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ADSORPTION OF ARGON AND n-ALKANES ON MASSIVE SOLID SURFACES

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Abstract. Piezogravimetric method has been used to study the adsorption of n-hexane on quartz crystal surface and of argon, n-hexane, n-heptane and n-octane on silaned-quartz crystal surface, at 26.7°C. All the isotherms are of type II, indicating multilayer adsorption, while small extrapolations in some cases indicate that the physical adsorption at high pressures is not necessarily infinite. The values for the surface area of the silaned-quartz surface and the cross-sectional areas of n-alkanes used have been calculated and compared with the values found in the literature.

The adsorption data obtained on powders or highly porous adsorbents of high surface area are complicated by the surface heterogeneity effects and the capillary and intergranular condensation and adsorption in pores causing hysteresis. To minimize these effects the use of polished ordered and homogeneous crystalline solids free from pores and crevices seems very promising. However, adsorption studies on such surfaces do not only allow a definite interpretation of the data, but also, when compared with the data obtained on powders, throw light on the surface heterogeneity. It is important, therefore, to employ adsorbents of homogeneous surfaces which will provide reproducible results.

Low-energy carbon surfaces have enjoyed widespread popularity as substrates for studies of adsorption of n-alkanes. Graphite, graphitized carbon black and Graphon offer good examples of such surface. A vast technical literature exists which illustrates the low-energy character and the homogeneity of these surfaces but the usual large surface areas employed have often interfered with the drawing of fundamental inferences from the experimental results. Even such a basic quantity as surface area of the adsorbent frequently remains indeterminate, and the measured quantities are usually relative. In this connection, the crystal surfaces seem to be promising since they can be regarded to be nearly homogeneous and well-ordered without surface imperfections, allowing more accurate treatment of the data in terms of microscopic models.

Using modified quartz crystal surface, the adsorption of argon at liquid-nitrogen temperature has been investigated; because of its inert character and its wide use for the determination of surface area. The use of nitrogen has been avoided in the present studies because of its strong polar interaction with certain adsorbents.^{1,2} Also, isotherms of n-hexane

on quartz crystal surface and n-hexane, n-heptane and n-octane on modified quartz surface have been obtained.

The BET equation has been widely used for the estimation of monolayer capacities and, hence, the determination of the surface area of the adsorbents. The use of the equation, however, is not without difficulty because of small range of pressures over which it is valid.³ Thus, a procedure termed the point B method has been used for the estimation of monolayer capacities.

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 vacuum system and circuits used in this work have been described, in detail, elsewhere.⁴ However, for convenience, Fig. 1 is given here which shows the details of the experimental cell and the quartz crystal mounting assembly.

Before use, the cell, stainless steel components and the crystal assembly were treated with chromic acid-sulphuric acid mixture followed by repeated rinsing with triply distilled water. Prior to each set of 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 crystal assembly mounted in the experimental cell and connected to the oscillator was placed in the air-stirred constant temperature thermostat and the whole system was evacuated for a period of about 24 hr, till the system attained a full stability shown by a constant value of the resonant frequency. As the temperature of the adsorbate vapour differed from

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that of the quartz surface, the former was preheated in a preliminary thermostating compartment before admitting it into the cell. 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 over a period of about 30 min for each run until the equilibrium has been attained. After the determination of a particular isotherm, the system was outgassed till a stable value for the resonant frequency was obtained again.

Special attention was paid to the purity of the adsorbate samples of n-alkanes which were provided by Matheson Coleman and Bell Co. listed as being of chromatquality (99.5% purity). They were passed through molecular sieve and then degassed by trap-to-trap distillation. Dichlorodimethylsilane, which was adsorbed on quartz crystal to produce silanated surface, was kindly provided by Dr. A.C. Lowe.⁵ It had been purified by trap-to-trap distillation under grease-free conditions. Argon, showing no detectable impurity by mass spectrometer, was

purchased from Matheson Co.

