Multilayer adsorption of nitrogen and alkanes by non-porous carbons and silicas

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Abstract – Multilayer adsorption isotherms of nitrogen (at 77K), isobutane (at 261K) and neopentane (2,2-dimethylpropane, at 273K) have been determined on a number of non-porous carbons and silicas. The results serve to strengthen the view that the structure of the adsorbent surface has very little effect on the development of the nitrogen multilayer. The adsorbent structure has a greater effect on the course of the isobutane and neopentane isotherms, but when plotted on a reduced basis the corresponding isotherms for carbon and silica do appear to coincide at $p/p^o > 0.6$ and $\theta > 2$. All the isotherms give linear FHH plots over a wide range of multilayer coverage.

INTRODUCTION

It was over thirty years ago that Kiselev first drew attention to the importance of expressing standard physisorption data in the form of amount adsorbed per unit surface area (ref. 1). In this manner it was demonstrated by Kiselev and his co-workers (refs. 2,3,4) that the shape of a physisorption isotherm is dependent on both the nature of the gas/solid system and the porosity of the solid. The approach led also to a systematic study of adsorbent-adsorbate interactions (refs. 5-7) and to the Kiselev classification of adsorption systems (ref. 8).

Whilst these developments were taking place in the USSR, other attempts were being made in Europe and the USA to determine standard adsorption isotherm data on well-defined surfaces. Much of this early work (refs. 9,10) was designed to provide a standard multilayer thickness curve which was required for the computation of pore size distribution. Interest was further stimulated by the introduction of the t-method (ref. 11) and other related empirical procedures for isotherm analysis (ref. 12).

Although it was soon appreciated that the original concept of a "universal" nitrogen isotherm (refs. 13,14) could not apply to the monolayer region (ref. 12) it was more difficult to establish the extent to which the multilayer isotherm is dependent on the surface structure. A long-standing problem has been the difficulty in finding acceptable non-porous reference materials (ref. 15), i.e. finely divided solids having reproducible and stable surface properties.

Various semi-empirical equations have been proposed to account for multilayer adsorption (refs. 16,17), but the underlying theoretical principles are still far from clear. In recent years particular attention has been given to the Frenkel-Halsey-Hill (FHH) equation (refs. 18,19)

$$\ln(p^o/p) = k \, \theta^r \tag{1}$$

in which θ is the number of layers (or surface coverage) at relative pressure p/p^o, and k and r are empirical constants. In the derivation of the FHH equation it is assumed that the adsorbed multilayer has the properties of a slab of liquid. If the adsorption forces are non-specific and the distance from the surface large enough, the value of r should be 3 (i.e. the Hill equation (ref. 19)). In fact, nearly all the apparently non-porous adsorbents studied so far (refs. 16,21-28) have been found to give lower values of r (e.g. in the case of nitrogen adsorption on silicas (ref. 23) $r = 2.65-2.75$). There is some indication (ref. 26) that the r value for nitrogen remains almost constant irrespective of the nature of the surface, but more work is required to confirm these few results.

The limited amount of evidence available (refs. 26-28) suggests that although the FHH equation can be applied to adsorption isotherms of other vapours the value of r will depend on the nature of the surface. However, because of the paucity of standard adsorption data for other adsorptives (ref. 26) the full scope of the FHH equation has yet to be established.

NON-POROUS ADSORBENTS

The new results presented here have been obtained with well-characterised carbons and silicas which have been used in previous adsorption studies (refs. 23,26,29,30). Particular care has been taken to select only those adsorbents which are believed to by truly non-porous, i.e. solids which have not exhibited any detectable microporosity or mesoporosity as revealed by inspection of the nitrogen isotherms and the corresponding α_s plots (refs. 12,15). It has been found essential to recheck the porosity of each sample after storage because of the tendency of all these finely divided materials to undergo slow ageing and compaction with the consequential development of porosity. These changes are usually manifested in the form of interparticle capillary condensation, which is associated with a distortion of isotherm shape in the multilayer range - with little or no observable hysteresis (ref. 15).

TABLE 1. Surface areas and porosity of silica and carbon samples[a].

