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Surface chemistry of polymers
Adsorption and absorption of gases by polyvinylchloride

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Summary. Nitrogen and carbon monoxide are physically adsorbed on polyvinylchloride between 78 and 86 K, without hysteresis. At higher temperatures, carbon dioxide (195 K), sulfur dioxide (273 and 293 K) and chloroethane (293 K) are strongly absorbed by the solid, with hysteresis. The possibility of trapping CO inside the solid indicates that PVC has an open structure at higher temperatures. The effect of heating on the polymer was also investigated.

Introduction. – Recent studies [1, 2] have shown that various gases were physically adsorbed by polyvinylidene chloride (PVDC) between 78 and 293 K. The absence of hysteresis indicates that PVDC has a closed surface even at room temperature, and no penetration can occur, provided the gas is not a specific solvent.

The adsorption of nitrogen on PVC and PVDC [1] suggested that the two surfaces were similar at low temperatures. The present study shows that the similarity does not hold at higher temperatures, where strong penetration into PVC takes place.

Experimental Part

The volumetric apparatus described earlier [2] was used, with a new calorimetric jacket shown in fig. 1.

The jacket is suspended by 4 nylon threads, and placed around the sample holder S. It consists of two concentric copper cylinders (A and B) both closed at their lower ends. A heating element (H) of 38 Ω is wound around A. A layer of asbestos string (8 mm diameter) and a disk of expanded polystyrene (D) provide a satisfactory thermal insulation from the constant temperature bath (T) in which the jacket is immersed. (A small thermal leak is needed for a good temperature control). The gap between S and cylinder A is filled with 80 g of fine copper powder in order to ensure a uniform temperature around the sample. This device proved to be very efficient.

Two copper-constantan thermocouples (not shown), placed against S, and with their cold junctions in the outside bath, were used to control the temperature inside the jacket. The temperature differences between the top and the bottom of the sample could be kept within ± 0.1 K, when the system operated near 86 K. (Heating current of 200 mA).

The level of liquid N_2 was kept about (1–2) cm below the top of the calorimetric jacket, which was sealed with a layer of wax (W), about 3–4 mm thick.

Materials. – The main research was concentrated on samples of an unstabilised industrial PVC, "Type G" (courtesy of *Lonza* AG), with a surface area of 2 m^2/g. Density measurements in helium at 293 K gave (1.46 ± 0.02) g/cm^3. The density in nitrogen at 293 K agreed with the He value.

Samples of a different origin, (*B.P.* United Kingdom, type 121), investigated previously [1], were also used for comparisons. The surface area was 5.4 m^2/g. Both solids were of poor cristallinity, as revealed by X-ray powder photographs.

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The samples were originally outgassed for 25–30 hours at room temperature, under 10^{-5} Torr, and for variable periods between runs, depending on the circumstances described below.

Oxygen-free nitrogen, helium of chromatographic purity, and sulfur dioxide (*Fluka* AG, stated 99.97% pure) were only passed through a cold trap before storage. Carbon monoxide and carbon dioxide, of industrial origin (about 95% pure), were purified by repeated condensations and evaporations. Chloroethane (about 98% pure) was purified in the same way.

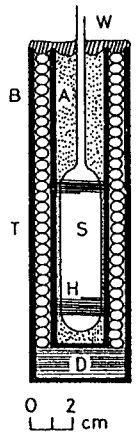

Fig. 1. *The calorimetric jacket*

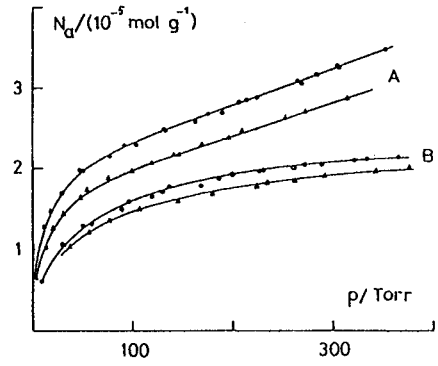

Fig. 2. *Isotherms for the adsorption of nitrogen on PVC type G at 77.6 K (A) and 86.3 K (B)*
(•) Untreated and (▲) heated samples

