6.7	54.0	5.3	58.7
Tetrahydrofuran	7.8	57.7	6.4	62.4
Diethyl ether	6.1	61.7	4.5	67.1
Di-isopropyl ether	6.2	64.1	5.2	67.4
Dibutyl ether	5.1	66.1	4.1	69.4
Methanol	-	-	6.0	52.0
Ethanol	8.2	46.9	5.6	55.7
n-Butanol	8.1	48.0	5.3	57.3
Isopropanol	7.9	49.0	5.0	58.7
3 Methyl 1 Butanol	7.6	50.0	4.7	60.0
Tertiary Butanol	8.2	50.6	5.9	58.4

For both series, the negative standard entropy change is seen in general to increase as the steric complexity of the donor molecule increases, in accordance with the trend expected theoretically.

2. ADSORPTION AT THE SOLID-SOLUTION INTERFACE

(a) ADSORPTION OF p-SUBSTITUTED PHENOLS FROM BENZENE

(i) Limiting Adsorption

The limiting adsorption values recorded in Table 52 have been evaluated from the composite isotherms (Figs. 34 and 35, p.123) by application of the empirical Jowett equation (57)¹¹⁵ which is independent of adsorption mechanism and has the form

$$\frac{n_1^s}{m} = A - (A-a)e^{-bx_1^L} \quad (57)$$

where n_1^s = moles of solute adsorbed by m gm of adsorbent

x_1^L = equilibrium concentration of solute

A = limiting adsorption value

a and b are constants.

Only the limiting adsorptions for those isotherms which show a definite plateau have been calculated.

TABLE 52

<u>Adsorbate</u>	<u>Limiting Adsorption Value / (m moles g⁻¹)</u>	
	<u>Silica</u>	<u>Alumina</u>
p-Methoxyphenol	1.09	0.58
p-Methylphenol	1.00	0.58
Phenol	0.98	0.60
p-Chlorophenol	1.00	0.56
p-Bromophenol	0.97	0.48
p-t-Butylphenol	0.75	0.42

In order to calculate the surface area requirement for each molecule from the limiting adsorption values it is necessary to know the surface area of the adsorbent which is available to solute and solvent molecules. Characterisation of the adsorbents by low temperature nitrogen adsorption has shown a probable pore radius of 1.75-2.0 nm for the silica assuming cylindrical shaped pores and a probable pore width of 2.0-3.0 nm for the alumina assuming slit-shaped pores. It is concluded that the whole of the surface areas of silica ($432 \text{ m}^2 \text{ g}^{-1}$) and alumina ($100 \text{ m}^2 \text{ g}^{-1}$)²² can be considered available to the adsorbate molecules.

In the case of alumina, the limiting adsorption values are seen to be similar in magnitude when the p-substituent is small and they represent a mean molecular area requirement on the surface of 0.27 nm^2 . Comparison with Adam's value of 0.24 nm^2 for the cross-sectional area of an aromatic molecule in a thin film on water¹¹⁶ suggests that the phenol covers the surface with an almost complete monolayer, the benzene molecules being almost totally excluded from the adsorbed phase at saturation.

In the case of silica, the limiting adsorption values, with the exception of p-t-butylphenol, are also of the same order and give rise to a mean molecular area requirement on the surface of 0.71 nm^2 . As the molecular area requirement of benzene is known to be 0.38 nm^2 from vapour phase adsorption studies (p. 82), then the area requirement of the phenol molecule on the silica surface will be 0.33 nm^2 , assuming that limiting adsorption corresponds to a solute-solvent molecular ratio of 1:1. This is in good agreement with the molecular area value of 0.34 nm^2 obtained for phenol when adsorbed

from n-hexane (Table 56) which because of its non polar nature would be expected to be almost completely excluded from the adsorbed phase at saturation. This value of 0.33 nm^2 is also reasonably consistent with the solute molecular area requirement on alumina (0.27 nm^2).

Thus for both surfaces, the phenol molecules can be considered to adopt a perpendicular orientation, the larger area requirement on silica possibly being due to a more angular disposition of the adsorbed molecule to the surface in order to maintain linearity and therefore stability of the hydrogen bond to the surface. In both cases the bulky nature of the t-bulky is seen to increase the molecular area requirement of p-t-butylphenol.

(ii) Index of Adsorption

On the basis of Everett's thermodynamic theory of adsorption from solution for perfect systems, the equilibrium constant of the phase exchange reaction



is given by

$$K = \frac{x_1^S \cdot x_2^L}{x_1^L \cdot x_2^S}$$

where K is related to the adsorption excess by the relation

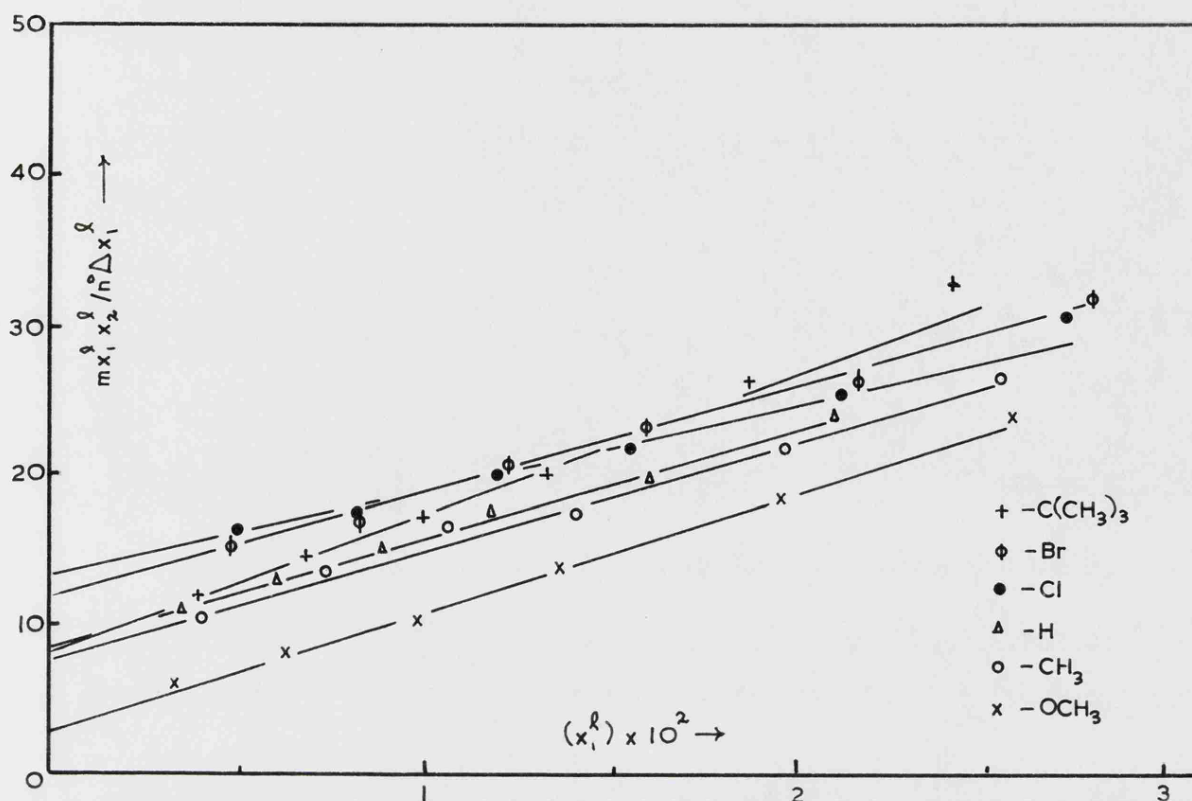
$$\frac{m x_1^L x_2^L}{n^0 \Delta x_1^L} = \frac{1}{n^S} \left(x_1^L + \frac{1}{(K-1)} \right) \quad (58)$$

x_1^L = mole fraction of component 1 in the liquid phase

- x_2^l = mole fraction of component 2 in the liquid phase.
 Δx_1^l = change in mole fraction of component 1 in the liquid phase on adsorption.
 n^S = total number of moles adsorbed at the surface of m gm adsorbent.
 n^0 = total number of moles present in the adsorption system.

On plotting $mx_1^l x_2^l / n^0 \Delta x_1^l$ against x_1^l for each of the compounds studied good straight lines are obtained for both adsorbents (Figs. 40 and 41) particularly when considering adsorption data in the middle concentration range of the isotherm. Values of n^S and K have been calculated from measurement of the slopes and intercepts of these lines and are recorded in Table 53. To assess the applicability of Everett's equation to these systems, the values of n^S obtained have been used to calculate a surface area value for the adsorbents considered. The mean molecular area requirements A_M of solute and solvent molecules on the surface have been calculated from the limiting adsorption data in Table 52 and from the appropriate area requirement of the benzene molecule on the surface (0.38 nm^2 for silica, 0.40 nm^2 for alumina²²). Allowance has been made in the assessment of the value of A_M for the slight variations from the 1:1 proportion of solute to solvent molecules present in the adsorbed phase at saturation.

