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Abstract

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STUDY OF COPRECIPITATION IN THE SYSTEM Zn^{2+}–Co^{2+}–$[Hg(SCN)_4]^{2-}$ BY THE METHOD OF RADIOMETRIC TITRATION

A considerable number of works have been devoted to the method of radiometric titration ($^{1-4}$), etc., but practically all of them are directed toward the use of this method for analytical purposes, and only in the work of Alimarin and Sirotina (^{5}) was an attempt made to use this method for studying the mechanism of coprecipitation. There are a number of methods that make it possible to follow the character of the distribution of components in precipitate–mother-liquor systems; however, they are rather lengthy in execution, since they presuppose the attainment of equilibrium between the mother liquor and the precipitate. In practice, however, in the majority of cases precipitates are isolated with a more or less rapid addition of the precipitating agent. Taking this into account, it seemed of interest to follow the distribution of the components of the system during the process of precipitate formation (as the precipitating agent is added) without prolonged standing, i.e., under nonequilibrium conditions. In our opinion, the method of radiometric titration offers this possibility, since it permits one to follow the distribution of the components both in the region preceding the equivalence point and in the region of excess precipitating agent.

As the object of investigation, the system Zn^{2+}–Co^{2+}–$[Hg(SCN)_4]^{2-}$ was chosen. It is known ($^{6-9}$) that, under equilibrium conditions, the tetrarhodanomercurates of zinc and cobalt form a continuous series of solid solutions. The solubilities in water of pure $Zn[Hg(SCN)_4]$ and $Co[Hg(SCN)_4]$ at 18° are, respectively, $1.75 \cdot 10^{-4}$ and $5.37 \cdot 10^{-4}$ mol/l (^{10}). Three types of mixtures were investigated: 1) $[Zn^{2+}] : [Co^{2+}] \ll 1$, i.e., an indicator amount of zinc was introduced; 2) $[Zn^{2+}] : [Co^{2+}] \gg 1$, i.e., an indicator amount of cobalt was introduced; 3) $[Zn^{2+}] : [Co^{2+}] = 1 : 1$. The change in the amounts of zinc and cobalt in the course of radiometric titration was monitored by the change in the activity of samples of the mother solution.

Table 1

Change in distribution coefficients during radiometric titration of mixtures

1 N $Li_2[Hg(SCN)_4]$, ml	D^{Zn}ind.:1	D^{Zn}1:1	D^{Co}1:ind	D^{Co}1:1	λZn^*ind.:1	λZn^*1:1	λCo^*1:ind	λCo^*1:1
0.1	400	6	0.56	0.17	200	6	0.55	0.17
0.2	23	2	0.55	0.49	20	1.95	0.57	0.51
0.4	4.55	1.59	0.47	0.63	2.90	1.47	0.52	0.68
0.6	7.84	1.66	0.42	0.60	2.93	1.44	0.52	0.69
0.8	10.12	1.65	0.34	0.61	2.41	1.31	0.52	0.76
1.0	22.49	4.39	0.17	0.23	2.14	1.59	0.54	0.63
1.2	26.42	22.02	0.07	0.04	1.87	1.94	0.51	0.52
1.5	15.59	20.57	0.08	0.05	1.63	1.75	0.55	0.57
2.0	10.44	12.18	0.10	0.08	1.49	1.54	0.58	0.65
3.0	8.07	8.97	0.17	0.11	1.41	1.42	0.68	0.70

* In calculating D^{Zn} and λ^{Zn}, the designations a, x, and $(a-x)$ correspond to the amounts of zinc, and b, y, and $(b-y)$ to the amounts of cobalt; in calculating D^{Co} and λ^{Co}, a, x, and $(a-x)$ were taken as the amounts of cobalt, and b, y, and $(b-y)$ as the amounts of zinc.

As indicators, the radioactive isotopes Zn^{65} and Co^{60} were used. The initial solution ($v = 20$ ml) in all cases contained 0.5 mmole of the mixture of Zn^{2+} and Co^{2+}. Titration was carried out with a 1 N solution of $Li_2[Hg(SCN)_4]$. For convenience in processing the results, the radiometric titration curves were constructed in co-

ordinates: milliliters of titrating agent—percent of the initial activity (i.e., the percent of the substance remaining in solution). The results of radiometric titration of mixtures of Zn^{2+} and Co^{2+} are given in Fig. 1. The discrepancy between the equivalence points and the theoretical value in titrating mixtures with the use of nonisotopic indicators is noteworthy. Similar deviations were observed in the experiments of Koreman et al. (^{11}) when nonisotopic Co^{60} was used in the radiometric titration of zinc with ammonium tetrarhodanomercurate. An anomalous course of the curves is also observed in Fig. 1, where Co^{60} was used as the indicator. To explain these facts we interpreted the radiometric titration data as follows. From these data the distribution coefficients D (homogeneous distribution) and λ (heterogeneous distribution) were calculated (see Table 1) from the formulas:

$$\frac{x}{a-x} = D\,\frac{y}{b-y}, \tag{1}$$

$$\ln\frac{a}{a-x} = \lambda \ln\frac{b}{b-y}, \tag{2}$$

where a and b are the initial amounts of zinc and cobalt; x and y are the amounts

Figure 1

Figure 1: Figure 1

of zinc and cobalt that have passed into the precipitate; $(a - x)$ and $(b - y)$ are the amounts of zinc and cobalt remaining in solution.

