

Test of the Nonane Method for Micropore Evaluation

Use of Nitrogen, n-Hexane and Carbon Tetrachloride as Adsorptives with Ammonium Phosphomolybdate, Phosphotungstate and Silicomolybdate as Absorbents

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Received 12th May, 1977

The adsorption isotherms of nitrogen, n-hexane and carbon tetrachloride on each of three microporous solids have been determined gravimetrically both before and after pre-adsorption of n-nonane. The solids were ammonium phosphomolybdate (APM), ammonium phosphotungstate (APT) and ammonium silicomolybdate (ASM), and a second series of experiments was carried out on compacts of the solids prepared at a pressure of 930 MN m^{-2} .

The nonane method for micropore evaluation was found to function satisfactorily when nitrogen was used for the determination of the isotherms, ASM being shown to be almost wholly microporous, APM to possess a small surface area ($\sim 4 \text{ m}^2 \text{ g}^{-1}$) and APT a considerable one ($\sim 59 \text{ m}^2 \text{ g}^{-1}$). With both APM and APT (ASM was not tested) the majority of the micropore volume survived compaction and was presumably therefore structural in nature, *i.e.*, contained within the lattice. The results obtained with hexane and carbon tetrachloride before pre-adsorption of nonane are explicable in terms of molecular sieve effects; but after pre-adsorption the uptake of both adsorptives was higher than that of nitrogen, probably because of their diffusion through the "stoppers" of nonane blocking the entrances to the micropores.

It is concluded that the applicability of the nonane method for micropore evaluation is restricted to adsorptives such as nitrogen which are used at temperatures much below ambient and which have low solubility in n-nonane.

It is now generally agreed¹ that within pores which are sufficiently narrow—micropores²—the overlap of adsorption fields from opposite walls^{3, 4} will manifest itself in enhanced adsorption at low pressures,^{5, 6} so that the isotherm becomes very steep in this region: the "knee" of the isotherm becomes sharper, and correspondingly the B.E.T. *c*-constant is much increased. The maximum value of pore width at which this micropore effect appears depends on the nature of both the adsorptive and the adsorbent, but for working purposes may be taken as 2 nm .^{2, 3, 7} The detection of micropores and the evaluation of micropore volume are matters of considerable significance in a number of contexts, including: the estimation of specific surface area by the B.E.T. method (if micropores are present the B.E.T. area will be too high),⁸ the adsorption of traces of vapour from a stream of carrier gas, as in chromatography or the removal of pollutants from air, and catalytic behaviour.

An estimate of the micropore volume may be obtained by expressing the height of the steep initial portion of the isotherm (the part preceding the knee) as a liquid volume; the estimate is inevitably crude however, since not only must the height be evaluated by mere inspection, but it contains an unknown contribution from the adsorption on the walls of the coarser pores and on the external surface. A sounder

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method, in principle, is to fill up the pores with some adsorptive which exerts a negligible pressure at the temperature of experiment;⁹ by measurement of the isotherm of, say, nitrogen, before and after the pre-adsorption, the micropore volume may be derived by subtraction. The suitability of n-nonane as pre-adsorbate, used in conjunction with nitrogen for the subsequent isotherm determination, was demonstrated by Gregg and Langford;⁸ other examples of its successful application have appeared from time to time.¹⁰⁻¹²

It was thought of interest to discover how far the nonane pre-adsorption method remains valid when adsorptives differing from nitrogen in physical characteristics, especially boiling point, are used for the determination of the isotherms. Accordingly n-hexane and carbon tetrachloride were selected as adsorptives, along with ammonium phosphomolybdate (APM), ammonium phosphotungstate (APT), and ammonium silicomolybdate (ASM) as adsorbents; from previous experience these three compounds were believed to possess considerable microporosity.^{13, 14} A second series of experiments was carried out on compacts of two of the solids (APM, APT) prepared at a pressure of 930 MN m⁻² (60 ton in⁻²).

EXPERIMENTAL

MATERIALS

The carbon tetrachloride and n-hexane were of Spectrosol grade (Hopkin and Williams), the latter being dried over a molecular sieve; the n-nonane (Philips Petroleum, stated purity 99%), was dried over sodium; all three adsorptives were freed from dissolved air by the usual freeze-thaw technique, before being passed into the appropriate storage reservoir. The nitrogen was of White Spot grade and before admission to the dosing system was dried by passage under slight excess pressure through a liquid nitrogen trap; the nitrogen was first allowed to condense in the trap and the gas for adsorption then bubbled slowly through the condensate.

