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Abstract

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ON SOME REGULARITIES OF COPRECIPITATION IN THE FORMATION OF ANOMALOUS MIXED CRYSTALS

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At the present time a very large number of cases are known of microquantities of impurities cocrystallizing with nonisomorphous carriers. The mixed crystals formed in this way are traditionally called "anomalous." For a long time already, in the study of coprecipitation phenomena, three basic formulas have been used:

Khlopin' s formula (^{1})

$$\frac{1}{V_{\mathrm{t}}} = K\frac{a-x}{V_{\mathrm{l}}}, \tag{1}$$

Henderson and Kracek' s (^{2})

$$\frac{x}{y} = D\frac{a-x}{b-y} \tag{2}$$

and Doerner and Hoskins' s (^{3})

$$\lg\frac{a}{a-x} = \lambda\lg\frac{b}{b-y}, \tag{3}$$

where x, y are the amounts of the micro- and macrocomponent in the precipitate; a, b are the initial amounts of the components in the solution; $V_{\mathrm{t}}, V_{\mathrm{l}}$ are the volumes of the solid and liquid phases.

It is worthwhile to consider the question of the extent to which these formulas, whose applicability under certain experimental conditions was originally proved for isomorphous systems, retain their significance in the transition to anomalous systems. In doing so, we shall consider systems in which no lower miscibility limit is observed, and at sufficiently small impurity concentrations, when no features of coprecipitation associated with the presence of an upper miscibility limit are detected.

If thermodynamic equilibrium has been established in an anomalous system of the type under consideration, then the applicability of formulas (1) and (2) is beyond doubt. As has already been shown earlier ([1], p. 173), these formulas are in principle analogous and are an application, to the case of coprecipitation, of the general law of equilibrium distribution of a substance between two phases. It may be noted, however, that formula (2) has already acquired a form associated with the notion specifically of isomorphous substitution. When this formula is used, the distribution of the element under study is usually compared with the distribution of that ion of the macrocomponent whose place the studied ion occupies in the crystal lattice. Ratner gave an analogous form to his formula as well, deriving it on the basis of thermodynamic concepts ([4]). However, if the study of coprecipitation is restricted to conditions of complete equilibrium in the system, then ideas about the character of substitution find only formal reflection in the calculation formulas, since the activity of the macrocomponent in the saturated solution is a constant quantity.

The situation is different in the case of coprecipitation from a supersaturated solution under conditions of logarithmic distribution. Under these conditions the activity of the macrocomponent in the solution changes during crystallization; therefore, ideas about the nature of the interaction between the components acquire fundamental significance and can be tested experimentally. In this connection

one may expect the applicability of formula (3) only in those cases where, in the formation of mixed crystals, substitution of the "ion-for-ion" type actually takes place and the corresponding ions compete in the crystallization process. Moreover, in the general case, when the ions forming the macrocomponent are present in the solution in nonequivalent amounts, in calculating the logarithm $\frac{b}{b-y}$ one must take the amounts of precisely that ion which is replaced in the solid phase by the element under study.

It is enough to consider several typical anomalous systems, for example Mn(II)–NH_4Cl ([5]), Ce(III)–K_2SO_4 ([6]), Ce(III)–$U(C_2O_4)_2$ ([7]), to become convinced that in such cases, without resorting to experiment, it is difficult to decide what place the microcomponent will occupy in the crystal lattice and whether, in the process of coprecipitation, it will compete with any ion of the macrocomponent. It is natural to suppose that the more the components differ in their properties, the less probable it is that they will compete in the coprecipitation process. In such cases one should rather speak of chemical interaction of the components, leading to the formation of complex double salts of variable composition. It seems expedient to consider three probable types of interaction between components in the formation of anomalous mixed crystals.

1. The components occupy analogous positions in the crystal lattice and compete with one another during crystallization (this case was considered by Derner and Hoskins ([3]), who studied the coprecipitation of radium with barium sulfate). 2. The transfer of the microcomponent into the crystals

does not depend on the concentration of the macrocomponent in the solution. 3. The presence of the macrocomponent in the solution promotes the transfer of the microcomponent into the precipitate (below, only the linear dependence of coprecipitation on the activity of the macrocomponent in the solution is analyzed).

