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The Porous Structure of Polymers and the Mechanism of Sorption

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A survey is made of the behaviour of polymeric sorbents and the role of the porous structure of polymers in the mechanism of sorption and in the thermodynamic affinity of solvents for the polymer. The list of references contains 301 items.

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I. INTRODUCTION

The properties of polymeric materials depend not only on the chemical structure and the dimensions of the macromolecules but also on the structure of the material, by which is usually understood the relative arrangement of macromolecules in space, their conformations, and also the internal structure of the units forming the macroscopic polymeric material and the nature of the interrelationship between them[1,2]. Furthermore, the concept of structure must include also looseness or emptiness, which are present in any material owing to the distances both between molecules and between coarser, supermolecular structures. In crystal chemistry these voids are indicated quantitatively by the packing coefficient[3,4]; the term "free volume" is usually applied to liquids[5]; and for porous solids various parameters of the porous structure are calculated[6].

A vast literature, summarised in several monographs[1,7,8], has been devoted to the structure especially of crystalline polymeric materials. These publications do not pay due attention to problems of the looseness of molecular packing and the porous structure of polymers, but are concerned mainly with the degree of ordering of the macromolecules and various morphological formations. Yet many papers have paid special attention to problems of the density of packing and the porous structure of polymers, but the regularities reported in them have not hitherto been summarised. Without knowledge of the porous structure of polymers and the density of their molecular packing it is impossible to describe the polymer structure, in particular of amorphous polymers, to understand the mechanism of the sorption of simple substances on polymers, or in general to comprehend the mechanism of the interaction of polymers with solvents.

The problem of the mechanism of sorption on polymers is of immense practical importance in connection with the expanding application of polymers as sorbents (ion-exchange resins and their frameworks, sorbents for gel-permeation chromatography)[9-11] and membranes (in particular for reverse osmosis[12-14]), as well as in connection with the sorption of simple substances by fibres, artificial leather[15,16], etc. Sorption effects play a large part in the permeability of polymers to gases and vapours[17,18]. Many processes in which polymers undergo chemical modification (e.g. the acetylation of cellulose, etc.) depend on the size of the pores, which act as transport arteries for penetration of the modifying agents to the reaction centres[19]. In this case an insufficiently developed porous structure may result in a non-uniform fibre of low quality. The mechanical and thermophysical properties of polymers are governed by their porous structure and the density of packing of the macromolecules[20,21]. It is therefore necessary to have a clear idea of the laws of the formation of the porous structure of polymers, and on the other hand also those of the production of monolithic polymers. The Reviewers have now made the first attempt to summarise all the information that has been published on this subject.

II. POROUS STRUCTURE OF MATERIALS AND ITS ESTIMATION

The concept of "porosity" and "pore" arose from consideration of the structure of solid mineral sorbents and catalysts. According to Dubinin's definition "pores are voids in solids ..."[22]; "porosity is a property of solids due to their structure and apparent in the presence of empty spaces—pores between individual grains, layers, crystallites, and other units of the coarse structure of a solid"[23]. The two definitions emphasise that the concept of porosity is applicable to solids, and that a pore is a space not between molecules but between supermolecular structures.

Table 1.

Method	Pore sizes, cm
Sorption	10^{-7}-10^{-5}
Chromatographic	10^{-7}-10^{-5}
Mercury porometry	10^{-7}-10^{-3}
Electron microscopy	10^{-6}-10^{-4}
Optical microscopy	$> 10^{-4}$
X-Ray diffraction	10^{-8}-10^{-5}

The porosity of solvents is usually assessed quantitatively by means of several parameters—specific surface S_{sp}, total pore volume W_0, pore radius r—and by means of differential distribution curves of pore volume with respect to radius. Methods of determination developed for mineral sorbents[24-26] are applied also to polymers. Each method covers a definite range of pore sizes (Table 1).

The most direct visual method is electron microscopy, which makes it possible to assess not only the dimensions but also the shape of the pores[27-29]; it is applied also to polymers[30-42]. X-Ray diffraction enables the effective radii of the finest pores to be determined[43,44]; in recent years this method has been widely applied to investigate ultramicrocracks in polymers[21,45], which are essentially micropores.

The sorption method was historically the first for evaluating the porous structure of sorbents, and has become classic. It consists essentially in studying the sorption of various substances from liquid and vapour media on solids and then using the resulting sorption isotherms to calculate the specific surface, the total pore volume, the pore radius, and the differential distribution curves. There exist many variants of this method and ways of calculating the parameters of the porous structure. The most common are the Brunauer–Emmett–Teller (BET) method for calculating specific surface[46,47] and the Dubinin–Radushkevich equation for calculating the total pore volume[48]. Despite the widespread use of the sorption method, it has several limitations, as indicated below.

1. It cannot estimate voids having $r < 7$ Å, since the quantity of substance sorbed by them is below the limits of sensitivity of the method.

2. Values of W_0, calculated by means of the Dubinin–Radushekvich equation or directly from the maximum quantity of substance sorbed[49], do not represent the true total pore volume, but indicate essentially the limiting volume of adsorption space, which, of course, depends on the size of the sorbed molecules: the larger the molecules the less accessible are the fine pores of the sorbent and hence the smaller the value obtained for W_0. In order to estimate the dimensions of the finer pores, therefore, use must be made of the sorption of substances having small molecules (nitrogen or argon); this is performed at temperatures at which their vapours condense (low-temperature sorption). In most cases the "porosity for nitrogen" of mineral sorbents exceeds the "porosity for benzene".[50] However, some workers[51,52] refer to quite marked changes in pore volume accompanying the cooling of certain mineral sorbents to temperatures (around −200°C) at which the sorption of nitrogen or argon is conducted, which may lead to incorrect results.

3. The parameters of the porous structure depend on the chemical surface structure of the sorbent, which in turn affects the area, occurring in the BET equation, occupied by a sorbate molecule in the adsorption layer and the degree of wetting of the surface by the liquid, i.e. the process of capillary condensation. Poor surface wetting hinders this process and leads to underestimates of the parameters[53].

4. Calculations based on the Thomson–Kelvin equation do not give true pore radii but essentially the radii of concave menisei of liquid condensed in the pores. A correction for the thickness of the adsorption layer must be made to obtain true pore radii[54,55].

5. The sorption method does not enable the size of very large pores to be estimated, in which capillary condensation is difficult because of the considerable distance between the walls.