The ammonium phosphomolybdate (NH₄)₃PMo₁₂O₄₀ (APM) was prepared by the method recommended by Thistlethwaite,¹⁵ the ammonium phosphotungstate (NH₄)₃PW₁₂O₄₀ (APT) was obtained by the addition of a saturated aqueous solution of ammonium chloride to a solution of phosphotungstic acid prepared by the method of Wu;¹⁶ and ammonium silicomolybdate (NH₄)₃HSiMo₁₂O₄₀ (ASM) was prepared from silicomolybdic acid by the method of Fourkey *et al.*¹⁷ All three solids were heated to 453 K in air to free them from volatile impurities such as ammonium chloride. Electron microscopy showed¹⁸ the APM to consist of well-defined hexagonal platelets many of them having a diameter in the range 200 to 500 nm; the APT was very spongy in appearance, and (at 50 000 magnification) no individual primary particles could be distinguished; and the ASM was intermediate in appearance, the edges of aggregates having rather sharper outlines than with APT, though it was difficult to distinguish any well-defined individual particles.

METHOD

The adsorption isotherms were measured gravimetrically with the aid of a Cahn RG electrobalance, the adsorbent being contained in a bucket of thin (0.025 mm) platinum foil weighing 0.26 g. For the nitrogen isotherms a special hangdown tube designed by Cutting¹⁹ was used; this had a base of Kovar metal sealed into the glass, and by means of a simple switching device the bucket could remain in contact with the metal base, which in turn was in direct contact with the liquid nitrogen of the bath, except when the reading of weight was actually being taken. (In the conventional gravimetric arrangement, an error of several percent may be obtained at the upper end of the isotherm, because the solid sample is appreciably higher in temperature than the bath).^{19, 20} The pressure of the vapour was measured by a transducer (Bell and Howell, 4-327-003). The solid was outgassed overnight at 463 K.

To prevent the bucket sticking to the layer of nonane condensed on the Kovar, the original procedure for pre-adsorption of nonane was modified: the outgassed adsorbent was exposed whilst at room temperature, rather than at 77 K, to the vapour of n-nonane, and then evacuated for several hours to remove adsorbed nonane from the external surface and the walls of meso and macropores.

Compaction was carried out in a die of 16 mm internal diameter. About 0.5 g of powder was placed into the die and was shaken down for half a minute; after insertion of the plunger the required pressure, 930 MN m^{-2} (60 ton in^{-2}), was applied for 15 min. The compact was then removed from the die and broken up into grains for loading into the bucket of the balance.

RESULTS AND DISCUSSION

In considering the results it is necessary to bear in mind the complicating effect of any constrictions in the micropores which are narrow enough to impede the passage of adsorbate molecules into the cavities beyond. If the width w of the entrance into a cavity is close to the critical dimension σ of the adsorptive molecule, then the passage of a molecule through the entrance will involve an energy of activation, and so will occur at a finite rate. If the ratio $\sigma : w$ falls within an appropriate range (not far from unity,^{21, 22} but difficult to specify exactly in the absence of a precise model) the energy of activation will be so high as to render the passage of molecules through the constriction excessively slow, so that the micropore will become only partially filled in the course of a measurement.^{23, 24} The result will be a type of hysteresis which extends to the lowest pressures ("low pressure hysteresis") and is therefore quite distinct from that accompanying capillary condensation in mesopores, which manifests itself in a closed hysteresis loop occurring at higher relative pressures.

