

Adsorption of Nitrogen, n-Butane and neo-Pentane on Chloro-Hydrocarbon Polymers

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Isotherms for adsorption of nitrogen at 78.3-92.4 K on powdered samples of polyvinyl chloride (PVC) and polyvinylidene chloride (PVDC) and of n-butane and neo-pentane on PVDC at 256.2-294 K have been measured in the monolayer region. Effective cross-sectional areas of adsorbed n-butane and neo-pentane, calculated from B.E.T. plots and based on nitrogen-determined surface areas, are comparable with values obtained from the densities of the liquids. For $\theta < ca. 0.5$, isosteric heats of adsorption of nitrogen on PVC correspond closely with those on PVDC. Isosteric heats for n-butane and neo-pentane show that PVDC has a low energy surface, and the heats for n-butane decrease significantly below the heat of liquefaction with increasing coverage. Lower heats of adsorption of n-butane, compared with neo-pentane, suggest that n-butane is adsorbed on PVDC in a perpendicular position rather than lying parallel with the surface. Nitrogen isotherms at 78 K on PVC of specific surface area $1.2 \text{ m}^2 \text{ g}^{-1}$ show evidence of stepwise adsorption, and nitrogen adsorption at 78 K on γ -hexachlorocyclohexane gives a specific surface area of $0.7 \text{ m}^2 \text{ g}^{-1}$ and a B.E.T. c value of 10.

Previous investigations of adsorption of gases and vapours on organic polymers have been mainly concerned with polytetrafluoroethylene (Teflon)¹⁻¹⁰ and purely hydrocarbon polymers such as polyethylene,^{2, 4, 8, 11} polypropylene,¹² polymethylmethacrylate,¹³ and polystyrene.^{9, 14} In this paper we present results for the adsorption of nitrogen on polyvinylchloride, $(\text{CH}_2\text{CHCl})_n$ and of nitrogen, n-butane and neo-pentane on polyvinylidene chloride, $(\text{CH}_2\text{CCl}_2)_n$; results for nitrogen adsorption on γ -hexachlorocyclohexane are also reported. Adsorption of argon and water vapour by polyvinylchloride (PVC) fibres has been investigated by Babkin *et al.*⁹

neo-Pentane and n-butane provide a useful basis for comparison of adsorption properties since, although the heats of liquefaction of the vapours are similar, some differences may arise in respect of the mode of orientation of n-butane on the surface. Beebe *et al.*¹⁵ compared calorimetric heats of adsorption of n-butane and neo-pentane on spheron-6. They found that at low coverage neopentane gave a lower heat than butane, despite its higher molar mass; the effective cross-sectional area (57 \AA^2) of neo-pentane was anomalously high compared with butane (45 \AA^2). Gregg and Sing,¹⁶ and McClellan and Harnsberger,¹⁷ have reviewed the widely differing results obtained for the cross-sectional area of n-butane.

One feature of interest arising from adsorption of gases on "low energy" solids such as Teflon concerns the mobility of the adsorbate. Graham³ concluded that nitrogen, at temperatures near 78 K was weakly adsorbed on Teflon as a "super-mobile", two-dimensional gas; abnormally low isosteric heats of adsorption indicated a multilayer film of low density. However, although nitrogen was also adsorbed on polypropylene¹² as a two-dimensional gas, it failed to show super-mobility, and adsorption of n-butane on Teflon⁵ showed entropy changes intermediate between those values representing two-dimensional mobility and localization.

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EXPERIMENTAL

Adsorption measurements were carried out using a conventional vacuum apparatus with a helical, quartz spring of sensitivity 4.1 cm g^{-1} . The sample bucket contained loads of up to 5 g, and the minimum detectable mass change was 0.1 mg. Gas pressures were measured with a mercury manometer. The section of the adsorption cell surrounding the spring was thermostatted at $30 \pm 0.1^\circ\text{C}$, and the lower section (23 cm) surrounding the sample bucket was enclosed by a calorimeter jacket constructed as follows. The glass wall of the cell was enclosed by a sheet of copper of thickness 0.5 mm, around which was wound a wire heating element of resistance 42Ω . The heating element was covered with a layer of asbestos string of 8 mm diam. and this in turn was enclosed by a closely fitting brass cylinder of thickness 3 mm. The top of the brass cylinder was sealed to the glass with Araldite, and, for nitrogen adsorption, the jacket was immersed in liquid nitrogen to a level about 2 cm below the Araldite seal. Temperatures of 78–93 K inside the cell were then obtained by varying the current through the heating element and were measured by means of two copper-constantan thermocouple junctions sealed inside the cell through a side arm, with their second junctions in the liquid nitrogen bath. The sample bucket was positioned between the two inner junctions, which were situated at heights of 6 and 10 cm from the base of the tube. With the jacket immersed in liquid nitrogen, and no heating of the element, the temperature of the sample was about 1 K above the temperature of the liquid-nitrogen bath; when the heating element was used to raise the temperature, the difference in temperature between the two inner junctions did not exceed 0.6 K. For adsorption of neo-pentane and n-butane, the calorimeter jacket was immersed either in water, ice, or a mixture of ice and salt. Samples were outgassed at room temperature in a vacuum of 10^{-5} mmHg, initially for 36 h, and subsequently, between adsorption runs, for 16 h.