The porous structure of solids can be investigated over a wide range of pore sizes by the method of mercury porometry, which enables pore radii to be measured from 30 to some 10^5 Å:[26,56-58] the larger pores (10^4–10^5 Å) are filled with mercury under pressures of ~ 1 atm; high pressures reaching 2500–4000 atm are used to fill the finer pores. The pore radii are calculated by means of the equation

$$r = -\frac{2\sigma \cdot \cos\theta}{p}, \qquad (1)$$

where σ is the surface tension of mercury at the experimental temperature, θ the angle of wetting, and p (in kgf cm^{-2}) the pressure. This method has recently begun to be widely used to examine the porous structure of polymeric materials—fibres[59-69], network copolymers, and ion-exchange resins based on them[34,70-75].

Difficulties arise also with mercury porometry, connected with the choice of numerical values for σ and θ, which depend on the nature and the purity of the surface, and may vary with pressure[26,60,76,77]. As a result of incorrect estimates for σ and θ, as well as their possible variation during an experiment, the error in the determination of pore size may reach 30–40%.[26,77] Furthermore, the high pressures applied may disrupt the structure of the sorbent[26,51,65,76-80]. Therefore this cannot be regarded as an absolute method for determining pore size[75,77].

III. CHARACTERISTICS OF POLYMERIC SORBENTS

All that has been stated above concerning the limitations on the sorption method and mercury porometry are fully applicable also to polymeric sorbents, which also possess specific features due to the properties and structure of the polymers. In the determination of the pore structure of polymers it must be borne in mind that they exist not only in the solid but also in the rubberlike-elastic state, so that the question naturally arises of whether the idea of pores and porosity is appropriate to such a state. From the definition of these concepts (Section II) it follows that pores are voids in a solid that do not change with time[81]. This concept is fully applicable to solid polymers (vitreous and crystalline) but inapplicable to polymers in a state of rubberlike elasticity. In this last case the "voids" or "holes" have a fluctuating character (just as in liquids): i.e. they change their forms and dimensions continuously under the influence of thermal motion. However, the permanent cavities produced in polymeric materials under special conditions, e.g. in foam rubbers, can be termed pores, and the articles themselves are porous.

Furthermore, the structure of polymeric sorbents is considerably more labile and far more sensitive to sorbent–sorbate interaction, temperature, and external pressure than is the structure of classic mineral sorbents (active carbons, silica gels, etc.). This faces the investigator with the problem of the conditions under which a particular method can be used to assess porous structure, and also the conditions of preparation of polymeric sorbents.

Any substance of high molecular weight swells on interaction with liquids and vapours of low molecular weight. Swelling is not simply the absorption of these substances by the pores of the former: it necessarily involves changes in the volume of the specimen and in its structure[82]. Hence the structure of a swollen polymer differs fundamentally, especially at high relative vapour pressures, from its original structure. Since a swollen polymer is not a solid, the "holes" or free volume it contains are fluctuating in character and are not pores. Therefore the terms used in the literature—"porosity of polymers in the hydrated state"[10], "pseudoporosity"[83], "latent porosity"[84-86]—are devoid of physical meaning.

Structural lability of a polymer develops also when the temperature is varied, which often leads to incorrect results in the investigation of the low-temperature sorption of nitrogen or argon vapour[87-94]. If the coefficient of thermal expansion of a sorbent is $\alpha \simeq 10^{-6}$ deg^{-1}, the specific volume may change by only 0.002–0.003 cm^3 g^{-1} when the temperature is lowered from 25 to −195°C, and this will hardly be apparent in its overall porosity. In such cases the porosity with respect to nitrogen, determined at −195°C, will exceed the porosity with respect to benzene, determined at 25°C, as was to be expected, and the method of low-temperature sorption is applicable. With many polymers, however, the coefficient of expansion is larger by factors of 10–10^2. For example, polystyrene and its copolymers have $\alpha = (1.8–2.7) \times 10^{-4}$ deg^{-1}, and for cellulose $\alpha = 4 \times 10^{-4}$ deg^{-1};[93,94] hence the volume of these compounds should decrease by 0.1 cm^3 g^{-1} when they are cooled by ~ 200 deg. If the pore volume of the polymer is of the same order, the porosity will almost disappear on cooling. In such cases the parameters of the porous structure determined with respect to nitrogen may be smaller than those with respect to organic compounds. This is illustrated by Table 2, which shows that, for specimens of well developed porosity (No. 4 and 5), such volume changes are insignificant, and the specific surface with respect to nitrogen is considerably larger than that with respect to methanol[94]. It is obviously for this reason that results obtained by Ružička and Kudlaček[95] for the sorption of argon vapour on viscose tyre cord agreed with those obtained by Paul and Bartsch[96] for high-strength viscose rayon fibre by mercury porometry. In the case of polymers having relatively undeveloped porosity, however, the low-temperature sorption of nitrogen or argon vapour must be applied with great caution[94].

Table 2. Parameters of the porous structure of polymers determined from the sorption of nitrogen and organic vapours[94].

No.	Polymer	S_{sp}, m^2 g^{-1}		W_0, cm^3 g^{-1}	
		N_2	CH_3OH	N_2	CH_3OH
1	Polystyrene	—	—	0.001	0.030
2	Copolymer of styrene + 4% *p*-dvb*	~0	5.1	~0	0.030
3	Copolymer of styrene + 20% *p*-dvb	~0	17.2	~0	0.070
4	Copolymer of styrene + 60% *p*-dvb**	278.4	88.4	—	0.460
5	Polymer based on 100% *p*-dvb**	423.8	94.2	—	0.440

* dvb = divinylbenzene.
** Synthesised in n-heptane.

The structural lability of polymers and polymeric sorbents is evident also in mercury-porometric measurements, since the high pressures used may develop forced elastic deformations in the specimen. In uniformly porous polymers, with all the pores filled with mercury at almost the same pressure, the pore walls may be compressed under multilateral pressure. When pores of different sizes are present, they are filled with mercury at different pressures, and the wall between a full pore and a still unfilled pore may be deformed by unilateral pressure, closing the pore. The possibility of the reversible compression of polymers during porometric measurements was mentioned in Ref. 65, but with some polymers no significant change in porosity occurs when they are tested in a porometer[75].

The peculiarities of polymeric sorbents also lead to certain demands on their preparation, mainly the need to remove from the pores various impurities of low molecular weight. With active carbons and other mineral sorbents this is usually achieved by prolonged heating in a vacuum at 300–400°C. Such heat-treatment is excluded with polymers because of their possible degradation or other chemical changes. But the removal of moisture or organic compounds by drying polymers even at lower temperatures (but above their glass points) is also hardly applicable because of shrinkage phenomena due to the plasticising action of low-molecular liquids that are present. Thus the vaporisation of water from moistened cellulose leads to its compaction[19].

