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Abstract

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ADSORPTION OF HEXANE AND BENZENE VAPORS ON NONRADIOACTIVE AND RADIOACTIVE SAMPLES OF BARIUM SULFATE

The introduction of radioactive isotopes into solid substances changes their physicochemical properties ($^{1-5}$). Although the nature of the phenomena occurring here is still not entirely clear, their influence on the properties of solids is unquestionable. It was of interest to investigate the adsorption properties of radioactive samples with respect to adsorption from the gas phase of substances of different structure, in particular polar and nonpolar ones. In work (^{6}), qualitative indications were obtained of an increase in methanol adsorption upon introduction of the radioactive sulfur isotope into K_2SO_4 powder; however, the small surface area hindered the obtaining of more precise information. In the present work, precipitates of barium sulfate containing radioactive sulfur, which can easily be obtained with a more developed surface, were taken as adsorbents.

The $BaSO_4$ precipitates in the present work were prepared by interaction of a $BaCl_2$ solution with a Na_2SO_4 solution containing S^{35}. A Na_2SO_4 solution ($pH = 7$) was used with a stable-carrier concentration of 3.9 mg/l and a specific activity with respect to S^{35} of 10 mCi/ml. Foreign salt impurities were practically absent. Among the radioactive impurities there was phosphorus, but not more than 0.01%. The $BaSO_4$ precipitate was washed in portions with a 10% solution of C_2H_5OH in distilled water.

Four $BaSO_4$ samples were obtained: one inactive and three active, with activities at the time of preparation of 96, 101, and 85 mCi/g. Before the adsorption experiments, the samples were evacuated in an adsorption apparatus (^{7}) at 200°. The specific surface area s of the samples was determined in the same apparatus from low-temperature adsorption of nitrogen and argon vapors by the BET method. The characteristics of the samples studied are given in Table 1.

Table 1

Characteristics of the investigated $BaSO_4$ samples

Samples	Initial radioactivity, mCi/g	Specific surface, m^2/g from nitrogen adsorption	Sample age before beginning adsorption measurement, days: hexane	Sample age before beginning adsorption measurement, days: benzene	Radioactivity of samples before adsorption measurement, mCi/g: hexane	Radioactivity of samples before adsorption measurement, mCi/g: benzene
Evacuated at 200° $BaSO_4$	0	4.3	–	–	–	–
$*BaSO_4$-1	96	4.6	187	167	21	25
$*BaSO_4$-2	101	8.0	42	56	72	65
$*BaSO_4$-3	85	7.3	7	10	80	77
Additionally evacuated at 400° $BaSO_4$	0	3.3	–	–	–	–
$*BaSO_4$-1	96	3.9	–	–	–	–
$*BaSO_4$-2	101	4.4	75	71	56	57
$*BaSO_4$-3	85	5.0	92	86	41	43

As adsorbates, *n*-hexane, benzene, methanol, nitrogen, and in some cases argon were used. Below are presented data on the adsorption of vapors of *n*-hexane* and benzene. The adsorption of hexane is due mainly to electrokinetic (dispersion) interaction with the surface of the adsorbent. The adsorption of benzene on surfaces bearing electric charges and dipoles occurs not only as a result of the action of electrokinetic (dispersion) forces and weak electrostatic induction forces, but also owing to the additional interaction of the electron cloud of the benzene molecule (chiefly its π bonds) with dipoles or ions on the adsorbent surface ([9], [10]).

Fig. 1. Isotherms of absolute values of adsorption of *n*-hexane vapor at 20° (A) and benzene at 50° (B) on a nonradioactive sample of $BaSO_4$ (200°) (1) and radioactive samples $BaSO_4$-1 (200°) (2), $BaSO_4$-2 (200°) (3), and $BaSO_4$-3

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

(200°) (4). Black points here and in Fig. 3, 4—desorption. At the top are shown the initial portions of the isotherms.

Fig. 1 gives the isotherms of absolute values of adsorption of vapors of *n*-hexane and benzene (calculated per unit surface area, determined from adsorption of nitrogen vapor) on a nonradioactive and three radioactive $BaSO_4$ samples evacuated at 200°. In the monomolecular region of surface coverage, especially at low coverages, the adsorption of these substances per unit surface area of the radioactive samples is greater than on the nonradioactive sample. Thus, for example, the absolute value of adsorption on sample $BaSO_4$-1 is approximately twice as large as on the nonradioactive sample for the more weakly adsorbed hexane at a relative pressure $p/p_s = 0.005$, and for the more strongly adsorbed benzene at $p/p_s = 0.0005$.

Fig. 2. Isotherms of absolute values of adsorption of benzene vapor at 50° on radioactive samples $BaSO_4$-1 (200°) (A) and $BaSO_4$-3 (200°) (B). Points 1, 3 are initially measured adsorption isotherms; points 2, 4 are measured a second time after holding the samples for 2 months.