Fig. 40



Adsorption of p-substituted phenols from benzene on to silica

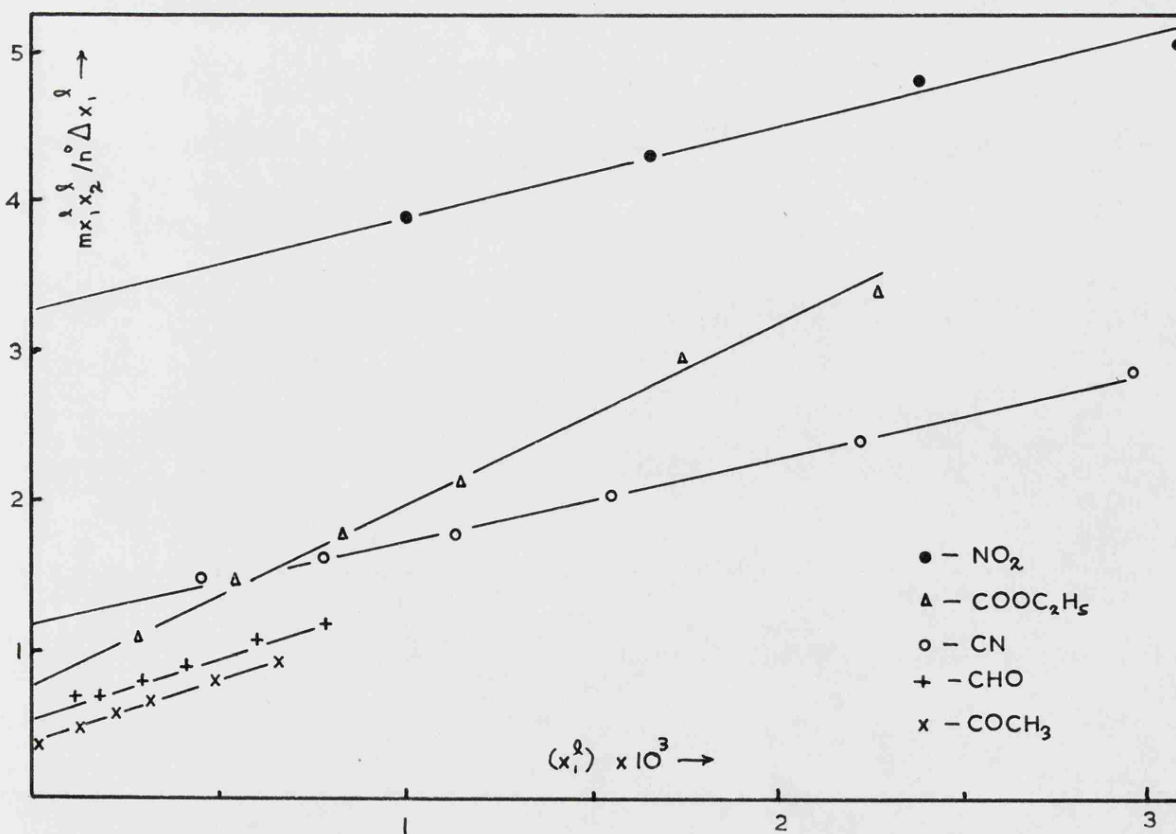
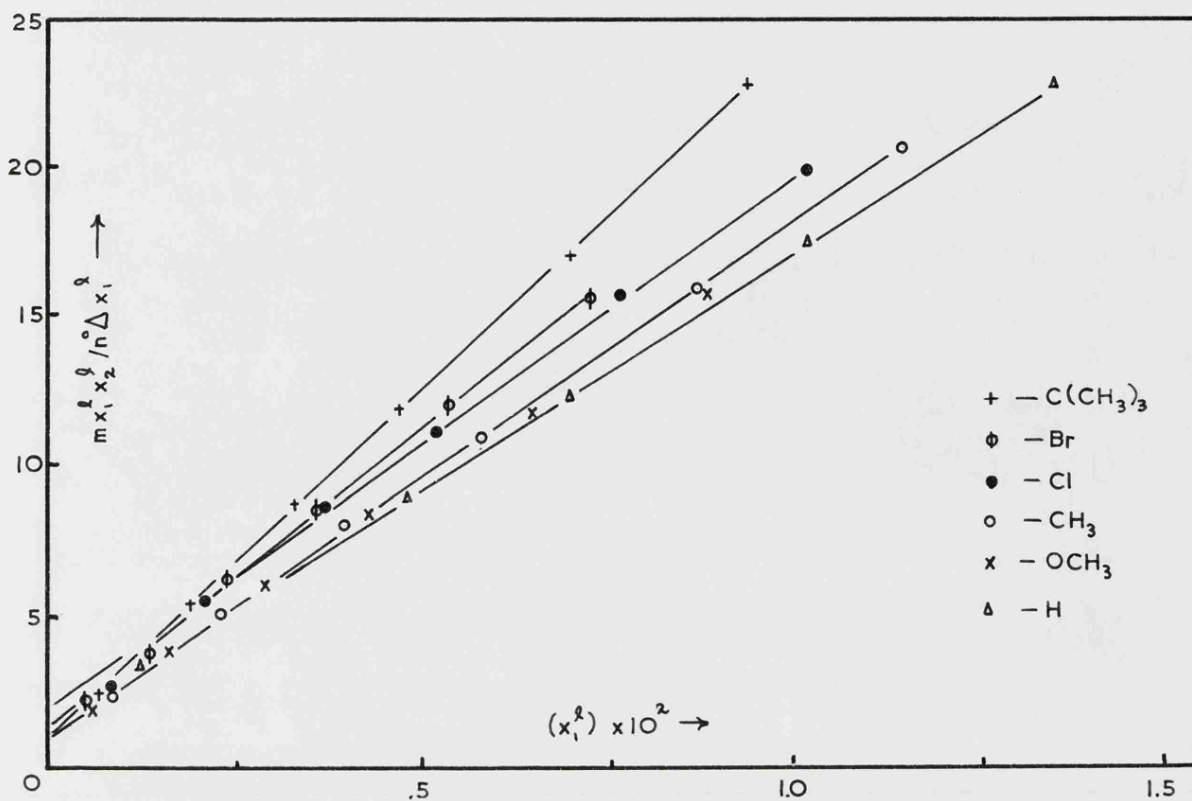


Fig. 41



Adsorption of p-substituted phenols from benzene on to alumina

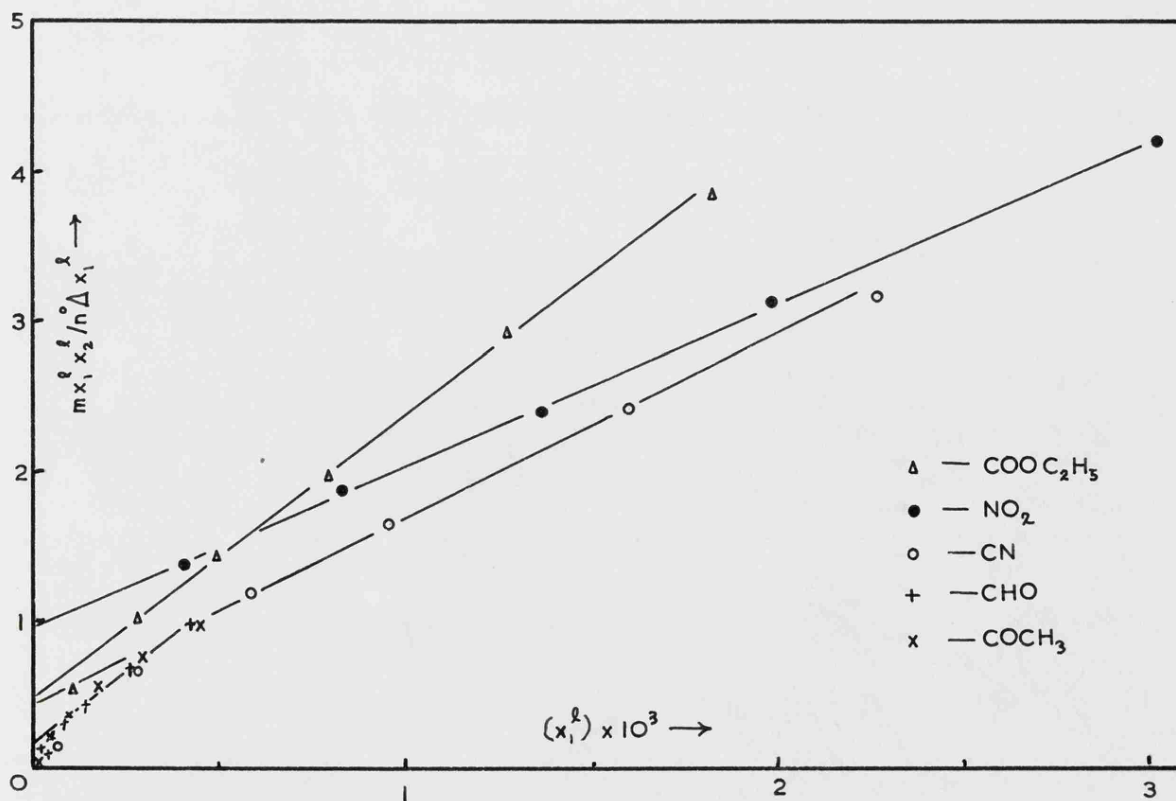


TABLE 53

p-substituent	Hammett σ^{32}	K	$n^S \times 10^3$ /mol	Mean Molecular Area A_M/nm^2	Calculated Surface Area $S/\text{m}^2\text{g}^{-1}$
<u>Silica</u>					
OCH ₃	-0.27	382	1.25	0.41	309
C(CH ₃) ₃	-0.20	100	1.15	-	-
CH ₃	-0.17	100	1.44	0.37	321
H	0	71	1.50	0.37	334
Cl	0.23	44	1.72	0.37	383
Br	0.23	66	1.45	0.37	323
COOC ₂ H ₅	0.67*	1,348	0.89	-	-
COCH ₃	0.87*	1,927	1.22	-	-
CN	1.00*	443	1.90	-	-
CHO	1.13*	1,436	1.29	-	-
NO ₂	1.27*	134	1.85	-	-
<u>Alumina</u>					
OCH ₃		1,665	0.588	0.27	96
C(CH ₃) ₃		3,116	0.419	-	-
CH ₃		1,813	0.577	0.27	94
H		1,133	0.614	0.27	100
Cl		1,515	0.520	0.27	84
Br		1,766	0.500	0.27	81
COOC ₂ H ₅		4,406	0.507	-	-
COCH ₃		5,636	0.634	-	-
CN		3,352	0.761	-	-
CHO		6,850	0.588	-	-
NO ₂		1,045	0.859	-	-

*enhanced values appropriate to reactions involving phenols.

In the case of silica, the surface area values obtained are seen to be about 25% lower than the B.E.T. nitrogen adsorption value of $432 \text{ m}^2\text{g}^{-1}$. As benzene is not the least interacting of solvents, it is not surprising that these adsorption systems do not strictly follow the requirements of equation (58).

In the case of alumina, good agreement is obtained between the surface area values calculated by equation (58) and the experimental surface area value of $100 \text{ m}^2\text{g}^{-1}$. As the benzene molecules are almost completely excluded from the alumina surface at saturation, and the adsorbed phase consists mainly of phenol molecules, this would seem to determine the closeness of approach of these systems to Everett's ideal model. It thus appears that non-ideality in the adsorbed phase is the major contribution to the deviation from the model in the case of adsorption on silica.

It is also of interest to consider whether the value of K calculated from equation (58) represents a measure of the adsorption tendency of the p-substituted phenols for the surface. The perpendicular orientation of the phenol molecules to the adsorbent surfaces indicates that the probable mechanism of adsorption is hydrogen bonding between the hydroxyl group on the surface and the functional OH group of the phenols. The electron density of the phenolic OH group and thus the adsorption tendency of the phenol for the surface will be altered by the presence of the p-substituent and a quantitative measure of this effect is provided by the Hammett substituent constant σ defined by:-

$$\log \left(\frac{K}{K_0} \right) = \sigma \rho$$

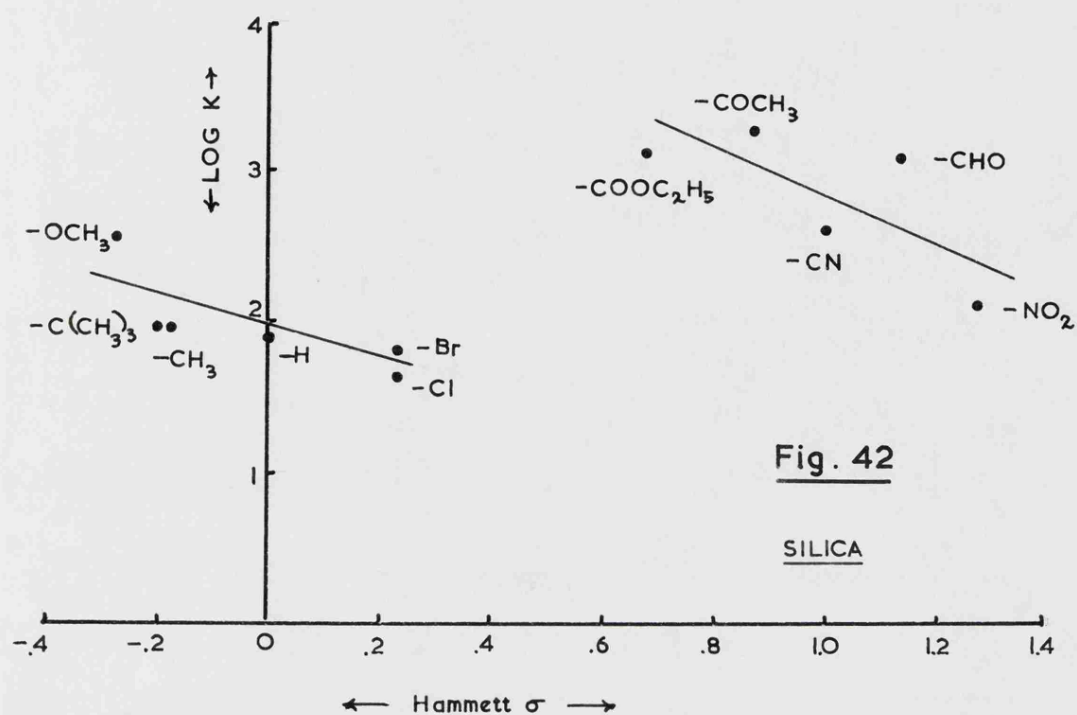
where K , K_0 are equilibrium or rate constants of substituted and unsubstituted benzene derivatives, respectively,

σ is a substituent constant varying with the nature and position of the substituent,

ρ is a reaction constant varying with the type of reaction, the physical conditions under which it takes place and the nature of the side-chain.