Polymeric sorbents can be subjected to lyophilic or freeze drying, first applied to biological materials. This method consists in the rapid cooling of moistened polymer specimens to the boiling point of liquid nitrogen, which leads to the sublimation of liquids present in the specimen. An advantage of lyophilic drying is the almost complete elimination of the effect of the capillary forces present in ordinary drying[97-102].

The best method for drying a polymer is inclusion, which consists in successive displacement of the liquid by treatment with various increasingly volatile miscible liquids which possess gradually diminishing affinity for the polymer. The last liquid should have as low a surface tension as possible. As a result, the polymer passes into a vitreous state, and its pores contain a readily vaporisable liquid interacting only slightly with the polymer. After removal of this liquid the polymer has more or less retained its original structure[19,67,68,98,99,103-105]. The classic example of this method is the inclusion of moistened cellulose: water is displaced by repeated treatments with methanol, and then with pentane, which is evaporated off[19].

Unfortunately, these characteristics of polymeric sorbents were ignored in many determinations of the porosity parameters, so that the results are unreliable[87,89,106,107]. For example, the specific surface of cellulose was calculated from the water-vapour sorption isotherms as 100–200 m^2 g^{-1},[87,106] values which are far too high, since cellulose swells strongly in water. If the sorbates used cause a given polymer to swell to different extents, different values of the specific surface will, of course, be obtained for the same specimen[107].

The incorrectness of such results was first pointed out by the Reviewers[108,109], who suggested the same approach as for mineral sorbents, i.e. to maintain the sorbent as far as possible rigid, retaining its structure unchanged during sorption. The appropriate sorbates were said to be "inert", a not altogether fortunate term, since absolutely inert sorbates and sorbents do not exist, as Hill showed[110-112]. Any sorbent—even if mineral—undergoes some perturbation under the influence of a sorbate, which is apparent in a change in state of the surface atoms[113-115] or even in a slight "subswelling" of the sorbent[116-119]. Henceforward, however, we shall employ the term "inert" to imply sorbates in which a polymer hardly swells at all.

Polymeric sorbents may undergo considerable disturbances under the influence of a sorbate. In order to obtain correct values for the parameters of their porous structure it is necessary to select for each polymer a

sorbate that will not cause its bulk swelling (the perturbation of a polymeric sorbent by the sorbate should not exceed that of a mineral sorbent).

During recent years comprehensive experimental information has been obtained on the sorption of "inert" vapours (i.e. those that do not cause swelling) on very many polymers[49,93,94,108,109,120-141]. Parameters of their porous structure have been calculated (by generally accepted methods) from the sorption isotherms. The BET and Dubinin–Radushkevich equations are applicable over the same ranges of relative vapour pressures as for mineral sorbents[108,120,130].

IV. CLASSIFICATION OF POLYMERIC SORBENTS AND THE POROUS STRUCTURE OF POLYMERS

The first few classifications of mineral and polymeric sorbents were based on the form of sorption isotherm, which was related to the type of surface coverage of the adsorbents by the adsorbate molecules. In particular, such a classification was proposed by Brunauer, Deming, Deming, and Teller (the BDDT classification), in which all published sorption isotherms were divided into five types differing in the character of the surface coverage[6,24]. A similar approach to the classification of polymeric sorbents was suggested by Rogers, who separated all known sorption isotherms on polymers into the four types[142] illustrated in Fig. 1. The first type of isotherms correspond to a linear relation between the concentration of the sorbed substance and the pressure, which characterises the absorption of a gas in conformity with Henry's law. The second type involve systems in which only a monolayer is adsorbed on the polymer surface. Isotherms of the third type are obtained for multimolecular adsorption when the energy of interaction between sorbent and sorbate molecules exceeds the intermolecular interaction energy in the sorbate. The fourth type corresponds to multimolecular adsorption when the former interaction energy is very much smaller.

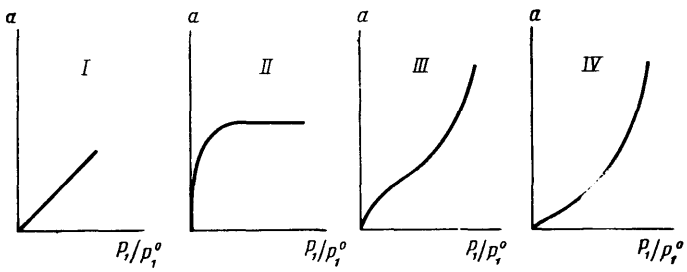


Figure 1. Types of sorption isotherms on polymers according to Rogers[142], where a is the equilibrium quantity sorbed in millimoles per gram of sorbent, and p_1/p_1^0 the relative vapour pressure.

Theories relating adsorption processes solely with surface state[24] were accompanied by the development of ideas on the role of sorbent porosity in adsorption processes, and classification of mineral sorbents were proposed according to pore size and shape. Thus there exist globular, slitlike, cylindrical, and bottle-shaped pores, as well as pores between round rods[116]. Pores are divided into closed, blind, and open pores[51,143]: the third group comprises pores, channels, and capillaries that are connected with one another and with the sorbent surface, serving as transport arteries for mass transfer; closed pores are mutually isolated and have no outlet to the surface; and blind pores are connected with the surface but are not interconnected. No unambiguous evidence has been published of the presence of one kind of pore or another. In most cases this must be judged from gas-permeability data[144,145]. The most fertile classifications of sorbents are those of Dubinin[6,22,146] and of Kiselev[147], which can be applied even to polymeric sorbents.

