

Surface Chemistry of Polymers
Physical Adsorption of Nitrogen, Argon, Sulfur Dioxide
and Neopentane on Polyvinylidene Fluoride

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Summary. The adsorption of nitrogen, argon, sulfur dioxide and neopentane on polyvinylidene fluoride has been measured by static methods and by gas-solid chromatography. The polymer has a homogeneous surface of low energy, which is not significantly affected by heating.

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1. Introduction. – In order to complete the present series of investigations, we wish to report the surface properties of polyvinylidene fluoride (PVDF), measured by static methods and by gas-solid chromatography (GSC). The physical adsorption of various gases on PVDF showed similarities with the case of polyvinylidene chloride (PVDC) [1] [2] and polytetrafluoroethylene (PTFE) [3].

2. Experimental. – The static measurements were carried out with the volumetric B.E.T. apparatus described earlier [2] [4]. Owing to minor improvements, the temperature of the calorimetric jacket could be kept constant within ± 0.1 K, between 78 and 95 K. For adsorption near room temperature, the temperature of the sample was kept constant within ± 0.05 K by using a cryomat (*Lauda*, type K 50 DW) with methanol as a refrigerant. This device proved to be better than the various cryoscopic mixtures and baths used previously. Each isotherm was repeated at least once. The chromatographic measurements were carried out as described earlier [5].

Polyvinylidene fluoride (trade name KYNAR) was supplied by the *Pennwalt Corp.* (Holland) and used without further treatment. The surface varied between 8 and 9 m²/g, depending on the samples. The adsorbates were oxygen-free nitrogen and argon (*Carba SA*, with a stated purity of 99.9%), sulfur dioxide and neopentane (*Fluka AG*, stated minimum purity of 99%). The latter were purified by repeated condensations and evaporations during which only the middle fractions were kept.

3. Results and discussion

Nitrogen adsorption, at 77.4, 87.3 and 97.4 K. The isotherms (type II) are shown in Fig. 1. The B.E.T. plot gave a surface area $S_m = (9.11 \pm 0.2)$ m²g⁻¹, assuming a molecular cross-sectional area of $16.2 \cdot 10^{-20}$ m² for N₂ at 78 K. The average isosteric heat of adsorption Q^{st} given by

$$\left(\frac{\partial \ln p}{\partial T} \right)_{n_a} = -Q^{st}/RT^2 \quad (1)$$

was derived from the three isotherms taken in pairs. Fig. 3 shows that this quantity is practically constant for surface coverages $\theta > 0.3$.

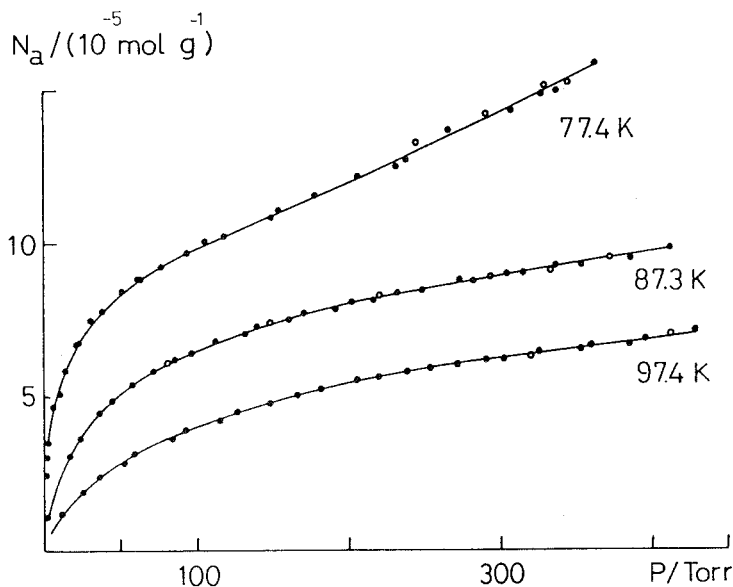


Fig. 1. Adsorption of nitrogen on PVDF

Argon adsorption, at 77.4, 87.3 and 97.4 K. The isotherms (type II) are shown in Fig. 2. Assuming a molecular cross-sectional area of $16.5 \cdot 10^{-20} \text{m}^2$ [6], $S_m = (9.4 \pm 0.2) \text{m}^2 \text{g}^{-1}$. This value agrees well with the result obtained with nitrogen. The cross-sectional areas usually suggested for Ar [7-9] are too small in the present case. The problem has already been discussed [6] [9].