[The critical dimension σ is a quantity difficult to assess with precision.²⁵ Minimum kinetic diameters, quoted by Walker,²² are $\sigma(\text{N}_2) = 0.37 \text{ nm}$ and $\sigma(\text{n-C}_4\text{H}_{10}) = 0.43 \text{ nm}$; Barrer^{26, 27} gives $\sigma(\text{N}_2) = 0.30 \text{ nm}$ (taking into account the elongated shape) and $\sigma(\text{n-paraffins}) = 0.49 \text{ nm}$. The value for carbon tetrachloride, calculated from the liquid density at ²⁸ 298 K, is $\sigma(\text{CCl}_4) = 0.57 \text{ nm}$. It therefore seems safe to say that $\sigma(\text{N}_2) < \sigma(\text{C}_6\text{H}_{14}) < \sigma(\text{CCl}_4)$. By way of partial confirmation, the order of chromatographic elution from molecular sieve 5A is: nitrogen, n-propane].²⁹

When the pre-adsorption procedure is carried out those micropores having unconstricted entrances will fill completely with nonane, so that the adsorptive, A, used for determination of the subsequent isotherm, will be excluded completely; the micropore volume can then be obtained from the difference between the isotherms of A before and after pre-adsorption respectively, as already explained.²⁶ If, however, the pores have narrow entrances, the nonane will tend to be adsorbed in the entrances, thereby blocking them in the manner of a stopper. If A is an adsorptive such as nitrogen which is used at very low temperature (77 K), it will still be excluded completely so that the micropore volume can be obtained as before; but if adsorptive A is the vapour of an organic liquid which is used at much higher temperature, say 298 K, and is soluble in nonane, one may expect that some molecules of A will penetrate the stopper, so that adsorptive A will no longer be completely excluded from the micropores; consequently the calculated value of the micropore volume will be erroneously low. Exactly this complication appears to be present when adsorptive A is n-hexane or carbon tetrachloride.

Because the feature of major interest in the present study is the pore volume of the adsorbents, it is convenient to plot the isotherms with the amount adsorbed expressed as a volume of liquid adsorbate, using the normal liquid density of the adsorptive A for the conversion.

NITROGEN

The isotherms of nitrogen will be dealt with first, since with this adsorptive the nonane pre-adsorption procedure gives consistent results for all three solids, both before and after compaction. With the loose powders, the nitrogen isotherm is of Type I for APM and ASM (fig. 1, curve 2; fig. 2, curve 7), and of Type II for APT (fig. 4, curve 19). The clear inference is that all three solids are microporous, APM and ASM almost wholly so, and APT possessing in addition a considerable "open" surface (walls of macropores). The isotherms after nonane pre-adsorption have the characteristics consistent with this inference: with APM and ASM the isotherm lies close to the pressure axis (fig. 1, curve 6; fig. 2, curve 10) and with APT it is much below, and almost parallel to, the isotherm before pre-adsorption (fig. 4, curve 24).

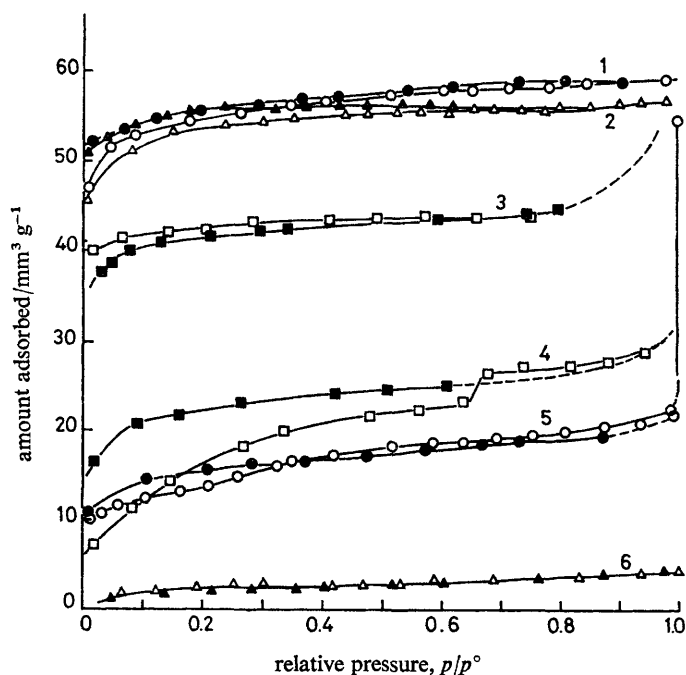


FIG. 1.—Adsorption isotherms on ammonium phosphomolybdate (APM) powder. 1, 2, 3, before pre-adsorption of n-nonane; 4, 5, 6, after pre-adsorption of n-nonane. Open symbols, adsorption; solid symbols, desorption. 2, 6, nitrogen (77 K); 1, 5, n-hexane (298 K); 3, 4, carbon tetrachloride (298 K).