SILICA	A_{BET} m^2g^{-1}	A_s m^2g^{-1}	POROSITY	CARBON	A_{BET} m^2g^{-1}	A_s m^2g^{-1}	POROSITY
Arc				Non-Graphitised			
Fransil	36		NP	Sooty Silica	84		NP
TK800	158	158	NP	Elftex 120	37	37	NP
TK900	136	135	NP	Vulcan 3	84	84	meso
Fume				Spheron 6	123	104	micro
Aerosil 200	192	192	NP	Graphitised			
Aerosil 300	313	318	meso	Vulcan 3G	70	86	NP
Precipitated				Sterling FT	10.3	12.4	NP
HiSil 233	131	123	micro	Graphon	91	103	NP
VN3	178	122	micro				

[a] NP = non-porous. micro = microporous. meso = mesoporous.

Some of the adsorbents considered are indicated in Table 1, where the BET areas and α_s areas (A_{BET} and A_s, respectively) are recorded along with an assessment of the texture. It can be seen that, in general, arc silicas and well graphitised carbons are the most suitable materials for study. Precipitated silicas (refs. 31,32), and also certain grades of Aerosil (ref. 29), tend to be microporous and/or mesoporous and are therefore not recommended.

The adsorption data obtained on the samples of alumina, chromia and titania have been taken from previous publications (refs. 33,34).

STANDARD ISOTHERMS

In order to compare the shapes of adsorption isotherms determined on non-porous adsorbents of different surface area it is expedient to express the amounts adsorbed in a reduced form. The normal procedure is to plot the amount adsorbed per unit area (i.e. following Kiselev, as μmol m^{-2}) against p/p^o. Typical results for the adsorption of nitrogen and argon at 77K are shown in Fig. 1. It is evident that the nitrogen isotherms on the non-porous forms of silica, alumina, chromia and titania are all virtually identical in shape and location, whereas the corresponding argon isotherms are not in such close agreement. These differences are consistent with earlier findings concerning argon adsorption and confirm that it is generally safer to use nitrogen for the routine determination of surface area and pore size distribution (ref. 12).

An alternative way of plotting the isotherm in a reduced form is to express the adsorption as a dimensionless quantity, e.g. $n/n_{0.4}$, where $n_{0.4}$ is the amount adsorbed at $p/p^o = 0.4$. This procedure has the advantage of making the reduced uptake independent of the BET method (which is invariably used to calculate the monolayer capacity, n_m). This is particularly important when considering the shape of nitrogen isotherms determined on adsorbents, such as high temperature aluminas and graphitised carbons, on which localisation of nitrogen molecules in the monolayer region of the isotherm is believed to occur (refs. 34,35). With these adsorbents it is found that, when reduced to unit surface area or plotted in the form n/n_m, nitrogen isotherms show significant deviations in both the multilayer and monolayer regions from the isotherms in Fig. 1 (ref. 36). However, if the amounts adsorbed are expressed in the reduced $n/n_{0.4}$ form good agreement is obtained in the multilayer region of the isotherm. This is illustrated by the results in Fig. 2 for nitrogen isotherms determined in various laboratories on a range of non-porous carbons (refs. 36-40). It is evident that differences