Two AT-cut crystals, A and B have been used during these studies. Each had an apparent (geometric) available area of 3.088 cm² and a mass of 0.0654 g. Crystal A was used as such but crystal B was coated with (CH₃)₂SiCl₂ by exposure to the vapour at 240°C for approximately 8 hr, and named surface 'BS2HA'. The term 'S2' is simply a convenient notation for dichlorodimethylsilane and the first letter stands for the designation of the crystal. The adsorption of the adsorbates was studied on these surfaces.

Results and Discussion

Figure 2 shows the adsorption and desorption of n-hexane on polished quartz surface. It has been displayed to show the reproducibility of the observations and for general comparison.

The Experimental n-Alkane Isotherms. The limitations on the precision of the experimental method placed a lower limit upon the actual pressure which could be studied. As a result comparatively few observations could be taken at relative pressures in the region leading up to monolayer formation. Difficulties were sometimes experienced at high relative pressures, when the marked extent of adsorption tended to lead to 'blacking out, i.e. to cessation of crystal vibration. A number of general points may be summarized as follows:

(i) The adsorption isotherms for both surfaces are of type II. They are reasonably reproducible,

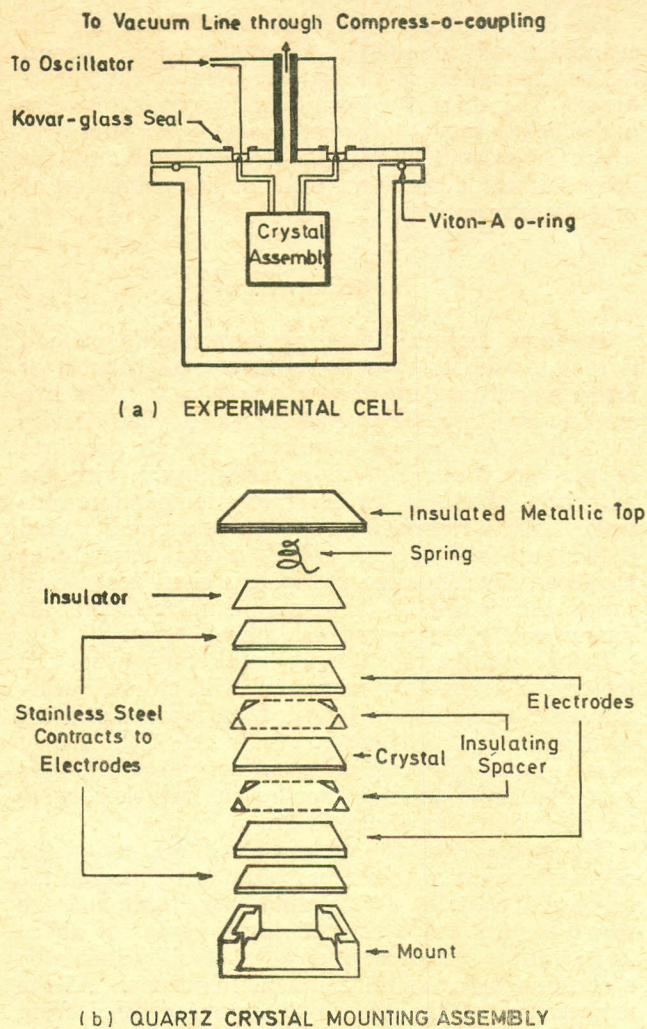


Fig. 1

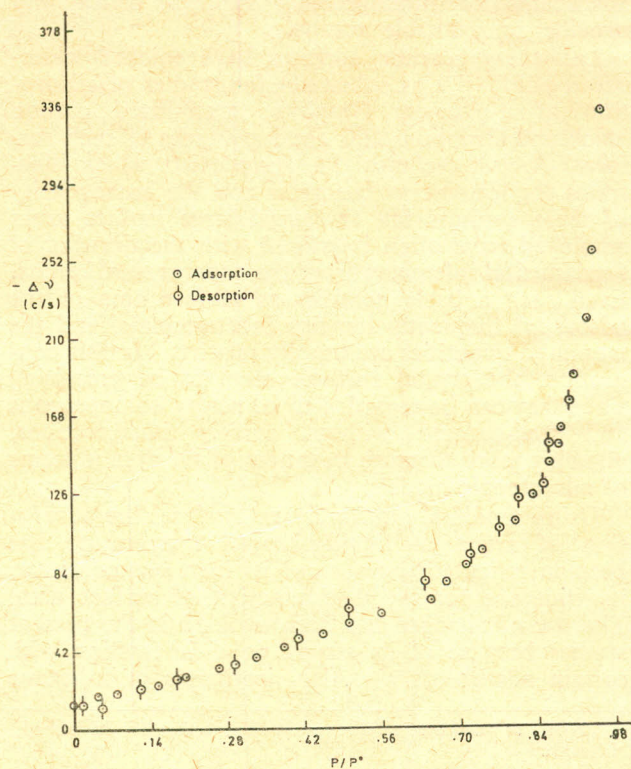


Fig. 2. Adsorption and desorption of n-Hexane on surface 'A'.

particularly at the lower temperature (see Fig. 2), and display negligible hysteresis.