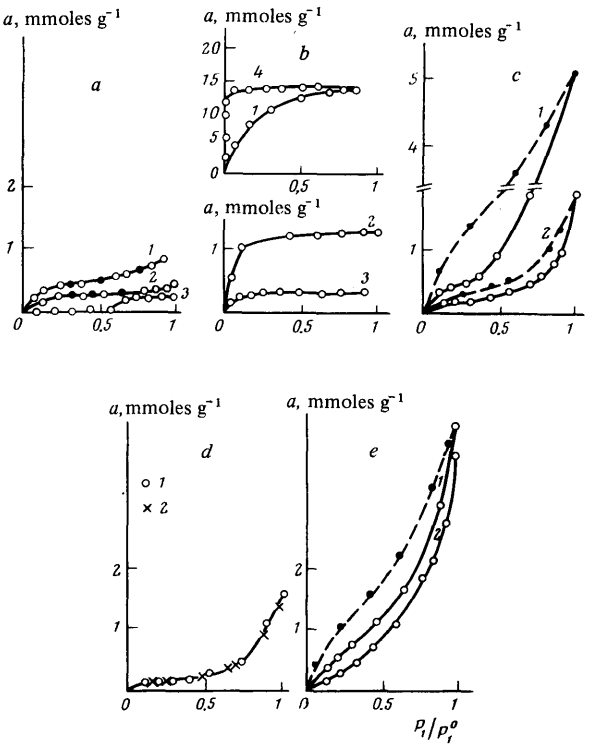


Figure 2. Sorption isotherms for vapours of "inert" liquids on different classes of polymeric sorbents, where the solid circles and broken curves denote desorption results. (*a*) Non-porous: 1) n-hexane on polyvinyl alcohol[108]; 2) benzene on polyvinylidene chloride[121]; 3) methanol on polyethylene[121]. (*b*) Microporous: 1) nitrogen on a macroscopically cross-linked isoporous polymeric sorbent based on polystyrene and *p*-bischloromethylbenzene; 2) water on polystyrene[148]; 3) n-hexane on cellulose[108]; 4) nitrogen on activated carbon[123]. (*c*) Sorbents containing continuous pores: 1) copolymer of styrene with *p*-divinylbenzene (in n-decane)[131]; 2) methanol on a polyarylate (DKh-1 brand)[237]. (*d*) Macroporous: 1) Styroflex film; 2) polystyrene film. (*e*) Mixed type: 1) copolymer of styrene with technical divinylbenzene (in n-heptane)[125]; methanol on a polyarylate (F-1 brand)[237].

Analysis of > 200 sorption isotherms for "inert" vapours on various polymers[49,93,108,109,120-141,148] enables them to be separated into the four main types illustrated in Fig. 2. The first type—non-porous sorbents (Fig. 2*a*)—are characterised by sigmoid isotherms without sorption hysteresis and with a small quantity of maximally absorbed sorbate. Such isotherms are observed with several crystalline polymers (polyvinyl alcohol, polyvinylidene chloride) and certain densely packed vitreous polymers (block poly(methyl methacrylate) and polystyrene). At low relative vapour pressures crystalline polyethylene sorbs hardly any vapour of the "inert" methanol, and insignificant sorption is observed only at higher relative vapour pressures. Such polymers are characterised by almost zero total pore volume W_0 and very small specific surfaces ($\sim 1-7$ m^2 g^{-1}).

The second type comprises microporous polymeric sorbents having pore radii up to 16 Å. Such fine pores cannot be penetrated by large sorbate molecules and many small molecules. Microporous sorbents are characterised by Γ-shaped isotherms (Fig. 2*b*), the plateau on which results not from surface saturation with sorbate molecules but from the inaccessibility of the fine pores to the penetration of many molecules. The concept of specific surface has no physical meaning for microporous polymeric sorbents[22,149-154], but the total pore volume may reach 0.5 cm^3 g^{-1}. Fig. 2*b* indicates that the initial portion of the sorption isotherms is considerably less steep on the polymeric sorbents than e.g. on microporous carbons[123,155] or zeolites[156-159]. This is understandable, since a large number of fine pores in the latter sorbents result from the removal of hydrogen chloride or water.

Polymeric sorbents of the third type have continuous pores with radii from 16 to 1000–2000 Å. Such polymers are characterised by sigmoid isotherms and large sorption hysteresis (Fig. 2*c*). They are able to absorb large quantities of a sorbate, their total pore volume reaching $W_0 \simeq 0.8$ cm^3 g^{-1} and their specific surface $\sim$ 700–900 m^2 g^{-1}.

Macroporous polymeric sorbents, having pore radii exceeding 1000–2000 Å, constitute the fourth type. According to Dubinin's hypothesis, sorption takes place on them in the same way as on non-porous sorbents, since the internal surface of such large cavities acts as an external surface. Indeed, Fig. 2*d* shows that the sorption isotherms for methanol on a non-porous Styroflex film and on a specially prepared macroporous specimen of polystyrene are completely identical.

It is often impossible to assign real polymers to a definite class of sorbents, and in particular it is a complicated task to obtain uniformly fine-pored sorbents, often termed "isoporous". The latter are obtained not by polymerisation or polycondensation but by the cross-linking of existing polymers[136,160-163]. The large majority of amorphous polymers are sorbents of structurally mixed type. They are characterised by slightly sigmoid isotherms (Fig. 2*e*) and possess pores of the most diverse dimensions, as is evident from Fig. 3. Such sorbents often exhibit no correlation between pore volume and specific surface. Thus, when large pores predominate, the pore volume may be large but the specific surface small; and conversely, in the presence of a large number of small pores, the sorbent has a large specific surface and a small pore volume[49,129,135].

Pore radii of the order of 10^2–10^4 Å indicate that the large cavities in the polymer are formed not between molecules but between coarse supermolecular structures, while the pore walls may be very densely packed. This suggests that amorphous polymers are structurally inhomogeneous, as is sometimes observed even with crystalline polymers. In isotactic polystyrene, for example, large pores are found situated between crystallites[122].

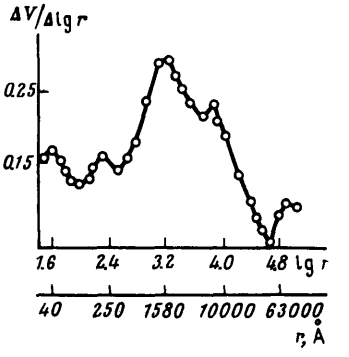


Figure 3. Differential curve of the distribution of pore volume with respect to radius for F-1 polyarylate, where ΔV is the volume of mercury filling pores of certain radii.

Porosity is not a property of a given substance but depends on its previous history. It is usually produced during preparation of the specimen. Several methods are available for obtaining porous polymers, and are used during synthesis and the moulding of articles. They usually involve heat-treatment of the material accompanied by removal of volatile products[123,161-170], with the introduction of special blowing agents[10,171], saturation of the polymers by gases under a high pressure which is subsequently released[172], or the introduction into monomers of suspensions of organic or inorganic solids which are later removed[173,174]. One process for obtaining porous polymers is synthesis in the presence of a solvent, whose removal leaves quite large cavities in the polymer. Very porous three-dimensional polymers can be synthesised in so called inert solvents, i.e. substances that are not involved in the polymerisation. Porous cross-linked copolymers (e.g. of styrene with divinylbenzene), employed in chromatography and also used as frameworks for macroporous ion-exchange resins, are produced in this way[9,10,31,32,83-86,136,174-180]. Shrinkage stresses arising on removal of the solvent then play an important part. They lead to shrinkage deformations and to contraction of the structural framework, i.e. to shrinkage of the whole material.

