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Abstract

Full Text

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PHYSICAL CHEMISTRY

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STUDY OF THE INFLUENCE OF THE SPECIFIC RADIOACTIVITY OF CERIUM OXALATE ON ITS SOLUBILITY

On the basis of the works ([1],[2]) and many subsequent ones, the radioactive-tracer method is widely used for determining the solubility of sparingly soluble substances. If the solubility of compounds is very low, preparations of high specific activity must be used. However, as established by investigations of recent years ([3]-[7]), the radioactive radiation of solids exerts a considerable influence on their physicochemical properties. In particular, V. I. Spitsyn, E. A. Torchenkova, and I. N. Glazkova ([8]) found that the kinetics of dissolution of barium sulfate and the actual value of its solubility in water depend on the specific radioactivity of preparations of $BaSO_4$ containing S^{35}.

In the present work the influence of specific activity on the solubility in water of cerium(III) oxalate, labeled with Ce^{144}, was studied. The radioactive isotope of cerium Ce^{144} (maximum β-radiation energy 0.3 MeV) has a half-life of 282 days and forms the short-lived daughter isotope Pr^{144} ($T_{1/2} = 17.5$ min.) with a maximum β-radiation energy of 2.97 MeV. Preparations of four activity levels were used: 0.0075; 0.046; 0.495; and 4.3 mCu/g.

Samples of cerium oxalate were prepared under identical conditions by precipitation from an acidic 0.5 N (with respect to HCl) solution of X-ray-spectroscopically pure $CeCl_3$ containing the radioactive isotope Ce^{144}, at the boiling temperature, with a fivefold excess of oxalic acid. The precipitate obtained was heated for one hour at 70–80°. For better maturation of the crystals, filtration was carried out after 24 hours. The precipitate was washed with water to a neutral reaction to methyl orange. The preparations thus obtained, after drying in air, in all cases corresponded to the hydrate $Ce_2(C_2O_4)_3 \cdot 10H_2O$. The cerium content was determined by igniting the initial oxalate at 700–800° to CeO_2. The oxalate ion was determined by titrating a hot sulfuric-acid solution containing an accurately weighed portion of cerium oxalate with potassium permanganate solution. The content of water of crystallization was calculated by difference.

To determine the solubility, 10 mg of cerium oxalate and 80 ml of twice-distilled water were placed in a vessel equipped with a screw stirrer and an oil seal. The experiments were carried out in a thermostat at 25°. Saturation was reached, as a rule, after 80-100 hours of stirring. Before sampling, stirring was stopped and the precipitate was allowed to settle for 30 min. The solution sample was carefully centrifuged and applied with a micropipette in 0.5-ml portions to special aluminum dishes—targets, after which it was evaporated to dryness. The volume of solution varied, depending on the specific activity of the initial salt, from 0.5 to 5.0 ml. The minimum counting rate (after subtraction of background) was 10 impulses/min. The solubility was calculated by the formula:

$$L = \frac{I_\mathrm{p} Q}{I \ v_\mathrm{p}} \cdot 1000, \tag{1}$$

where L is the solubility in mg/l, I_p is the activity of the solution in counts/min, v_p is the volume of the solution in ml, Q_st is the content of cerium oxalate in the standard in mg, and I_st is the activity of the standard in counts/min. The standards were prepared by dissolving an exact weighed portion of the initial cerium oxalate in hydrochloric acid.

The results of four series of experiments are given in Table 1 and show that, with an increase in the specific activity of cerium oxalate, its solubility,

Table 1

Solubility of $^*\mathrm{Ce_2(C_2O_4)_3 \cdot 10H_2O}$ in water at 25°

Specific activity (N	Specific activity (N	Solubility
counts/min • g	mCu/g	(L), mg/l
$5.00 \cdot 10^6$	0.0075	0.87 ± 0.02
$3.06 \cdot 10^7$	0.046	0.75 ± 0.02
$3.30 \cdot 10^8$	0.495	0.50 ± 0.04
$2.86 \cdot 10^9$	4.30	0.33 ± 0.03

Fig. 1. Solubility in water of cerium oxalate of different specific activity at 25°.

as determined by the Ce^{144} indicator, decreases. The composition of the bottom phase in this case practically does not change.

As Fig. 1 shows, the solubility of cerium oxalate depends linearly on the logarithm of the specific radioactivity of the preparation and is expressed by the equation:

$$\lg N = aL + b. \tag{2}$$

Indeed, if the data of Table 1 are used for a quantitative calculation of the closeness of the relationship (R) between the solubility (L) and the specific activity (N) of cerium oxalate, we obtain $R = 0.99$, which indicates a direct functional dependence $L = f(\lg N)$. The value of R was calculated by the formula

$$R = \frac{n\sum_1^n L\lg N - \sum_1^n L \sum_1^n \lg N}{\sqrt{\left[n\sum_1^n L^2 - \left(\sum_1^n L\right)^2\right]\left[n\sum_1^n (\lg N)^2 - \left(\sum_1^n \lg N\right)^2\right]}}, \tag{3}$$

where R is the closeness of the relationship, L is the solubility in mg/l, N is the specific activity in mCu/g, and n is the number of averaged experimental points. Applying the method of least squares, one can calculate the values of the parameters a and b in equation (2) for the analytical calculation of the solubility of cerium oxalate at any specific activity. The parameters of equation (2) were calculated from the formulas:

$$a = \frac{n\sum_1^n L\lg N - \sum_1^n L \sum_1^n \lg N}{n\sum_1^n L^2 - \left(\sum_1^n L\right)^2}, \tag{4}$$

$$b = \frac{\sum_1^n L^2 \sum_1^n \lg N - \sum_1^n L \sum_1^n L\lg N}{n\sum_1^n L^2 - \left(\sum_1^n L\right)^2}, \tag{5}$$

and led to the values $a = -4.93$ and $b = 2.235$.

Substituting the values of the parameters into equation (2), one can find the value of the solubility at very low specific activity. Taking $N = 1.0 \cdot 10^{-6}$ mCu/g, we obtain $L = 1.65$ mg/l.

The literature data on the solubility of cerium oxalate ($^{9-11}$) differ greatly and lie in the range from 0.55 to 1.45 mg/l calculated for the 10-hydrate. The most reliable among them may be considered the solubility values obtained by volumetric and gravimetric methods (^{10,11}), equal respectively to 1.32 and 1.45 mg/l. These values are in good agreement with the calculation given above.

In conclusion, it should be noted that the effect of the radiation of the radioactive indicator used on the solubility of sparingly soluble compounds must be taken into account when using the tracer-atom method.

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