Detailed examination reveals minor differences between the three solids. The isotherm on ASM measured before pre-adsorption showed no hysteresis (fig. 2, curve 7) implying the absence of pores, or pore entrances, having a width close to $\sigma(\text{N}_2)$; and the fact that after pre-adsorption of nonane the uptake of nitrogen was scarcely detectable (fig. 2, curve 10) indicates that the porosity falls almost completely within the micropore range.

On APM the isotherm is more rounded at the low pressure end than on ASM, and it shows slight hysteresis extending to the lowest pressures (fig. 1, curve 2); a small proportion of pores must therefore possess entrances with widths close to $\sigma(\text{N}_2)$. After pre-adsorption of nonane the isotherm of nitrogen is much lower, but

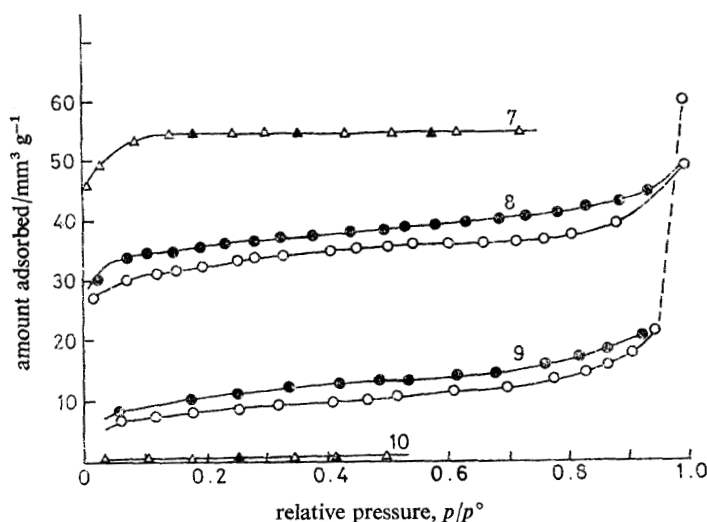


FIG. 2.—Adsorption isotherms on ammonium silicomolybdate (ASM) powder. 7, 8, before pre-adsorption of n-nonane; 9, 10, after pre-adsorption of n-nonane. Open symbols, adsorption; solid symbols, desorption. 7, 10, nitrogen (77 K); 8, 9, n-hexane (298 K).

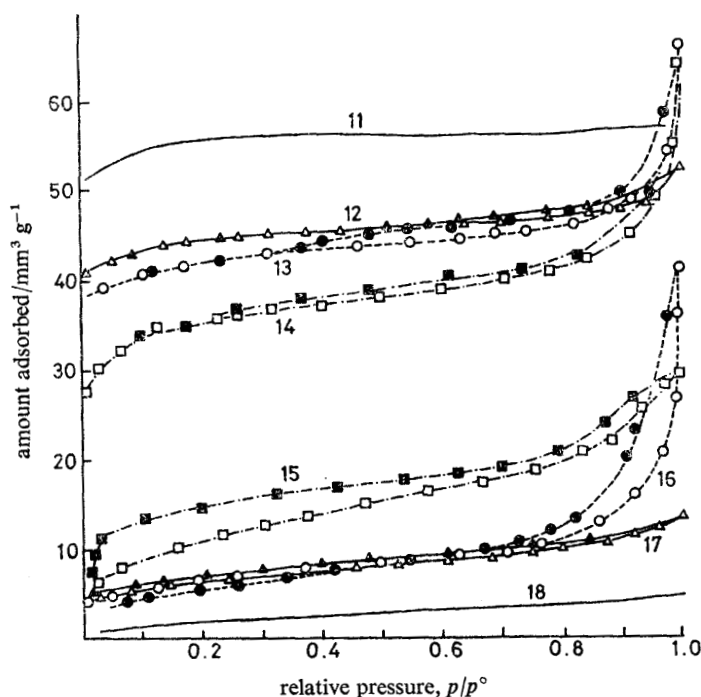


FIG. 3.—Adsorption isotherms on ammonium phosphomolybdate (APM) compact. 12, 13, 14, before pre-adsorption of n-nonane; 15, 16, 17, after pre-adsorption of n-nonane. Open symbols, adsorption; solid symbols, desorption. 12, 17, nitrogen (77 K); 13, 16, n-hexane (298 K); 14, 15, carbon tetrachloride (298 K). The isotherms of nitrogen on the loose powder are shown for reference: 11, before, 18, after, n-nonane pre-adsorption.

