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Abstract

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THE EFFECT OF COMPLEX FORMATION ON THE SEPARATION OF ELEMENTS BY COCRYSTALLIZATION

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At present, for the separation of chemically analogous elements, the methods most often used are chromatography, extraction, and cocrystallization. The use of the phenomenon of complex formation has made it possible to increase significantly the efficiency of the first two methods. At the same time, there are a number of publications in the literature ($^{1-3}$) from which it follows that the use of complexones makes it possible to improve the separation of elements by the method of cocrystallization. However, the material published in the literature is purely empirical, and on its basis no attempt has been made at a theoretical calculation of the efficiency of separation of elements. The only exception is the work (^{4}), on the basis of which a calculation can be made of the cocrystallization coefficient in the presence of complex-forming agents. But the authors consider a case rarely encountered in practice, when only the microelement forms a complex compound with the given addend. Of much greater interest is the case when complex compounds are formed by both components participating in the cocrystallization process.

As is known, the distribution of a microelement between the crystalline phase and the solution obeys Khlopin' s law (^{5}):

$$\frac{x}{y} = D_0 \frac{[A^\bullet]}{[A^{\bullet\prime}]}, \tag{1}$$

where x and y are the amounts of the micro- and macroelement in the precipitate; $[A^\bullet]$ and $[A^{\bullet\prime}]$ are the contents of the components in the solution; D_0 is the cocrystallization coefficient. This coefficient may lie within the limits $0 < D_0 < \infty$. The more D_0 differs from 1, the better the separation of the elements will proceed.

When a complex-forming agent is introduced into the system, complex compounds of the macro- and microelement are formed in the solution, having different stabilities, which will lead to a change in the ratio $[A^\bullet]/[A^{\bullet\prime}]$, and this, in turn, will affect the change in the practically determined coefficient D.

In order for the precipitate to be in equilibrium with the solution, it is necessary that only part of the macroelement be bound in a complex. If we are dealing with such systems in which, among the series of complex compounds of the macro- and microelement, only one has high stability, then this compound will predominate over a wide range of addend concentrations. Then the concentration of the macroelement present in the ionic state is expressed by the equality

$$[A^{\bullet\prime}] = [A^{\bullet}_{\text{total}}] - [AB]'. \tag{2}$$

where $[AB]'$ is the concentration of the macroelement bound in the complex.

If the ratio of the stability constants of the complex compounds of the microelement (β) and macroelement (β'), as well as the ratio $[AB]'/[A^{\bullet\prime}]$, is known, then the concentration of the microelement present in the ionic state can be found:

$$[A^{\bullet}] = \frac{[A_{\text{total}}]}{1 + \frac{\beta}{\beta'}\frac{[AB]'}{[A^{\bullet\prime}]}}. \tag{3}$$

Substituting (2) and (3) into equality (1), and also carrying out the simplest transformations, we find

$$D_0 = \frac{x[A'_{\text{total}}]}{y(A_{\text{total}})} + \frac{x[AB]'}{y[A']}\,\frac{\left(\dfrac{\beta}{\beta'} - 1\right)}{\left\{1 + \dfrac{\beta}{\beta'}\,\dfrac{[AB]'}{[A']}\right\}}. \tag{4}$$

The first term of this equation is the practically determinable coprecipitation coefficient D. Then, solving (4) with respect to D, and also taking (1) into account, we obtain

$$D = D_0\,\frac{\left\{\dfrac{[AB]'}{[A']} + 1\right\}}{\left\{\dfrac{\beta}{\beta'}\,\dfrac{[AB]'}{[A']} + 1\right\}}. \tag{5}$$

It is not difficult to show that under the conditions $[A'] \ll \dfrac{\beta}{\beta'}[AB]'$ and $[A'] \ll [AB]'$, equation (5) is simplified:

$$D = D_0\frac{\beta'}{\beta},$$

and the practical coprecipitation coefficient reaches its limiting value.

The correctness of the relation (5) found by us was checked using the example of the distribution of Sr^{90} between the solution and the solid phase of barium nitrate. It turned out that the coprecipitation coefficient of strontium in the absence of a complexing agent at 25° is $D_0 = 0.13 \pm 0.01$. When complexon III, which binds strontium into a more stable complex than barium, is introduced into the system, the coprecipitation coefficient of strontium decreases. The results obtained are given in Table 1.