The plots of $\log K$ against σ from the data in Table 53 are given in Figs. 42 and 43. For silica (Fig. 42), two distinct correlations are found for the phenols studied, both showing the same trend of decreasing $\log K$ with increasing electron-attracting power of the p-substituent (increasing σ), whereas for alumina (Fig. 43), a linear plot of slightly increasing $\log K$ with increasing σ is observed, the two exceptions being p-t-butyl phenol and p-nitro phenol.

An explanation of the two correlations observed in the case of adsorption on silica may be sought in terms of the difference in solubility of the two groups of phenols in benzene. To allow for this difference in solubility, the adsorption isotherms Figs. 34 and 35 (p. 123,124) have been replotted in the form of $n^0 \Delta x_1^L / m$ against $x_1^L / (x_1^L)_S$ (Figs. 44 and 45).



Adsorption of p-substituted phenols from benzene

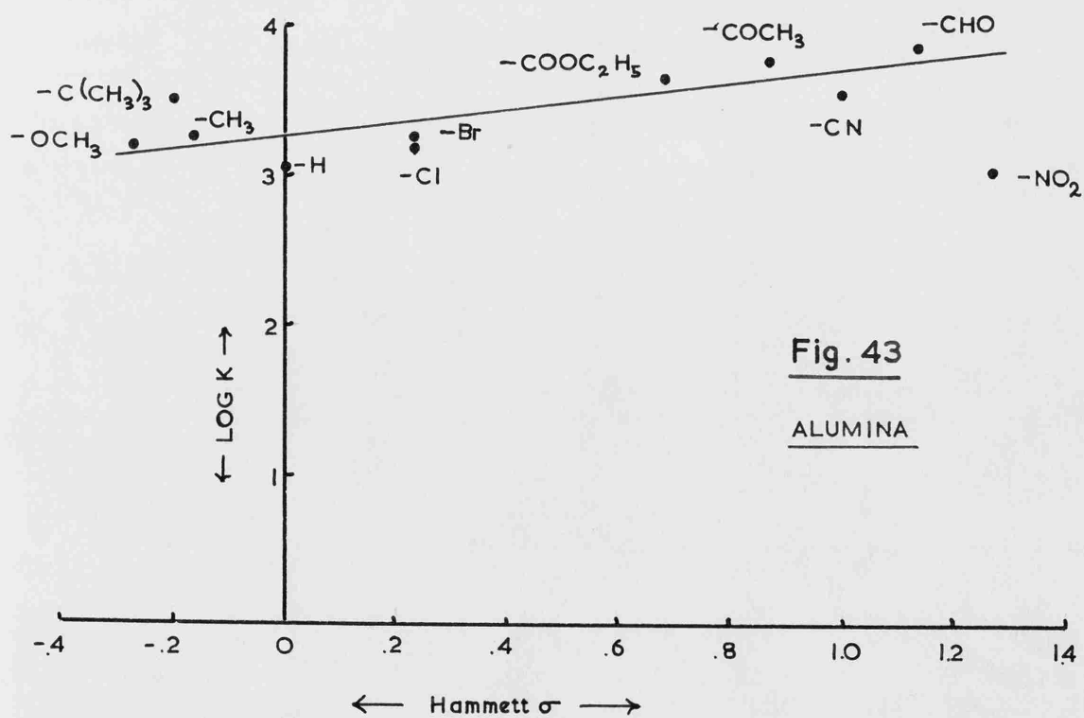
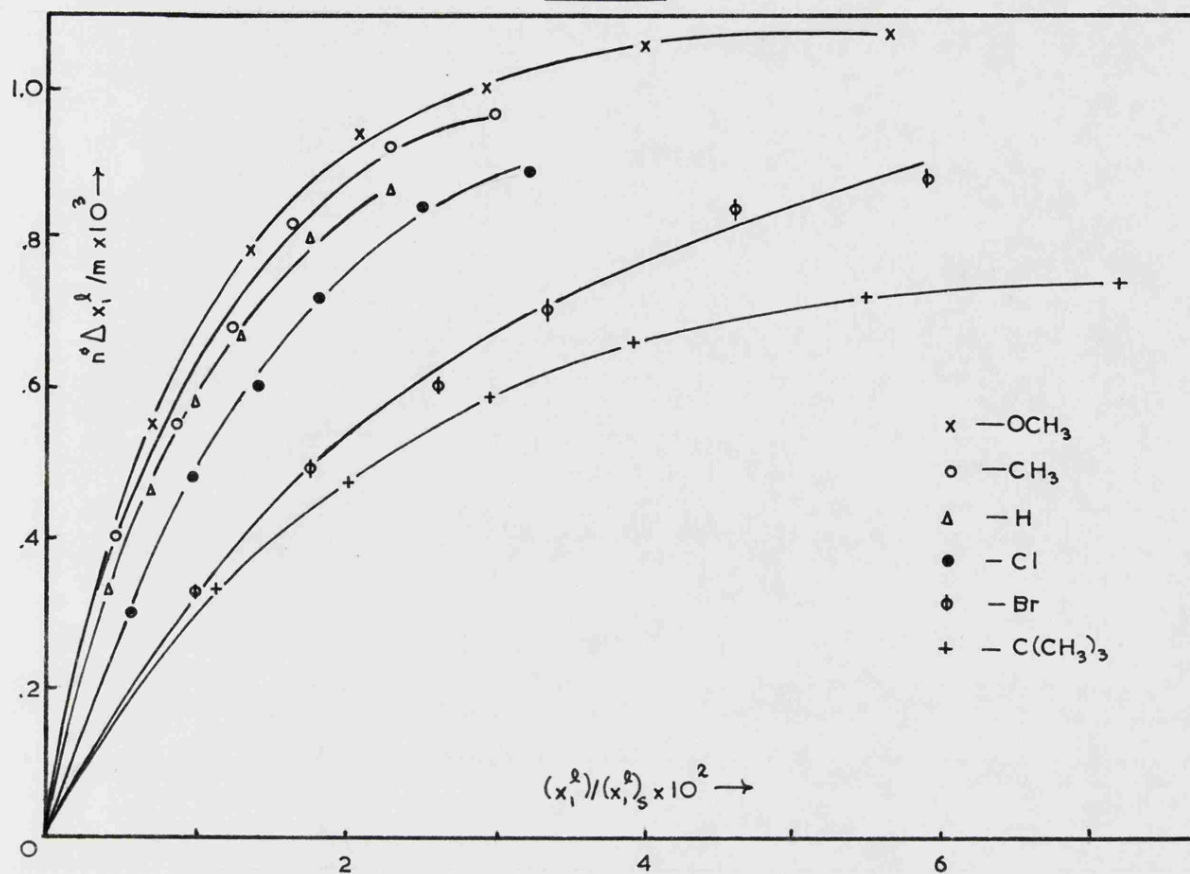