MATERIALS

Polyvinylchloride, suspension resin, type 113, and emulsion resin, type 121, were supplied by B.P. Chemicals (U.K.) Ltd., and polyvinylidene chloride, No. EP-961-10-17 was supplied by The Dow Chemical Co. γ -hexachlorocyclohexane was supplied by B.D.H. These materials were used as supplied.

Nitrogen, supplied by British Oxygen Co. and stated to be oxygen-free was purified using a drying column (CaCl_2 and silica gel) and a liquid nitrogen trap. neo-Pentane and n-butane, both of research grade, were obtained from Phillips Petroleum Co.

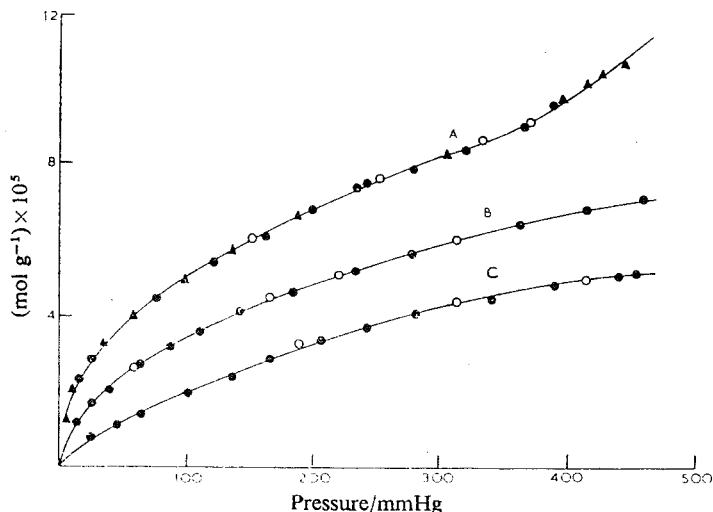


FIG. 1.—Isotherms for the adsorption of nitrogen on PVC (121) at 78.5 K (A), 85.0 K (B) and 92.4 K (C). Adsorption, \bullet , \blacktriangle ; desorption, \circ .

RESULTS AND DISCUSSION

Fig. 1-4 show the isotherms, respectively, for nitrogen on polyvinyl chloride (PVC) at 78.5, 85.0 and 92.4 K, nitrogen on polyvinylidene chloride (PVDC) at 78.3 and 92.4 K, neo-pentane on PVDC at 273.2 and 294 K, and n-butane on PVDC at 256.2, 273.2 and 294 K. Desorption results showed that there was no hysteresis, although with butane, much slower attainment of desorption equilibrium, compared with the other gases, occurred after about the mid-way stage of each of the isotherms

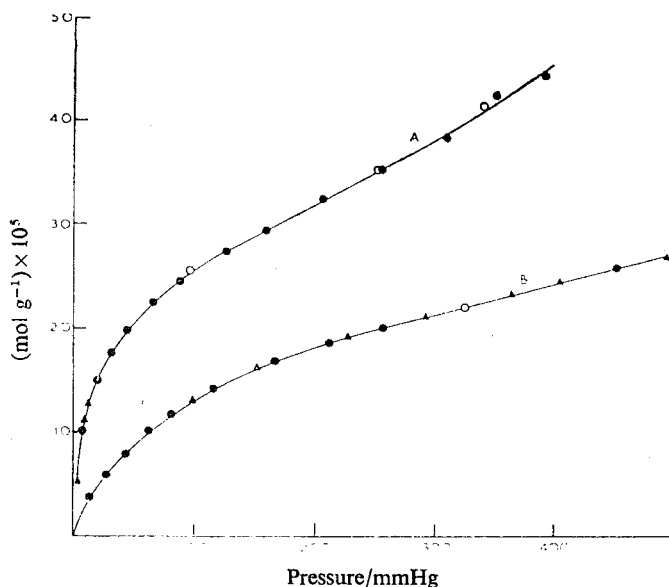


FIG. 2.—Isotherms for the adsorption of nitrogen on PVDC at 78.3 K (A) and 9.24 K (B). Adsorption, ●▲; desorption, ○△.