in the degree of graphitisation have a significant effect on the isotherm shape at low pressures but that the multilayer region is affected to a much lesser extent.
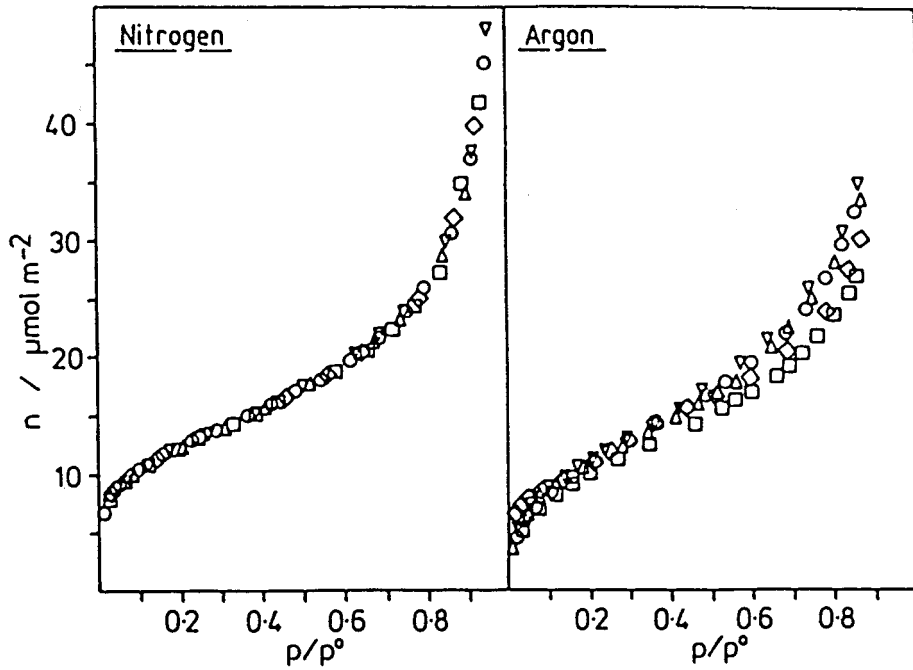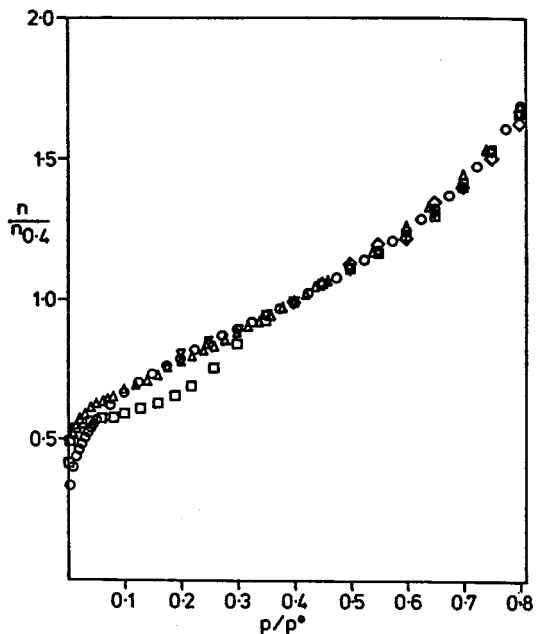

Fig. 1. Reduced nitrogen and argon isotherms.
   O TK800 (ref. 29)   □ Fransil (ref. 29)   △ Alumina (ref. 34)
   ◇α-chromia (ref. 33)   ▽ Anatase (ref.23)

Fig. 2. Standard nitrogen isotherms for carbon.
   O Brunel (ref. 26)
   □ Kiselev (ref. 40)
   ◇ Dubinin (ref. 37)
   ▽ Pierce (ref. 38)
   △ Rodriguez-Reinoso (ref. 36)

A similar picture emerges when isotherms of other vapours are compared. The results in Figs. 3 and 4 illustrate the influence of surface structure on the shape of isotherms of hydrocarbon vapours. In the case of both isobutane and neopentane (2,2-dimethylpropane) the knee of the isotherm is much sharper with the high energy carbon surface than with the silica surface. However, at higher pressures there is much less difference between the corresponding isotherms.
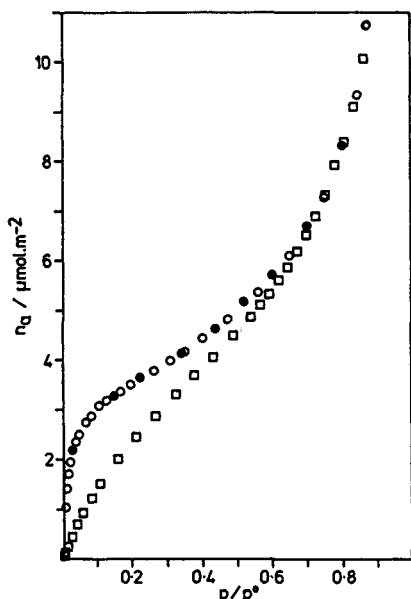
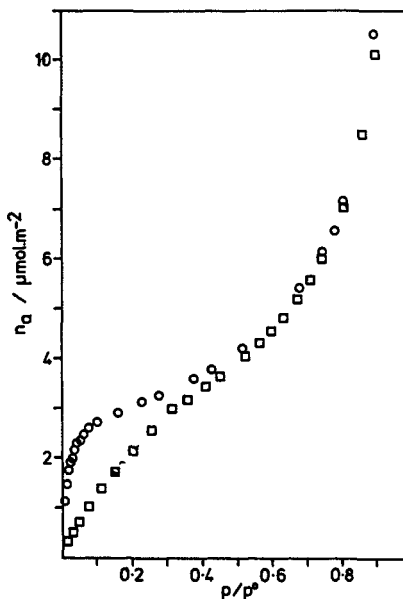Fig. 3.   Isobutane isotherms.   O Elftex   □ TK800