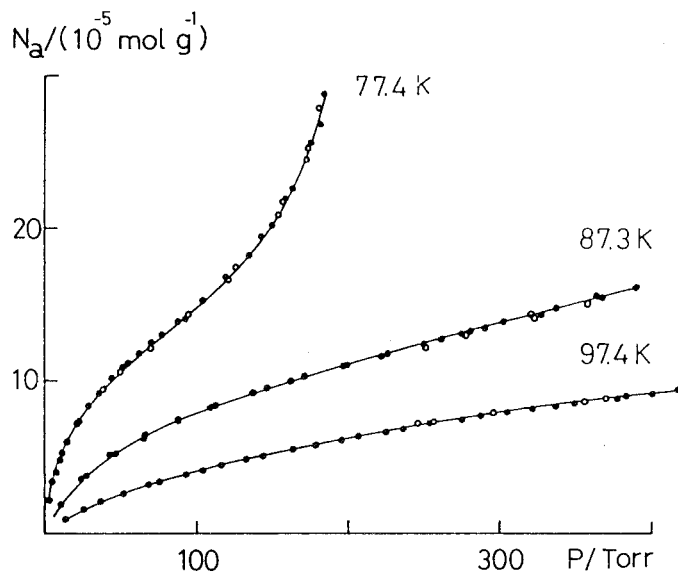


Fig. 2. Adsorption of argon on PVDF

The isosteric heats of adsorption are shown in Fig. 3. They are close to the average enthalpy of liquefaction, with a slight increase near half-coverage.

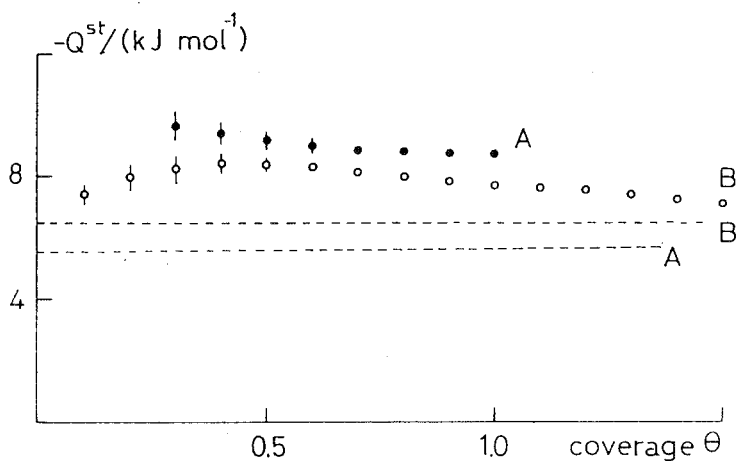


Fig. 3. Isosteric heats of adsorption of nitrogen (A) and argon (B) on PVDF. The broken lines refer to the corresponding enthalpies of liquefaction (near 78 and 87 K)

Neopentane adsorption, at 253.1, 263.1, 273.15 and 278.1 K. The isotherms (type III) are shown in Fig. 4. This type of isotherm does not yield reliable values for S_m .

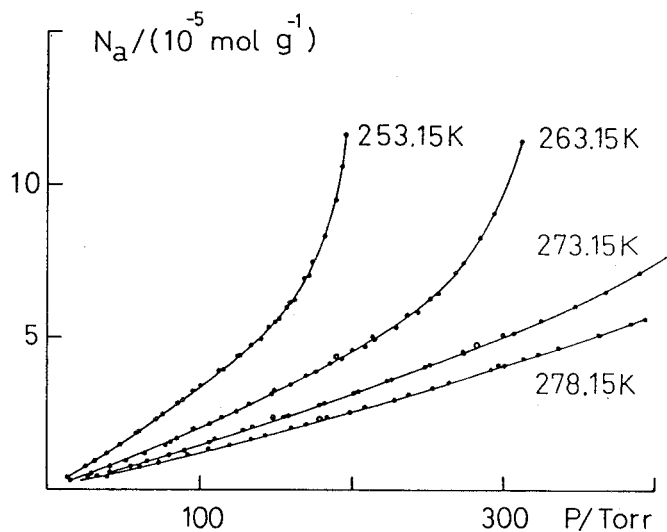


Fig. 4. Adsorption of neopentane on PVDF

The average isosteric heat of adsorption (Fig. 6), derived from the isosters, is somewhat smaller than the average heat of condensation, but constant and equal to (-20 ± 0.5) kJ/mol.

