Chemistry

1960

SovietRxiv

Abstract

Full Text

Chemistry

V. I. Kuznetsov and P. D. Titov

Co-extraction of Tungsten and Certain Other Elements

(Presented by Academician A. P. Vinogradov, October 2, 1959)

Whereas the phenomena of coprecipitation and cocrystallization have been well studied, the co-extraction of elements has been investigated only poorly. Only isolated facts are known that may be assigned to this phenomenon.

Because solid phases are absent in extraction, adsorption phenomena, which underlie many cases of coprecipitation and cocrystallization, are absent. In extraction, only at the phase boundary can processes similar to adsorption occur; however, these processes also proceed very weakly.

Co-extraction occurs by other mechanisms; probably foremost among them is the formation of mixed compounds.

Table 1

Influence of dilution on the extraction of tungsten and molybdenum by aniline (pH of the aqueous phase after extraction 4.3–4.5)

Concentration of elements, γ/ml	Distribution coefficients	Distribution coefficients
Concentration of elements, γ/ml	W^VI	Mo^VI
10 000	4900	420
1 000	800	42
100	140	5.4
10	30	1.5
1	9	–

Sometimes co-extraction is associated with the transition of an element into a compound in the form of which it is extracted better than in the form of the initial product. The co-extraction of pentavalent vanadium with tungsten and phosphorus is known, owing to the formation of a well-extracted mixed phosphotungstovanadic heteropoly acid ([1]). The ease of formation of this latter compound made it possible to use it for the colorimetric determination of small amounts of vanadium ([2]).

In a number of other cases of co-extraction described in the literature, when the extraction of elements into a nonaqueous solvent increases substantially, the formation of new, well-extracted compounds is less obvious. As examples one may cite the increase in extractability of ruthenium by a benzene solution of caprylic acid after the addition of copper (^{3}), or of methyl isopropyl ketone after the introduction of lead salts (^{4}). Other cases of co-extraction have also been described, the mechanism of which is unclear (^{5}–^{7}).

The authors observed a clear example of co-extraction by the mechanism of formation of mixed compounds in studying the extraction of tungsten and molybdenum from a hydrochloric-acid medium by aniline. In this case tungsten and molybdenum are extracted by the so-called ion mechanism (^{8}) in the form of anilinium polytungstates or polymolybdates, the anions of which are formed upon acidification of soluble tungstates and molybdates. At sufficiently high dilution of tungstates and molybdates after acidification of their solutions, the required polyanions do not arise, and therefore extraction of both tungsten and molybdenum from dilute solutions proceeds more weakly than from more concentrated ones. After acidification of an aqueous solution of sodium tungstate or molybdate with hydrochloric acid to an acidity of 1.5 N and shaking with an equal volume of aniline, tungsten and molybdenum pass into the aniline layer with distribution coefficients that rapidly decrease as the concentration of the elements falls (Table 1).

But if not too small amounts of molybdate or vanadate are added to a dilute solution of alkaline tungstate, and then the whole mixture is acidified with hydrochloric acid to the same acidity (1.5 N), the distribution coefficients of tungsten increase substantially. The results of experiments carried out with tungsten labeled with W^{185} or W^{187} are given in Table 2*.

Obviously, tungstates form mixed polyanions with molybdates or vanadates, in the form of whose salts tungsten is extracted. The tendency of these elements to form mixed compounds can be seen from the example of the existence of well-known mixed heteropoly acids (9).

Table 2

Influence of the presence of molybdenum and vanadium on the tungsten distribution coefficients
(the mean values from 2 determinations are indicated)

Concentration of W^{VI}, γ/ml	Distribution coefficients W, without additives	Distribution coefficients W, with Mo^{VI} 500 γ/ml	Distribution coefficients W, with Mo^{VI} 250 γ/ml	Distribution coefficients W, with V^{V} 500 γ/ml	Distribution coefficients W, with V^{V} 250 γ/ml
1.0	9.0	4450	38	4670	29
0.1	5.0	1600	–	1700	–

Concentration of W^{VI}, γ/ml	Distribution coefficients W, without additives	Distribution coefficients W, with Mo^{VI} 500 γ/ml	Distribution coefficients W, with Mo^{VI} 250 γ/ml	Distribution coefficients W, with V^{V} 500 γ/ml	Distribution coefficients W, with V^{V} 250 γ/ml
0.01	2.5	250	–	295	–
0.001	1.3	18	–	40	–

Coextractions of this kind are possible not only for tungsten, but also for other elements capable of forming polynuclear oxy-oxo ions, sometimes called "polymers" in the literature. Thus, niobium can be coextracted with tungsten, and also with vanadium. In extraction with aniline, the distribution coefficients of niobium at low concentrations of the latter are small, and they likewise decrease as its concentration decreases. But these coefficients increase sharply if a coextracting element is introduced into the alkaline niobate solution and then the whole mixture is acidified.

Table 3

Coextraction of niobium with tungsten and vanadium at 20°

Concentration of Nb, γ/ml	Distribution coefficients Nb, without additives	Distribution coefficients Nb, upon addition up to 500 γ/ml W	Distribution coefficients Nb, upon addition up to 500 γ/ml V^{V}
1.0	5.2	330	37
1.0	5.0	240	35
0.01	0.45	280	25
0.01	0.67	250	–
0.01	0.87	–	–

Table 3 gives the results of the corresponding experiments. To an alkaline solution of potassium niobate labeled with Nb^{95}, of "carrier-free" grade, an alkaline solution of sodium tungstate or vanadate was added; the mixture was thoroughly stirred, acidified with hydrochloric acid to an acidity of 1.5 *N*, and then extracted with an equal volume of aniline.

