Chemistry

Corresponding Member of the Academy of Sciences of the USSR A. V. NIKOLAEV, V. A. GRIGOR' EV

1964

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR A. V. NIKOLAEV, V. A. GRIGOR' EV

COPRECIPITATION OF THALLIUM (I) WITH ZINC, COBALT, AND CADMIUM TETRATHIOMERCURATES

Most studies on the coprecipitation of microimpurities with sparingly soluble precipitates have been devoted to systems that include simple ions. In this connection, processes in which complex compounds participate are of undoubted interest. In practice, one most often encounters processes involving the capture by precipitates of various cations; therefore, the study of systems with complex anions is of definite interest. From this point of view we selected the complex tetrathiomercurate ion $[Hg(SCN)_4]^{2-}$ ($K_{\text{dissoc}} \approx 10^{-22}$) (1), which forms sparingly soluble compounds with a number of divalent cations (2). It has been shown (2) that the properties of these compounds are affected by the nature of the outer-sphere cation; in particular, as the cation radius increases, an increase in the solubility of the salt in water is observed. To clarify the influence of the nature of the outer-sphere cation on the magnitude of capture of the cation microimpurity, we used the zinc, cobalt, and cadmium tetrathiomercurates (Table 1).

Table 1

Dependence of the solubility of tetrathiomercurates in water (25°) on the cation radius

No.	Cation	Ion radius, Å	Solubility, mol/l*
1	Zn^{2+}	0.83	$1.72 \cdot 10^{-4}$
2	Co^{2+}	0.82	$5.92 \cdot 10^{-4}$
3	Cd^{2+}	1.03	$2.11 \cdot 10^{-3}$

* Our data.

Fig. 1. Capture isotherms of thallium by precipitates of $Co[Hg(SCN)_4]$ (I), $Zn[Hg(SCN)_4]$ (II), and $Cd[Hg(SCN)_4]$ (III)

As the distributing component, the monovalent thallium cation (and its radioactive isotope Tl^{204}) was used. The capture isotherms of thallium (I) by precipitates of zinc, cobalt, and cadmium tetrathiomercurates, obtained by the "two-indicator" method, are presented in Fig. 1. These isotherms are characterized by the presence of three regions, depending on the concentration

thallium in solution. Region A is characterized by a constant relative magnitude of capture, independent of the initial concentration (up to $\sim 10^{-5}$ mol/l) of thallium in solution, i.e., by a crystallization coefficient const (Fig. 1a); in region B a sharp decrease is observed in the relative magnitude of thallium capture by the precipitates $M[Hg(SCN)_4]$, which is probably due to attainment of the saturation limit of the precipitates with respect to thallium (Fig. 1b). And, finally, region C corresponds to the separation of thallium as an independent solid phase in the form $Tl_2[Hg(SCN)_4]$. The solubility of thallium(I) tetrathiocyanatomercurate, determined by us using the radioactive isotope Tl^{204}, is $1.6 \cdot 10^{-3}$ mol/l at 25°. The character of the capture isotherms shown in Fig. 1 indicates the presence in these systems of an upper miscibility limit; thus, thallium capture does not proceed by the type of formation of true mixed crystals. Similar behavior of the distributing substance, as is known for a number of other systems ([3]), is explained by the formation of intra-adsorption compounds. The magnitude of thallium capture by the precipitate $Co[Hg(SCN)_4]$ is greater than for $Zn[Hg(SCN)_4]$ and $Cd[Hg(SCN)_4]$, although this could not have been expected from the solubility ratios (see Table 1). One of the methods that makes it possible to distinguish cocrystallization from adsorptive capture may be the addition of multivalent ions to the solution. However, as our investigations have shown, the presence of multivalent cations (Fe^{3+}, Al^{3+}, Sc^{3+}) has no substantial effect either on the magnitude or on the character of thallium capture by precipitates $M[Hg(SCN)_4]$. The magnitude and character of the capture also do not change substantially in the pH interval from 1 to 7. These facts do not permit, in the strict sense, assigning the processes of coprecipitation of thallium(I) with zinc, cobalt, and cadmium tetrathiocyanatomercurates to ordinary adsorption processes.