Table 1

Dependence of the coprecipitation coefficient of strontium with $Ba(NO_3)_2$ on the degree of binding of barium into a complex

Experiment No.	$\frac{[AB]'^*}{[A^{\bullet\prime}]}$	D	$\frac{\beta}{\beta'}$
1	1.63	0.00648	31.8
2	0.456	0.0116	33.6
3	0.195	0.0235	28.7
4	0.0652	0.0509	26.4
5	0.0195	0.0829	30.7
Average			30.2

* $[AB]'/[A^{\bullet\prime}]$ = [Ba] in the complex / [Ba$^{\bullet\bullet}$] in the ionic state.

It follows from the table that the experimentally found coprecipitation coefficient decreases as the amount of barium bound into a complex increases. At the same time, the ratio of the stability constants of the strontium and barium complexes, calculated from equation (5), remains constant within the limits of experimental error, which confirms the applicability of relation (5).

Thus, knowing D_0 and β/β', one can by calculation determine the amount of complexing agent that must be introduced into the system in order to achieve the required completeness of separation of the components.

It should be noted that the value $\beta/\beta' = 30.2$ found by us differs from the value 7.44 known in the literature (6). This is due to the fact that the coprecipitation experiments were carried out under conditions of high ionic strength (sodium nitrate concentration 500 g/l), and the values of the activity coefficients of the components were not taken into account.

Up to this point we have considered the influence of complex formation of the components on their separation under conditions of equilibrium conduct of the process. At the same time, it is known that equilibrium coprecipitation is, from the point of view of element separation, less effective than nonequilibrium coprecipitation, described by the Doerner—Hoskins equation (7). The process of coprecipitation, in accordance with the Doerner—Hoskins equation, proceeds during slow crystallization of the solid phase, when the surface of the growing crysis constantly in thermodynamic equilibrium with the solution. This is expressed by the equation

$$\frac{dx}{a-x} = \lambda_0 \frac{dy}{b-y}, \tag{6}$$

where x and y are the amounts of the micro- and macrocomponent in the solid phase, and a and b are the total contents of the micro- and macrocomponent in the system; λ_0 is the cocrystallization coefficient, and, as Khlopin showed (^{5}), $\lambda_0 = D_0$.

It is evident that introducing a complexing agent into the system will require replacing λ_0 by λ, where λ must be equal to D. Then from equations (5) and (6) we obtain

$$\frac{dx}{a-x} = \lambda_0 \frac{\left\{\frac{[\mathrm{AB}]'}{[\mathrm{A}']} + 1\right\}}{\left\{\frac{\beta}{\beta'}\frac{[\mathrm{AB}]'}{[\mathrm{A}']} + 1\right\}} \frac{dy}{b-y}. \tag{7}$$

In this case two methods of precipitating the solid phase are possible:

1. A complexing agent is introduced into the system in such an amount that only part of the macro- and microelement is bound into the complex. Then, by carrying out slow precipitation, a certain amount of the macroelement initially present in the ionic state is transferred into the precipitate.
2. At first the macro- and microelement are completely converted into complex compounds. Then slow decomposition of the complexes is carried out, as a result of which the elements gradually pass into the ionic state and, in the presence of an excess of precipitant, form a solid phase. In this case it is assumed that the concentration of the macroelement present in the ionic state does not change during precipitation.

In the first case the variable quantity will be $[\mathrm{A}']$. Expressing $[\mathrm{A}']$ through b, y, and $[\mathrm{AB}]'$, and performing the simplest transformations, we obtain

$$\frac{dx}{a-x} = \lambda_0 \frac{dy}{b + [\mathrm{AB}]'v\left(\frac{\beta}{\beta'} - 1\right) - y}, \tag{8}$$

where v is the volume of the solution.

Integration of the left-hand side of equation (8) from 0 to x and of the right-hand side from 0 to y gives

$$\ln\frac{a}{a-x}=\lambda_0\ln\frac{b-[\mathrm{AB}]'v+\dfrac{\beta}{\beta'}[\mathrm{AB}]'v}{b-[\mathrm{AB}]'v-y+\dfrac{\beta}{\beta'}[\mathrm{AB}]'v}. \tag{9}$$

Since $[\mathrm{A}''_{\mathrm{init}}]v=b-[\mathrm{AB}]'v$, and $[\mathrm{A}''_{\mathrm{fin}}]v=b-[\mathrm{AB}]'v-y$, equation (9) assumes the final form:

$$\ln\frac{a}{a-x}=\lambda_0\ln\frac{[\mathrm{A}''_{\mathrm{init}}]+\dfrac{\beta}{\beta'}[\mathrm{AB}]'}{[\mathrm{A}''_{\mathrm{fin}}]+\dfrac{\beta}{\beta'}[\mathrm{AB}]'}. \tag{10}$$