Cases of coextraction similar to those considered may be of interest: 1) for purposes of concentrating the corresponding elements from dilute solutions in analytical determinations, since the extraction can be sufficiently selective; 2) for studying the ability of elements to form mixed polynuclear oxy-oxo ions and other mixed particles that have been insufficiently studied.

Let us emphasize that, for carrying out experiments similar to those described, it is expedient to use substances which, like aniline, form cations of medium, not excessively high ionic weight. If amines or other cation-forming compounds of excessively high molecular weight are used—for example, such as methyl violet —then, owing to their ability to extract "monomeric" tungstate ions, cases of coextraction similar to those considered are observed less distinctly.

The inability of aniline to extract tungsten in the form of normal anilinium tungstate is demonstrated by the absence of tungsten extraction in the extraction of unacidified solutions of sodium tungstate. Considerations that the absence of extraction from unacidified solutions may be due to an insufficient concentration of anilinium cations under these conditions are rejected by the results of experiments with benzylamine.

Benzylamine $C_6H_5CH_2NH_2$ (mol. wt. 107) differs little in molecular weight from aniline $C_6H_5NH_2$ (mol. wt. 93), but it is a stronger base than aniline. The dissociation constants for aniline and benzylamine at 25° are, respectively, $4.0 \cdot 10^{-10}$ and $2.4 \cdot 10^{-5}$; benzylamine is miscible with water. It is easy to calculate that, for example, in a 50% solution of benzylamine in a medium with pH 9.5, the concentration of benzylaminium cations will be of the order of 3.5 mol/l, as compared with the tungsten concentration, equal to $3 \cdot 10^{-3}$ mol/l. Nevertheless, from unacidified solutions of sodium tungstate with pH 9.5 (after extraction), neither benzylamine containing 10% dibenzylamine nor its mixture with aniline (1 : 1) extracts tungsten. At a tungsten concentration of 1 mg/ml, the distribution coefficients of tungsten in both cases are less than 0.01.

Table 4

Extraction of W and Mo by aromatic amines from 0.05 *N* solutions of sodium tungstate and molybdate, acidified to an acidity of 0.5 *N* with respect to HCl

Amines	Distribution coefficients	Distribution coefficients
	W	Mo
Aniline	1500	90
m-Toluidine	1050	130
p-Xylidine	1000	300
m-Xylidine	875	240
α-Naphthylamine	625	225

Extraction and coextraction of tungsten and molybdenum can be observed not only with aniline. Benzylamine and its mixture with dibenzylamine are not suitable for this purpose, since the amine phase in equilibrium with a medium of pH 4.2–4.5 cannot exist. Amines with weaker basic properties—such as *m*-toluidine ($K^{25} = 5.5 \cdot 10^{-10}$), *p*-xylidine ($K^{25} = 9.6 \cdot 10^{-10}$), *m*-xylidine ($K^{25} =$

---

* Experiments with a tungsten concentration of 1.0 γ/ml and higher were carried out with W^{185}; experiments with lower concentrations were carried out with W^{187}.

$6.3 \cdot 10^{-10}$), molten α-naphthylamine (m.p. 50°, $K = 9.9 \cdot 10^{-11}$), and similar ones—extract tungsten or molybdenum in the same way as aniline (Table 4).

The cases considered of coextraction of tungsten and niobium, which are of practical interest because they indicate the possibility of increasing the extractability of these elements from dilute solutions, can, of course, be extended to a number of other elements as well. Many elements are capable of forming polynuclear oxo-oxo ions, and, with an appropriate experimental design, coextraction can be observed for many elements. All such cases of coextraction proceed by the mechanism of formation of mixed compounds.

There are indications in the literature of cases of a relatively small increase in the extractability of some elements upon the introduction into their solutions of large amounts of other, well-extractable elements. Thus, it is noted that, for example, Cs, Ca, Sr, La from their solutions not containing uranyl nitrate are extracted by methyl butyl ketone more weakly than from solutions containing much well-extractable uranyl nitrate ([5]).

It is difficult to say whether the increase in extractability of these elements observed in these cases should be regarded as the result of true coextraction, or whether it is caused by some other reasons.

Institute of Geochemistry and Analytical Chemistry
named after V. I. Vernadsky
Academy of Sciences of the USSR

Received
21 IX 1959

CITED LITERATURE

1. V. G. Shcherbakov, R. M. Veitsman, Zav. lab., **20**, 663 (1954).
2. A. P. Vinogradov, DAN, **10**, 249 (1931).
3. R. W. West, T. G. Lyons, J. K. Carlton, Anal. chim. acta, **6**, 403 (1952).
4. R. W. West, J. K. Karlton, ibid., **6**, 406 (1952).
5. V. M. Vdovenko, L. N. Lazarev, Khim. nauka i prom., **4**, 230 (1959).
6. R. W. Dadson, G. J. Forney, E. H. Swift, J. Am. Chem. Soc., **58**, 2573 (1936).
7. Taichi Sato, J. Inorg. and Nucl. Chem., **9**, 188 (1959).
8. V. I. Kuznetsov, Usp. khim., **23**, 654 (1954).

9. A. M. Kokorin, Doctoral dissertation, Kishinev, 1955.

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