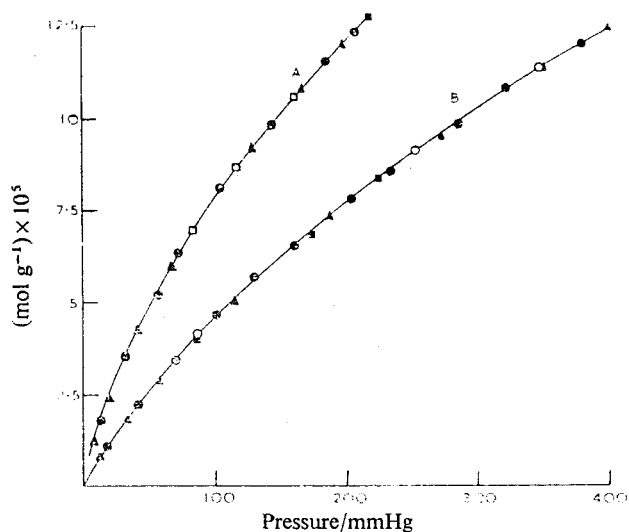


FIG. 3.—Isotherms for the adsorption of neopentane on PVDC at 273.2 K (A) and 294 K (B). Adsorption, ●▲■; desorption, ○□.

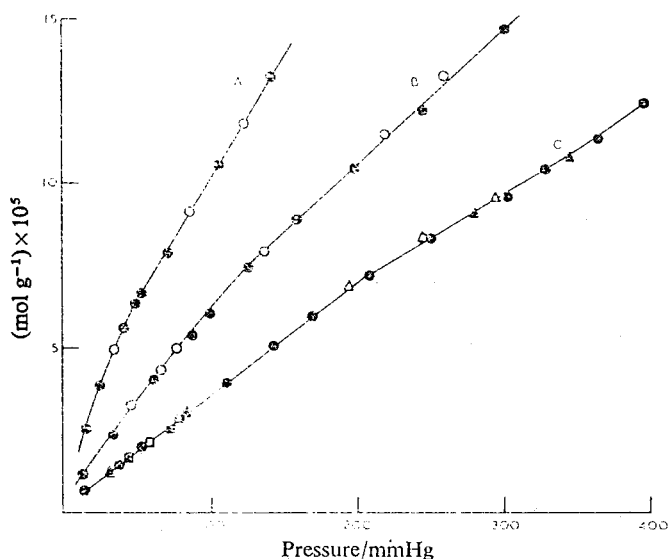


FIG. 4.—Isotherms for the adsorption of n-butane on PVDC at 256.2 K (A), 273.2 K (B) and 942 K (C). Adsorption, ●▲■; desorption, ○△□.

shown. Measurements taken on separate occasions at a given temperature, after further outgassing, and changes in isotherm temperature during a run, showed good reproducibility. Nitrogen adsorption measurements on PVDC at 78.3 K, carried out about 3 weeks after the neo-pentane and n-butane runs, gave the same isotherm as in fig. 2. Thus, if any penetration of organic vapour and swelling of the polymer has occurred under the present conditions, it does not cause any significant irreversible change in the surface.

B.E.T. plots corresponding to the nitrogen isotherms gave specific surface areas, assuming a value of 16.2 \AA^2 for the cross-sectional area of nitrogen, of $5.4 \text{ m}^2 \text{ g}^{-1}$ (PVC) and $24 \text{ m}^2 \text{ g}^{-1}$ (PVDC). The effective cross-sectional area of neo-pentane, calculated from B.E.T. plots for neo-pentane on the basis of the surface area from nitrogen adsorption, was $39 \pm 1 \text{ \AA}^2$; this is considerably lower than the values^{15, 18} of 57 and 62 \AA^2 found on carbon, and is close to the value¹⁹ of 41 \AA^2 for graphitized carbon and to the value of 37.0 \AA^2 calculated from the liquid density at 283 K using a packing factor of 1.091. Similarly, B.E.T. plots for the butane isotherms gave a mean value of $29 \pm 5 \text{ \AA}^2$ for the cross-sectional area of n-butane, which may be compared with the value of 32.1 \AA^2 corresponding to the liquid density at 273 K. Values in the range $32\text{--}55 \text{ \AA}^2$ have been reported^{15-17, 20} for n-butane on other adsorbents, and calculations by Beebe *et al.*²¹ for a molecule lying parallel with the surface gave $35.4\text{--}40 \text{ \AA}^2$.