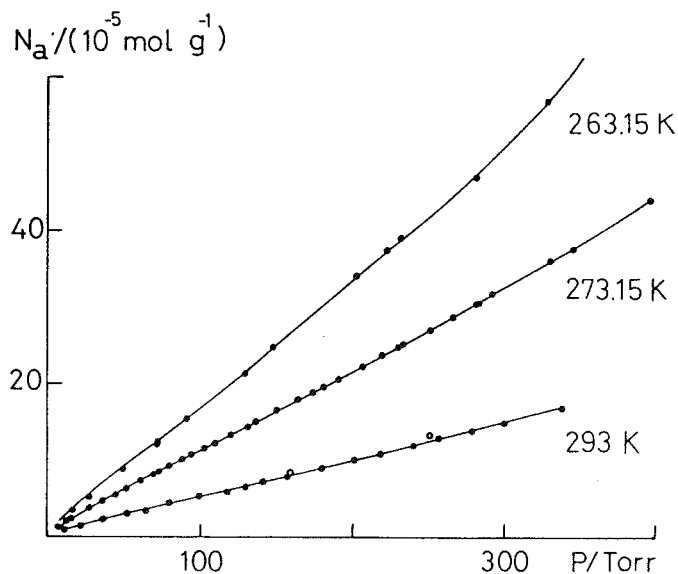


Fig. 5. Adsorption of sulfur dioxide on PVDF

Adsorption of sulfur dioxide, at 263.1, 273.15 and 293.1 K. The isotherms (Fig. 5) are practically linear for the whole pressure range considered. The value of the cross-sectional area A_m had to be assumed from measurements on PVDC [2] ($A_m = 24 \cdot 10^{-20} \text{ m}^2$, against $19 \cdot 10^{-20} \text{ m}^2$ from liquid density measurements), in order to compute θ . The isosteric heats of adsorption (Fig. 6) fall rapidly, to become virtually equal to the enthalpy of liquefaction at the average temperature $\bar{T} = 273 \text{ K}$.

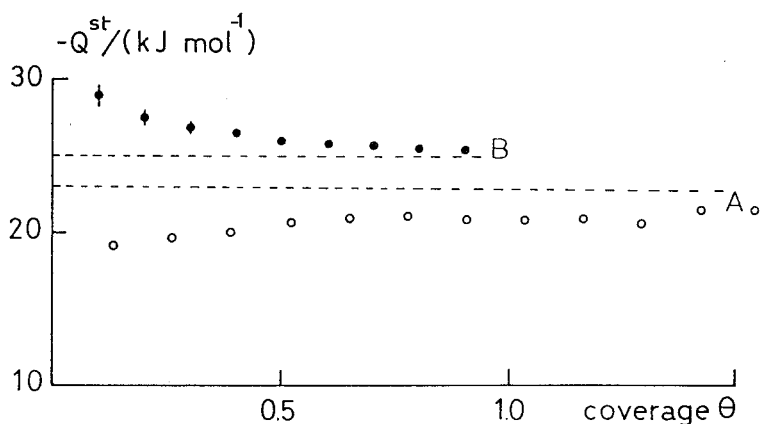


Fig. 6. *Isosteric heats of adsorption of neopentane (A) and sulfur dioxide (B) on PVDF. The broken lines refer to the corresponding enthalpies of liquefaction (near 263 and 273 K)*

The adsorption isotherms of the four gases show that there is no penetration or retention on the surface of PVDF, unlike PVC [4] [5]. Moreover, by using the gas-solid chromatography techniques described earlier [5] with methanol and neopentane as molecular probes, it was shown that PVDF is not affected by heating to about 360 K [10]. Heating to 420 K reduces the surface area, without affecting the enthalpy of adsorption of methanol at low coverage. The reduction of S_m is not surprising, since $T_f = 444 \text{ K}$ for crystalline PVDF. The heats of adsorption of neopentane and sulfur dioxide at low coverage, measured by GSC near room temperature, are consistent with the static measurements. This confirms the homogeneous character of the surface of polyvinylidene fluoride.

Entropy calculations of the type described earlier [2] were also carried out. Comparisons with the predictions for two-dimensional gases show that nitrogen and argon are quite mobile at 87 K, the entropy of adsorption being 10–12 J/mol · K larger than the value predicted for the loss of one degree of translation (42 J/mol · K). *Graham* [3] found that nitrogen was super-mobile, when adsorbed on the surface of polytetrafluoroethylene in the same temperature region. For argon, on the other hand, the loss of entropy was equal to the value predicted for the two-dimensional gas. In the case of adsorption on polypropylene [11], nitrogen and argon are slightly super-mobile. The results for PVDF are consistent with these observations. It also is found that neopentane and sulfur dioxide are slightly super-mobile on PVDF, near 270 K.

The various investigations show that the halogenated polymers have similar surfaces, of low energy. In the case of PVC, however, a slight complication arises from the penetration of certain molecules and from the modifications caused by thermal and chemical treatments [4] [5] [10]. The problem of adsorption potentials on these surfaces will be dealt with later.

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