DETERMINATION OF THE SPECIFIC SURFACE AREA AND PORE VOLUME OF SOLID POLYMERIC SORBENTS

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DETERMINATION OF THE SPECIFIC SURFACE AREA AND PORE VOLUME OF SOLID POLYMERIC SORBENTS

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Work in recent years has established a definite interrelation between the thermodynamic regularities of the processes of dissolution of polymers and their physical state. Thus, the interaction of a number of glassy polymers with low-molecular liquids—polystyrene (1), polymethyl methacrylate (2), cellulose (3), and others—is accompanied by the evolution of heat and a sharp decrease in the entropy of the liquid being sorbed. Changes of this kind are characteristic of the processes of vapor adsorption by solid porous sorbents (3), in connection with which the conclusion was drawn that the indicated polymers, while in the glassy state, behave as microporous sorbents. The microporosity of such polymers is the result of the loose packing of their macromolecules. At the same time it was shown that, during sorption of vapors by polyvinyl alcohol, heat absorption and a slight increase in the entropy of the liquid being sorbed are observed, which was associated with the dense packing of the macromolecules of this polymer (1). All these works made it possible to put forward a new formulation of the question concerning the intermediate position of high-molecular compounds between low-molecular liquids and colloidal sorbents (1). Closest to low-molecular liquids are highly elastic polymers with flexible chains; then come high-molecular glasses with dense packing, polymeric loosely packed glasses, and solid porous sorbents of the activated-carbon and silica-gel type.

Taking into account the great similarity in the dissolution of elastic polymers with low-molecular liquids, during the last 20 years the thermodynamic regularities developed for true solutions of low-molecular compounds have been successfully applied to solutions of these polymers (4). However, these regularities proved completely unsuitable when considering the processes of dissolution and swelling of glassy polymers (1). In particular, the proposition that solutions in which one of the components has large molecular dimensions are characterized by a sharp increase in entropy, many times exceeding the ideal value (5), cannot in general be recognized as correct.

All this indicates the necessity of developing a new way of approaching the processes of interaction of high-molecular glasses with solvents. Such a new approach may be to treat polymers in the glassy state as solid sorbents and to

Fig. 1. Sorption isotherms of methyl alcohol on polystyrene. 1 —mol. wt. 456000, 2 —mol. wt. 133000

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Fig. 2. Sorption isotherms of n-hexane. 1 —cellulose, 2 —polyvinyl alcohol, 3 —triacetylcellulose

Figure 2: Fig. 2. Sorption isotherms of n-hexane. 1 —cellulose, 2 —polyvinyl alcohol, 3 —triacetylcellulose

apply to them methods that make it possible to quantitatively evaluate their porosity.

One of such methods, which has become widespread, is the sorption method. However, the sorption isotherms obtained up to now cannot unambiguously testify to the porosity of a polymer. This ambiguity is due to two reasons: 1) in all experiments, vapors of liquids were used in which the polymers swelled, that is, during the sorption process a change in the structure of the sorbent took place; 2) the sorbing capacity

polymer in the case of swelling is determined not only by the degree of packing of the macromolecules, but also by the flexibility of their chains.

These difficulties can be avoided by using vapors of liquids that are inert with respect to the given glassy polymer. In this case the structure of the polymer does not change during the sorption process and chain flexibility is not realized.

We investigated the sorption of vapors of inert liquids by polystyrene, polyvinyl alcohol, cellulose, and triacetylcellulose. As sorbents we used two fractions of polystyrene, of molecular weight 456000 and 133000, powdered triacetylcellulose of molecular weight 140000, polyvinyl alcohol of molecular weight 17000, and industrial linter. As inert liquids for polystyrene, methyl alcohol was taken; for the other polymers, *n*-hexane. The sorption of vapors of these liquids has been well studied on active carbons and silica gels ([6,7]). For the investigation we used an apparatus described earlier ([1]). Equilibrium at a temperature of 25° was established within 3-5 hours. The results of the measurements are presented in Figs. 1 and 2, from which it is seen that the isotherms differ from one another.

Fig. 1. Sorption isotherms of methyl alcohol on polystyrene. 1 —mol. wt. 456000, 2 —mol. wt. 133000

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The sorption isotherms of methyl alcohol on polystyrene and of *n*-hexane on cellulose are identical to the sorption isotherms of vapors of these same liquids on silica gel ([3]). According to the classification of A. V. Kiselev ([9]), this type of sorption isotherm is characteristic of homogeneous finely porous sorbents. In this case, for the small molecules of methyl alcohol a slight sorption hysteresis is observed. The sorption isotherm of *n*-hexane on polyvinyl alcohol resembles the isotherms obtained on nonporous sorbents (^{3}). Finally, for triacetylcellulose a typical S-shaped isotherm was obtained, with convexity relative to the ordinate axis at low relative vapor pressures and concavity at high ones. Such isotherms are characteristic of more coarsely porous sorbents. Thus, from consideration of the external form of the isotherms it follows that polystyrene and cellulose are finely porous sorbents, triacetylcellulose has larger pores, and polyvinyl alcohol is a nonporous sorbent. These data fully agree with the results of previous investigations, according to which polystyrene (^{1,10}), triacetylcellulose (^{1}), and cellulose (^{2}) have a loose packing of molecules, whereas polyvinyl alcohol is densely packed (^{1,11}). From Fig. 1 it follows that the sorption isotherm of the sample of molecular weight 133000 lies below the isotherm of the sample of molecular weight 456000. This indicates

indicates an increase in loosening with increasing molecular weight of polystyrene, which has also been observed previously (^{12}).

We have attempted to quantitatively estimate the degree of porosity of these polymers, using for this purpose the BET method and the method of M. M. Dubinin and L. V. Radushkevich.

As is known, the basic equation of Brunauer, Emmett, and Teller (BET) was derived for S-shaped adsorption isotherms (^{13}). However, in a number of works this method is formally applied to calculate the specific surface area and pore volume of sorbents of varying degrees of porosity, up to nonporous sorbents of the $BaSO_4$ and $PbSO_4$ type (^{8}). The method of M. M. Dubinin and L. V. Radushkevich is applicable to finely porous sorbents.

Table 1

Specific surface areas and pore volumes

Sorbent	S, m^2/g	W_0, cm^3
Polystyrenemol. wt. 456000	61.09	0.0315
Polystyrenemol. wt. 133000	30.52	0.0154
Cellulose	42.64	0.0323
Triacetyl cellulose	50.69	0.0838
Polyvinyl alcohol	3.59	–

In our cases the BET equation is applicable in the range of relative pressures from 0.05 to 0.03, that is, in the region in which it is generally applicable. The equation of M. M. Dubinin and L. V. Radushkevich is applicable in the region of low relative vapor pressures.

Table 1 gives the calculated values of specific surface area and pore volumes for the polymers studied. It follows from the table that high-molecular-weight polystyrene, cellulose, and triacetyl cellulose may be assigned to finely porous sorbents with a slightly developed specific surface. With decreasing molecular weight of polystyrene, the specific surface area and pore volume decrease. The pore volume of high-molecular-weight polystyrene is about 1.5%, that of cellulose 3%, and that of triacetyl cellulose on the order of 8% of the total volume of the polymer. The specific surface area of polyvinyl alcohol is very small and corresponds to the values of the specific surface area of nonporous sorbents ([8]).

The results obtained indicate the possibility of a quantitative assessment of the porosity of polymers by studying the sorption of inert liquids on them.

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