Isosteric heats of adsorption corresponding to the isotherms of fig. 1-4 are plotted against coverage θ , in fig. 5 (nitrogen) and fig. 6 (n-butane and neo-pentane). Values of θ ref to the B.E.T. monolayer quantities for the three gases. Vertical lines through the data points representing heats calculated from isotherms at three temperatures show the differences between the heats from the two pairs of temperatures. The lower pair of temperatures gave the higher heats in each case, and with butane the average difference may be compared with the change in heat of liquefaction with temperature (indicated on the ordinate). Fig. 5 also shows for comparison, as broken curves, the approximate heat curves for nitrogen adsorbed on polyethylene¹¹

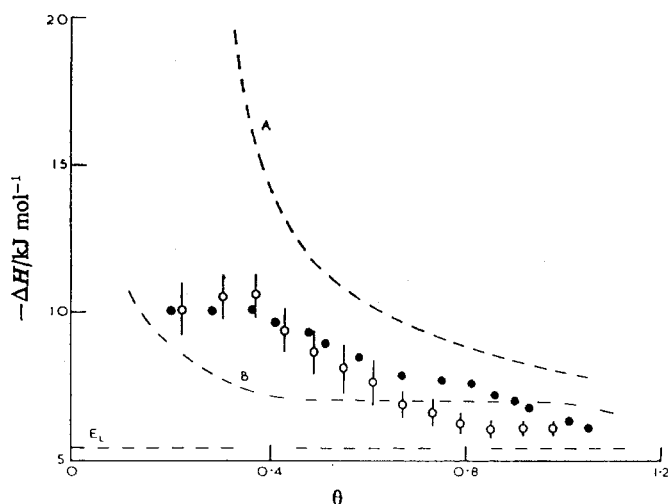


FIG. 5.—Isosteric heats of adsorption of nitrogen on PVC, \circ ; PVDC, \bullet ; polyethylene (ref. (11)), A; and polypropylene (ref. (12)), B. E_L indicates the heat of liquefaction of nitrogen near 85 K.

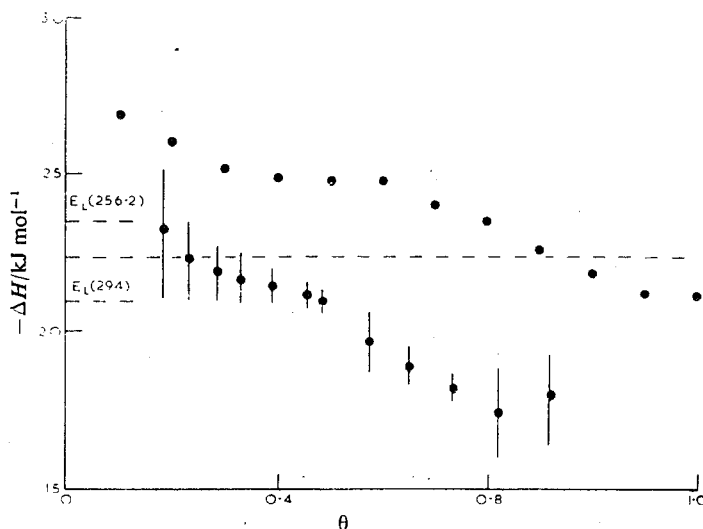


FIG. 6.—Isosteric heats of adsorption of neo-pentane, \bullet ; and n-butane, \blacklozenge on PVDC. Broken lines indicate heats of liquefaction E_L of n-butane at 256.2, 273.2 and 294 K. E_L for neo-pentane at 283 K lies between the values for n-butane at 256.2 and 273.2 K.

and polypropylene.¹² The low-coverage part of the curve for polyethylene, which is not shown, continues to increase sharply to about 33 kJ mol^{-1} at $\theta \sim 0.2$. For PVC and PVDC, the nitrogen heats at values of θ between *ca.* 0.2 and 0.4 are about the same, which indicates that the nitrogen adsorption mechanism in this range is similar for both PVC and PVDC; molecular models representing the polymer surfaces show that probable sites for adsorption involve “depressions” formed by closely grouped chlorine atoms. At higher coverage, beyond $\theta \sim 0.4$, the nitrogen heat curves for PVC and PVDC are characteristic of heterogeneous parts of the surface and are approximately parallel to the polyethylene curve.