Results and discussion. – *Nitrogen* was adsorbed at 77.6 and 86.3 K, and the isotherms are shown in fig. 2. They are of type II, without hysteresis. The B.E.T. plot gave a surface area of 2.05 m^2/g (using the value of $A_m = 16.2 \times 10^{-20}$ m^2 per molecule). The isosteric heats of adsorption are shown in fig. 3. Earlier results for nitrogen adsorption on the BP 121 sample [1], in the same temperature range, are also shown for reference.

In connection with chromatographic investigation (to be published later), the effect of heating the sample was also investigated by the static B.E.T. method. Samples of PVC were kept in the sample holder at 80–81° for periods up to 30 hours,

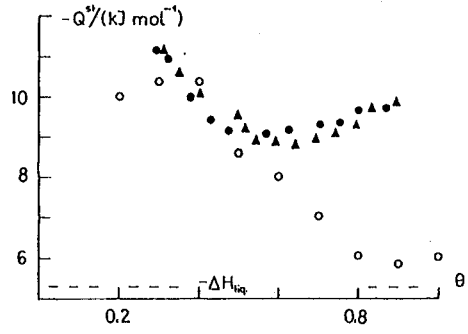

Fig. 3. *Isosteric heats of adsorption for nitrogen on PVC*
(•) Untreated and (▲) heated samples of type G. (○) Type 121, untreated

and under reduced nitrogen pressure (a few torr). This temperature is slightly above T_g, the glass transition of PVC (78–80°). The samples were then outgassed at room temperature for 15–20 h, and nitrogen was readsorbed at 78 and 86 K. The isotherms for a sample heated for 9 h are also shown in fig. 1. The B.E.T. surface area was about 10% smaller after the treatment, but the isosteric heats of adsorption did not change in the range $0.3 < \theta < 0.9$, as shown in fig. 3. Chromatographic experiments, on the other hand, revealed that the heat of adsorption of methanol between 40 and 80° dropped from −42 to −30 kJ/mole at low coverage. This decrease in heterogeneity is consistent with the decrease in surface area by heating.

X-ray powder photographs did not show significant changes in the structure of the polymer after heating.

Carbon monoxide is also physically adsorbed at 78 and 86 K, without hysteresis, as shown in fig. 4. The cross-sectional areas of CO are 15.5 and 16.7 Å² at 77.6 and 86.3 K respectively. They compare well with the values of 16.0 and 16.8 Å² calculated from liquid densities [3].

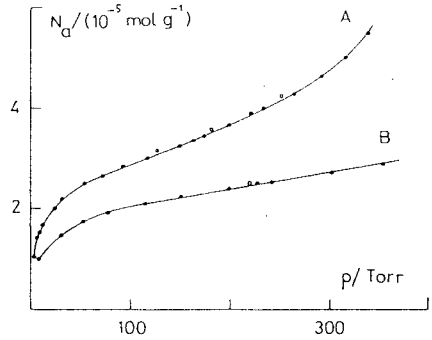

Fig. 4. *Isotherms for the adsorption of carbon monoxide on PVC type G, at 77.6 K (A) and 86.3 K (B)*

The isosteric heats of adsorption for $0.5 < \theta < 1.5$ are shown in fig. 5. There is a slight increase in the monolayer region.

When the clean solid was cooled from room temperature to 78 K in the presence of CO, a new isotherm was obtained. The absence of hysteresis and the parallelism

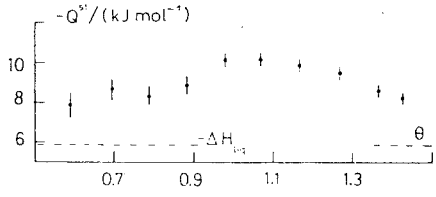

Fig. 5. *Isosteric heats of adsorption for CO on PVC type G*

with the original isotherm suggested that a constant amount of carbon monoxide had been trapped inside the solid as the temperature was lowered.

