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Isosteric Heats of Adsorption for Nitrogen Adsorbed on Microporous Silica

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Nitrogen adsorption isotherms at three different but similar temperatures were determined on samples of microporous silicas prepared by a freeze–thaw technique. A maximum in the plot of the isosteric heat of adsorption against coverage was observed on all the samples investigated. It is suggested that the effect can be explained in terms of lateral interaction between adsorbate molecules being important in the narrowest pores whilst in the larger micropores surface heterogeneity may play a predominant role. The microporosity of the silicas is established by adsorbing adsorbates of different molecular size and noting the adsorption capacity at a relative pressure near saturation.

THE preparation and ageing of microporous silica have been described.[1,2] This microporous silica had been prepared by a technique of freeze–thawing in which a silica sol is first frozen and then thawed to give a suspension of silica flakes which upon drying and degassing yield a microporous adsorbent which is plate-like in physical structure. In the present investigation three of the samples of silica were subjected to 'molecular probe analysis' in which the nature of the micropores was investigated by adsorbing a series of vapours of differing molecular size. Nitrogen was adsorbed on the samples at a series of temperatures and the isosteric heats of adsorption calculated.

EXPERIMENTAL

Sols of silicic acid were prepared by passing a solution of sodium metasilicate down a column of the hydrogen form of the exchange resin Zeocarb 225 maintained at 20 °C. The sol was adjusted to various pH's with 2N-HCl, the samples described here namely 1, 2, and 3 had pH's in the sol stage of 3·00, 2·25, and 1·40 respectively.

The sol was frozen at −78 °C in solid carbon dioxide-acetone for 1 h, then allowed to thaw at room temperature for 18 h. The suspensions of flaky, plate-like silica were centrifuged, dried in a vacuum desiccator for 18 h, degassed under high vacuum for two days followed by 2 h at 150 °C, after which time they had achieved constant weight.

A series of vapours of different molecular size were adsorbed on the samples by use of a gravimetric balance sensitive to 0·05 mg.[3] Nitrogen was adsorbed on the silicas at temperatures of 77·4, 87, and 90 K by use of liquid nitrogen, liquid argon, and liquid oxygen respectively. The temperature was continually checked with a copper-constantan thermocouple and it was found that by containing the liquid coolant in a Dewar vessel with the liquid boiling continuously maintained a constant temperature. The nitrogen, which was supplied as oxygen-free by British Oxygen Co., had a stated purity of 99·99% but was found to contain traces of water which were removed by passage through a trap of liquid nitrogen.

In order to ensure complete reversibility the complete isotherms were first plotted by use of an oil manometer to record the low pressures, the density of the oil being determined by calibration against a mercury manometer for each adsorption run. A complete isotherm normally took about 12 h but it could take much longer depending on the number of points taken at low pressures. Because

an adsorption run took so long the reversibility was not determined during the actual sorption experiment but after completing the series of three isotherms on a sample, nitrogen was admitted to the degassed sample at a low pressure and adsorbed at 77·4 K. After ensuring that the point coincided with the previously determined isotherm the temperature was raised to 87 K and the new readings taken and checked with the 87 K isotherm. The temperature was then raised to 90 K, readings taken again, and after confirmation that the three points fitted their respective isotherms the process was reversed and the points duplicated indicating that the process was thermodynamically reversible. This procedure was repeated four times at various stages on the isotherms, one series of points taking up to 6 h at low pressures.
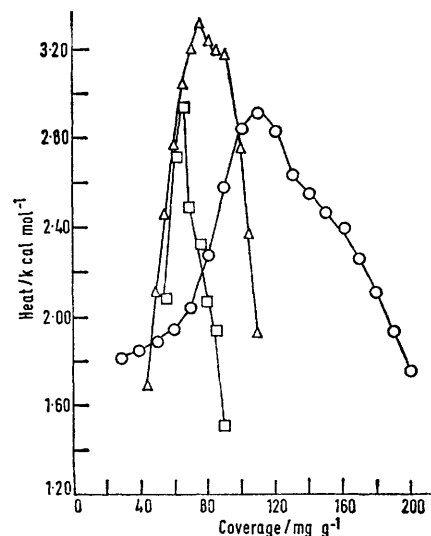
Plot of isosteric heats of adsorption against coverage for microporous silicas; $\bigcirc$, Sample 3; $\triangle$, sample 1; $\square$ sample 2; the latent heat of condensation is at 1·32 kcal mol^{-1}

RESULTS

Plots of log P/(cmHg) against the reciprocal of the absolute temperature of adsorption were drawn at various coverages and straight-line plots were obtained. From the slopes of the plots the isosteric heats of adsorption were calculated from the Clausius–Clapeyron equation. Plots of the variation of heat of adsorption with coverage are shown in the Figure and Table 1 gives, for the 77·4 K

[1] D. Dollimore and T. Shingles, *J. Colloid and Interface Sci.*, 1969, **29**, 601.

[2] D. Dollimore and T. Shingles, *J. Appl. Chem.*, 1969, **19**, 218.

[3] G. R. Heal, *J. Sci. Instr.*, 1966, **43**, 289.

isotherms, values of the relative pressure and of the fraction of the pore volume filled at the peak of the maxima in the heat of adsorption curves.

TABLE 1

Heat of adsorption maxima

Sample	pH of preparation	Points at which maximum occurs on heat of adsorption plots (taken from isotherms at 77.4 K)		
		Coverage (X)/mg g⁻¹	X/X_s	$10^4 P/P_0$
3	1·40	110	0·512	3·795
1	3·00	75	0·586	2·879
2	2·25	65	0·619	1·378

N.B. Microporosity increases going down the Table.