This phenomenon was investigated in detail by Rebinder[181], Ostrikov et al.[182-190], Vlodavets et al.[191-193], etc. The shrinkage stresses may result in contraction of the material by factors of 8–10[194], with the pore walls coming together and in some cases completely closing the pores[181,185,191]. The magnitude of the shrinkage stresses depends on the surface tension of the liquid[67,98,103-105,185,194-198], the nature of the sorbent, and the shrinkage capacity of the latter[199]. With perfectly rigid materials (porous silicate glasses, ceramics) shrinkage phenomena are almost completely absent. Elastic polymers exhibit the largest shrinkage. Hence the polymer framework should be as inelastic as possible to obtain a highly porous

structure during removal of the inert solvent, as has been demonstrated experimentally for the cross-linked frameworks of styrene–divinylbenzene copolymers[200]. This is achieved by introducing a large number of cross-links during synthesis and selecting as inert solvent a "poor" solvent that does not plasticise the polymers. Cross-linked copolymers of highly developed porosity are therefore obtained in the presence of large quantities of thermodynamically "bad" solvents and with a large quantity of the cross-linking agent in the reaction mixture[31,32,34,49,70-72,84-86,124,125,131,136,173,174,176,180,201-224].

Analogous effects are observed also in the synthesis of linear polymers, as has been shown for a series of polyarylates[133,135]. Thus polymers of desired porosity can be obtained by varying the conditions of the synthesis. A porous structure can be conferred on polymers also by varying the conditions under which they are moulded, as has been demonstrated for fibres[64,67,68,225-228] and films[129,132,229-237].

V. RELATIONS BETWEEN PARAMETERS OF THE POROUS STRUCTURE OF POLYMERS, THEIR FREE VOLUME, AND THE PACKING COEFFICIENT

As already mentioned, besides the term "porosity" there exist other concepts connected with "empty" spaces in materials—the free volume and the packing coefficient—the problem of whose relationship has been discussed previously[238].

The term "packing coefficient" was first applied by Kitaigorodskii to crystals[3,4], but subsequently began to be used for amorphous solids and liquids, and also to describe the molecular packing of polymers[239-243]. This coefficient is the ratio of the actual volume of the molecules in 1 g or 1 mole of the substance to its specific (or molar) volume at the given temperature:

$$K = \frac{V_W}{V_T}. \qquad (2)$$

The intrinsic volume of molecules is calculated from the intermolecular distances and the lengths of the chemical bonds between the atoms, obtained by X-ray diffraction[4,240]. For most low-molecular and polymeric crystals the packing coefficient lies in the range $K = 0.68–0.8$,[3] and for monolithic amorphous polymers it fluctuates between 0.662 and 0.723.[240]

The free volume is usually understood to be the volume not occupied by the mass of the given substance, but different authors calculated it differently. Thus Frenkel'[5] understood by free volume the excess volume of a specimen at a given temperature in comparison with its volume at the absolute zero:

$$V_F = V_T - V_0. \qquad (3)$$

Hildebrand and Bondi termed the quantity V_F calculated by means of Eqn. (3) the expansion volume, and proposed that the free or empty volume V_E should be calculated by means of the formula[244,245]

$$V_E = V_T - V_W, \qquad (4)$$

in which V_T is the volume of the body at the given temperature and V_W is the actual volume of its molecules.

The empty volume and the packing coefficient are related by the simple formula

$$1 - K = V_E/V_T, \qquad (5)$$

from which it follows that in crystals, even with the densest packing of their atoms and molecules, the free or empty volume constitutes 20–32% of the total volume. Yet sorption experiments show that typical crystalline solids are non-porous sorbents. Hence 20–32% of the volume of crystalline solids represents "ultramicroscopic voids" inaccessible to even the smallest gas molecules, e.g. hydrogen[246]. Diffusion in the lattice of such crystals as sodium chloride, etc. is possible only when they contain defects or at high temperatures[246].

As already mentioned, crystalline polymers are in most cases also non-porous solvents, for which calculations show that V_E fluctuates within the range 0.2–0.3 $cm^3\ g^{-1}$.[237,238] If Eqn. (4) is formally used to calculate V_E for a porous polymer, the very high values of 2–4 $cm^3\ g^{-1}$ are obtained. This empty volume obviously includes the whole total pore volume. Thus the free or empty volume of a porous polymer always exceeds its total pore volume. However, the quantity W_0 calculated from sorption data does not represent the total pore volume, since it depends on the relation between the size of the pores and that of the sorbate molecules (Section II). This led to introduction of the concept of the maximum pore volume W_0^{max}, representing the volume of all the pores into which molecules of any size can penetrate[238].

A hypothetical case can be imagined in which a polymer contains pores of various sizes, while the pore walls are packed as in an ideal crystal, so that

$$W_0^{max} = V_T - V_{id.cr}. \qquad (6)$$

This recalls an equation often used to calculate the total porosity[25,98,105] or the so called porosity factor[31]

$$P = 1/\rho_{app} - 1/\rho_{tr}, \qquad (7)$$

in which ρ_{app} and ρ_{tr} are the apparent and true densities of the material respectively[31]. The former density is determined pyknometrically with a liquid that does not wet the material and hence does not penetrate its pores (most often mercury), or is calculated from geometrical considerations[25,247]. The true density is also determined pyknometrically but with a liquid that wets the polymer and hence is able to penetrate its pores. For non-porous materials $\rho_{app} = \rho_{tr}$. For porous materials, even if microporous, these quantities may differ markedly. Therefore the method used to determine the density of a polymer must always be indicated.