(ii) As expected, the extent of physical adsorption of n-hexane on quartz surface is considerably greater than that on silanated surface (Table 1).

(iii) The extent of physical adsorption decreases on silanated surface at fixed temperature and relative pressure as the molecular weight of the adsorbate is raised.

One special point should be noted. In some cases, the relative pressure was raised to unity by increasing the temperature of the liquid adsorbate sample above that of the experimental cell. Experimental observations could then sometimes be taken, although the values assigned both to v and to P/P_0 are much less reliable. The interesting feature is that these observations lend considerable support to the view that the extent of physical adsorption at $P/P_0 = 1$ is not necessarily infinite⁶ (Fig. 5).

Argon Adsorption. The adsorption of argon upon the silanated quartz surface was measured at liquid nitrogen temperature. The observed results are shown by the isotherm (Fig. 6).

TABLE 1. COMPARISON OF THE EXTENT OF PHYSICAL ADSORPTION OF n-HEXANE ON SURFACES 'A' AND 'BS2HA'.

P/P_0	$-\Delta v$ for surface 'A' (c/s)	$-\Delta v$ for surface 'BS2HA' (c/s)
0.01	20.0	8.2
0.14	25.2	13.6
0.21	28.5	18.3
0.28	33.6	23.7
0.35	40.0	29.1
0.42	46.5	36.0
0.49	52.6	42.8
0.56	63.0	51.0
0.63	72.0	60.0
0.70	84.0	72.0
0.77	102.8	84.0
0.84	127.6	108.0
0.91	189.0	140.0
0.98	—	186.0

TABLE 2. COMPARAISON OF THE EXTENT OF PHYSICAL ADSORPTION OF n-ALKANES ON SURFACE 'BS2HA'.

P/P_0	$-\Delta v$ or n-Hexane (c/s)	$-\Delta v$ for n-Octane (c/s)	$-\Delta v$ for n-Octane (c/s)
0.14	13.6	11.4	10.8
0.28	23.7	20.2	18.7
0.42	36.0	30.6	29.9
0.56	51.0	42.3	42.0
0.70	72.0	70.0	60.1
0.84	108.0	118.0	88.2
0.98	186.0	174.0	162.0