Fig. 4.   Neopentane isotherms

THE FHH EQUATION

FHH plots corresponding to the nitrogen isotherms in Fig. 2 are given in Fig. 5. It can be seen that over the range of pressures from $0.4p^o$ to $0.8p^o$ the plots are linear. Furthermore, extrapolation of the linear region to high pressures gives good agreement with the experimental data of Kiselev (ref. 40), Pierce (ref. 38) and ourselves (ref. 39). Similar results have also been obtained for the adsorption of nitrogen by non-porous silicas and other oxides (refs. 23-25). In this case the linear region of the FHH plot frequently extends to pressures much greater than $0.8p^o$. Where deviations from linearity are found, they generally occur in a positive direction (i.e. the uptake is greater than predicted by extrapolation of the FHH equation) and are often associated with the presence of a capillary condensation hysteresis loop at high pressures. In view of this it is surprising that negative deviations are observed in Fig. 5. More work is required in order to confirm and explain this behaviour.
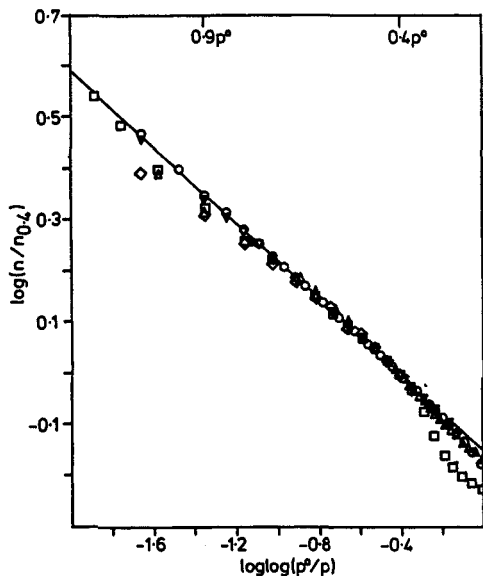

Fig. 5.   FHH plots for nitrogen on carbon.
O Brunel (ref. 26)   ◇ Dubinin (ref. 37)
□ Kiselev (ref. 40)   ▽ Pierce (ref. 38)
        △ Rodriguez-Reinoso (ref. 36)

TABLE 2.   FHH r values.

Adsorptive	N_2	C_3H_8	$i-C_4H_{10}$	$neo-C_5H_{12}$
Temperature	77K	196K	261K	273K
Graphitised C	2.70	2.55	2.34	2.21
Ungraphitised C	2.70	2.50	2.25	2.17
Silica	2.70	–	2.00	2.00
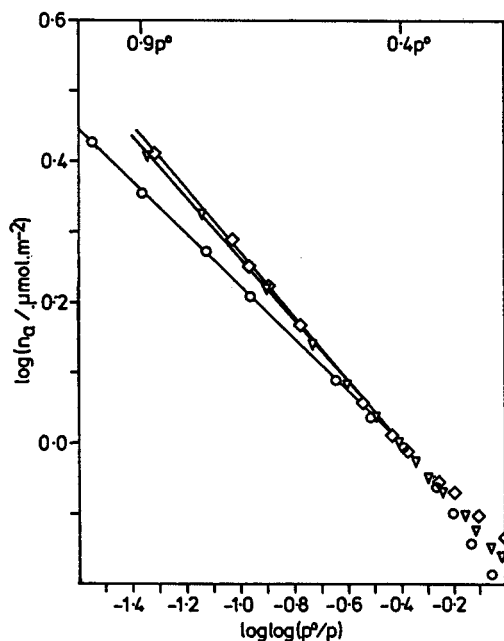
Fig. 6. FHH plots for Elftex

