STRUCTURE OF RADIOACTIVE PRECIPITATES

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Abstract

Full Text

PHYSICAL CHEMISTRY

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STRUCTURE OF RADIOACTIVE PRECIPITATES

(Presented by Academician V. I. Spitsyn, 19 XI 1962)

A characteristic property of solid radioactive preparations is the considerable heterogeneity of their surface in comparison with nonradioactive samples, which was first shown by means of electron-microscopic photographs (^{1}). These features of the surface structure of radioactive crystals are evidently formed in the process of separation of the solid phase and subsequently remain almost unchanged.

Fig. 1. Change in the magnitude of the surface of sulfates of Ca, Sr, Ba as a function of specific radioactivity (m Cu/g).
1 –$BaSO_4{}^*$; 2 –$CaSO_4{}^* \cdot 2H_2O$, 3 –$CaSO_4 \cdot 2H_2O^*$; 4 –$SrSO_4{}^*$

In the present work the specific surface of precipitates of radioactive sulfates of Ca, Sr, and Ba, as well as the size distribution of the crystals of these salts, was studied. The radioactive preparations were obtained by precipitation at 70° by simultaneous mixing of equinormal solutions of the corresponding chloride and sodium sulfate, containing a definite amount of the required radioisotope. The concentration of $CaCl_2$ was $2N$, and of $SrCl_2$ and $BaCl_2$, $1N$. The pH value of these solutions, through addition of HCl, was ~ 2. The Na_2SO_4 solution had pH $\simeq 6$. After separation, the precipitates were vigorously stirred for another 1 hour at 70°, and then were slowly cooled and allowed to stand for 3 days at ordinary temperature. Thereafter the solid phase was separated from the mother liquor, washed with a 50% alcohol-water mixture until a negative reaction for Cl^- ions was obtained, and dried to constant weight at the corresponding temperature: $BaSO_4$ and $SrSO_4$ at 200°, $CaSO_4 \cdot 2H_2O$ at 60°.

The preparation of sulfates of Ca, Sr, and Ba was always carried out under strictly constant conditions. Only the content of the radioactive preparation in the solution was varied. The isotopes used were: S^{35}, a pure β-emitter, $T_{1/2} = 87.1$ days, $E_{(\beta)\,\max} = 0.169$ MeV, in the form of Na_2SO_4; Ca^{45}, a β-

Fig. 2. Crystal-size distribution in precipitates

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emitter, $T_{1/2} = 164$ days, $E_{(\beta)\,\mathrm{max}} = 0.254$ MeV, in the form of $CaCl_2$.

The particle-size distribution was studied on Figurowski' s balance (2), and the specific surface area was determined with Deryagin' s apparatus (3), and, for some samples, by the BET method. Both methods of measuring the surface gave coincident results within an error of ±8%. It may be concluded that typical pores are absent in the precipitates studied. Work on Figurowski' s balance was carried out in 50% alcoholic solutions both with dried samples and with samples taken directly after washing. The specific radioactivity of $CaSO_4{}^* \cdot 2H_2O$, $S_2{}^*SO_4$, and Ba^*SO_4 was determined with a 4π-counter.

Figure 1 shows how the surface of sulfates of Ca and Ba changes as a function of their specific radioactivity. For all the compounds studied,

a decrease in specific surface area is observed at small amounts of radioisotope. Then, as a rule, with increasing specific radioactivity of the samples, the surface area increases. This phenomenon is intensified for the more finely dispersed and less soluble precipitate $BaSO_4$. On the other hand, the effect of additions of different isotopes in the case of $CaSO_4$ proves to be very similar (curves 2 and 3). It should be noted that, upon

Fig. 2. Distribution of crystals by size in $BaSO_4$ precipitates of different specific radioactivity. 1—nonradioactive sample; precipitates containing S^{35}, mCu/g: 2 —0.01; 3—0.1; 4—1; 5—10; 6—100

storage in air of the preparations studied (up to 1 year), the magnitude of their surface area does not change. Thus, prolonged self-irradiation of the precipitates as S^{35} or Ca^{45} decays does not exert a substantial influence on the state of the surface.

Figure 2 gives the results of dispersion analysis of barium sulfate precipitates. Along the ordinate is plotted the distribution function dQ/dr, characterizing the relative content of particles of a given size in the preparation under study. It can be seen that, as the specific radioactivity of barium sulfate increases, not only is there a tendency toward a decrease in the particle size of the precipitate, but also a change in the character of the distribution curve. The latter is reflected, for example, in the appearance of two maxima on the curve, beginning with a specific radioactivity of 1 mCu/g. For samples of $CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$, and $SrSO_4$, analogous results were obtained.

Any dispersed system can be characterized by means of the coefficient of heterogeneity U (2)

Figure 3

Figure 3: Figure 3

$$U = \Delta a \sqrt{\frac{\sum n_i}{2 \sum n_i v^2}},$$

where Δa is the difference between two successive particle sizes, v is the difference between the mean size and the size of the i-th particle, and n_i is the number of particles of the given size. When $U = 0$, the system is perfectly heterogeneous; if, however, U approaches infinity, the system consists of identical particles. Consequently, a decrease in U indicates an increase in the heterogeneity of the particles in the system.

As can be seen from Fig. 3, the values of U for all the radioactive precipitates studied are lower in comparison with the nonradioactive preparations. Thus, radioactive radiation increases the heterogeneity of the precipitating sulfates.

The phenomena described can be explained as follows. In the process of formation of a radioactive precipitate, the structure of its surface and the particle size are determined by two main factors. Radioactive radiation causes the formation of an increased number of crystallization centers in the volume of the solution and, consequently, leads to the production of a more highly dispersed precipitate. In addition, radioactive crystals under such conditions possess a nonuniform surface structure ([1]).

Fig. 3. Values of the nonuniformity coefficient U for precipitates of sulfates of Ca, Sr, and Ba:
1—$SrSO_4$; 2—$CaSO_4 \cdot 2H_2O$; 3—$CaSO_4 \cdot 2H_2O$; 4—$BaSO_4$.

On the other hand, as was shown earlier, radioactive precipitates recrystallize at a higher rate than nonradioactive ones ([4]). For this reason, particles containing radioactivity become coarser in solution much more rapidly, and their specific surface decreases. These factors, acting simultaneously, exert opposite effects on the solid phase that forms. As a consequence, it is evident that a minimum in the values of the specific surface is observed on the curves in Fig. 1 as a function of the specific radioactivity of sulfate precipitates.

If one proceeds from the proposed mechanism of formation of highly radioactive precipitates, then inactive preparations obtained under external irradiation (for example, by β-particles) of the solutions being mixed should have a larger surface area than the same preparations obtained under ordinary conditions. Experiments specially set up in this direction confirmed our supposition.

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