is still well above the pressure axis (fig. 1, curve 6); it is almost parallel to the (desorption) branch of the isotherm before pre-adsorption, the separation between the two isotherms, which is a measure of the micropore volume, being $51\text{--}53\text{ mm}^3\text{ g}^{-1}$. Above its B.E.T. point B, this isotherm (curve 6) has a slight but finite slope, so that the solid must possess a small "open" surface, of area $\sim 4\text{ m}^2\text{ g}^{-1}$.

The isotherm on APT shows no hysteresis, so pore entrances of width close to $\sigma(\text{N}_2)$ are absent (fig. 4, curve 19), but the clear type II character points to the presence of a considerable "open" surface ($\sim 59\text{ m}^2\text{ g}^{-1}$) made up of the walls of macropores. From the vertical separation of the near-parallel isotherms before and after pre-adsorption respectively (fig. 4, curves 19 and 24), the micropore volume is $\sim 48\text{ mm}^3\text{ g}^{-1}$. The presence of low pressure hysteresis in isotherm 24 suggests that a small proportion of entrances are of such shape and width (say 1.5 nm) as to be incompletely blocked by the nonane.

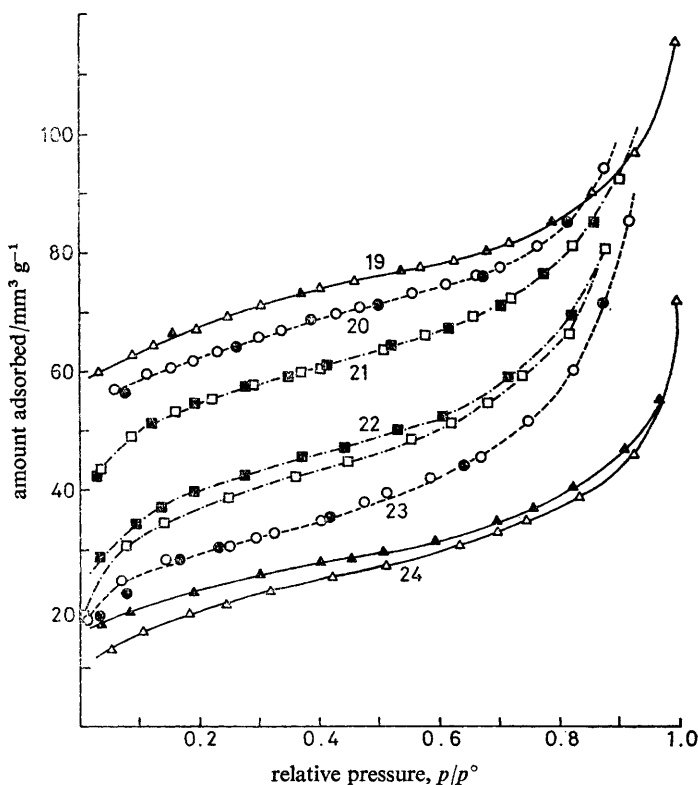


FIG. 4.—Adsorption isotherms on ammonium phosphotungstate (APT) powder. 19, 20, 21, before n-nonane pre-adsorption; 22, 23, 24, after n-nonane pre-adsorption. Open symbols, adsorption; solid symbols, desorption. 19, 24, nitrogen (77 K); 20, 23, n-hexane (298 K); 21, 22, carbon tetrachloride (298 K).

The compaction of the powders (APM and APT only) again leads to results of a not unexpected nature. The isotherm on APM remains of type I, but it is lowered by $\sim 11\text{ mm}^3\text{ g}^{-1}$, and hysteresis has disappeared (fig. 3, curves 12 and 11). Thus, compaction has closed off, or perhaps eliminated entirely, a group of pores 11 mm^3 in volume, which includes all those with entrances of width close to $\sigma(\text{N}_2)$. After pre-adsorption of nonane the isotherm is much lowered, the micropore volume,

estimated from the vertical separation of the near-parallel branches (fig. 3, curves 12 and 17), being $37 \text{ mm}^3 \text{ g}^{-1}$. Interestingly, isotherm 17 lies distinctly above the corresponding isotherm (18) on the uncompact powder and has an increased slope above B.E.T. Point B, so that the specific surface has been increased by compaction; this is reasonably explained in terms of the fracture, and consequent reduction in average particle size, during compaction.