Fig. 44



Adsorption of p-substituted phenols from benzene on to silica

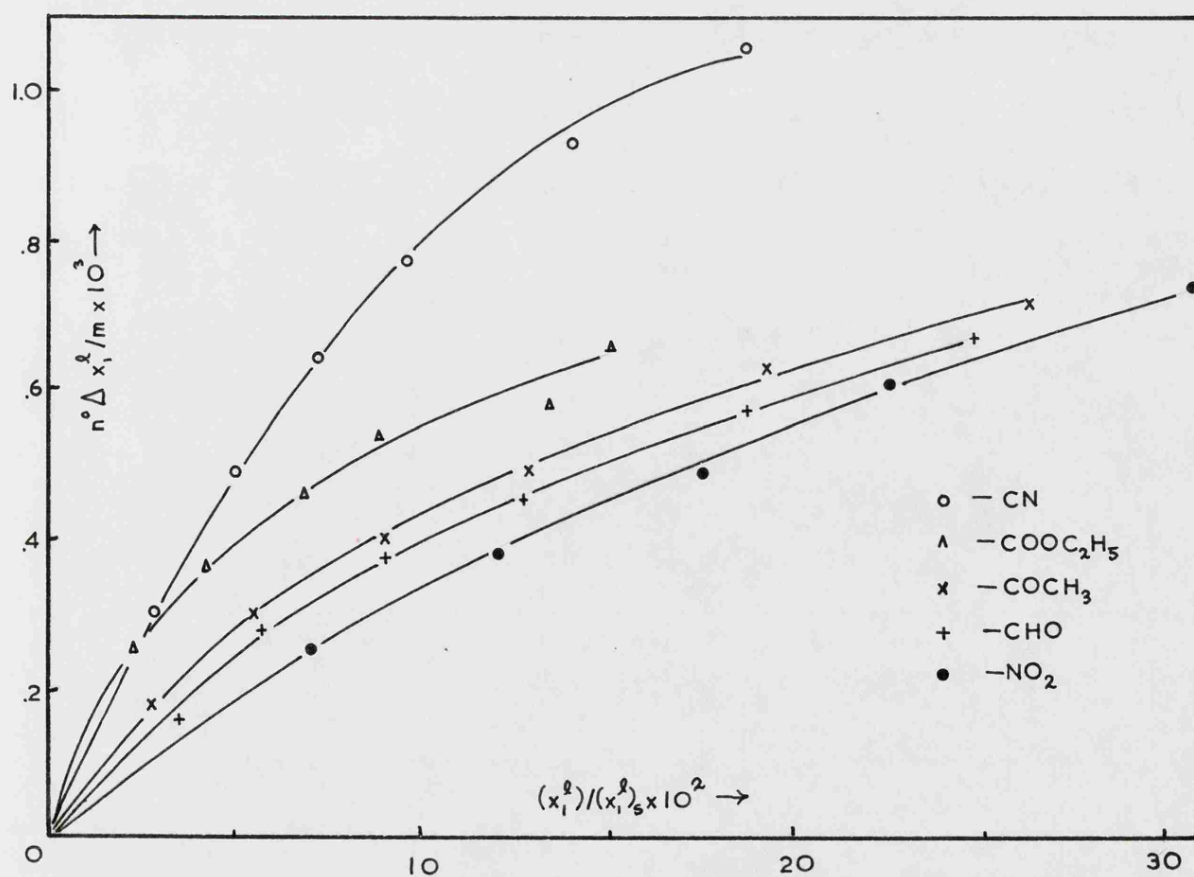
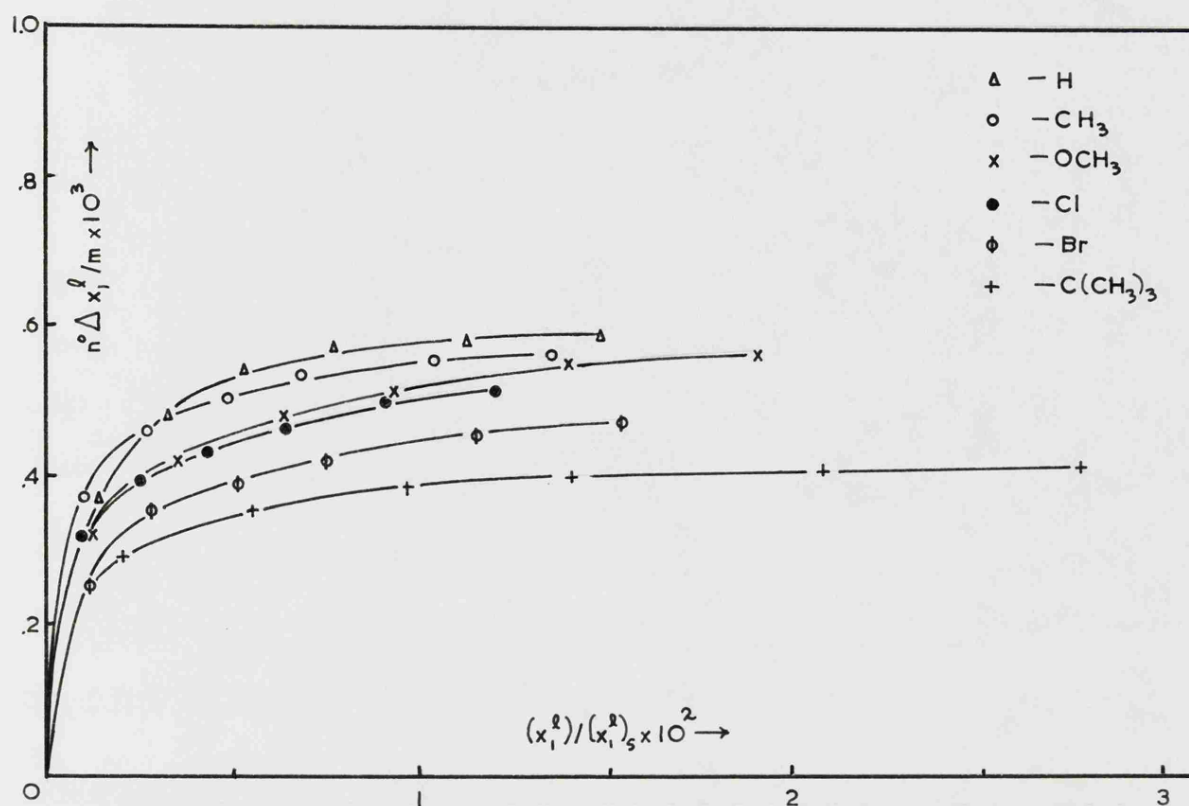
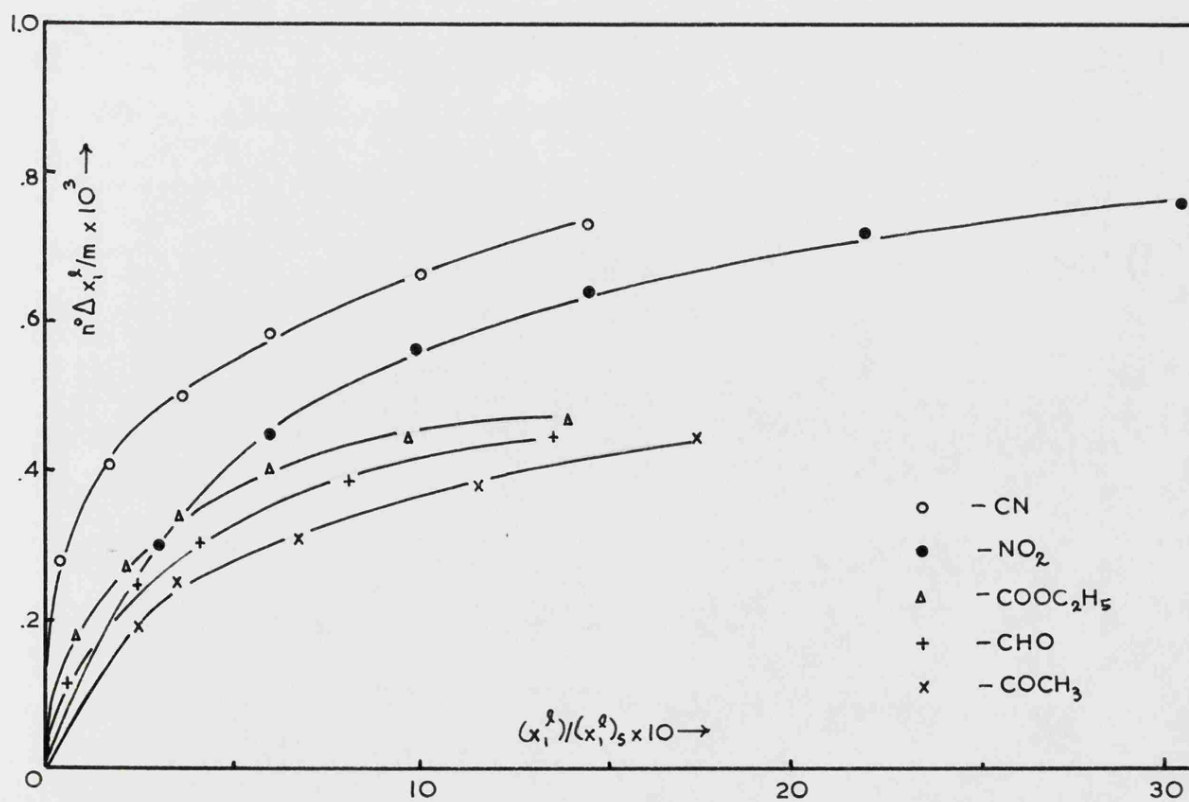


Fig. 45



Adsorption of p-substituted phenols from benzene on to alumina



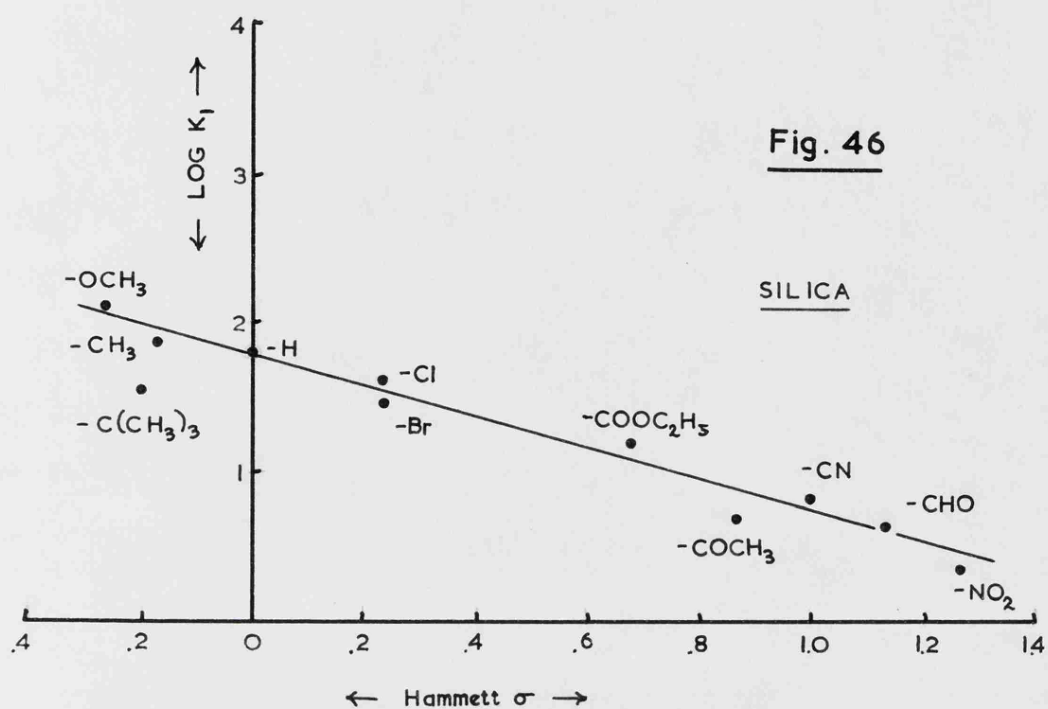
Equation (58) then becomes

$$\frac{mx_1^{\ell}x_2^{\ell}}{(x_1^{\ell})_s n^0 \Delta x_1^{\ell}} = \frac{1}{n^S} \left[\frac{x_1^{\ell}}{(x_1^{\ell})_s} + \frac{1}{(x_1^{\ell})_s (K-1)} \right] \quad (59)$$

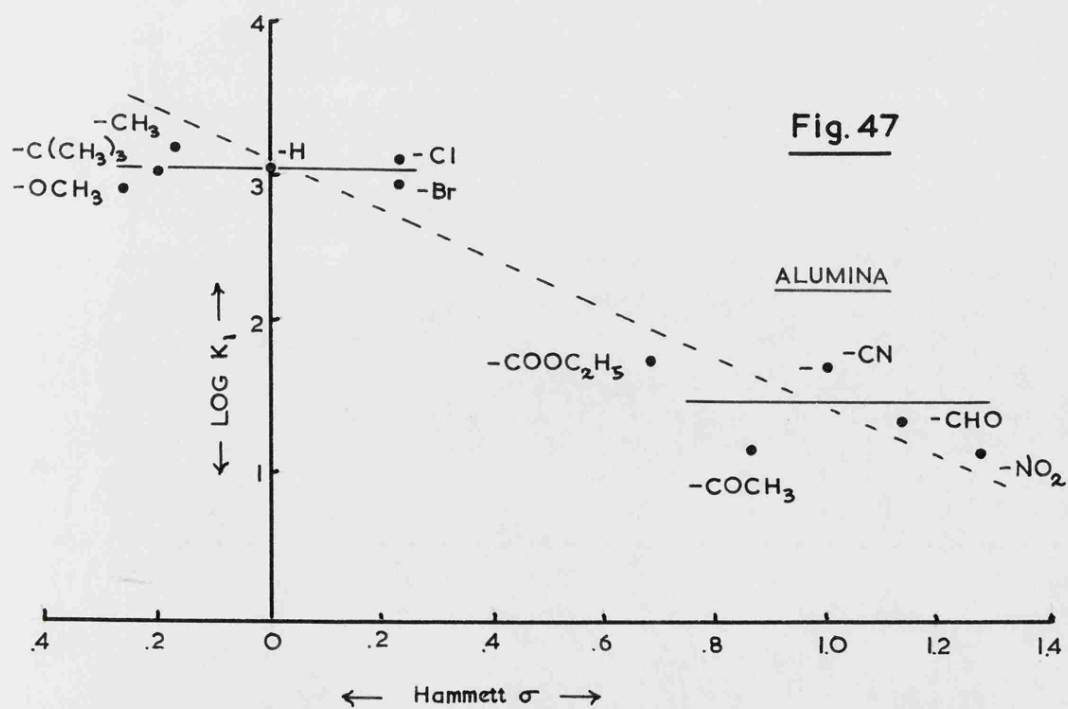
giving the same slope of $1/n^S$ as previously, but a different intercept leading to the evaluation of K_1 where $K_1 = (x_1^{\ell})_s (K-1)$. The values of K_1 obtained for the two adsorbent systems considered are recorded in Table 54 and the plots of $\log K_1$ against σ are shown in Figs. 46 and 47.