Nitrogen adsorption isotherms at 78 K on a sample of PVC of lower specific surface area and on γ -hexachlorocyclohexane are shown in fig. 7. The slight stepwise appearance of the PVC isotherm suggests some degree of homogeneity of the polymer surface; in this connection, the nitrogen heats (fig. 5) for the higher area sample of PVC (and PVDC) at values of θ from about 0.2 to 0.4 are approximately independent of coverage, whereas the heats for polyethylene fall sharply in this range.

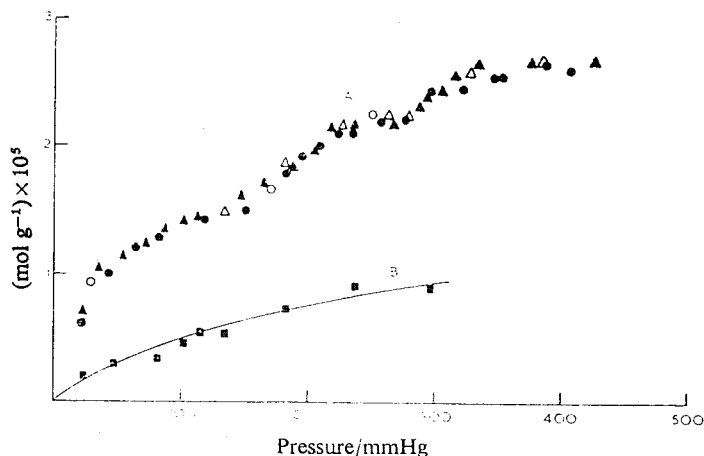


FIG. 7.—Isotherms for the adsorption of nitrogen at 78 K on PVC (113), A, and on γ -hexachlorocyclohexane, B. Adsorption, \bullet , \blacktriangle , \blacksquare ; desorption, \circ , \triangle .

Linear B.E.T. plots for the first "step" of the PVC isotherm (fig. 7) and for γ -hexachlorocyclohexane gave specific surface areas and c values (in parenthesis) of $1.2 \text{ m}^2 \text{ g}^{-1}$ (70) and $0.7 \text{ m}^2 \text{ g}^{-1}$ (10) respectively. These c values may be compared with values for nitrogen of 62 for PVDC and 27 for the higher area sample of PVC. The relatively low value of c for γ -hexachlorocyclohexane, indicating a low average heat in the first layer, is noteworthy; the physical adsorption behaviour of molecular solids has been discussed by Dormant and Adamson.²² The c values from the B.E.T. plots for *n*-butane and neo-pentane were 4 and 7 respectively.

The heats of adsorption of both *n*-butane and neo-pentane on PVDC (fig. 6) are significantly lower than the calorimetric heats,¹⁵ at corresponding values of θ , for these vapours on spheron-6, reflecting the "low-energy" character of the polymer surface. With spheron-6, higher heats of *n*-butane at low coverage compared with neo-pentane were attributed¹⁵ to the ability of *n*-butane to lie flat on the surface, each CH_3 or CH_2 contributing to the heat. The reverse situation seems to hold with PVDC, since the heats for neo-pentane are higher in accordance with its higher molar mass. This may be taken as evidence that *n*-butane is not adsorbed in a parallel position on PVDC. An additional feature shown by fig. 6 is that the heats for *n*-butane, and to a lesser extent, neo-pentane, decrease to below the heat of liquefaction. Similar behaviour observed with adsorption of Ar, N_2 and CF_4 on Teflon has been attributed³ to formation of an adsorbed film of unusually low density.

