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ADSORPTION ON HOMOGENEOUS SURFACE

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Abstract. Piezogravimetric method has been used to study the adsorption of H_2O, CH_3OH, C_2H_5OH, n-C_3H_7OH and n-C_4H_9OH on polished quartz crystal surface, at 26.7°C. The isotherms of type II, tending to meet the saturation pressure line. The BET equation was found to be valid up to $p/p^o = 0.4$. The values of the molecular cross-sectional areas of the alcohols showed a horizontal orientation on the quartz crystal surface.

The BET equation,[1] generally used for the estimation of surface areas of adsorbents, from vapour adsorption, dates from 1938 and it succeeded the 'Point B' method[2] which constitutes an alternative method for the measurement of volume or mass adsorbed. Its one of the important aspects is that in order to arrive at a simple analytical expression its authors assumed the surface to be homogeneous (alongwith a few other assumptions) which is rarely the case in practice. After severe simplifications, it is put in the form :

$$\frac{p}{v(p^o-p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \cdot \frac{p}{p^o} \tag{1}$$

such that by plotting the left hand side against p/p^o, v_m and c can be obtained. Applying equation (1) to experimental data, it appears that linearity, in general, holds only over the range $0.05 \leq p/p^o \leq 0.30$, although in some cases, it persists up to a relative pressure of 0.40.

A consequence of the limited range of validity of equation (1) is that the BET theory understimates the extent of adsorption at very low pressures, and is an overestimate at high relative pressures. The various objections which have been raised to the theory tend to be focussed upon these regions. The objections, and proposed modifications to the equation may be found elsewhere.[3] Here, attention is confined to one particular aspect. Whatever the faults of the theory, it does imply that the extent of adsorption tends towards infinity as p/p^o approaches 1; this is in accordance with many experimental studies which are said to display isotherms of type II. The measurement of the extent of adsorption at high relative pressures is, however, experimentally difficult and the region has received much less attention than the low pressure region which leads to the formation of a monolayer. Yet, grounds for supposing that the extent of adsorption at p/p^o is sometimes finite, have been published.[4–7]

With these views in mind, Brunauer and his coworkers[8] published a modification of the BET theory to account for finite adsorption at saturation in which they introduced a number k which describes the strength of the attractive force field of the adsorbent, and so varies from one adsorbent to another. In fact, as k decreases, the value of v_m increases, other forces being equal; thus the surface area calculated by means of the new BET equation should be larger. However, due to the practical difficulties in the application of the new BET equation, preference is given to the older, and widely tested, approach, although the isotherms obtained in the present studies tend to intersect the p^o line.

Experimental

The core feature of the piezogravimetric method is that a suitably chosen quartz crystal, capable of resonating at its characteristic frequency between two exciting electrodes, be coupled with an ancillary device for measuring frequency shifts at various pressures of the adsorbate vapour, at equilibrium with the adsorbent phase, in an accurately temperature-controlled cell. The experimental system alongwith the details of the experimental cell and quartz crystal mounting assembly have been described, in detail, elsewhere.[9]

As usual, the cell, stainless steel components and the assembly were cleaned with a mixture of chromic acid–sulphuric acid followed by repeated rinsing with triply distilled water. Before taking observations, the cell with crystal assembly, was heated at 240°C and the vacuum line was thoroughly baked at 80°C for about 48 hr.

The experimental system was placed in an air-thermostat and evacuated for a period of about 24 hr, till the resonant frequency was stable. At each run the vapour was introduced gradually by increasing the pressure in small steps. Following the introduction of vapour the frequency was monitored as a function of time until the equilibrium has been attained. After the determination of a particular isotherm, the system was out-gassed till a stable value for the resonant frequency was obtained again.

The quartz crystal used was AT-cut, and highly polished with an apparent (geometric) available area of 3.088 cm^2, and a mass of 0.0654 g. The adsorption of the adsorbates was studied on this surface.

Results and Discussions

The total surface area of the quartz crystal was calculated from argon adsorption, at liquid nitrogen temperature, and was found to be approximately 7.8 cm^2 (rugosity being about 2.5).

