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Abstract

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A NEW VARIETY OF ANOMALOUS MIXED CRYSTALS

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Until quite recently (1) it was assumed that all anomalous mixed crystals, in contrast to isomorphous ones, must have a lower miscibility limit. At present, however, a large number of anomalous systems are known in which the lower limit is absent, and mixed crystals form at an arbitrarily small concentration of one of the components. It is precisely such systems that are of greatest interest for radiochemistry.

In (2) it was shown that, in anomalous systems that do not have a lower limit, special laws of precipitation should also be observed, differing from the laws of coprecipitation in isomorphous systems. Depending on the character of the interaction between the components, anomalous systems were divided into three groups, the differences between which manifest themselves during the formation of mixed crystals from a supersaturated solution under conditions of logarithmic distribution. Moreover, only in the case of systems formed by components that are relatively close in their properties can one expect coprecipitation to proceed in accordance with the Doerner–Hoskins formula:

$$\lg \frac{100}{100-x} = \lambda \lg \frac{b}{b-y}. \tag{1}$$

For systems formed by components that differ strongly in their properties, the following formulas were derived:

$$\lg \frac{100}{100-x} = \chi \frac{y}{V}, \tag{2}$$

$$\lg \frac{100}{100-x} = \nu \frac{y\left(b-\frac{y}{2}\right)}{V^2}, \tag{3}$$

where x, y are the amounts of the micro- and macrocomponent in the precipitate; $100, b$ are the initial amounts of the components in solution; V is the volume of the solution.

In contrast to formulas (1) and (2), the applicability of formula (3) to any coprecipitation processes has not been demonstrated experimentally.

As was already noted (2), the microcomponent will pass into the solid phase in accordance with formula (3) only in the case of a linear dependence of coprecipitation on the concentration of the microcomponent in solution. In general, it is advisable to assign to a special group of anomalous systems those systems in which the elementary act of cocrystallization is described by the equation

$$\frac{dx}{dy} = \nu \frac{100 - x}{V} \left(\frac{b - y}{V} \right)^n, \tag{4}$$

where $n > 0$.

If necessary, the integration can readily be carried out also for values of n different from unity. For all anomalous systems

for this group, an increase in the capture of the microcomponent with increasing concentration of the macrocomponent cation in the solution should be characteristic. The existence of regularities of this kind could be expected in the coprecipitation of a radioelement capable of being present in solution in the form of a multicharged complex anion with a salt of a monovalent metal. Therefore, in the present work the coprecipitation of microquantities of thorium with silver oxalate was studied. Systems of this type, for example Zr(IV)–K_2SO_4, have already been studied earlier (4).

The advantage of the chosen system lies in the comparatively low solubility of the microcomponent, which makes it possible to vary the precipitation conditions within rather broad

Table 1

Initial Ag conc. in soln., mg/ml	Amount of Ag in precipitate, mg/ml	HNO_3 conc., M	Amount of thorium-234 in precipitate, %	Initial Ag conc. in soln., mg/ml	Amount of Ag in precipitate, mg/ml	HNO_3 conc., M	Amount of thorium-234 in precipitate, %
0.79	0.58	0.2	5.4	2.96	2.80	0.2	96.1
0.79	0.58	0.2	5.2	1.58	1.21	0.5	8.9
1.98	1.75	0.2	73.0	1.58	1.13	0.5	8.6
1.98	1.80	0.2	67.5	3.95	3.45	0.5	69.8
2.96	2.77	0.2	96.2	3.95	3.48	0.5	72.3

Table 2

Initial Ag conc. in soln., mg/ml	Amount of Ag in precipitate, mg/ml	HNO_3 conc., M	Mean $H_2C_2O_4$ conc., M	Amount of thorium-234 in precipitate, %	Initial Ag conc. in soln., mg/ml	Amount of Ag in precipitate, mg/ml	HNO_3 conc., M	Mean $H_2C_2O_4$ conc., M	Amount of thorium-234 in precipitate, %
2.00	0.89	0.2	0.008	59.5	2.00	0.88	0.5	0.017	28.8
2.00	1.53	0.2	0.011	68.2	2.96	1.52	0.5	0.015	50.7
2.00	1.21	0.5	0.037	22.5	2.96	1.48	0.5	0.010	50.6
2.00	1.23	0.5	0.037	22.2	2.96	1.26	0.5	0.013	43.1
2.00	1.02	0.5	0.028	25.2	2.96	1.20	0.5	0.010	44.6
2.00	1.13	0.5	0.027	27.0	3.95	1.14	0.5	0.010	48.4
2.00	0.90	0.5	0.021	29.6	3.95	1.18	0.5	0.005	50.6
2.00	0.95	0.5	0.020	29.2	3.95	1.48	0.5	0.009	60.3
2.00	0.92	0.5	0.017	30.8	3.95	1.41	0.5	0.006	58.2

limits the precipitation conditions. In the work the isotope thorium—Th^{234} was used. The preparation of this isotope is described in the article (5). First of all it was established that thorium is indeed capable of coprecipitating with silver oxalate. It turned out that a considerable part of the thorium is captured by well-formed crystals of silver oxalate during slow crystallization, and that thorium is distributed throughout the entire volume of the solid phase. Adsorption of thorium on prepared crystals of silver oxalate was practically not observed. Preliminary experiments also showed that, at the intensity of stirring of the solution that was attained during the precipitation process, well reproducible results can be obtained if the mean crystallization rate does not exceed 1 mg Ag/ml · h.

