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Abstract

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DYNAMIC METHOD FOR INVESTIGATING THE STRUCTURE AND SPECIFIC SURFACE AREA OF ADSORBENTS

(Presented by Academician M. M. Dubinin, 25 VIII 1956)

The primary adsorption process of monomolecular adsorption for macroporous and nonporous adsorbents is determined chiefly by the magnitude and nature of the surface of the adsorbent. The completion of the sorption process—polymolecular adsorption and capillary condensation or, correspondingly, capillary stratification—depends on the porous structure of the adsorbent ($^{1-3}$). The process of adsorption by porous bodies under dynamic conditions can be divided into two periods: "before breakthrough" and "after breakthrough" (^{4}). The "before breakthrough" period is characterized by a constant sorption rate, chiefly by a process of monomolecular adsorption. The "after breakthrough" period is characterized by a decreasing sorption rate. The determining factor here is internal diffusion, which depends to a greater degree on the structure of the adsorbent; consequently, by studying the dynamics of sorption, one can obtain an idea of the structure of the adsorbent.

Table 1

Adsorption values a, mM/g, obtained under static and dynamic experimental conditions

Samples	By phenol	By phenol	By benzyl alcohol	By benzyl alcohol	By thymol	By thymol
Samples	static	dynamic	static	dynamic	static	dynamic
KSM	2,040	2,070	1,740	1,790	1,300	1,170
KSK	1,653	1,500	1,450	1,420	0,945	0,890
173-	0,690	0,710	0,560	0,571	0,245	0,246
172-	0,264	0,262	0,264	0,277	0,188	0,117
171-	0,066	0,052	0,066	0,050	0,033	0,026
55	0,412	0,421	0,351	0,338	0,166	0,135

To investigate the structure of adsorbents on the basis of this idea, we chose

Fig. 1

Figure 1: Fig. 1

the method of "molecular probes," proposed by M. M. Dubinin (5,6), with the modification that the experiments of "molecular probing" were carried out under dynamic conditions at solution flow rates ensuring the establishment of adsorption equilibrium. If, in studying adsorption from solutions by static methods, one can judge the adsorption process only from the initial and final data, without being able to observe the very interesting features associated with the kinetics of the adsorption process, then, on passing to dynamic conditions for conducting experiments, from the form of the resulting "breakthrough curves" one can judge the rate of the sorption process, as well as the structure of the adsorbent.

High-molecular compounds were taken as "molecular probes" : phenol, benzyl alcohol, and thymol (5-methyl-2-isopropylphenol). Carbon tetrachloride served as the solvent, as an indifferent and weakly adsorbed solvent.

Method of investigation. A solution of the adsorbed substance in carbon tetrachloride was passed through a layer of sorbent placed in a chromatographic column. In our experiments the rate ···

the rate of flow of the solution did not exceed 10–15 ml/hr. The sorbent layer had a constant height of 7.5 cm. In this way we ensured, as far as possible, constant conditions for carrying out the experiment. To construct the exit curve of a portion of solution that had passed through the sorbent layer, samples were taken for determination of the adsorbed substance content in them regularly every 0.5 ml. The content of the adsorbed substance in the effluent solution was determined interferometrically.

Fig. 1. Exit curves for thymol solutions of different concentrations in CCl_4 on sample No. 55: 1 –0.49 mM/l, 2 –0.359 mM/l, 3 –0.208 mM/l, 4 –0.161 mM/l.

The results were represented graphically: the volume of the investigated solution that had passed through the sorbent layer was plotted on the abscissa axis, and the concentration of the effluent solution, calculated from the calibration curve, on the ordinate axis.

First of all it was necessary to make sure that adsorption equilibrium was established in the dynamic experiments. The results of comparing adsorption values obtained under dynamic and static experimental conditions are given in Table 1; they show that, in our dynamic experiments carried out under standard conditions, adsorption equilibrium was attained.

It was further necessary to determine the influence of the concentration of the "molecular probe" solution on the shape of the exit curve under the other standard conditions of the experiment. We obtained exit curves for a solution of thymol in carbon tetrachloride on sample 55 (suyfunite) with the thymol concentration varied from 0.161 to 0.495 mM/l, i.e., by a factor of three. The areas

Fig. 2

Figure 2: Fig. 2

Fig. 3. Breakthrough curves for phenol (a), benzyl alcohol (b), and thymol (v) in a solution of CCl4 on standard silica gels; curve numbers, see Fig. 2

Figure 3: Fig. 3. Breakthrough curves for phenol (a), benzyl alcohol (b), and thymol (v) in a solution of CCl4 on standard silica gels; curve numbers, see Fig. 2

bounded by the exit curves and the coordinate axes practically coincide, as can be seen from Fig. 1. Hence it may be assumed that, during adsorption from solution, a monomolecular coating of the adsorbent surface takes place, and from the indicated areas the adsorption values and the specific surface areas of the adsorbents can be determined.