It should be noted that under the condition

$$\frac{\beta}{\beta'}[\mathrm{AB}]'\ll[\mathrm{A}''_{\mathrm{fin}}]$$

the effect of complex formation is insignificant, and equation (10) assumes the usual Doerner–Hoskins expression:

$$\ln\frac{a}{a-x}=\lambda_0\ln\frac{[\mathrm{A}''_{\mathrm{init}}]}{[\mathrm{A}''_{\mathrm{fin}}]}. \tag{11}$$

In the second case the variable will be $[\mathrm{AB}]'$. Then, expressing in (7) $[\mathrm{AB}]'$ through b, y, and $[\mathrm{A}'']$, and carrying out the transformations, we find

$$\frac{dx}{a-x}=\lambda_0\frac{\beta'}{\beta}\frac{dy}{b-[\mathrm{A}'']v+\dfrac{\beta'}{\beta}[\mathrm{A}'']v-y}. \tag{12}$$

Integration of this equation from 0 to x for the left-hand side and from 0 to y for the right-hand side leads to the solution

$$\ln\frac{a}{a-x}=\lambda_0\frac{\beta'}{\beta}\ln\frac{b-[\mathrm{A}'']v+\frac{\beta'}{\beta}[\mathrm{A}'']v}{b-[\mathrm{A}'']v-y+\frac{\beta'}{\beta}[\mathrm{A}'']v}. \tag{13}$$

Since $[\mathrm{AB}]'_{\mathrm{initial}}v=b-[\mathrm{A}'']v$, and $[\mathrm{AB}]'_{\mathrm{final}}v=b-y-[\mathrm{A}'']v$, equation (12) takes the final form:

Table 2

Dependence of the practical cocrystallization coefficient on the degree of barium precipitation

Experiment No.	Degree of barium precipitation, %	λ	Deviation from mean
1	21.5	0.0030	−0.0002
2	32.7	0.0077	+0.0045
3	32.7	0.0049	+0.0017
4	43.1	0.0027	−0.0005
5	55.1	0.0022	−0.0010
6	64.6	0.0017	−0.0015
7	75.9	0.0016	−0.0016
8	86.2	0.0021	−0.0011
Mean		0.0032	

$$\ln \frac{a}{a-x} = \lambda_0 \frac{\beta'}{\beta} \ln \frac{[\mathrm{AB}]'_{\mathrm{initial}} + \frac{\beta'}{\beta}[\mathrm{A}'']}{[\mathrm{AB}]'_{\mathrm{final}} + \frac{\beta'}{\beta}[\mathrm{A}'']}. \tag{14}$$

Comparison of equations (10) and (14) shows that the second route of precipitation makes it possible to achieve greater efficiency in the separation of elements.

Equation (14) was verified on the same system that had been studied in the preceding experiments.*

A solution containing $Na_2[Ba(EDTA)]$ and sodium nitrate in an amount of 500 g/l was saturated with barium nitrate, after which Sr^{90} was introduced. Then, with stirring, a solution of copper nitrate was slowly added to a definite volume of the solution. In this process the reaction

$$\mathrm{Na_2[Ba(EDTA)] + Cu(NO_3)_2 \rightarrow Na_2[Cu(EDTA)] + Ba(NO_3)_2}.$$

took place. The barium displaced from the complex formed a solid phase of nitrate. The rate of precipitate formation was 0.1 g/hour. After completion of the experiment the precipitate was separated and the amount of strontium cocrystallized with barium nitrate was determined. On the basis of the data obtained, the values of the practical cocrystallization coefficient were calculated from equation (14):

$$\lambda = \lambda_0 \frac{\beta'}{\beta}$$

(see Table 2).

It is evident from the table that λ does not depend on the degree of barium precipitation. The value found, $\lambda = 0.0032 \pm 0.0015$, is close to the value calculated from previous data (cocrystallization under equilibrium conditions): $\lambda = 0.0043$.

Thus, the experimental results confirm the correctness of the theoretical conclusions.

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REFERENCES

1. V. G. Khlopin, A. P. Ratner, DAN, A, **27**, 723 (1930).
2. H. Käding, Zs. phys. Chem., A, **162**, 174 (1932).
3. L. Gordon, K. Shaver, Anal. Chem., **25**, 784 (1953).
4. K. B. Zaborenko, V. V. Fomin, I. V. Kolosov, DAN, **123**, 688 (1958).
5. V. G. Khlopin, Tr. Gos. Radium Inst. AN SSSR, **4**, 34 (1938).
6. K. B. Yatsimirskii, V. P. Vasil' ev, *Stability Constants of Complex Compounds*, Izd. AN SSSR, 1959, p. 173.
7. H. A. Doerner, W. M. Hoskins, J. Am. Chem. Soc., **49**, 738 (1927).

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