Table 3 lists some typical values for the parameters V_E and W_0^{max} and for the packing coefficients. It includes apparent polymer densities, which for polyisobutylene, polyethylene, and poly(vinyl acetate) are identical with the true densities. For the first four polymers in Table 3 we see that $W_0^{max} \simeq 0$, so that the empty volume V_E is the volume of ultramicroscopic cavities, which fluctuates from 0.26 to 0.35 $cm^3\ g^{-1}$. However, these polymers differ in their density of packing, which is especially clearly shown in the values of V_E expressed in $cm^3\ mole^{-1}$ monomer unit: its value is least for crystalline polyethylene, which has the highest packing coefficient. A less densely packed polymer is polyisobutylene, for which $K = 0.678$; it is followed by polystyrene and poly(vinyl acetate). These data show that polystyrene is a loosely packed polymer, as follows also from heats of dissolution[248,249]. It is interesting that these last two polymers have almost the same packing coefficients, and the values for all amorphous polymers are very closely similar[240]. The empty volume V_E calculated in $cm^3\ mole^{-1}$ is probably a more sensitive measure of density of packing.

Polyarylates possess very high values of W_0^{max}, V_E ($cm^3\ g^{-1}$), and V_E ($cm^3\ mole^{-1}$). The porosity of these polymers is a consequence of their synthesis in solvents. Values of K calculated formally by means of Eqn. (2) for such polymers are far smaller than for non-porous polymers. Such low packing coefficients indicate not a low density of molecular packing but a loose packing of supermolecular structures. Consequently porosity and density of molecular packing are inadequate concepts.

Table 3. Densities, free volumes, maximum pore volumes, and packing coefficients of polymers[237,238,240].

No.	Polymer	ρ_{app}, g cm^{-3}	V_E, cm^3 g^{-1}	V_E, cm^3 $mole^{-1}$	W_0^{max}, $cm^3\ g^{-1}$	K_{pol}
1	Polyethylene (100% cryst.)	1.00	0.26	7.2	~0	0.740
2	Poly(vinyl acetate)	1.189	0.28	24.1	~0	0.665
3	Polystyrene	1.05	0.32	33.3	0.06	0.666
4	Polyisobutylene	0.912	0.35	10.6	0	0.678
5	Polyarylate based on phenolphthalein and isophthalic acid—F-1 (synthesised in chlorinated biphenyl)	0.90	0.82	367.3	0.58	0.477
6	Polyarylate based on phenolphthalein and terephthalic acid—F-2 (in acetone)	0.77	0.74	355	0.49	0.426

VI. MECHANISM OF THE SORPTION OF SIMPLE SUBSTANCES BY POLYMERS

The absorption of one substance by another, e.g. of a liquid by another or of gases by liquids, is in general termed sorption. More often, however, this term implies the absorption of molecules of gases, vapours, or liquids or of ions by solids, which can occur by two mechanisms[24]. (1) The substance is absorbed only on the surface, whether external or internal. Such a process is termed adsorption. It is divided into physical adsorption, when the adsorbate interacts with the adsorbent by van der Waals forces, and chemisorption, when chemical reactions occur between them. (2) Molecules of the sorbate penetrate inside the solid, entering the force field existing between its atoms, ions, or molecules throughout. Here, too, two processes may occur: the gas or vapour can either dissolve in the solid or form a chemical compound with it. For the most part adsorption and dissolution occur simultaneously, and are combined under the general term sorption.

The mechanism of the sorption of low-molecular substances on polymers is complicated and depends on many factors, including the phase constitution and the physical state of the polymer, its porous structure, its chemical structure, the flexibility of the chains, intermolecular interaction, and the thermodynamic affinity of the polymer for the sorbate. Depending on the magnitude of this last factor the polymer may be perturbed to different extents and the mechanism of sorption may be different.

1. Mechanism of the Sorption of "Inert" Sorbates on Polymers

If the polymer does not swell in the sorbate vapour, the mechanism of sorption does not differ fundamentally from that on mineral sorbents. Thus physical adsorption takes place on non-porous crystalline or elastic polymers (we ignore chemical interaction between polymer and sorbate).

Interacting centres of a microporous sorbent are distributed throughout its volume. With such sorbents, therefore, a mechanism of bulk filling of pores can be regarded as "dissolution" of the gas or "inert" vapour in the bulk of the specimen[22,154,250-252]. The mechanism operating with sorbents containing continuous pores involves coverage of the pore walls layer by layer, coalescence of the multilayers, and capillary condensation. Coalescence does not take place in macroporous sorbents owing to the distance between the pore walls, so that capillary condensation is absent, and only physical adsorption is observed.

Information on the mechanism of adsorption will be given by heats of adsorption, which has been discussed in detail by Kiselev et al. for hydrocarbons on graphitised carbon black, a typical non-porous adsorbent[253-256]. They showed that at low surface coverage the hydrocarbon molecules are oriented parallel to the surface. A similar conclusion has been reached by Ostrovskii et al.[257,258] in an investigation of the heats of adsorption of hydrocarbons on poly-*p*-divinylbenzene. This work showed that the BET theory of multimolecular adsorption does not apply to polymeric sorbents, which was attributed to surface non-uniformity. Analysis of possible reasons for such inhomogeneity indicated that the inconsistency with the BET theory might be due to swelling of the polymer, which will be considered in greater detail in the following subsection.

2. Mechanism of the Sorption of Non-inert Vapours on Polymers

Any substances in which polymers swell will be regarded as non-inert liquids and their vapours. Sorption of the vapours is most typical in the case of polymers. Numerous papers have appeared on the sorption of the most diverse vapours on various polymers—Long[259-267], Park[268-270], Gregor[271,272], Kargin et al.,[273-281] Tager et al.,[282-288] Lipatov et al.,[289] Papkov and Fainberg[15], and others. Inspection of the immense amount of information existing on the sorption of various substances on different polymers enables certain generalisations to be made and several mechanisms of sorption of non-inert substances typical of polymers to be distinguished. Thus with dense packing of macromolecules porosity is absent and physical adsorption is impossible. The sorption of non-inert vapours on densely packed polymers (elastic or vitreous, linear and cross-linked) must be regarded as true dissolution of the vapour in the polymer "matrix". However, dissolution has different mechanisms according as the temperature is above or below the glass point.

The mechanism of the dissolution of vapours in the elastomeric polymers (above the glass point) is fluctuational: i.e. the process consists in sorbate molecules and monomer units or segments of the polymer chain changing places. Because of the great flexibility of the chain these interchanges are possible from the very first portions of gas or vapour absorbed: i.e. disturbance of the sorbent and essentially mutual dissolution of the components begin at the lowest values of p_1. Typical sorption isotherms on elastic polymers are always concave [? convex] to the abscissae axis throughout the range of relative vapour pressures (Fig. 4*a*). The worse is the solvent thermodynamically, the lower is the sorption isotherm situated, and a non-solvent remains almost unabsorbed by the elastomers. The overall process depends on the affinity of the

solvent for the polymer and on the flexibility of the polymer chain. With the same flexibility the sorption of a given substance on different elastomers is described by a single curve[277].