Fig. 7. FHH plots for TK800

O Nitrogen ▽ Isobutane ◇ Neopentane
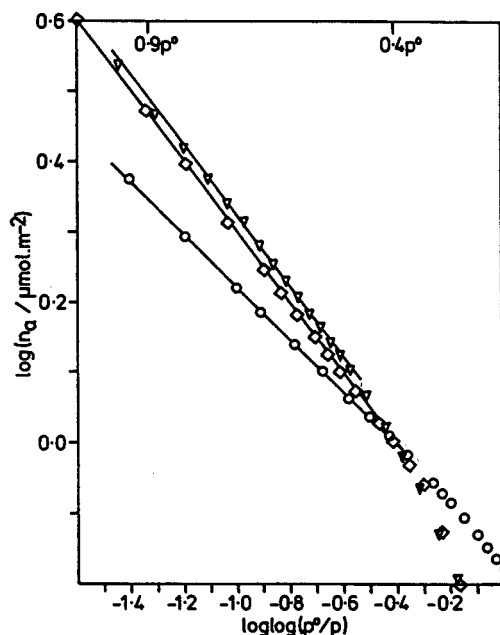
Most workers have found that the value of r for nitrogen adsorption by non-porous carbons and oxides is ca. 2.7 (refs. 23-25,38). The presence of even a relatively small amount of microporosity will increase the r value without affecting the range of linearity of the plot (ref. 23). Capillary condensation, on the other hand, decreases the r value and also restricts the range of linearity (ref. 23). It is important to appreciate that the shape of the isotherm in the multilayer region may be distorted by capillary condensation even if the hysteresis loop closes at a high pressure (ref. 24) and it is possible that reduction in the r value could provide a sensitive test to detect the occurrence of reversible capillary condensation (ref. 12).

FHH plots for the adsorption of nitrogen, isobutane and neopentane by samples of non-porous carbon and silica are given in Fig. 6 and Fig. 7. It can be seen that although the plots are linear over wide ranges of pressure there are significant differences in the slope for each adsorptive. Table 2 lists r values for a number of adsorptives determined on the various non-porous silicas and carbons. The values were obtained by fitting the FHH equation over the range of pressures from $0.4p^{\circ}$ (slightly higher in the case of isobutane on silica) to $0.85p^{\circ}$. It can be seen that the r value increases in the order silica (hydroxylated or dehydroxylated) < ungraphitised carbon < graphitised carbon. In other words the r value increases as the adsorbent-adsorbate is increased (refs. 22,24).

Although the r value given by a particular adsorptive appears to be dependent on the nature of the adsorbent surface, the variation is relatively small when adsorbents of just one chemical type (i.e. silica or carbon) are considered. Thus it should be possible to define standard adsorption isotherms for organic adsorptives as well as for nitrogen and to use these to analyse organic vapour isotherms by the α_s method (ref. 26). Much more work using well defined non-porous adsorbents is still required in order to establish how far this principle can be extended.

The lower limit of the linear range of most of the FHH plots in Figs. 5-7 is ca. $0.4p^{\circ}$, corresponding to a nominal surface coverage of about 1.5 layers. It is interesting to note that in his reassessment of the Harkins-Jura method Rouquerol also found that a surface coverage of about 1.5 layers was sufficient to mask the direct effects of surface heterogeneity (ref. 41). In addition, it is well known that differential enthalpies of adsorption become similar to enthalpies of condensation and that, when the liquid is adopted as the standard state, differential entropies of adsorption approach zero, at nominal surface coverages of between 1 and 2 monolayers (ref. 16). At such a low surface coverage the properties of the adsorbed film are unlikely to be exactly the same as those of the bulk fluid and the FHH equation must therefore be regarded as an essentially empirical relationship.

CONCLUSIONS

The results presented here strengthen the view that the structure of the adsorbent surface has only minimal influence on the development of the nitrogen multilayer at 77K. Thus nitrogen isotherms determined on a wide range of non-porous carbons and silicas appear to be almost coincident at $p/p^o > 0.4p^o$ and $\theta > 1.5$. Furthermore, it has been confirmed that the nitrogen FHH plots are linear over a very wide multilayer range (ca. 1.5-5 nominal layers) and that in the absence of interparticle capillary condensation $r = 2.70 \pm 0.05$.

The multilayer isotherms of propane, isobutane and neopentane have been found to be more dependent on the chemical nature of the adsorbent (i.e. carbon or silica). In these cases the range of linearity of the FHH plot is not always as extensive as that of nitrogen.

Comparison of the isotherm data with results obtained in other laboratories reveals that further work is required to establish whether there are detectable differences in form and location of nitrogen isotherms at high p/p^o. For this purpose it will be essential to give more attention to the selection of non-porous reference materials and to the conditions of outgassing and the choice of experimental technique.

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