Table 1 gives the results obtained in precipitating increasing amounts of silver oxalate by gradual addition of oxalic acid. In this case the concentration of oxalic acid during precipitation was not taken into exact account. In Table 1, as in all subsequent tables, all concentrations refer to the volume of the solution at the end of precipitation.

The observed sharp increase in the percentage of thorium precipitated with increasing amount of precipitate already makes it possible to conclude that coprecipitation proceeds in the spirit of equation (4). But in order to clarify more precisely the features of coprecipitation, it is necessary separately to assess the influence of the concentration of the cation and anion of the macrocomponent. The data given in Table 2 provide an idea of the dependence of coprecipitation on the concentration

oxalic acid. Comparing the results of experiments carried out at an unchanged initial silver concentration and not very different amounts of precipitate, one can establish that when the concentration of oxalic acid is decreased to 0.02 M (in 0.5 M HNO_3) the capture of thorium increases somewhat,

Table 3

Initial conc. of Ag in solution, mg/ml	Amount of Ag in precipitate, mg/ml	Amount of thorium-234 in precipitate, %	v, ml^2/mg^2	x, ml/mg	λ
3.95	0.55	29.3	0.074	0.274	2.32
3.95	0.72	36.0	0.075	0.270	2.22
3.95	1.14	48.4	0.075	0.252	1.95
3.95	1.18	50.6	0.077	0.259	1.99
3.95	1.41	58.2	0.083	0.269	1.97
3.95	1.48	60.3	0.085	0.272	1.97
3.95	1.50	59.0	0.081	0.258	1.86
3.95	1.77	69.0	0.094	0.287	1.97
3.95	2.32	69.0	0.079	0.219	1.32
3.95	2.80	70.6	0.075	0.190	0.99
3.95	2.94	72.7	0.077	0.192	0.95
2.96	0.40	16.2	0.070	0.192	1.21
2.96	1.20	44.6	0.091	0.214	1.14
2.96	1.26	43.1	0.083	0.194	1.02
2.96	1.50	50.5	0.091	0.202	1.00
2.00	0.77	20.8	0.082	0.132	0.48
2.00	0.95	29.0	0.103	0.157	0.53
2.00	0.95	27.4	0.096	0.146	0.50

whereas in the interval 0.020–0.005 M it remains practically constant. This peculiar dependence is apparently due to the fact that not only the state of thorium in solution depends on the concentration of oxalic acid, but, during formation of the solid phase, competition is also possible

Table 4

Experiment no.	Concentration of $H_2C_2O_4$, M before precipitation	Concentration of $H_2C_2O_4$, M after precipitation	Mean conc. of Ag, mg/ml	Amount of thorium-234 in precipitate, %	λ'
1	0.0995	0.0944	1.03	6.6	1.30
2	0.0995	0.0946	1.11	5.7	1.16

Experiment no.	Concentration of $H_2C_2O_4$, M before precipitation	Concentration of $H_2C_2O_4$, M after precipitation	Mean conc. of Ag, mg/ml	Amount of thorium-234 in precipitate, %	λ'
3	0.0497	0.0453	1.05	11.8	1.35
4	0.0398	0.0339	1.37	21.6	1.52
5	0.0398	0.0341	1.39	22.2	1.63
6	0.0298	0.0246	1.44	27.0	1.64
7	0.0298	0.0251	1.49	25.2	1.69
8	0.0248	0.0202	1.50	27.0	1.53
9	0.0224	0.0180	1.53	29.2	1.58
10	0.0224	0.0182	1.55	29.6	1.69
11	0.0398	0.0339	0.85	9.1	0.59
12	0.0398	0.0341	0.80	8.9	0.60

between the complex anion $[Th(C_2O_4)_3]^{2-}$ and certain forms of oxalic acid $(C_2O_4^{2-}, HC_2O_4^-)$.

To check the applicability of any of the formulas given above, a special series of experiments was carried out in which the concentration of oxalic acid during precipitation was maintained within 0.020–0.005 M (the concentration of nitric acid in all experiments was 0.5 M). The results obtained (Table 3) show that coprecipitation is satisfactorily described by formula (3).

Finally, Table 4 gives the results of a series of experiments, using which one can calculate, by formula (1), the values of the distribution coefficient-

of thorium precipitation (denoted λ') with respect to oxalic acid (concentration of HNO_3 0.5 M).

Judging from the data obtained, the notion of the possibility of competition between the thorium complex and certain forms of oxalic acid is apparently correct. The coefficient λ', under some change in the precipitation conditions, remains approximately constant (experiments 1-3 and 4-10 in Table 4). However, as was to be expected, a considerable change in the concentration of silver in the solution clearly affects the coprecipitation of thorium. This is especially evident in experiments 4, 5 and 11, 12 of Table 4.

Thus, in order to characterize fully the behavior of thorium in the system under study, it is necessary to take into account the dependence of coprecipitation on the concentration of the cation of the macrocomponent, the change in the state of thorium in solution when the concentration of the anion of the macrocomponent is changed, and the competing action of this anion.

The results obtained confirm that, when studying coprecipitation under conditions of logarithmic distribution, it is possible to discover special regularities that make it possible not only to distinguish anomalous mixed crystals from isomorphous ones, but also to establish the existence of distinctive varieties of anomalous mixed crystals.

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