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THE EFFECT OF THE RADIOACTIVITY OF BARIUM SULFATE ON ITS SORPTION PROPERTIES

Radioactive radiation can cause a variety of changes in solids, amounting mainly to various disturbances of their crystal lattice (^{1}) and to the appearance of electric charges on the surface (^{2}). This, in turn, should affect the physicochemical properties of solids and, in particular, the rate of isotope-exchange reactions in heterogeneous systems (^{3}), catalytic activity (^{4}), sorption processes, and other phenomena (^{5}).

The authors of the present communication studied the effect of radioactivity on the sorption properties of solids. As the sorbent, barium sulfate, which had previously been well studied ($^{6-8}$), was chosen. The adsorption on it from aqueous solutions of the acidic orange dye (Orange AT2B) $(C_{16}H_{11}O_4N_2S)Na$ and of two basic dyes—methylene blue $(C_{16}H_{18}N_3S)Cl$ and brilliant green $(C_{27}H_{35}N_2)Cl$—was studied. The source of radioactive radiation was S^{35}, introduced into barium sulfate during its precipitation. S^{35} emits only β-particles of low energy ($E_{\max} = 0.169$ MeV) and has a sufficiently long half-life ($T_{1/2} = 87.1$ days). As an emitter it has a number of advantages: it makes it possible to work with preparations of high specific activity with minimal shielding; its radiation is almost completely absorbed within the $BaSO_4$ precipitate. In addition, the effect of the radiation on the liquid phase proves to be insignificant, since the solubility of $BaSO_4$ is low and the amount of radioactive sulfur entering the solution is small.

Table 1

Characteristics of the precipitates used
$BaSO_4$

Preparation No.	Specific surface, m^2/g	Specific activity, mCi/g
1	0.74	0

Preparation No.	Specific surface, m^2/g	Specific activity, mCi/g
2	0.68	0.01
3	0.68	0.1
4	0.78	1
5	0.76	4
6	0.78	10

The $BaSO_4$ preparations were prepared according to Kolthoff (^{7}) and Rutgers (^{8}). Hot $0.1\,N$ solutions of $BaCl_2$ and Na_2SO_4, containing a definite amount of S^{35}, were poured together at the same rate (over 30 min, 200 ml of each solution) with stirring. The stirring was then continued for 1 hour while heating to 70-80°. After this the precipitates were allowed to stand in the mother liquor for 16 hours. They were then washed free of Na^+, Cl^-, and Ba^{2+} ions, since the barium salt was added with some excess so that as few radioactive SO_4^{2-} anions as possible would remain in solution. Finally, the precipitates were washed twice with ethyl alcohol and dried at 80-100° to constant weight. The characteristics of the precipitates obtained are given in Table 1.

The specific surface area of the $BaSO_4$ precipitates was determined by a visual-microscopic method (magnification 1350×). The results obtained agree well with the data obtained by Rutgers (^{8}) by the same method and by an electron-microscopic method, as well as in the study of the absorption of various dyes by a $BaSO_4$ precipitate (^{7,8}).

The procedure of our experiments was as follows: 3 g of precipitate at a temperature of $25 \pm 0.5°$ were shaken for 4 hours with 15 ml of a dye solution of the corresponding concentration. After this, the dye content in the liquid phase was determined by the spectrophotometric method using SF-4 and SF-2M instruments (the latter permits operation at the absorption maximum). The measurement error lay within 3-4%. Preliminary experiments established the time required for equilibrium to be established between the solid and liquid phases; it usually did not exceed 1 hour. The dye concentration was studied within the range from 10 to 200-250 mg/l. The solutions were characterized by the following pH values: acid orange, 5.5-5.8; methylene blue, 6.2-6.9; brilliant green, 3.9-4.6.

The results of the investigation are shown in Figs. 1, 2, and 3. All data were obtained from three parallel experiments. The deviation from the mean did not exceed 5%. It was established that the acid orange dye is absorbed most strongly by the $BaSO_4$ precipitate; its sorption is an order of magnitude higher than that of the other dyes studied. Methylene blue is sorbed somewhat more than brilliant green.