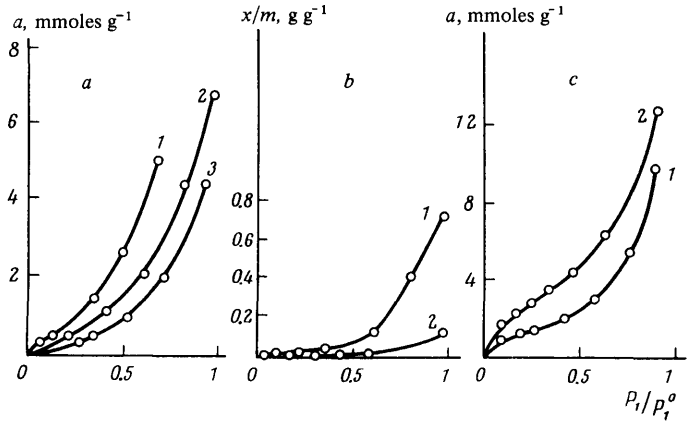


Figure 4. Types of sorption isotherms for vapours of non-inert liquids on polymers, where x/m is the equilibrium quantity sorbed expressed in grams: (*a*) 1) n-hexane on natural rubber[276]; 2) toluene on polyisobutylene[284]; 3) benzene on nitrile rubber (SKN-18)[282]; (*b*) 1) dioxan on polyurethane[287]; 2) ethanol on polyvinyl alcohol[276]; (*c*) 1) benzene on porous polystyrene[288]; chloroform on a polyarylate[237].

At temperatures below the glass point segmental motion of the chain is almost completely absent, so that interchanges between vapour molecules and chain units are difficult. The mechanism of dissolution of the vapour consists in the penetration of its molecules into existing cavities, of which there are few in densely packed polymers. The process is facilitated by the mobility of side-groups, but this effect is apparently insignificant, since at low pressures p_1 the quantity of substance dissolved lies beyond the sensitivity of the sorption method. Sorption begins to be appreciable at definite values of p_1, at which a fluctuational mechanism of swelling and dissolution of the polymer becomes possible. The sorption isotherms therefore have the form illustrated in Fig. 4*b*[278,287].

A more complicated mechanism of sorption of non-inert vapours is observed with porous vitreous polymers. The sorption isotherms are sigmoid with an initial section convex towards the ordinate (Fig. 4*c*). This portion corresponds to the vitreous state of the system[288]; the point of inflexion on the curve lies in the range of sorbate concentrations in the polymer at which the system passes, at the experimental temperature (25°C), from the vitreous state into one of rubberlike elasticity.

At higher relative vapour pressures the shape of the isotherm resembles that for elastomers: i.e. the mechanism of the absorption of a vapour by a polymer is analogous to the mechanism of sorption on rubberlike polymers. Sorption isotherms of this type have been obtained with cross-linked copolymers[271,272], polyamides[276], cellulose nitrate and acetate[290], and polystyrene[291]. Analysis of such sigmoid isotherms led to the conclusion[106,112,276,291,292] that the initial convex portion of the isotherm represents physical adsorption, and the concave portion corresponds to dissolution of the polymer, the main argument being that the former obeys the BET equation, and the latter the Flory equation.

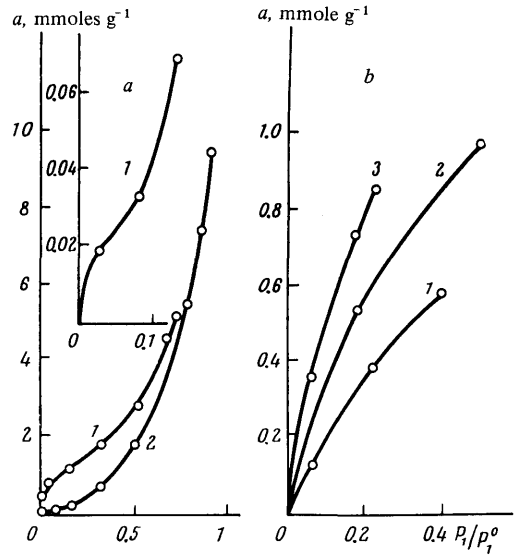


Figure 5. Sorption isotherms for the vapours of different liquids on specimens of polystyrene[288]. (*a*) Benzene vapour on polystyrene: 1) porous; 2) non-porous. (*b*) Initial portions of sorption isotherms on porous polystyrene for the vapours of: 1) methanol; 2) cyclohexane; 3) benzene.

A recent study of the sorption of various vapours on polymeric sorbents of the same chemical nature but differing in porosity has shown[288] that the height of the convex upwards section is greater the greater the porosity of the polymer, and for the same porosity the greater the thermodynamic affinity of the sorbate for the polymer (Fig. 5). This indicates the simultaneous occurrence of the processes—physical adsorption of the sorbate in the pores of the polymer and swelling of the rest of the polymer, i.e. of the pore "walls" or the polymer "matrix"—which cannot be separated. However, their simultaneous occurrence leads to very important conclusions.

Firstly, the specific surface of the polymer itself cannot be calculated when sorbates in which the polymer swells are used: i.e. the BET equation is not applicable to such a case.

Secondly, since physical adsorption is superimposed on swelling, the parameters of the thermodynamic affinity of the solvent for the polymer calculated from the sorption isotherms should depend on the porous structure of the polymer. In fact, different values of the chemical-potential difference for the solvent calculated by means of the equation

$$\Delta\mu_1 = RT \ln p_1/p_1^0, \qquad (8)$$

should be obtained for the same degree of absorption of the sorbate. When the corresponding difference $\Delta\mu_2$ for the polymer is calculated by means of the Gibbs–Duhem equation, different values are also obtained for specimens differing in porosity.

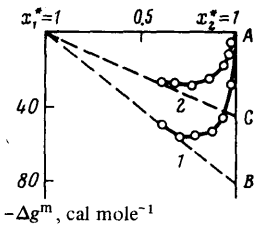


Figure 6. Dependence of Δg^m on apparent mole fraction x_2^* of the polymer (x_1^* is the apparent mole fraction of the solvent) for cyclohexane on polystyrene[288]: 1) porous; 2) non-porous.