TABLE 54

<u>p-substituent</u>	<u>Index of Adsorption K_1</u>	
	<u>Silica</u>	<u>Alumina</u>
OCH ₃	133	768
C(CH ₃) ₃	34	1,050
CH ₃	74	1,541
H	64	1,030
Cl	40	1,282
Br	29	837
COOC ₂ H ₅	17	57
COCH ₃	5	14
CN	7	53
CHO	4	22
NO ₂	2	14



Adsorption of p-substituted phenols from benzene



In the case of silica, a good linear plot is now observed (Fig. 46) in which $\log K_1$ decreases with increase in the Hammett σ constant and is suggestive of a type of surface hydrogen bonding in which the oxygen atom of the OH group of the phenol is bonded to a hydrogen atom of a physically adsorbed surface water molecule or surface hydroxyl group. An increase in Hammett σ increases the acidity of the phenol molecule and correspondingly decreases the tendency of the OH group to react with an acidic hydrogen atom site on the silica surface. The introduction of the saturation mole fraction $(x_1^L)_s$ into equation (58) accounts for the effect of changes in solubility of the phenols in the liquid phase on adsorption at the solution/silica interface.

In the case of alumina, the plot of $\log K_1$ against Hammett σ (Fig. 47) can be interpreted in two ways:-

- (i) Phenols with high saturation mole fractions give a linear plot of negligible slope as do phenols of low solubility in benzene. The affinity of the latter group of phenols is less than that of the former group for the alumina surface. The effect of adsorbate solubility in the liquid phase on adsorption at the solution-alumina interface can be assumed virtually constant but different for the two groups of phenols, over the range of $(x_1^L)_s$ values considered. In consequence, the Hammett σ plot should reflect only changes occurring in the adsorption affinity of the phenols for the surface when the p-substituent is varied. These affinities are so strong that the linear plots observed are of almost zero slope implying that the nature of the p-substituent has little effect. It is difficult to understand

however why those phenols with strongly electron attracting p-substituents and less soluble in benzene have lower affinities for a basic surface.

- (ii) A fair correlation between decreasing $\log K_1$ with increasing Hammett σ is obtained for the majority of phenols studied, the slope of the plot being even greater than the corresponding one for silica. This seems surprising in view of the more basic nature of the alumina surface and no adequate explanation can be offered.

The adsorption affinities of the p-substituted phenols for the two adsorbent surfaces can be compared by plotting the logarithm of the K_1 values for silica against those for alumina from the data in Table 54. A reasonable correlation is observed (Fig. 48) which clearly shows the alumina surface to be a stronger adsorbing surface for the p-substituted phenols than the silica surface.

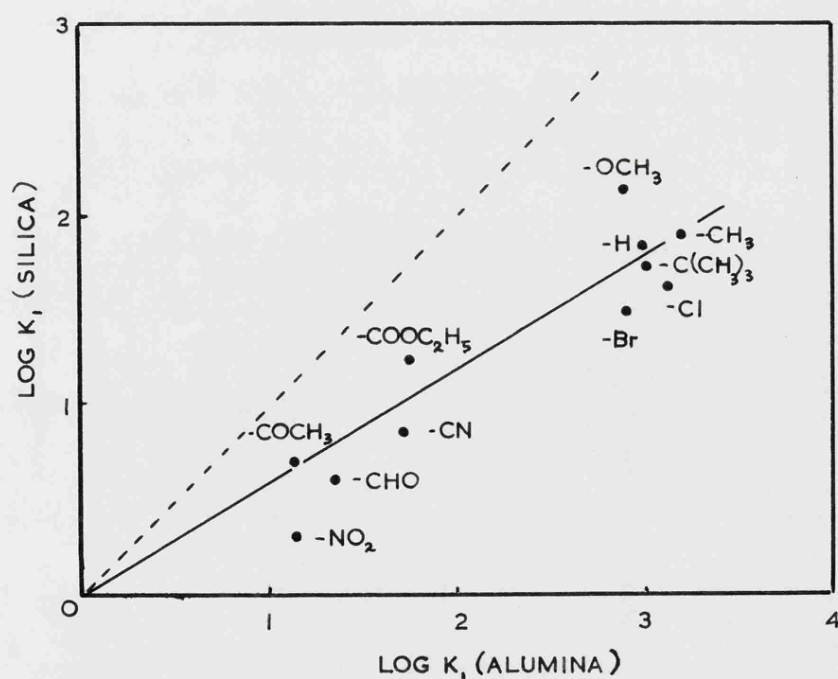


Fig. 48

(b) ADSORPTION OF PHENOL FROM DIFFERENT SOLVENTS

(i) Individual Isotherms

Although in the case of adsorption from dilute solution, the composite isotherm is almost identical to that of the individual isotherm of the solute, solvent adsorption may still be appreciable over the concentration range studied. To calculate the individual isotherms, it is usual to assume monolayer adsorption and obtain n_1^s and n_2^s by application of the following equations discussed in the 'Introduction'.

$$\frac{n^0 \Delta x_1^\ell}{m} = n_1^s x_2^\ell - n_2^s x_1^\ell$$

and

$$\frac{n_1^s}{(n_1^s)_m} + \frac{n_2^s}{(n_2^s)_m} = 1$$

The molecular area requirements of the solvent molecules on the surface and the calculated $(n_2^s)_m$ values are given in Table 55.

The $(n_1^s)_m$ value for phenol on silica was taken as $2.12 \times 10^{-3} \text{ mol g}^{-1}$ corresponding to monolayer adsorption of phenol from n-hexane assuming complete exclusion of the latter from the adsorbed phase at saturation.

The $(n_1^s)_m$ value for phenol on alumina was taken as $0.691 \times 10^{-3} \text{ mol g}^{-1}$ calculated from Adam's value of 0.24 nm^2 for the cross-sectional area of an aromatic molecule in a thin film on water¹¹⁶.

TABLE 55

<u>Adsorbent</u>	<u>Solvent</u>	<u>Molecular Area Requirement</u>	$(n_2^s)_m$
		A_M/nm^2	$\times 10^3/\text{mol}$
<u>Silica</u>	n-hexane	0.44*	1.63
	cyclohexane	0.41*	1.75
	carbon tetrachloride	0.37 ¹⁰⁷	1.94
	toluene	0.50 ¹¹⁷	1.44
	benzene	0.38	1.89
<u>Alumina</u>	cyclohexane	0.39 ⁹⁹	0.41
	carbon tetrachloride	0.37 ¹⁰⁷	0.45
	benzene	0.40**	0.42
	tetrahydrofuran	0.42**	0.40
	dioxan	0.42**	0.40

* The molecular area requirement was obtained by comparison of the Catalin molecular model with that for benzene.

** Determined experimentally by vapour phase adsorption^{22,31,118}.

The composite and calculated individual isotherms for the adsorption of phenol from various solvents are shown in Figs. 49 and 50. The limiting adsorption values calculated from the individual isotherms by application of the Jowett equation are given in Table 56.

TABLE 56

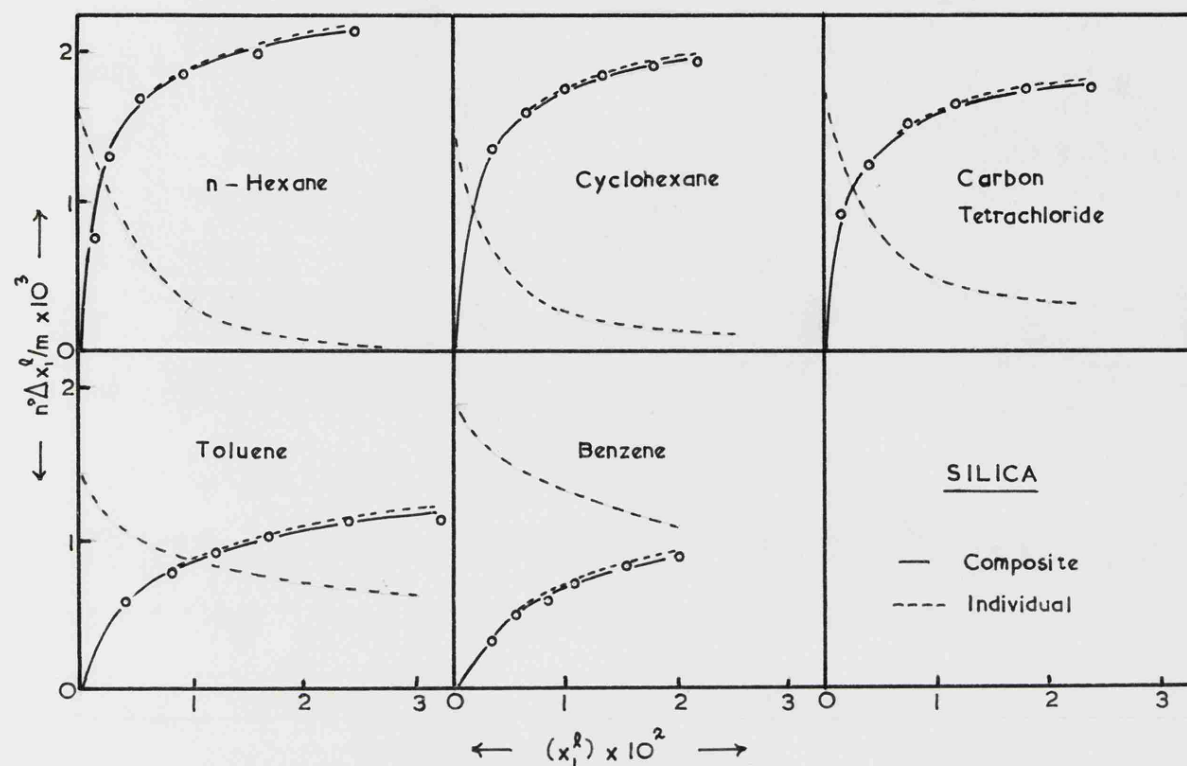
<u>Adsorbent</u>	<u>Solvent</u>	<u>Limiting Adsorption Value / (m moles g⁻¹)</u>	
		<u>Solute</u>	<u>Solvent</u>
<u>Silica</u>	n-hexane	2.12	-
	cyclohexane	2.02	0.07
	carbon tetrachloride	1.82	0.21
	toluene	1.24	0.60
	benzene	0.98	1.02
<u>Alumina</u>	cyclohexane	0.65	0.03
	carbon tetrachloride	0.61	0.05
	benzene	0.60	0.05
	tetrahydrofuran	0.22	0.27
	dioxan	0.17	0.30