With APT, compaction produces the kind of change commonly found with powders, *viz.*, that the isotherm, originally of type II, acquires a type IV character with a well-defined hysteresis loop (fig. 5, curve 26): the particles have been pushed so close together that the spaces between them have been reduced to mesopore size. The very considerable lowering of the isotherm consequent on compaction (fig. 5, *cf.* curves 26 and 25) corresponds to a substantial loss of surface area, from 59 to

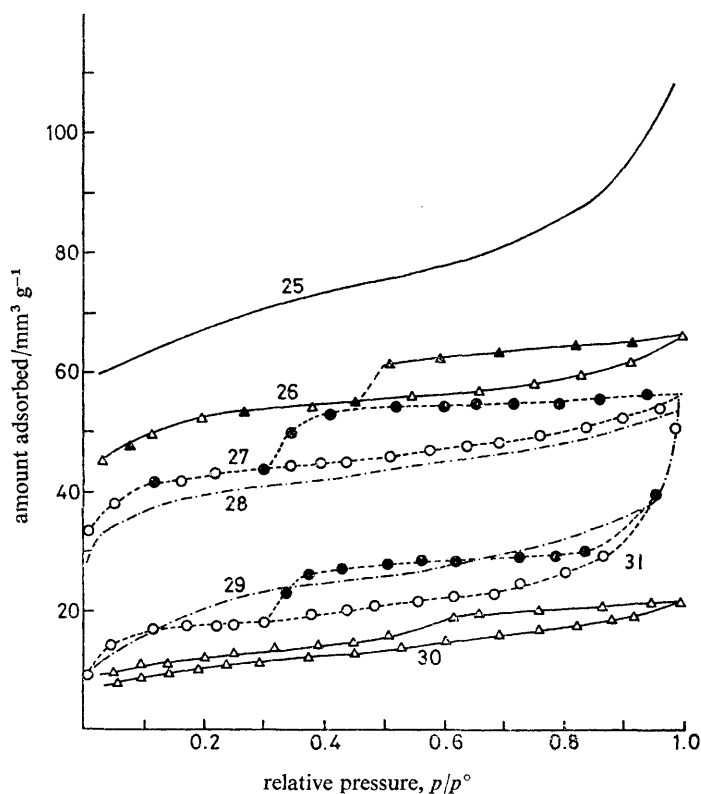


FIG. 5.—Adsorption isotherms on ammonium phosphotungstate (APT) compact. 26, 27, 28, before n-nonane pre-adsorption; 29, 30, 31, after n-nonane pre-adsorption. Open symbols, adsorption; solid symbols, desorption. 26, 30, nitrogen (77 K); 27, 31, n-hexane (298 K); 28, 29, carbon tetrachloride (298 K). 25 is the nitrogen isotherm on the loose powder before n-nonane pre-adsorption, shown for reference. For clarity, only the adsorption branches are shown in isotherms 28 and 29. The complete isotherms for carbon tetrachloride are given in fig. 6.

$26 \text{ m}^2 \text{ g}^{-1}$, as estimated from the B.E.T. point B uptakes after subtraction of the micropore contribution; it is readily explicable in terms of a cold welding of contiguous particles of powder under the action of the applied pressure, an effect again well known with powders if they are composed of sufficiently soft material.

After pre-adsorption of nonane, the isotherm is again much lower than before

pre-adsorption, the separation of the corresponding adsorption branches being $43 \text{ mm}^3 \text{ g}^{-1}$ (fig. 5, curves 26 and 30) so that compaction has reduced the freely accessible micropore volume by $5 \text{ mm}^3 \text{ g}^{-1}$.