The indicated ideas, as applied to the elementary act of coprecipitation, may be written as follows:

$$\frac{dx}{dy} = \lambda_0 \frac{a}{a'}, \qquad \frac{dx}{dy} = \varkappa_0 a, \qquad \frac{dx}{dy} = \nu_0 a a';$$

or, after replacing the activities of the micro- and macrocomponent in the liquid phase (a and a') by concentrations:

$$\frac{dx}{dy} = \lambda \frac{a-x}{b-y}, \tag{4}$$

$$\frac{dx}{dy} = \varkappa \frac{a-x}{V}, \tag{5}$$

$$\frac{dx}{dy} = \nu \frac{a-x}{V} \cdot \frac{b-y}{V}. \tag{6}$$

If the components have the formulas MA_n and $\mathrm{M'A}_m$, where M is the radioelement under study and A is the common anion, then it is understood that x and y in equations (4-6) are the amounts of M and M′. In connection with the transition from the activities of the components to the concentrations of the corresponding metals, the "true" constants λ_0, $\varkappa_0$, ν_0 are replaced by the coefficients λ, $\varkappa$, ν, which will be constant only at an unchanged concentration of the common anion and at constant ionic strength of the solution. It is also essential that during precipitation the equilibrium between the various complex forms of the components not be disturbed.

If the coefficients $\varkappa$, ν and the volume of the solution do not change in the crystallization process, then integration of equations (5) and (6) presents no difficulties and leads to the formulas:

$$\lg \frac{a}{a-x} = \varkappa \frac{y}{V}, \tag{7}$$

$$\lg \frac{a}{a-x} = \nu \frac{y\left(b - \frac{y}{2}\right)}{V^2}. \tag{8}$$

(Integration of equation (4) gives the Doerner and Hoskins formula.) For the application of formulas (7) and (8), the experimental conditions must be the same as for the application of formula (3): that is, precipitation must occur from a homogeneous supersaturated solution, and the crystals that separate must not undergo substantial recrystallization.

The applicability of the logarithmic and of the derived semilogarithmic formulas was checked for the case of coprecipitation of small amounts of calcium with uranium and thorium oxalates. The β-active isotope Ca^{45} was used as an indicator. The results obtained are given in Tables 1 and 2. The procedure for similar experiments was described earlier (^{7}).

Table 1

Coprecipitation of calcium with uranium oxalate
Composition of solution: 1.0 M HCl, 0.10 M $H_2C_2O_4$

Solution volume, ml	Amount of uranium, mg	Amount of uranium, mg	Amount of calcium, cpm/min·10^3	Amount of calcium, cpm/min·10^3	χ, ml/mg	λ	ν, ml^2/mg^2
	in precipitate	in solution	in precipitate	in solution			
100	2.6	44.7	7.5	40.0	2.9	0.85	22
100	5.0	15.7	18.0	47.0	2.8	1.2	15
100	7.9	20.2	27.5	38.5	3.0	1.6	12
100	11.6	12.1	38.4	27.0	3.3	1.3	18
100	16.9	11.3	45.5	17.5	3.3	1.4	17
100	17.4	3.2	34.5	13.4	3.2	0.68	27
100	18.6	1.7	48.5	19.9	2.9	0.50	26
100	19.2	1.5	35.0	11.9	3.1	0.52	28
50	9.4	0.9	17.1	5.4	3.3	0.59	29
150	7.3	32.3	22.2	52.5	3.1	1.7	13
				Average	3.1$±$0.2		

Table 2

Coprecipitation of calcium with thorium oxalate
Composition of solution: 0.5 M HCl, 0.10 M $H_2C_2O_4$

Solution volume, ml	Amount of thorium, mg	Amount of thorium, mg	Amount of calcium, cpm/min·10^3	Amount of calcium, cpm/min·10^3	χ, ml/mg	λ	ν, ml^2/mg^2
	in precipitate	in solution	in precipitate	in solution			
200	2.2	13.9	5.0	62.0	3.1	0.53	41
200	18.2	4.9	44.0	43.5	3.3	0.45	47
200	4.9	0.1	7.7	35.8	3.5	0.05	270
100	3.5	6.2	9.5	34.0	3.1	0.55	39
100	5.7	4.0	16.0	28.5	3.4	0.50	50
100	8.1	1.6	22.2	23.6	3.6	0.37	64
100	9.3	0.4	22.6	20.4	3.5	0.23	69
				Average	3.4$±$0.2		

Coprecipitation of calcium is satisfactorily described by formula (7). It should be emphasized that, under the same conditions, coprecipitation of cerium(III) and thorium (uranium X_1) with uranium oxalate (7,8) proceeded in accordance with the logarithmic formula (3). If the process of cocrystallization is described by formula (7), then the completeness of precipitation of the impurity is determined by the mass of precipitate separated from a unit volume of solution. The crystals formed must always contain a supersaturation amount of the microcomponent, and only in the case when its concentration does not change during precipitation will homogeneous crystals arise.

The difference between formulas (3, 7, 8) is clearly manifested when the degree of precipitation of the carrier is varied over wide limits, which is readily achieved when working with sparingly soluble salts. It is quite probable that formulas (3, 7, 8) do not exhaust all possible cases of interaction between the components in the process of coprecipitation. As is evident from the foregoing, in order to elucidate the regularities governing the formation of anomalous mixed crystals, the study of coprecipitation under conditions of a logarithmic distribution is of great importance.

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