The effect of competition between solute and solvent molecules for the adsorbing surface is clearly seen in the individual isotherms, the increasing order of solvent/surface interaction being:-

for silica n-hexane < cyclohexane < carbon tetrachloride
 < toluene < benzene

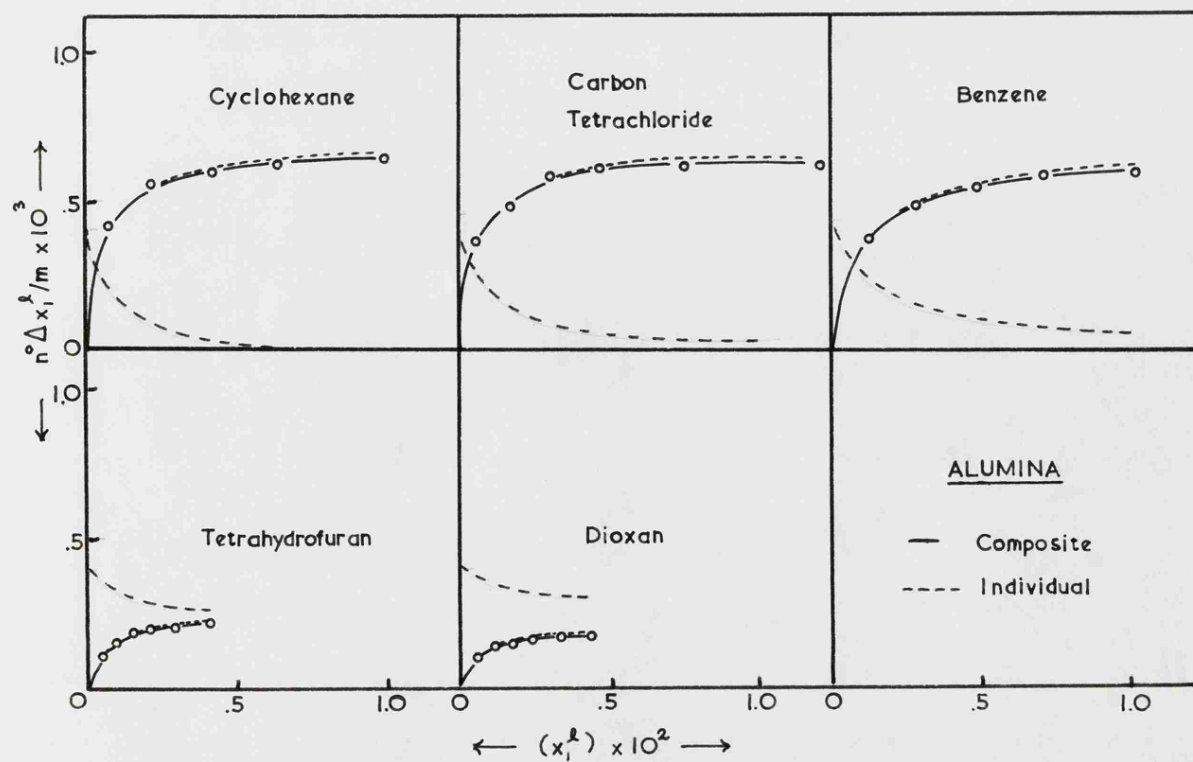
for alumina cyclohexane < carbon tetrachloride < benzene
 < tetrahydrofuran < dioxan.

Fig. 49



Adsorption of phenol from different solvents

Fig. 50



(ii) Index of Adsorption

Adsorption parameters n^S and K of equation (58) have been calculated for each adsorption system from the plots of $mx_1^L x_2^L / n^0 \Delta x_1^L$ against x_1^L (Figs. 51 and 52), and are recorded in Table 57. Values of K_1 have not been calculated since the $(x_1^L)_S$ values concerned are of a similar magnitude. The mean molecular area requirements in Table 57 have been calculated from

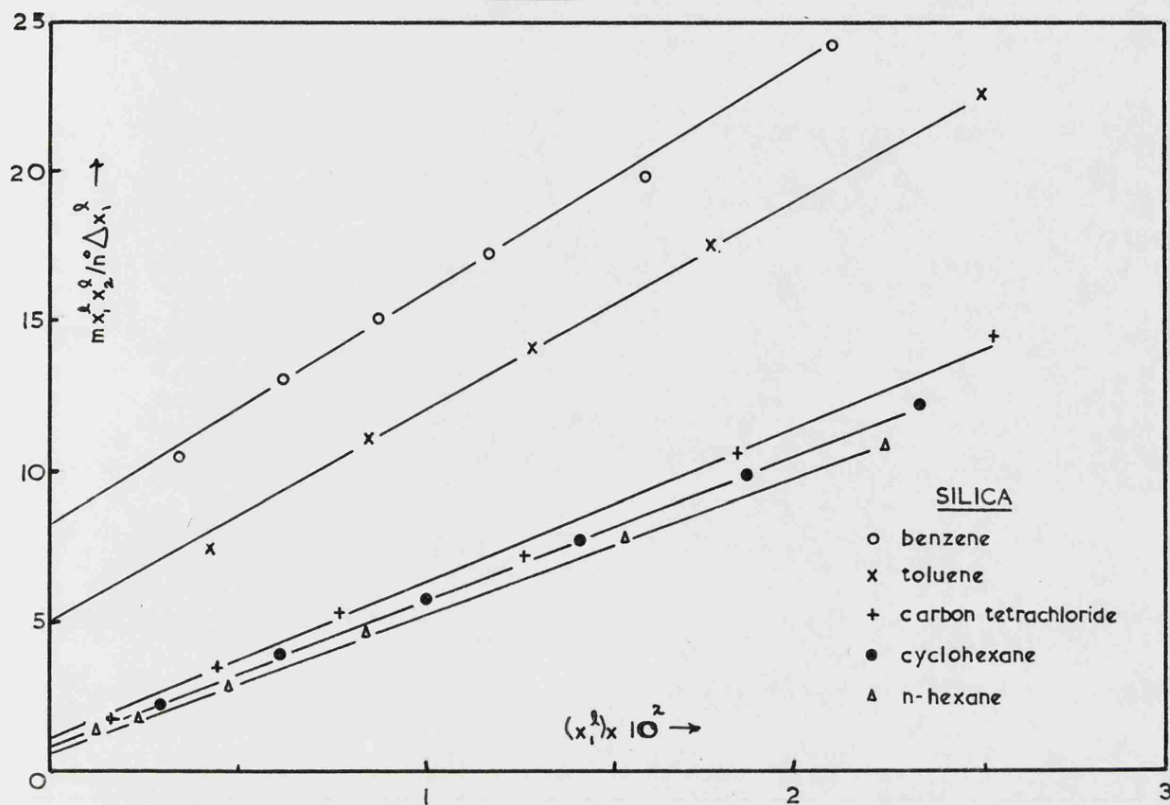
$$\left(\frac{n_1 A_1 + n_2 A_2}{n_1 + n_2} \right)$$

where A_1 = molecular area requirement of phenol on the adsorbent surface (silica 0.33 nm^2 , alumina 0.24 nm^2)

A_2 = molecular area requirement of solvent on the adsorbent surface (Table 55)

n_1, n_2 = moles of solute and solvent respectively, on the adsorbent surface at saturation (Table 56).

Fig. 51



Adsorption of phenol from different solvents

Fig. 52

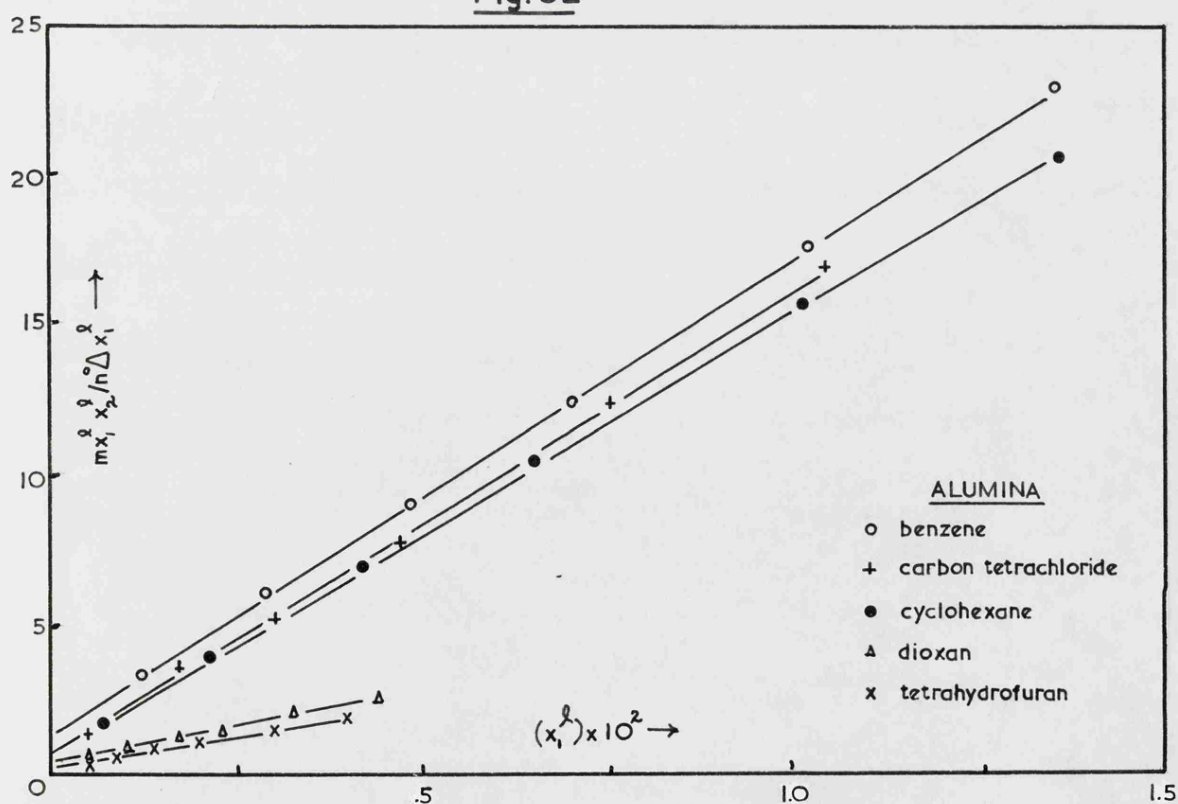


TABLE 57

Solvent	E_T^{114}	K	$n^S \times 10^3$	Mean Molecular Area A_M	Calculated Surface Area S
	/kJ mol ⁻¹		/mol	/nm ²	/m ² g ⁻¹
<u>Silica</u>					
n-hexane	129.3	691	2.18	0.34	432
cyclohexane	130.5	592	2.05	0.34	420
carbon tetrachloride	136.0	380	2.00	0.35	422
toluene	141.8	123	1.51	0.40	364
benzene	144.3	71	1.50	0.37	334
<u>Alumina</u>					
cyclohexane	130.5	1,616	0.72	0.25	108
carbon tetrachloride	136.0	1,502	0.66	0.27	107
benzene	144.3	1,133	0.61	0.27	100
tetrahydrofuran	156.5	2,015	0.23	0.36	51
dioxan	150.6	2,039	0.18	0.36	40

For silica, with the exception of the phenol-benzene system, the agreement between the calculated surface areas and the B.E.T. value of $432 \text{ m}^2 \text{ g}^{-1}$ implies a better conformity to the idealised theory adsorption at the solid-solution interface than in the case of the p-substituted phenol-benzene systems. This is presumably due to the fact that deviations from thermodynamic ideality are less in solvents other than benzene and particularly so in the adsorbed phase. Also, of importance in this connection is the fact that the surface is predominantly occupied by phenol molecules at limiting adsorption.