The compaction experiments were limited to one pressure only; it is not possible, therefore, to decide whether the results obtained merely represent one stage in a continuous process, or whether the micropores which are eliminated during the compaction are qualitatively different from those pores which are not. On the whole it would seem that those pores which are able to survive the high pressure involved must be contained within the actual lattice of the solid, whereas those that are removed consist of narrow gaps between the primary and secondary particles. The former group ($37 \text{ mm}^3 \text{ g}^{-1}$ in volume for APM and $43 \text{ mm}^3 \text{ g}^{-1}$ for APT) would presumably not be removed by any compacting pressure lower than that required to bring about actual chemical decomposition; and the latter group (11 and $\sim 5 \text{ mm}^3 \text{ g}^{-1}$ in volume respectively) are eliminated by the cold welding of contiguous particles of solid, which as already postulated accounts for the loss of specific surface on compaction.

HEXANE AND CARBON TETRACHLORIDE

The results with these two adsorptives are less straightforward than with nitrogen, and in some ways unexpected. The relative positions of the isotherms in the absence of nonane pre-adsorption can, on the whole, be explained in terms of molecular size and shape of the adsorptives, but those after nonane pre-adsorption need further explanation: there is little doubt that carbon tetrachloride and hexane can penetrate the "stoppers" of nonane to such an extent as to render them unsuitable for use in the nonane method for micropore detection and evaluation.

On uncompact APM the isotherm of hexane is quite close to that of nitrogen (actually slightly above it—fig. 1, curve 1) and shows hysteresis at all pressures, but the isotherm of carbon tetrachloride lies much below those for both nitrogen and hexane, and has a steep initial portion $\sim 35 \text{ mm}^3 \text{ g}^{-1}$ high, with considerable hysteresis throughout. The simplest explanation is that a proportion of the micropores, $\sim 35 \text{ mm}^3 \text{ g}^{-1}$ in volume, are freely accessible to all three adsorptives, but that the remainder ($\sim 51 - 35 = 16 \text{ mm}^3 \text{ g}^{-1}$ in volume) are freely accessible to nitrogen and hexane but offer hindrance to the entrance of carbon tetrachloride because of its larger molecular size.

Surprisingly, the isotherms of both adsorptives, measured after pre-adsorption of nonane, lie very considerably above the isotherm for nitrogen.

It is difficult to explain this result other than by supposing that the molecules of both adsorptives are able to diffuse through the "stoppers" of nonane which plug the entrances to the micropores, a view supported by the presence of hysteresis at all pressures. That such diffusion occurs with hexane and carbon tetrachloride but not with nitrogen may be attributed to the higher temperature of measurement which would accelerate diffusion, and also to the greater solubility of hexane and carbon tetrachloride in n-nonane; an additional factor is that at the temperature of measurement n-nonane is solid in the case of nitrogen (77 K) but liquid in the case of the other two adsorptives (298 K).

The hexane isotherm of the compact of APM (fig. 3, curve 13) lies close to that for nitrogen and, except at low pressures (where it is less rounded than the nitrogen isotherm), is almost parallel to the hexane isotherm for the loose material. Thus the $11 \text{ mm}^3 \text{ g}^{-1}$ of pores which, as noted earlier, have been closed to nitrogen by compaction, are likewise closed to hexane and must therefore have had entrances

$\sim \sigma(\text{C}_6\text{H}_{14})$ in width, *viz.*, ~ 0.49 nm. After nonane pre-adsorption the hexane isotherm (fig. 3, curve 16) on the compact is (except at high relative pressures) close to the nitrogen isotherm—a state of affairs therefore quite different from that found with the uncompact APM; the carbon tetrachloride isotherm on the other hand is considerably lower before (curve 14), and higher after, nonane pre-adsorption than those of nitrogen and hexane (curve 15), just as was found with the uncompact solid. A similar comment applies, *viz.*, that the position of curve 14 is explained by a molecular sieve effect and that of curve 15 by diffusion through the nonane stoppers. It remains unexplained, however, how diffusion through the nonane stoppers can occur with carbon tetrachloride but not with n-hexane.

With ASM the measurements were confined to the uncompact powder, and did not include carbon tetrachloride as adsorptive (fig. 2). The hexane isotherm before nonane pre-adsorption lies well below the corresponding nitrogen isotherm and hysteresis is present at all pressures (curves 7 and 8); a molecular sieve effect is strongly indicated. After nonane pre-adsorption the hexane isotherm, as in the case of APM, is much above the nitrogen isotherm (*cf.* curves 9 and 10), and the explanation in terms of penetration of nonane stoppers again suggests itself.