Fig. 6 illustrates the mean free energies of mixing calculated by means of the formula

$$\Delta g^m = x_1^* \Delta\mu_1 + x_2^* \Delta\mu_2$$

as a function of the apparent mole fractions of the components. It is evident that they also depend on the porosity of the polymer. The difference between the free energies of interaction of the sorbate with porous and non-porous polymers is obviously the work required to form the pores, which can be calculated from the equations[288]

1 mole of units of non-porous polymer + solvent = soln. I – ΔG_{np}
1 mole of units of porous polymer + solvent = soln. II – ΔG_{por} ,

where ΔG_{por} and ΔG_{np} are the respective free energies of mixing of a large quantity of solvent with 1 mole of monomer units. Hence

non-porous polymer → porous polymer + $\Delta G_{por} - \Delta G_{np}$.

The difference $\Delta G_{por} - \Delta G_{np}$ represents the change in free energy accompanying transfer from the non-porous to the porous sorbent: i.e. it is the work of pore formation A_{por}. Values of ΔG_{por} and ΔG_{np} can be calculated from the dependence of Δg^m on x_2^*.[293] In Fig. 6 the intercept $AB = \Delta G_{por}$ (in calories per mole of monomer units in the polymer), while $AC = \Delta G_{np}$. The difference between them is the work of pore formation:

$$BC = AB - AC = \Delta G_{por} - \Delta G_{np} = A_{por} .$$

Values of A_{por} are independent of the nature of the sorbate, but increase with the porosity of the specimen[288].

The porous structure of a polymer influences also the magnitude and sign of the parameter χ_1 calculated by means of the Flory–Huggins equation[294]

$$\ln p_1/p_1^0 = \ln(1-\varphi_2) + \varphi_2 + \chi_1\varphi_2^2, \qquad (9)$$

in which φ_2 is the volume fraction of the polymer. The concentration dependence of χ_1 is different for porous and non-porous specimens of a polymer (Fig. 7). For the latter the parameter increases with polymer concentration[294,295]. For a porous polymer χ_1 is a decreasing function of concentration at small dilutions, and the concentration dependence reaches negative values (curve 2). Similar curves have been observed by Moore[290] for solutions of cellulose ethers, probably as a consequence of the sigmoid isotherms and the loose packing of these polymers. The above results indicate that Eqn. (9) holds only for the second stage of sorption, when the porous structure of the polymer has broken down and only swelling develops. If adsorption on the surface and sorption in the mass (swelling) take place simultaneously, the Flory–Huggins equation (9) cannot be applied.

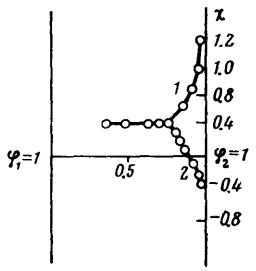


Figure 7. Concentration dependence of χ_1 (where φ_1 and φ_2 are the volume fractions of solvent and polymer respectively) for benzene on polystyrene[288]: 1) non-porous; 2) porous.

3. Role of the Porous Structure of Polymers in Sorption from Liquid Media and Vapours

An interesting phenomenon observed in the study of sorption processes is the Schroeder effect[296], according to which the quantity of a given substance absorbed by a polymer from a liquid medium always exceeds the quantity absorbed from the vapour state. It was first observed for the gelatin–water system. Analogous results were later obtained by other investigators[297–299] for the systems formed by agar-agar with water, unvulcanised and vulcanised rubber with organic liquids (alcohols, tetrachloromethane) and their vapours, and also liquid mixtures of benzene with alcohol and the mixed vapours sorbed on vulcanised rubber. The nature of the effect still remains an open question[299]. Schroeder himself[296] and the other investigators[297–299] attributed it to experimental error—fluctuations of temperature, the impossibility of achieving absolute saturation of the vapour, disregard of surface tension, a slower rate of sorption from liquid and vapour media, etc.

A more recent paper[300] has suggested, in addition to the above reasons, that the phenomenon may be due also to the presence of pores, which are filled with a liquid but not with a vapour. This hypothesis has been tested experimentally on several porous and non-porous polymers with both inert and non-inert liquids and their vapours[301]. It was found that with non-inert liquids, when the polymer swells, the Schroeder effect is not observed: i.e. the same equilibrium quantity of a substance is sorbed from liquid and vapour media. A difference is present only in the kinetics: liquids are sorbed more rapidly than are vapours (Fig. 8*a*, *b*). In the sorption of "inert" substances on porous polymers differences are observed not only in the

kinetics but also in the equilibrium quantities sorbed (Fig. 8*c*): liquids are sorbed in far greater quantities than are their vapours.

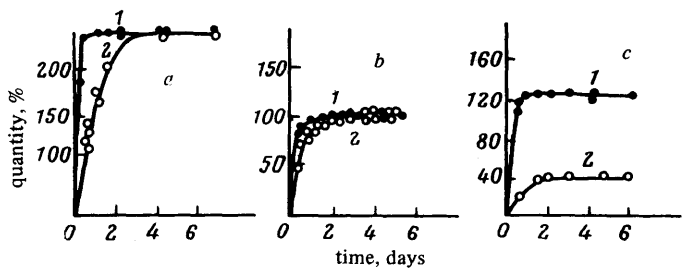


Figure 8. Rate curves for absorption by polymers from: 1) liquids; 2) vapours[301]: *a*) "non-inert" benzene on non-porous copolymer of styrene with 6% of divinylbenzene; *b*) "non-inert" benzene on macroporous copolymer of styrene with 20% of divinylbenzene; *c*) "inert" methanol on macroporous copolymer of styrene with 20% of divinylbenzene.

This last phenomenon is attributed to different mechanisms by which pores are filled. A liquid fills all the pores, including large pores, whose dimensions make them accessible to its molecules. But a vapour is sorbed by a more complicated mechanism, involving a series of successive stages—adsorption from the vapour on the pore walls with formation of multimolecular layers, coalescence of the latter with appearance of a concave meniscus, and then condensation of the vapour. Since the vapour pressure is lower the smaller the radius of curvature of a concave surface, capillary condensation occurs preferentially in fine pores (of continuous type). In coarse pores, as remarked in Section VI, 1, coalescence of multilayers and hence capillary condensation do not occur owing to the distance between the pore walls. Such pores may therefore remain unfilled by the "liquefied" vapour.

Thus development of the Schroeder effect depends both on the porous structure of the polymer and on the thermodynamic affinity of the low-molecular substance for the polymer. The absorption of substances that cause swelling involves a redistribution and partial disappearance of pores. Therefore the equilibrium quantity sorbed does not depend on whether it has been sorbed from the liquid or from the vapour.

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