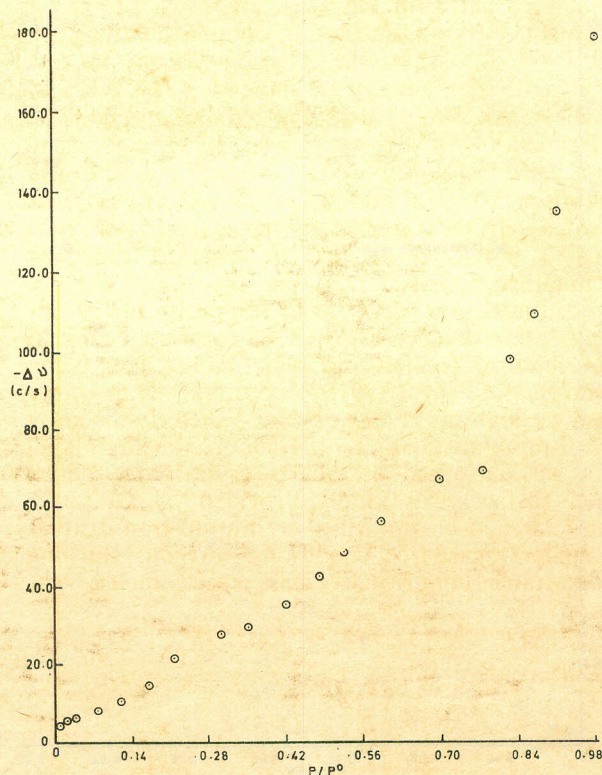


Fig. 3. Adsorption of n-Hexene on surface 'BS 2 HA' at 26.7°C

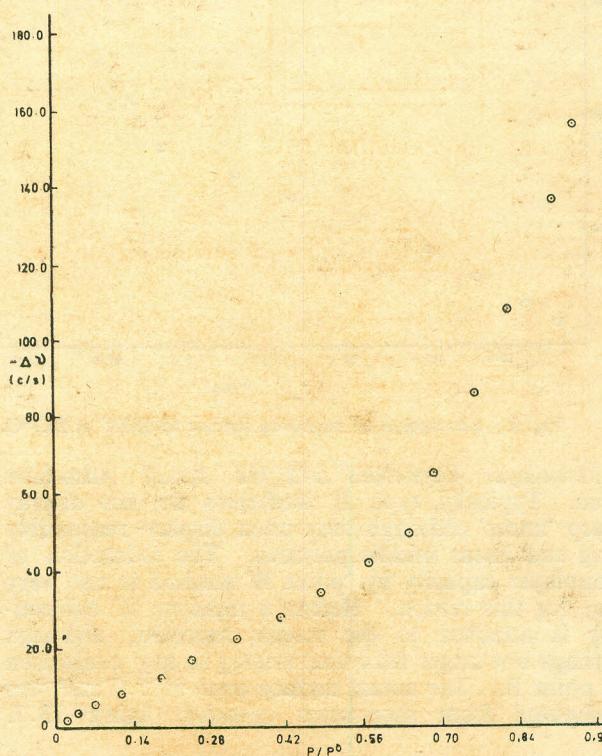


Fig. 4. Adsorption of n-Heptane on surface 'BS2HA' at 26.7°C

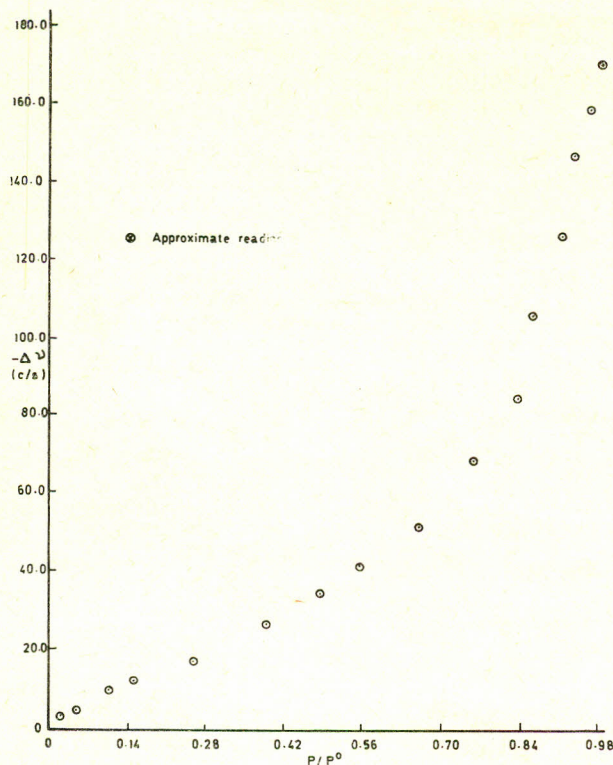


Fig. 5. Adsorption of n-Octane on surface 'BS2HA' at 26.7°C.