The influence of the size and shape of the molecules of the adsorbed substance, i.e., of the molecular probes, was revealed by dynamic experiments on the selected adsorbent. During adsorption on highly dispersed solids, an increase in the size of the adsorbate molecules leads to a decrease in the accessible surface area of the adsorbent. An inverse linear dependence has been established of adsorption values on the areas occupied by the adsorbent molecules and on the number of carbon atoms in the molecule (Fig. 2). The values of the molecular areas—

Fig. 2. Dependence of the adsorption value on the size of the adsorbing molecule. Samples: 1 —171-b, 2 —172-b, 3 —55, 4 —173-b, 5 —KSK, 6 —KSM.

of our "molecular probes" were determined by us with the standard KSK silica gel.

The results of dynamic investigations under standard conditions using a solution of one of the alcohols show a sharp difference in the breakthrough curves for the standard KSK and KSM silica gels. The area bounded by the breakthrough curve and the coordinates—the concentration and volume of solution—is proportional to the value of the specific surface area and differs sharply for the comparison standards (KSK and KSM), as shown in Fig. 3. The breakthrough curves for various natural sorbents, in their form, occupy a certain intermediate position.

Fig. 3. Breakthrough curves for phenol (*a*), benzyl alcohol (*b*), and thymol (*v*) in a solution of CCl_4 on standard silica gels; curve numbers, see Fig. 2

By the molecular-probe method under dynamic conditions, the porous structure of natural sorbents of the Far East of various origins was investigated (32 samples using three molecular probes). The method of "molecular probes" under dynamic experimental conditions can provide a quantitative characterization of the porous structure of adsorbents. The limiting value of adsorption a_∞ will be

Fig. 4. Outlet curves for a solution of phenol in CCl_4 on diatomites (1, 2), decomposed new tuffs (3–5) and gumbrin (6). For comparison, outlet curves on KSK and KSM are given. Samples: 1 –345, 2 –327, 3 –55, 4 –172-6, 5 –173-6, 6 –304, 7 –KSK, 8 –KSM

Figure 4: Fig. 4. Outlet curves for a solution of phenol in CCl_4 on diatomites (1, 2), decomposed new tuffs (3–5) and gumbrin (6). For comparison, outlet curves on KSK and KSM are given. Samples: 1 –345, 2 –327, 3 –55, 4 –172-6, 5 –173-6, 6 –304, 7 –KSK, 8 –KSM

composed of two factors: a_1, the amount of adsorption "before breakthrough," and a_2, the amount of adsorption after "breakthrough" up to complete saturation

$$a_\infty = a_1 + a_2.$$

Table 2

Comparison of the amount of adsorbed substance (mM/g) up to the breakthrough point (a_1) and from the breakthrough point to adsorption saturation (a_2) on various adsorbents

Adsorbent	For phenol a_1	For phenol a_2	For thymol a_1	For thymol a_2
KSM	1.770	0.304	1.008	0.162
KSK	1.420	0.080	0.743	0.147
171	0.042	0.022	0.004	0.022
172	0.262	0.261	0.095	0.069
173	0.624	0.088	0.112	0.134
55	0.351	0.070	0.052	0.083
223	0.274	0.095	0.044	0.058

For macroporous adsorbents, the value a_1 will chiefly determine their adsorption capacity, while the value a_2 will be small. For finely porous adsorbents, with a sufficiently large value of a_1, the value a_2 may also be large. The values of a_1 and a_2 for a number of natural sorbents and standard silica gels are given in Table 2.

By the shape of the outlet curves it is possible to classify natural sorbents: for example, diatomites have outlet curves that bring them close to coarse-pore sorbents; gumbrin–to fine-pore sorbents, etc. (Fig. 4).

Thus, from the experimental data presented it is clear that the application of the "molecular probe" method under dynamic conditions makes it possible:

Fig. 4. Outlet curves for a solution of phenol in CCl_4 on diatomites *(1, 2)*, decomposed new tuffs *(3–5)* and gumbrin *(6)*. For comparison, outlet curves

on KSK and KSM are given. Samples: *1* –345, *2* –327, *3* –55, *4* –172-6, *5* –173-6, *6* –304, *7* –KSK, *8* –KSM.

1) to relate the kinetics of the sorption process to the porous structure of the adsorbent;
2) to apply a simple procedure for a dynamic experiment, with the concentration in the effluent stream recorded interferometrically or refractometrically;
3) to obtain an idea of the structural type of the adsorbent under study and to determine its specific surface area in a very short time, since a dynamic experiment lasts from two to four hours;
4) to obtain a quantitative representation of the characteristics of the porous structure of the adsorbent as component values of adsorption "before breakthrough" and "after breakthrough."

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