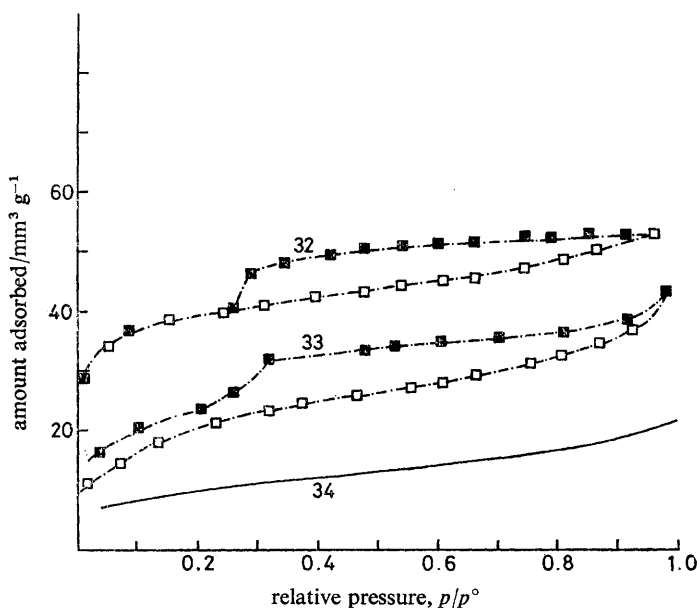


FIG. 6.—Adsorption isotherms of carbon tetrachloride (at 298 K) on ammonium phosphotungstate (APT) compact. Open symbols, adsorption; solid symbols, desorption. 32, before, 33, after, n-nonane pre-adsorption. 34, isotherm of nitrogen after n-nonane pre-adsorption, shown for reference. Curves 32 and 33 correspond respectively to curves 28 and 29 of fig. 5.

The results for APT can be understood in the light of those already described for the other two solids. With the uncompact material the hexane isotherm lies below the nitrogen isotherm, the carbon tetrachloride isotherm being lower still (fig. 4, curves 19, 20 and 21). These relative positions are explicable in terms of molecular sieve action. After nonane pre-adsorption the relative positions of the isotherms for the three adsorptives are reversed (curves 24, 23 and 22); diffusion through nonane stoppers is again indicated, and is confirmed by the fact that a second run with carbon tetrachloride resulted in a raising of the isotherm still further.

On compacted APT both hexane and carbon tetrachloride, like nitrogen, give type IV isotherms with well-defined hysteresis loops (fig. 5 and 6), confirming that a system of mesopores has been produced by compaction. The relative positions of the three adsorptives are the same as for the uncompacted material, and are to be explained in a similar manner: molecular sieve action before pre-adsorption of nonane, and penetration of the nonane stoppers after pre-adsorption. The absence of low pressure hysteresis from the hexane isotherm after pre-adsorption of nonane is slightly puzzling (fig. 5, curve 31), in view of its clear presence in the isotherms of the other two adsorptives (fig. 5, curve 30 and fig. 6, curve 33).

CONCLUSIONS

(1). The nonane pre-adsorption method can be successfully used for micropore evaluation when nitrogen, but not n-hexane or carbon tetrachloride, is used for the isotherm determination. The breakdown of the method with these organic adsorptives is probably to be attributed to their ability to penetrate the adsorbed nonane which blocks the pore entrances, in virtue of their solubility in nonane and the higher temperature of measurement.

The applicability of the method appears to be restricted to adsorptives such as nitrogen which (a) are used at temperatures far below ambient, and (b) have low solubility in solid nonane.

(2). The samples of ammonium phosphomolybdate, ammonium phosphotungstate and ammonium silicomolybdate studied all possess a high degree of microporosity after heat treatment at 453 K. The major portion of this microporosity is probably structural in nature, *i.e.* is contained in the lattice of the solid. Whilst the properties of these three substances, like those of the salts of heteropolyacids in general, vary in detail according to the exact mode of preparation, it is reasonable to infer that considerable microporosity is a general property of such salts in view of the essential similarity of their lattice structure.

One of us (M. M. T.) thanks the Government of Pakistan for the grant of study leave.

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