For alumina, good agreement between calculated and experimental surface area values is again obtained when considering relatively non-polar solvents but large deviations from the requirements of equation (58) are observed for solvents capable of strong specific interaction such as dioxan and tetrahydrofuran.

The E_T parameter has been used as a quantitative measure of solvent reactivity and the plots of $\log K$ against E_T for the two adsorbents considered are presented in Fig. 53. For comparison, plots of the limiting adsorption values for phenol given in Table 56 against E_T are shown in Fig. 54.

In the case of silica, the linearity of the plots observed, reveal the quantitative dependence of the affinity of phenol adsorption on solvent reactivity, the direction of the trend being as expected.

In the case of alumina, the independence between $\log K$ and E_T again reflects the strong affinity between the phenol and the surface which

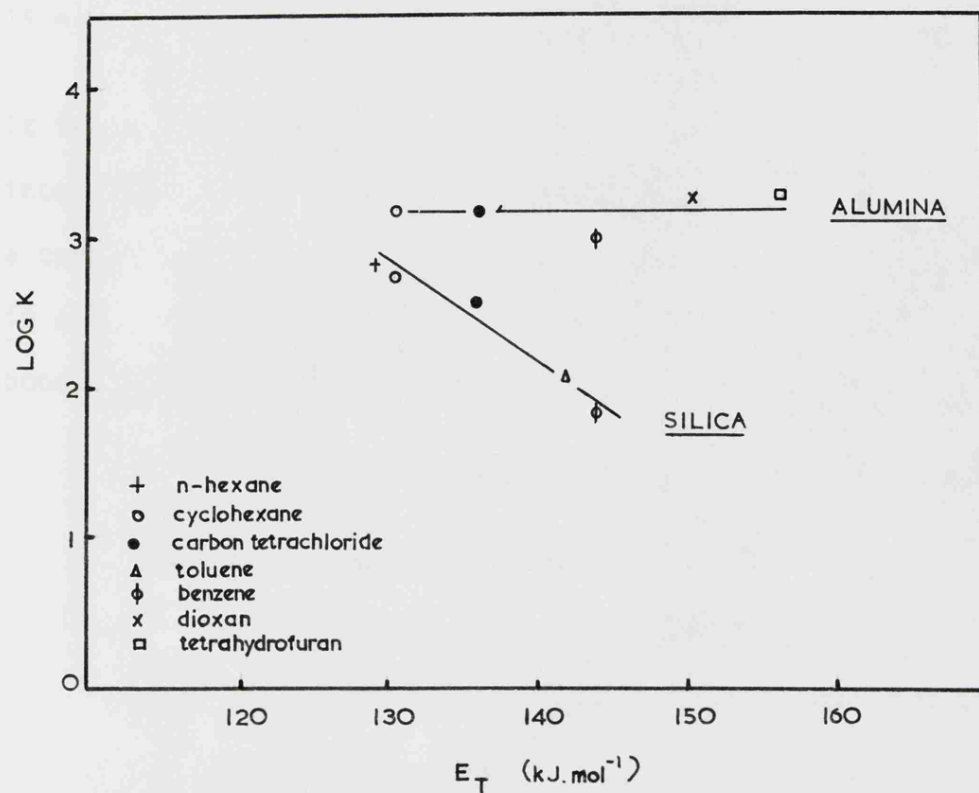


Fig. 53

Adsorption of phenol from different solvents

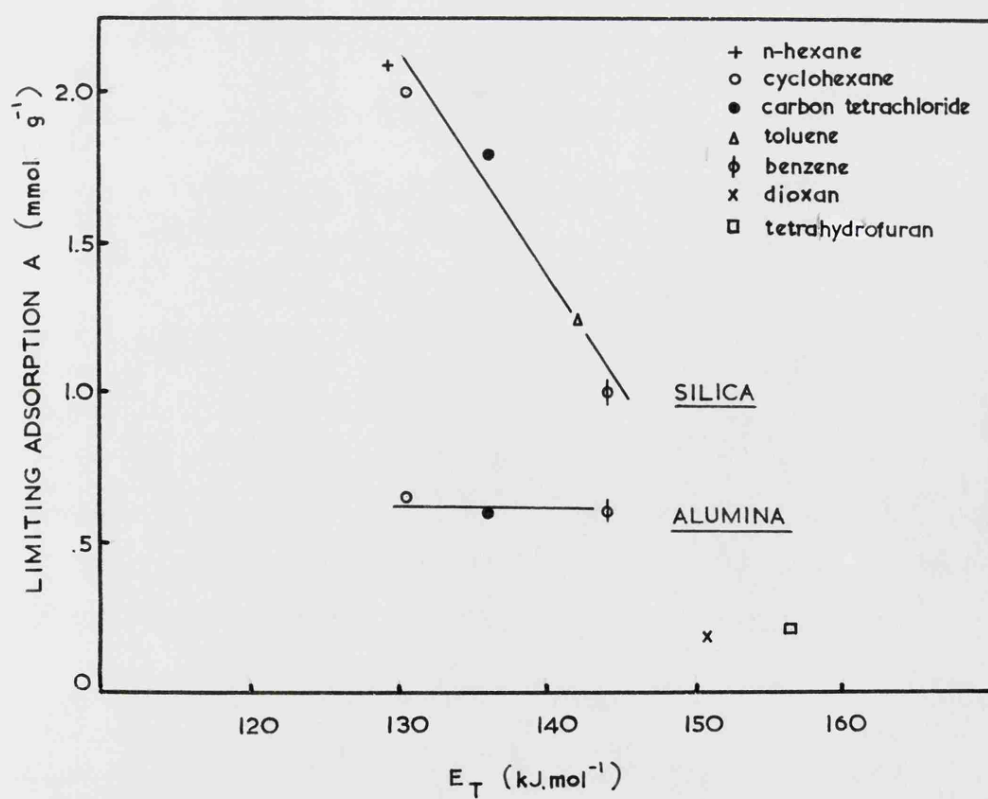


Fig. 54

is almost unaffected by adsorptive-solvent reactivity in solution.

It is thus seen that the process of adsorption at a solution-solid interface is analogous to that of association in solution in that a defined index of adsorption is related to the E_T solvent parameter in a similar manner to the association constant of the hydrogen bonding process of phenol to various solvents.

A P P E N D I X

COMPUTER PROGRAMS

1. Calculation of Association Constant

```

      DIMENSION CD(10),AM(10),RAM(10),RCD(10),RK1(10),RK2(10),
1EM(10),C(10),AK(45),DEV(45),RAK(20),RDEV(20),NAM(80),AO(10)
      READ(2,28)NM
28  FORMAT(I2)
      DO 52ND=1,NM
      READ(2,1)(NAM(K),K=1,40)
      1  FORMAT(40A2)
      WRITE(3,2)(NAM(K),K=1,40)
      2  FORMAT(1H1,40A2,/)
      WRITE(3,11)
11  FORMAT(10X44HCALCULATION OF EQUILIBRIUM CONSTANT NAGAKURA)
      READ(2,10)N
10  FORMAT(I1)
      READ(2,15)(CD(I),AM(I),I=1,N)
15  FORMAT(F10.5,F10.3)
      READ(2,20)CA,AMF
20  FORMAT(E10.4,F10.3)
      SUMX=0.0
      SUMY=0.0
      SUMX2=0.0
      SUMXY=0.0
      FN=N
      DO 41 I=1,N
      AO(I)=AM(I)-AMF
      RAM(I)=1.0/AO(I)
      RCD(I)=1.0/CD(I)
      SUMX=SUMX+RAM(I)
      SUMY=SUMY+RCD(I)
      SUMX2=SUMX2+RAM(I)**2
      SUMXY=SUMXY+RAM(I)*RCD(I)
41  CONTINUE
      EMNLS=((FN*SUMXY)-(SUMX*SUMY))/((FN*SUMX2)-(SUMX*SUMX))
      CNLS=(SUMY-SUMX*EMNLS)/FN
      EQKNA=-CNLS
      WRITE(3,12)
12  FORMAT(/,19X5HEQKNA,12X5HEMNLS,/)
      WRITE(3,13)EQKNA,EMNLS
13  FORMAT(16XF8.3,8XF9.5)
      WRITE(3,14)
14  FORMAT(/,15X2HCD,13X2HAM,12X3HRC,4X3HRA,/)
      WRITE(3,16)(CD(I),AM(I),RCD(I),RAM(I),I=1,N)
16  FORMAT(11XF8.5,8XF6.3,8XF9.5,8XF9.5)
      WRITE(3,17)
17  FORMAT(/,15X2HCA,13X3HAMF,/)
      WRITE(3,18)CA,AMF
18  FORMAT(11XE12.5,4XF6.3)
      EA=AMF/CA
      SUM=0.0
      DO 42 I=1,N
      CC=(EQKNA*CD(I)*CA)/(1.0+EQKNA*CD(I))
```

```

      EC=(AM(I)-EA*(CA-CC))/CC
42 SUM=SUM+EC
      AVEC=SUM/FN
      EC1=AVEC-100.0
      EC2=AVEC+100.0
      DO 43 I=1,N
      RK1(I)=AO(I)/((EC1-EA)-CA-CD(I)+(CD(I)*CA*(EC1-EA))/AO(I)
      RK2(I)=AO(I)/((EC2-EA)-CA-CD(I)+(CD(I)*CA*(EC2-EA))/AO(I)
      EM(I)=(RK2(I)-RK1(I))/(EC2-EC1)
43 C(I)=RK1(I)-EM(I)*EC1
      K=0
      DO 44 I=1,N
      DO 44 J=1,N
      IF(I-J)45,44,44
45 K=K+1
      AK(K)=(EM(I)-EM(J))/(EM(I)*C(J)-EM(J)*C(I))
44 CONTINUE
      WRITE(3,19)
19  FORMAT(/,10X46HCALCULATION OF EQUILIBRIUM CONSTANT ROSE DRAGO)
      WRITE(3,21)
21  FORMAT(/,15X3HRK1,13X3HRK2,11X2HEM,19X1HC,/)
      WRITE(3,22)(RK1(I),RK2(I),EM(I),C(I),I=1,N)
22  FORMAT(8XF10.6,6XF10.6,7XE12.5,7XE12.5)
      NR=0
      NSUM=N*(N-1)/2
54 SUMK=0.0
      SUMK2=0.0
      FM=NSUM
      DO 46 K=1,NSUM
      SUMK=SUMK+AK(K)
46 SUMK2=SUMK2+AK(K)**2
      SD=SQRT(((SUMK2)-(SUMK**2)/FM)/(FM-1.0))
      AVK=SUMK/FM
      J=1
      M=1
      L=0
      DO 47 K=1,NSUM
47 DEV(K)=AK(K)-AVK
      WRITE(3,23)
23  FORMAT(/,15X3HAVK,13X2HSD,12X3HEC1,14X3HEC2,/)
      WRITE(3,24)AVK,SD,EC1,EC2
24  FORMAT(11XF7.3,9XF8.5,9XF7.1,10XF7.1)
      WRITE(3,25)
25  FORMAT(/,20X2HAK,27X3HDEV,/)
      WRITE(3,26)(AK(K),DEV(K),K=1,NSUM)
26  FORMAT(17XF10.6,18XF10.6)
      DO 48 K=1,NSUM
      IF(ABS(DEV(K))-SD*2.0)50,50,51
50 AK(J)=AK(K)
      AK(K)=AK(J)
      J=J+1
      GO TO 48
51 RAK(M)=AK(K)
      RDEV(M)=DEV(K)
      M=M+1