As is seen from the data of Table 1, in all cases the distribution of both zinc and cobalt does not occur in accordance with the law of homogeneous distribution. The largest deviations from the regularity are especially noticeable at the beginning of formation of the solid phase (addition of the first portions of precipitant), and also near the equivalence point. In all cases the distribution coefficient of zinc considerably exceeds that for cobalt. The distribution coefficients prove to be closer to constant values if the law of heterogeneous distribution, Eq. (2), is used for the calculation. As follows from the data of Table 1, during the radiometric titration λ remains a more or less constant value when indicator amounts of cobalt are coprecipitated with the precipitate of zinc tetrarhodanomercurate. The curves presented in Fig. 2 show how the composition of mixed crystals changes as the solid phase separates during the process

Fig. 1. Radiometric titration of mixtures of zinc and cobalt, carried out with different indicators.
a $-[\mathrm{Zn}^{2+}] : [\mathrm{Co}^{2+}] = \mathrm{ind.} : 1$; b $-1 : 1$; v $-1 : \mathrm{ind.}$

radiometric titration. Analysis of the curves in Fig. 2a shows that, upon separation of the first portions of the solid phase, preferential enrichment of the mixed crystals with zinc occurs. Subsequently there is a gradual equalization of the ratio of the amounts of zinc and cobalt in the solid phase, which in the limit tends to unity when the precipitant is in excess. The distribution of the components in the precipitate during the gradual separation of the latter has, as is seen from Fig. 2b, a dual character. With microquantities of one of the components (curves 1, 3), their distribution in the precipitate is nonlinear. In the case, however, where the components were present in the initial solution in macroquantities (curve 2), their distribution in the precipitate obeys a linear relationship, although anomalous deviations from linearity are also observed here in the region of nucleation. As is seen from Fig. 2c, the distribution of the components in the precipitate during the gradual separation of the solid phase proceeds according to a logarithmic law; moreover, at certain stages of radiometric titration this distribution occurs in different quantitative ratios. The coefficients of layer-by-layer enrichment of the growing crystals, K, which are determined as the tangent of the angle of inclination of the straight line, may serve as a quantitative characteristic of individual rectilinear sections of the curves in Fig. 2c:

$$\frac{\Delta \lg x^{\mathrm{Zn}}}{\Delta \lg y^{\mathrm{Co}}} = \mathrm{tg}\, \alpha = K. \qquad (3)$$

Figure 3

Figure 2: Figure 3

Upon addition of the first portions of the precipitant $Li_2[Hg(SCN)_4]$ to a solution containing macroquantities of cobalt, a rather slow course of the process of separation of $Co_2[Hg(SCN)_4]$ crystals is observed, although the solubility product of this compound has been reached. This, in all probability, is explained by the formation of solutions supersaturated with respect to this salt. In the case of zinc, appreciable formation of supersaturated solutions does not occur. Evidently, therefore, there is strong enrichment of the first portions of the solid phase with zinc.

Fig. 2. Change in the composition of the solid phase in the course of radiometric titration:
1—$[Zn^{2+}] : [Co^{2+}] =$ ind. : 1; 2—1 : 1; 3—1 : ind.

portions of precipitate deposited by zinc (see Table 1 and Fig. 2 *a, b*). The enrichment coefficient K' (see Fig. 2 *c*, curves 1, 2) refers to the process of separation of mixed crystals from solutions supersaturated with respect to $Co[Hg(SCN)_4]$. Point (*a*), in all probability, corresponds to the moment at which supersaturation is removed. The segment of the straight line with enrichment coefficient K'' corresponds to the coprecipitation of cobalt with the precipitate $Zn[Hg(SCN)_4]$; K''' corresponds

Fig. 3. Change in the concentration of mixtures of zinc and cobalt during radiometric titration: *a*—Zn^{65} indicator; *b*—Co^{60} indicator; 1—$[Zn^{2+}] : [Co^{2+}] =$ ind. : 1; 2—1 : 1; 3—1 : ind.

to the coprecipitation of zinc with the precipitate $Co[Hg(SCN)_4]$. Point (*b*) symbolizes the transition from one type of coprecipitation to another. Since the magnitude $K^{IV} \to 0$, in the section (*c*—*g*) coprecipitation of practically pure cobalt occurs.

Thus, during the gradual separation of mixed precipitates in the system Zn^{2+}—Co^{2+}—$[Hg(SCN)_4]^{2-}$, a considerable enrichment of the precipitate with zinc is observed during the period of nucleation. Subsequently there is a successive enrichment of the growing crystals with cobalt, and the distribution of the components occurs according to a logarithmic dependence. In the final crystals there is a decrease in the relative amounts of zinc from the center to the periphery and the reverse order of enrichment of the crystals with cobalt.

As shown in Fig. 3, the change in the total concentrations of zinc and cobalt during radiometric titration is not the same when different indicators are used. Moreover, the solubility data under these conditions (the horizontal branches of the curves) differ rather substantially. Consequently, if the nature of the distribution of the components during precipitate formation is not taken into account, the use of nonisotopic indicators to determine the solubility of various compounds will give only very approximate values.

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Note: Figure translations are in progress. See original paper for figures.