Fig. 1. Sorption of methylene blue by $BaSO_4$ precipitate of different specific activity.
1 —inactive precipitate; 2 —0.01 mCu/g; 3 —0.1 mCu/g; 4 —1 mCu/g; 5 —4

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

mCu/g; 6 –10 mCu/g.

It should be noted that the magnitude of the sorption of both basic dyes decreases with increasing specific radioactivity of barium sulfate. A precipitate with an activity of 10 mCu/g is characterized by a sorption capacity for methylene blue equal to 15 γ/g (inactive: 50 γ/g), and for brilliant green 20 γ/g (inactive: 30 γ/g). Conversely, the sorption of acid orange increases with increasing radioactivity of the $BaSO_4$ preparation. At an activity of 10 mCu/g, the sorption capacity of the precipitate is 455 γ/g (inactive: 380 γ/g). Figure 4 shows the dependence of the magnitude of dye sorption on the specific radioactivity of $BaSO_4$. For methylene blue within the activity range 0.01–10 mCu/g, the sorption capacity li-

Fig. 2. Sorption of brilliant green by $BaSO_4$ precipitate of different specific activity. Designations as in Fig. 1.

Fig. 3. Sorption of acid orange by $BaSO_4$ precipitate of different specific activity. Designations as in Fig. 1.

linearly on the logarithm of the specific activity of $BaSO_4$. For brilliant green, a sharp drop in the sorption value is observed in the sorbent-activity interval 0.01–0.1 mCi/g; a further increase in the specific radioactivity of the precipitate to 10 mCi/g does not cause any appreciable decrease in its sorption capacity.

The question arose whether the decrease in adsorption of the basic dyes studied with increasing radioactivity of the sorbent was only apparent, and whether it might depend on their decolorization under the action of radiation. To test this supposition, special experiments were carried out. Labeled sodium sulfate was added to the dye solution, the activity of which with respect to S^{35} exceeded the S^{35} content in the liquid phase above the $BaSO_4$ precipitate with a specific activity of 10 mCi/g by factors of 10, 100, and 500. At definite time intervals the dye concentration was checked by the spectrophotometric method. It turned out that the dyes taken were resistant to the action of β-radiation from S^{35} for 40–50 hours, even at an S^{35} concentration of up to 8 mCi/l. Such an S^{35} concentration greatly exceeds its content in the equilibrium solutions studied.

Fig. 3

Figure 3: Fig. 3

Figure 4. Effect of $BaSO_4$ activity on dye sorption. 1—methylene blue, 2—brilliant green, 3—acid orange

Figure 4: Figure 4. Effect of $BaSO_4$ activity on dye sorption. 1—methylene blue, 2—brilliant green, 3—acid orange

Fig. 4. Effect of the activity of $BaSO_4$* on the sorption of dyes. 1—methylene blue, 2—brilliant green, 3—acid orange.

In addition, equilibrium dye solutions over barium sulfate precipitates with a specific activity of 10 mCi/g were shaken not for 4 hours, as was usually done, but for 16 and 32 hours. It turned out that in this case as well there were no further changes in the dye concentration. Thus, in our experiments the change in dye sorption by barium sulfate precipitates of different specific activity cannot be attributed to destruction of the dye under the action of S^{35} radiation.

Evidently, there were also no appreciable chemical or radiation-chemical changes in the liquid phase that could have affected the stability of the dyes or the magnitude of their adsorption. This view is confirmed by the fact that, within the limits of measurement error, the pH values for the equilibrium solutions did not change in comparison with the initial dye solutions.

We suppose that the observed change in dye sorption is connected with the appearance of a positive charge on the precipitate of radioactive barium sulfate due to its continuous emission of β-particles. Obviously, the magnitude of this charge increases with increasing specific activity of the precipitate. In such a case, on a radioactive sorbent that is a β-emitter, a basic dye possessing a colored cation should be sorbed less well, while an acid dye with a colored anion should be sorbed better than occurs in the presence of a nonradioactive sorbent. This is precisely the picture we observed in the experiments described above.

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