Figure 1 shows the adsorption curves of various adsorbates on the surfaces of the quartz crystal. Due to some limitations on the precision of experimental method at very low pressures, comparatively

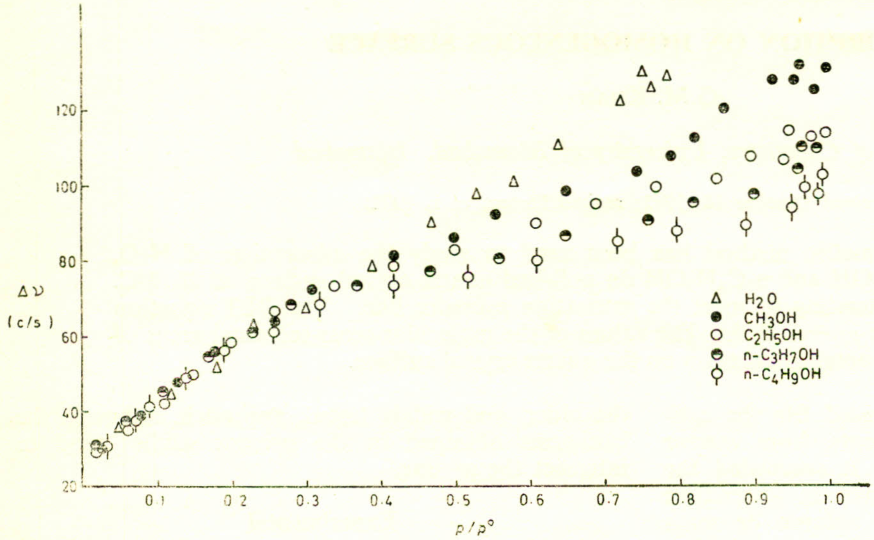

Fig. 1. Adsorption of water and various aliphatic alcohols on quartz crystal surface at 26·7°C.

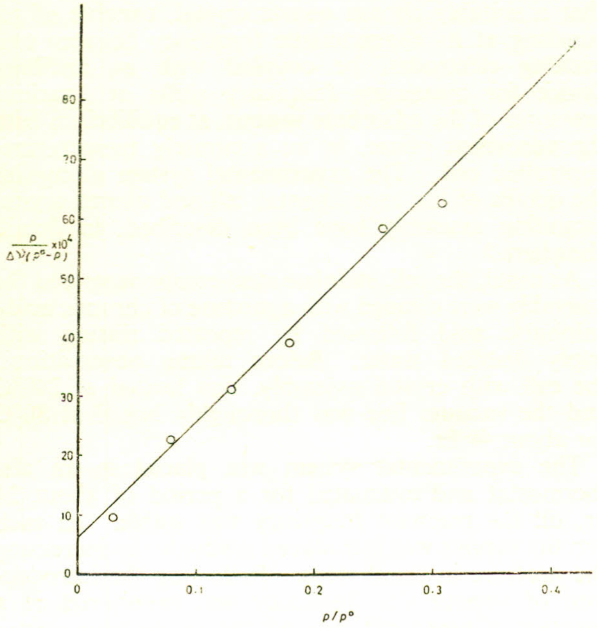

Fig. 2. BET plot for CH_3OH on quartz crystal at 26·7°C.

few observations could be taken in this region. Difficulties were also experienced at high relative pressures but an approximate path of the curve can easily be visualized. The adsorption isotherms are of type II and tend to approach the saturation pressure line.

One of the conditions for the determination of the monolayer capacity of a massive plane solid from an adsorption isotherm is that the isotherm shall have a sharp knee. With an isotherm of this kind, it is possible to evaluate the monolayer capacity, with fair accuracy, with the aid of a BET plot or merely by reading off the adsorption at point B.

In the present case, the monolayer capacities were calculated by using BET equation which was found to be valid up to $p/p^\circ \simeq 0.4$ (Fig. 2). These values of the monolayer capacities were used to determine the cross-sectional areas of the adsorbates, employing the following equation:

TABLE 1. THE CALCULATED CROSS-SECTIONAL AREAS OF THE ADSORBATES.

Adsorbate	H_2O	CH_3OH	C_2H_5OH	n–C_3H_7OH	n–C_4H_9OH
Cross-sectional Area (Å)	7·2	13·1	18·8	24·6	30·0

$$A = \frac{Mc}{M_w} NA \cdot A_m \cdot 10^{-16} \qquad (2)$$

Where A, the actual area (cm^2); A_m, the cross-sectional area of the adsorbed molecule ($Å^2$); Mc, the monolayer capacity; M_w the mol wt of the adsorbate; and N_A is the Avogadro's number.

The calculated cross-sectional areas (Table 1) indicate that the molecules of the adsorbates are not necessarily arranged vertically on the quartz crystal surface, with their polar end groups attached to the quartz surface. There is almost a constant difference of about 6 $Å^2$ in the calculated cross-sectional areas and it seems probable that the molecules are closely packed, oriented on the surface horizontally, and are localized due to very strong attraction by the quartz surface; the finite extent of adsorption to less than three monolayers strongly supports this idea.

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