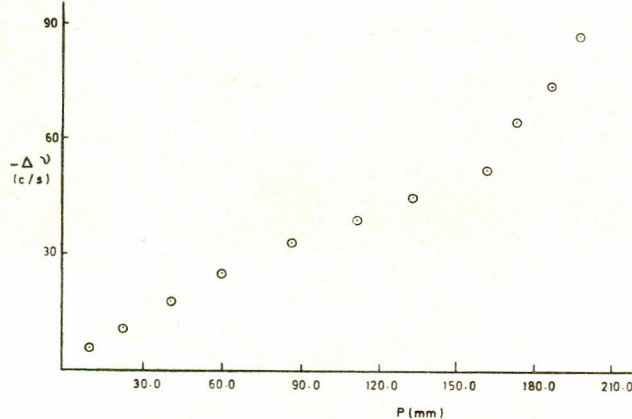


Fig. 6. Adsorption of argon on surface 'BS2HA' at 26.7°C.

Monolayer Capacities and the Actual Adsorbent Area. Typically, type II isotherms do not display sharp 'knees' although they often display reasonably long and linear middle portions. The estimation of monolayer capacity by 'point B' method is not very easy for this reason. Hence, a measure of subjectivity is attached to the results reported, although perhaps not larger than that arising in any evaluation of point B. The actual surface area of 5.9 cm² was computed from monolayer capacity, using 13.7 Å² for argon cross-sectional area, employing the following equation.

TABLE 3. CALCULATED ADSORBENT AREA, A , AND COMPARISON OF CALCULATED CROSS-SECTIONAL AREAS, A_m , OF VARIOUS ADSORBATES WITH THOSE FROM LITERATURE.

n-Alkane	A_m used for calculations (Å ²)	Calculated area, A (cm ²)	A_m (Å ²) from Kiselev and others a, b	A (Å ²) calculated
n-Butane	—	—	39.5 ^a , 40.8 ^b	—
n-Pentane	—	—	45	—
n-Hexane	51.5	6.0	51.5, 51.0	53.4
n-Heptane	57.3	5.8	57.3	58.0
n-Octane	61.0	5.3	61.0, 71.5 ^a	62.4
Argon	13.7	5.9	—	—

^a Ref. 8; ^b Ref. 9.

$$A = \frac{m_c}{M_w} N_A \cdot A_m \cdot 10^{-16}$$

where A is the actual area (cm²), A_m is the cross-sectional area of the adsorbed molecule (Å²), m_c is the monolayer capacity, M_w is the molecular weight of the adsorbate, and N_A is Avogadro's number.

The calculated adsorbent areas based upon Kiselev's⁷ suggested adsorbate cross-sectional areas (Table 3) are sufficiently consistent as to suggest that the general approach cannot be seriously in error, and that the average values are of the right order of magnitude. Although the procedure is at least to some extent cyclic (adsorbate areas, estimated in various ways, are used to determine the real areas of adsorbents), the chief check is the constancy in the areas so calculated. Table 3 shows the back-calculated cross-sectional areas of the adsorbates together with the corresponding values reported in the literature.^{8,9} These back-calculated values are quite consistent, display a more regular increment per —CH₂ group than those of Kiselev, and indicate that the adsorbed n-alkane molecules in the first layer must lie parallel to the adsorbent surface in close-packed regular array.

One more point, improved determination of the primary interactions in the first adsorbed layer, and estimation of adsorbent surface area, can be expected when increasing emphasis is laid upon plane, massive surface with rugosities close to unity.

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