Fig. 2. A —radiometric titration of cobalt (I), zinc (II), cadmium (III) in the presence of thallium, $C^0_{Tl} = 5 \cdot 10^{-6}$ mol/l; **B** —change in the composition of the precipitates during titration

The data of radiometric titration of solutions of zinc, cobalt, and cadmium salts in the presence of thallium(I), labeled with Tl^{204}, are presented in Fig. 2A. When thallium ions are present in the initial solution in concentrations less than 10^{-5} mol/l, coprecipitation occurs as the tetrathiocyanatomercurate precipitates are gradually formed. An excess of precipitant has practically no effect on the magnitude of capture. Such behavior of microimpurities is more characteristic of cocrystallization processes (true or anomalous) than of adsorption processes. The distribution of thallium (Fig. 2B) in the crystals of the precipitates $M[Hg(SCN)_4]$ (where $M = Zn^{2+}, Co^{2+}, Cd^{2+}$) does not proceed according to a linear regularity, as occurs in the case of formation of true mixed crystals

Fig. 3. Radiometric titration curves

Figure 2: Fig. 3. Radiometric titration curves

([4]). In the region of supersaturated solutions (on curves I and III, segment *ab*) such a dependence is realized. However, after the supersaturation is removed (at point *b*), the change in the composition of the precipitates in the process of gradual

the release of the solid phase occurs not with a constant coefficient of "layer-by-layer enrichment." In the case of significant thallium concentrations in the initial solution (more than 10^{-2} mol/l), the radiometric titration curves have the form shown in Fig. 3. For the thallium–cobalt and thallium–zinc pairs, there is initially precipitation of the less soluble $Co[Hg(SCN)_4]$ and $Zn[Hg(SCN)_4]$, and then thallium is precipitated in the form $Tl_2[Hg(SCN)_4]$. In the case of the thallium–cadmium pair, the less soluble thallium tetrarhodanomercurate is initially precipitated. These cases, in principle, may be used for the quantitative determination of zinc, cobalt, and cadmium by the method of radiometric titration with the use of the nonisotopic radioactive indicator Tl^{204}.

Fig. 3. Radiometric titration of mixtures of thallium with cobalt (I), zinc (II), cadmium (III);
$[Tl^+] : [M^{2+}] = 1 : 1$ (in g-eq.). Indicator: Tl^{204}.

The facts presented above indicate that the coprecipitation of thallium with precipitates $M[Hg(SCN)_4]$ cannot, strictly speaking, be assigned to any of the already known types, since in this case features characteristic both of processes of formation of anomalously mixed crystals and of intra-adsorption systems appear simultaneously. Known analogous facts ([5,6]) indicate that in a number of cases it is difficult to draw a strict distinction between the phenomena of internal adsorption and the formation of anomalously mixed crystals. What is beyond doubt is only that the coprecipitation of thallium(I) with the tetrarhodanomercurates of zinc, cobalt, and cadmium has the character of a volume distribution. Uptake (III) has a different character and is noticeably smaller in magnitude.

Received
20 I 1964

REFERENCES CITED

1. A. M. Golub, T. I. Tsitsurina, *Scientific Notes of Kiev University*, **16**, No. 15, 101 (1957).

2. M. Czalis, A. Swinarski, *Roczn. Chem.*, **31**, issue 4, 1101 (1957).

3. M. S. Merkulova, S. A. Potapova et al., *ZhFKh*, **31**, 5, 1056 (1957).

4. A. V. Nikolaev, V. A. Grigor' ev, *DAN*, **155**, No. 4 (1964).

5. O. Hahn, *Applied Radiochemistry*, 1947, p. 105.

6. M. S. Merkulova, *ZhNKh*, **3**, 1, 25 (1958).

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