```

```

      L=L+1
48  CONTINUE
      IF(L-1) 52,53,53
53  WRITE(3,27) (RAK(M),RDEV(M),M=1,L)
27  FORMAT(//,17XF10.6,18XF10.6)
      NR=NR+1
      NSUM=J-1
      IF(NR-6) 54,52,52
52  CONTINUE
      CALL EXIT
      END

```

2. Calculation of Surface Area by Gas Adsorption

```

      DIMENSION DP(50),DT(50),DM(50),EP(50),ET(50),EM(50),VA(50),
1  RP(50),RV(50),C(10),VM(10),SA(10),AM(10),RPM(10),NAM(80)
      READ(2,1) (NAM(K),K=1,40)
1  FORMAT(40A2)
      WRITE(3,2) (NAM(K),K=1,40)
2  FORMAT(1H1,/,40A2,/)
      READ(2,3) N
3  FORMAT(I2)
      READ(2,4) VRT,VNT,PO,AREA,MSA,WT
4  FORMAT(F5.2,F9.2,F8.2,F9.2,5XI1,F11.2)
      READ(2,5) (DM(I),DP(I),EM(I),ET(I),EP(I),I=1,N)
5  FORMAT(F5.2,F8.1,F9.2,F9.2,F8.1,F9.2)
      VAD=0.0
      SBN=0.0
      DO 10 I=1,N
      DT(I)=DT(I)+273.20
      DNR=DP(I)*(148.9+DM(I)*0.2059)/DT(I)+SBN
      ET(I)=ET(I)+273.20
      ENR=EP(I)*(148.9+EM(I)*0.2059)/ET(I)
      SBN=EP(I)*(VRT/ET(I)+VNT/77.2)
      VNR=DNR-ENR-SBN
      VA(I)=3.5947*VNR/WT+VAD
      VAD=VA(I)
      RP(I)=EP(I)/PO
      RV(I)=EP(I)/(VA(I)*(PO-EP(I)))
10  CONTINUE
      PMR=0.40
      M=0
21  SUMX=0
      SUMX2=0
      SUMY=0
      SUMXY=0
      NM=0
      DO 20 I=1,N
      IF(RP(I)-0.05) 20,20,22
22  IF(RP(I)-PMR) 23,23,20
23  NM=NM+1
      SUMX=SUMX+RP(I)

```



```

SUMY=SUMY+RV(I)
SUMX2=SUMX2+RP(I)*RP(I)
SUMXY=SUMXY+RP(I)*RV(I)
20 CONTINUE
M=M+1
TNI=(SUMX*SUMXY-SUMY*SUMX2)/(SUMX*SUMX-SUMX2*NM)
SLO=(SUMY-NM*TNI)/SUMX
C(M)=1.0+SLO/TNI
VM(M)=1.0/(SLO+TNI)
RPM(M)=PMR
PMR=PMR-0.025
IF(PMR-0.25)24,21,21
24 L=M
WRITE(3,6)
6 FORMAT(12X2HDM,6X2HDT,7X2HDP,7X2HEM,6X2HET,7X2HEP,
27X4HP/PO,8X2HVA,27X10HP/VA(PO-P),/)
WRITE(3,7)(DM(I),DT(I),DP(I),EM(I),ET(I),EP(I),RP(I),
3VA(I),RV(I),I=1,N)
7 FORMAT(9XF6.2,F8.1,F9.2,F9.2,F8.1,F9.2,F11.5,F12.4,E16.5)
IF(MSA-1)25,25,26
25 CONTINUE
DO 27 M=1,L
27 SA(M)=VM(M)*AREA*0.26872
WRITE(3,8)
8 FORMAT(/,32X8HMAX.P/PO,7X1HC,11X2HVM,8X12HSURFACE AREA,/)
WRITE(3,9)(RPM(M),C(M),VM(M),SA(M),M=1,L)
9 FORMAT(/,33XF6.3,F11.2,F13.3,F16.3)
GO TO 29
26 CONTINUE
DO 28 M=1,L
28 AM(M)=AREA*3.7214/VM(M)
WRITE(3,11)
11 FORMAT(/,32X8HMAX.P/PO,7X1HC,11X2HVM,8X14HMOLECULAR AREA,/)
WRITE(3,12)(RPM(M),C(M),VM(M),AM(M),M=1,L)
12 FORMAT(/,33XF6.3,F11.2,F13.3,F17.3)
29 CALL EXIT
END

```

3. Calculation of Pore Size Distribution

```

DIMENSION VOLD(50),T(50),X1(50),X2(50),X3(50),A(50),A1(50),
LA3(50),R1(50),R3(50),RKX(50),RDX1(50),RDX3(50),RDXM(50),
2RN(50),RN1(50),DVGAS(50),DVLIQ(50),V1(50),V2(50),C(50),
3SACUM(50),VPORE(50),SPORE(50),DVDD(50)
READ(2,1)M,NSP,XA,XB,XC
1 FORMAT(I2,3XI1,3F7.2)
READ(2,2)(VOLD(J),J=1,M)
READ(2,3)(T(J),J=1,M)
2 FORMAT(8F10.1)
3 FORMAT(8F10.2)
IF(NSP-1)5,5,7
5 WRITE(3,6)
6 FORMAT(1H1,/,10X64HCALCULATION OF PORE SIZE DISTRIBUTION
1ASSUMING CYLINDRICAL PORES)
GO TO 9
7 WRITE(3,8)
8 FORMAT(1H1,/,10X64HCALCULATION OF PORE SIZE DISTRIBUTION
1ASSUMING SLIT SHAPED PORES)

```

```

9 MSUM=M-1
  SA=0.0
  C(1)=0.0
  DO 10 J=1,MSUM
    XA=XA-0.02
    X1(J)=XA
    XB=XB-0.02
    X2(J)=XB
    XC=XC-0.02
    X3(J)=XC
    A(J)=ALOG(X2(J))/2.303
    RKX(J)=-4.05/A(J)
    A1(J)=ALOG(X1(J))/2.303
    R1(J)=-4.05/A1(J)
    A3(J)=ALOG(X3(J))/2.303
    R3(J)=-4.05/A3(J)
    J1=J+1
    DVGAS(J)=VOLD(J)-VOLD(J1)
    DVLIQ(J)=DVGAS(J)*34.68/22400.0
    IF(NSP-1)11,11,12
11 RDX1(J)=R1(J)+T(J)
    RDX3(J)=R3(J)+T(J1)
    RDXM(J)=RKX(J)+(T(J)+T(J1))/2.0
    RN(J)=RDXM(J)**2/(RDXM(J)-T(J1))**2
    RN1(J)=RN(J)*(T(J)-T(J1))*1.0E-4
    C(J1)=(RDXM(J)-(T(J)+T(J1))/2.0)/RDXM(J)
    V2(J)=RN1(J)*SA*C(J)
    GO TO 13
12 RDX1(J)=R1(J)+2.0*T(J)
    RDX3(J)=R3(J)+2.0*T(J1)
    RDXM(J)=RKX(J)+T(J)+T(J1)
    RN(J)=RDXM(J)/(RDXM(J)-2.0*T(J1))
    RN1(J)=RN(J)*(T(J)-T(J1))*1.0E-4
    V2(J)=RN1(J)*SA
13 V1(J)=RN(J)*DVLIQ(J)
    VPORE(J)=V1(J)-V2(J)
    DVDD(J)=VPORE(J)/(RDX1(J)-RDX3(J))
    SPORE(J)=2.0E+4*VPORE(J)/RDXM(J)
    SACUM(J)=SA+SPORE(J)
    SA=SACUM(J)
10 CONTINUE
14 FORMAT(/,5X4HVOLD,8X1HT,9X2HX1,8X2HX2,8X2HX3,7X1HA,10X3HRKX,
  16X4HRDXM,6X2HRN,14X3HRN1,/)
15 FORMAT(/,5X5HDVGAS,8X5HDVLIQ,11X2HV1,13X2HV2,12X5HVPORE'
  16X5HSPORE,5X5HSACUM,5X4HRDXM,11X4HDVDD,/)
16 FORMAT(F10.1,4F10.2,F10.4,2F10.3,F10.4,E20.5)
17 FORMAT(F10.2,F15.6,3F15.8,3F10.3,F15.7)
  WRITE(3,14)
  WRITE(3,16) (VOLD(J),T(J),X1(J),X2(J),X3(J),A(J),RKX(J),
1RDXM(J),RN(J),RN1(J),J=1,MSUM)
  WRITE(3,15)
  WRITE(3,17) (DVGAS(J),DVLIQ(J),V1(J),V2(J),VPORE(J),SPORE(J),
1SACUM(J),RDXM(J),DVDD(J),J=1,MSUM)
  CALL EXIT
  END

```

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ABSTRACT

The adsorption characteristics at alumina-silica-solution interfaces have been studied for solutions consisting of phenol dissolved in different solvents and for a series of p-substituted phenols dissolved in benzene.

Characterisation of the adsorbent surfaces has been attempted by low temperature nitrogen adsorption, vapour phase adsorption of benzene and dehydration experiments. Molecular area requirements of the adsorptives have been determined from the adsorption isotherms and these indicate that the phenols are perpendicularly orientated to the adsorbent surfaces.

By application of a thermodynamic equation derived by Everett on the basis of an ideal adsorption system, the adsorption affinities of the phenols for the silica surface have been calculated and are found to be related, on the one hand, logarithmically to the Hammett p-substituent parameter and on the other, to the solvent parameter E_T when considering the adsorption of phenol itself. The virtual independence of the affinity of the p-substituted phenols for alumina has been attributed to the much stronger bonding of the phenols to the alumina surface than to the silica surface. Calculation of surface area values from Everett's equation using the experimentally determined molecular area requirements have shown that deviations from ideality arise principally from interactions in the adsorbed phase.

Hydrogen bonding in the solution phase has been studied for phenol bonding to ether and alcohol type donors in non polar solvents. The

logarithm of the association constant has been correlated with the solvent parameter E_T , the change in standard free energy on association, $(-\Delta G^\ominus)$, increasing with increase in donor reactivity. The enthalpy change on association, $\Delta H^\ominus$, has been determined from the temperature coefficient of the association constant and found to be virtually constant for the complexes studied. Variations in $\Delta G^\ominus$ have been considered to arise principally from changes in the negative entropy of association, $(-\Delta S^\ominus)$, which increase as the steric complexity of the donor molecule increases, this trend being as predicted theoretically.