The results of the adsorption of vapours of different molecular size are summarised in Table 2. This shows the amount adsorbed at a relative pressure of 0·95 expressed as an equivalent volume of liquid. The adsorption isotherms were Type I except where stated and the data show

TABLE 2

Comparison of the pore volumes of various adsorbates on samples 1, 2, and 3

Adsorbate	Pore volumes/ml g⁻¹		
	Sample 1	Sample 2	Sample 3
Carbon dioxide	0·285	0·175	0·149
Carbon monoxide	0·288	0·172	0·145
Nitrogen	0·266	0·155	0·130
Nitrous oxide	0·240	0·156	0·130
Methane	0·236		
Ethane	0·248	0·129	0·103
Propane	0·208	0·115	0·090 *
Cyclopropane	0·253		0·078
Argon	0·227	0·128	
Butane	0·220	0·120	0·088 *
Benzene	0·220	0·113 *	0·058 *
Carbon tetrachloride	0·193	0·051	0·010
Neopentane	0·193	0·0587 *	

* These values are taken from the desorption loop of the isotherm.

Value for pore volume of carbon tetrachloride on Sample 3.

that the smaller adsorbate molecules were adsorbed in a greater volume than the larger adsorbate molecules. In the context used here the term micropore refers to pores less than about 10—15 Å and the results indicate that a whole range of pore sizes exist between the smallest and the largest adsorbate molecules. Table 2 indicates that the extent of microporosity increases going from sample 3 to 1 to 2 and in fact silica sample 2 acted as a non-porous adsorbent towards carbon tetrachloride.

DISCUSSION

Results of a similar nature have been reported but explanations for the observed results have not been very conclusive. Pace and Siebert[4] adsorbed nitrogen on

[4] E. L. Pace and A. R. Siebert, *J. Phys. Chem.*, 1960, **64**, 961.
[5] R. A. Beebe, J. Biscoe, W. R. Smith, and C. B. Wendell, *J. Amer. Chem. Soc.*, 1947, **69**, 95.
[6] L. E. Drain and J. L. Morrison, *Trans. Faraday Soc.*, 1952, **48**, 840.
[7] L. E. Drain and J. L. Morrison, *Trans. Faraday Soc.*, 1953, **49**, 654.

graphon and obtained a maximum adsorption heat at about 2·8 kcal mol⁻¹ which is very similar to those reported here. Beebe, Biscoe, Smith, and Wendell[5] and Drain and Morrison[6,7] said that decrease in heats of adsorption in the first layer was due to the physical heterogeneity of the surface or to repulsive interactions between the adsorbed atoms. Hockey and Pethica[8] observed that when adsorbing benzene on two aerosils there was an initial sharp decrease in heat of adsorption followed by a maximum. They concluded that this was due to a number of surface micropores in the silica, and that co-operative adsorption into these pores occurred at a relatively low pressure.

The Figure shows that a maximum is given in the plots of heat of adsorption against coverage. According to Gregg and Sing[9] heterogeneity of the surface leads to high initial heats of adsorption which fall off as the high-energy sites become occupied. Lateral attraction between adsorbate molecules may lead to a heat maximum at higher coverages.

In a system such as that present in the microporous plate-like silicas reported here the picture is more complicated. In the case of sample 2, multilayers cannot form because the pores are less than two adsorbate molecular diameters in width. Initially adsorption will occur in the smallest pores, provided they are large enough for the nitrogen molecule to enter, and the fact that the pores are so small will result in the adsorbate molecules being packed with an effectively higher density than would be the case in an open or large-pored system. The heat of adsorption will thus rise at the lower coverages and reach a maximum, at which point the surface heterogeneity will begin to play a predominant role and adsorption will take place in the larger micropores though in the case of sample 2 these will still be less than two molecular diameters in width. Whilst one often refers to pores as cylinders it is certainly not the case with these silicas. Adsorption could be occurring both in the silica network and between the layers of the plate-like structure so although interaction between molecules may be restricted in one direction owing to the width of the pores or separation of the sheets it will certainly not be the case in the plane of the layers of the silica plates. We have not plotted data below a coverage of around 30 mg/g, and the variation of the heat of adsorption in this region is not discussed.

Table 1 shows that the more microporous the silica the higher is the percentage coverage at the maximum heat of adsorption and the lower is the relative pressure. In other words the more microporous the sample then the more prolonged is the influence of the lateral attraction forces. The fact that the relative pressure is lower at the maximum for the most microporous sample indicates that adsorption potential is greater the smaller the pores are, as is to be expected. An interesting

[8] J. A. Hockey and B. A. Pethica, *Trans. Faraday Soc.*, 1962, **58**, 2017.
[9] S. J. Gregg and K. S. W. Sing, ' Adsorption, Surface Area and Porosity,' Academic Press, New York, 1967, p. 56.

observation on the heat maximum is that it corresponds to an inflection point observed when the isotherms are plotted according to the Dubinin–Radushkevich [10] equation. This would support the argument that adsorption was initially occurring in the narrowest of the pores, giving rise to high lateral attractions between molecules, where the adsorption potential is at its highest.[11]

[10] M. M. Dubinin, 'Chemistry and Physics of Carbon,' E. Arnold, London, 1966, vol. 2, pp. 51—118.
[11] T. G. Lamond and H. Marsh, *Carbon*, 1964, **1**, 281.