This property was investigated by repeating the operation with larger quantities of CO in the gas phase. From the final equilibrium pressure at 78 K (a few Torr) and the knowledge of the real isotherm, the amount trapped in the polymer could be

calculated. The sample was then pumped on for about $^1/_2$ h, until a pressure of about 10^{-2} Torr was reached.

When the sample was allowed to warm up to room temperature, the gas trapped by the solid was gradually released.

The trapping of CO could be explained by the existence of gaps between the chains of the amorphous (and atactic) PVC. These gaps are probably closed at low temperatures owing to the contraction of the solid.

The penetration into the polymer near room temperature is also revealed by the strong *absorption* of sulfur dioxide shown in fig. 6.

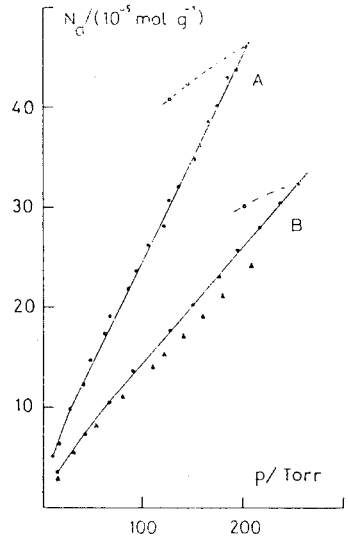

Fig. 6. *Isotherms for the absorption of SO_2 by PVC at 273 K (A) and 293 K (B)* (•) type G and (▲) type 121

The absorption isotherms for SO_2 at 273 and 293 K are linear, but show hysteresis on desorption (absorption equilibrium was reached after 30–45 min., but desorption took much longer).

If absorption was reversible, the corresponding isosteric heat would practically be equal to the latent heat of condensation of SO_2 near 283 K (−24 KJ/mole).

The penetration of SO_2 was also observed for the sample of PVC 121 at 293 K (fig. 6). The isotherms are very close, which suggests that the internal structures are similar for the two samples. In the case of PVC 121, the equilibrium was reached faster, owing to its larger surface area and consequently its larger number of penetration sites.

Carbon dioxide was also absorbed by PVC at 195 K. The somewhat smaller amounts and the longer equilibrium times observed (over 2 h) suggest a more restricted penetration.

Chloroethane, which is virtually the structural monomer of PVC, was also strongly absorbed at 293 K. In this case, however, there was probably a solvent effect combined with the penetration, because equilibrium could not be reached, even after

several hours. One could obtain a family of linear isotherms (with strong hysteresis), and corresponding to 2,3 or 4 h of equilibrium for each point.

The strong affinity of chloroethane for chlorinated polymers was also revealed by measurements on PVDC.

At 293 K there is adsorption (and no longer penetration) of CH_3CH_2Cl and the isotherm is linear up to $p/p_0 = 0.5$, corresponding to an approximate coverage of $\theta = 2$.

The adsorption equilibrium is reached after 45 min. only but there is a strong hysteresis on desorption, indicating some kind of retention.

About 40 h of pumping were needed to clean the surface. This contrasts with the behaviour of sulfur dioxide, neopentane and butane adsorbed on PVDC in the same temperature range [1, 2] and which have surface areas similar to the surface area of chloroethane.

Conclusion. – The present study, combined with previous investigations, shows that at low temperatures PVC and PVDC may be similar because of the Cl groups present on both surfaces. At higher temperatures, however, penetration effects appear with PVC. This may be caused by the poor cristallinity of the solid, owing to its atactic structure. In the case of PVDC, on the other hand, the structure is much simpler and the cristallinity is higher. Hence, there are fewer or no penetration sites at all between the chains.

This is also in agreement with the (relatively) lower penetration of water into a chlorinated PVC (63% Cl), as observed by *Babkin* & *al.* [4] near room temperature.

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