It is seen from Table 1 that the three radioactive samples differ from one another mainly in the lifetime before measurement of adsorption isotherms on them. The radioactive samples studied had similar and s—

similar radioactivity, but very different radioactivity at the moment of measurement of the adsorption isotherms. From Fig. 1 it is seen that the absolute adsorption isotherms of hexane on samples $BaSO_4$-1 and $BaSO_4$-2, with different specific activities before the measurements (21 and 72 mCi/g), approximately coincide, whereas the absolute adsorption isotherms of hexane on samples $BaSO_4$-2 and $BaSO_4$-3, with close specific activities (72 and 80 mCi/g), differ greatly; i.e., the magnitude of the activity of these samples at the given moment practically did not affect their adsorption properties. This conclusion was confirmed by special experiments to study the influence of the aging time of radioactive samples on their adsorption capacity. After the adsorption isotherms of benzene had been measured on samples $BaSO_4$-1 and $BaSO_4$-3, the samples were kept for another 2 months, and then the adsorption isotherms of benzene were again measured on them. The results of the measurements are shown in Fig. 2, from which it is seen that additional prolonged aging of the previously aged sample

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* Previously, the adsorption of *n*-hexane vapor on barium sulfate was studied in (^{8}).

$BaSO_4$-1, as well as of the fresh sample $BaSO_4$-3, did not lead to any change in their adsorption properties. This indicates that a possible change in the state of the surface of already formed solid sulfate as a result of the ongoing β-decay of S^{35} has no substantial effect on the adsorption of benzene—a substance highly sensitive to changes in the electric field of the surface of adsorbents ([7], [9], [10]).

Fig. 3. Isotherms of the absolute values of adsorption of hexane vapor at 20° on $BaSO_4$ samples aged at 200° (1, 3, 5) and 400° (2, 4, 6). Points 1, 2—nonradioactive $BaSO_4$ samples; points 3, 4, 5, 6—radioactive samples $BaSO_4$-2 (3, 4) and $BaSO_4$-3 (5, 6).

Fig. 4. Isotherms of the absolute values of adsorption of benzene vapor at 50° on $BaSO_4$ samples aged at 200° (1, 3, 5) and 400° (2, 4, 6). Points 1, 2—nonradioactive $BaSO_4$ samples; points 3, 4, 5, 6—radioactive samples $BaSO_4$-1 (3, 4) and $BaSO_4$-3 (5, 6).

At the same time, from Fig. 1 it is seen that, in the region of small surface coverages, the adsorption of hexane and benzene vapors referred to unit surface area increases with increasing initial radioactivity of the sample.

These results make it possible to suppose that introducing activity in the form of SO_4^{*2-} into the solution when obtaining radioactive $BaSO_4$ precipitates led to samples with a surface more active for adsorption than that of the nonradioactive sample.

It might have been expected that, if this increased adsorption capacity is associated with the formation of a more heterogeneous surface* in the radioactive barium sulfate samples, then upon removal of the surface heterogeneity the increased adsorption capacity should decrease relatively more in the radioactive samples than in the nonradioactive one. To test this assumption, after experiments with the samples evacuated at 200°, they were additionally evacuated in the apparatus at 400° for approximately 30 h. The specific surface area of the samples was checked by low-temperature adsorption of nitrogen vapor. The characteristics of the samples after this treatment are given in Table 1. It is evident from the table, first of all, that the specific surface area of the samples decreases upon calcination in vacuum, and more strongly for the more highly dispersed radioactive samples.

In Figs. 3 and 4, the isotherms of the absolute adsorption values of hexane and benzene vapors are compared for samples evacuated at 200 and 400°. Calcination in vacuum sharply lowers the adsorption properties toward hexane and benzene for all samples, and the adsorption capacity per unit surface area decreases to a greater extent for the radioactive samples than for the nonradioactive one. Thus, for example, the adsorption of hexane vapor at a relative pressure $p/p_s = 0.005$, after increasing the calcination temperature from 200 to 400°, decreases by approximately a factor of 3 for the nonradioactive sample, and by approximately a factor of 7 for the radioactive sample $BaSO_4^*$-2.

With an increase in the calcination temperature of the samples from 200 to 400°, not only do the magnitudes of adsorption change sharply, but the character of the isotherms also changes: in the region of small p/p_s, they become practically linear instead of convex. This also confirms the assumption made above that the surface of the samples evacuated at 200° is very heterogeneous, and more so for the radioactive samples than for the nonradioactive one. Evacuation to 400° leads to a sharp decrease in the surface heterogeneity of all these samples.

Thus, the study of vapor adsorption on samples subjected to additional calcination in vacuum at 400° confirms the conclusion drawn above that the addition of radioactive salt $Na_2SO_4^*$ during preparation promotes the formation of precipitates with increased adsorption capacity, whose surface has a very heterogeneous structure, more heterogeneous than the surface of the nonradioactive sample. Calcination in vacuum at 400°, however, makes the surface of all these samples significantly more homogeneous and gives it practically the same adsorption capacity.

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* This heterogeneity may be either geometrical, associated with the structure of the precipitates, or chemical, associated with the special features of the surface structure and hydration shell.

Note: Figure translations are in progress. See original paper for figures.