The butane adsorption results for θ values in the range 0.2-0.5 conformed approximately to the two-dimensional van der Waals equation of state,

$$P = K \frac{\theta}{1-\theta} \exp \left[\frac{\theta}{1-\theta} - \frac{2\alpha}{RT\beta} \theta \right],$$

where α and β are constants, and K is Henry's constant. Values of K at 256.2, 273.2 and 294 K were 110, 138 and 147 mmHg respectively, and the value of $2\alpha/\beta$ for the three plots was 7.9 kJ mol^{-1} ; the latter may be compared with the value of 7.53 kJ mol^{-1} reported²⁰ for n-butane on graphitized carbon. Following the procedure of de Boer,²³ as used by Hoory and Prausnitz,²⁰ and using a value of 21.8 kJ mol^{-1} (fig. 6) for the isosteric heat of adsorption, the integral change of entropy ΔS_s^a for adsorption of n-butane from a reference standard gas pressure, 760 mmHg, to a reference spreading pressure of $0.338 \text{ dyn cm}^{-1}$, was calculated to be $-27 \text{ J mol}^{-1} \text{ K}^{-1}$ at 273.2 K. For a mobile, two-dimensional film, with a loss of one degree of translational freedom, the entropy change, ΔS_s^{tr} , according to Hoory and Prausnitz's result corrected to 273.2 K, is $-49.67 \text{ J mol}^{-1} \text{ K}^{-1}$. Similar observations with Teflon,³ for which the decrease in entropy on adsorption of nitrogen was less than that associated with the loss of one degree of translational freedom, have been described in terms of "super-mobility" of the adsorbed film, and possibly involving retention of part of the translational entropy as a vibration normal to the surface. If we assume that n-butane is adsorbed on PVDC in the standing-up position, with no change in rotational entropy from the gas phase, then the vibrational contribution would be $+ca. 23 \text{ J mol}^{-1} \text{ K}^{-1}$. Hoory and Prausnitz's calculations²⁰ for n-butane on graphitized carbon at 298 K give a value of $+20.5 \text{ J mol}^{-1} \text{ K}^{-1}$ for the vibrational entropy term, the adsorbed molecule in this case lying flat.

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¹ J. J. Chessick, F. H. Healy and A. C. Zettlemoyer, *J. Phys. Chem.*, 1956, **60**, 1345.

² W. Thompson, *Physica*, 1960, **26**, 890.

³ D. Graham, *J. Phys. Chem.*, 1962, **66**, 1815.

⁴ J. W. Hightower and P. H. Emmett, *J. Polymer Sci. A*, 1964, **2**, 1647.

⁵ D. Graham, *J. Phys. Chem.*, 1965, **69**, 4387.

⁶ J. W. Whalen, W. H. Wade and J. J. Porter, *J. Colloid Interface Sci.*, 1967, **24**, 379.

⁷ W. H. Wade and J. W. Whalen, *J. Phys. Chem.*, 1968, **72**, 2898.

⁸ B. G. Aristov and A. V. Kiselev, *Kolloid Zhur.*, 1967, **29**, 631.

⁹ I. Yu. Babkin, Yu. M. Gordeev and A. I. Krasnogorov, *Kolloid Zhur.*, 1967, **29**, 765.

¹⁰ J. W. Whalen, *J. Colloid Interface Sci.*, 1968, **28**, 443.

¹¹ A. C. Zettlemoyer, A. Chan and E. Gamble, *J. Amer. Chem. Soc.*, 1950, **72**, 2752.

¹² D. Graham, *J. Phys. Chem.*, 1964, **68**, 2788.

¹³ J. E. Lohr and J. J. Scholz, *J. Colloid Sci.*, 1965, **20**, 846.

¹⁴ R. F. Hoburg, G. S. Handler and J. J. Scholz, *J. Colloid Interface Sci.*, 1968, **27**, 642.

¹⁵ R. A. Beebe, G. L. Kington, M. H. Polley and W. R. Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 40.

¹⁶ S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, (Academic Press, London, 1967), p. 81.

¹⁷ A. L. McClellan and H. F. Harnsberger, *J. Colloid Interface Sci.*, 1967, **23**, 577.

¹⁸ W. F. K. Wynne-Jones, *Proc. Symp. Colston Res. Soc.*, 1958, **10**, 38.

¹⁹ N. N. Avgul, A. V. Kiselev and I. A. Lygina, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. trans.)*, 1962, 717.

²⁰ S. E. Hoory and J. M. Prausnitz, *Trans. Faraday Soc.*, 1967, **63**, 455.

²¹ R. A. Beebe, M. H. Polley, W. R. Smith and C. B. Wendall, *J. Amer. Chem. Soc.*, 1947, **69**, 2294.

²² L. M. Dormant and A. W. Adamson, *J. Colloid Interface Sci.*, 1968, **28**, 459.

²³ J. H. de Boer, *The Dynamical Character of Adsorption* (The Clarendon Press, Oxford, 1953), p. 170.