Chemistry

D. I. Ryabchikov, I. K. Tsitovich, M. K. Torpudzhiyan

1964

SovietRxiv

Abstract

Full Text

Chemistry

D. I. Ryabchikov, I. K. Tsitovich, M. K. Torpudzhiyan

Mineral Ion Exchangers Based on Titanium

(Presented by Academician A. P. Vinogradov, January 10, 1964)

At present much attention is being devoted to the search for mineral ion exchangers with high exchange capacity which, unlike synthetic ion-exchange resins, possess high thermal and radiation stability. A number of works are known that are devoted, in this respect, to the study of zirconium compounds, for which the property of forming polymer chains is characteristic ([1–5]). Meanwhile, we had previously established that $Ti(OH)_4$ possesses an exchange capacity higher than that of zirconium hydroxide and phosphate ([6]). Therefore we undertook a systematic investigation of the ion-exchange properties of sparingly soluble titanium compounds. In doing so we proceeded from the assumption that for titanium, as for zirconium, the formation of polymer chains is characteristic—

$$-\mathrm{Ti}-\mathrm{O}\ldots-\mathrm{Ti}-\mathrm{O}-\mathrm{Ti}-\ldots\mathrm{O}-\mathrm{Ti}-$$

which can be cross-linked by polybasic acids into a three-dimensional network, and can also retain acidic ion-exchange groups on the free bonds of titanium atoms.

We synthesized and tested as ion exchangers: titanyl hydrogen phosphate (precipitant—HPO_4^{2-} in the presence of KOH), titanyl dihydrogen phosphate (precipitant—$H_2PO_4^-$ in the presence of KOH), titanyl hydroarsenate and chromate, metatitanic acid and potassium metatitanate, and titanyl oxyquinolinate.

In addition, we attempted to obtain titanyl molybdate and tungstate. It has repeatedly been indicated in the literature that the composition and properties of zirconium ([4,7]) and titanium ([8]) compounds depend strongly on the method by which they are obtained. Moreover, salts formed by titanium and weak acids (such as, in particular, molybdic and tungstic acids) practically cannot be obtained, since they are completely hydrolyzed in aqueous solutions (without heating) with the formation of $Ti(OH)_4$. However, in our view, colloidal titanium hydroxide, coagulating under the action of MoO_4^{2-} and WO_4^{2-} anions, sorbs these ions, and the resulting precipitates are not pure titanium hydroxide but its adsorption compounds with acid anions. Therefore we considered it possible provisionally to call the products obtained titanyl "molybdate" and "tungstate."

To obtain titanyl "molybdate," high-purity titanium sponge was dissolved in $2N$ H_2SO_4, Ti(III) was oxidized to Ti(IV) with nitric acid, and an alkaline solution of ammonium molybdate was added (until an alkaline reaction). The precipitate was treated with $2N$ KOH solution and dried in air.

Similarly, to obtain titanyl "tungstate," the same initial Ti(IV) solution was taken and treated with a mixture of K_2WO_4 with an excess of KOH. The precipitate was washed on a filter with bidistilled water and dried in air.

The absorption by all the sorbents listed of Cr(III), Fe(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) was investigated; these were taken only in the form of sulfates, in order to exclude the influence of different anions on sorbability. All solutions were prepared in bidistilled water from reagents of "chemically pure" and "pure for analysis" grades.

The experiments were carried out under dynamic conditions, as described by us earlier ([6]).

Before carrying out the experiments, the columns with sorbents were washed with bidistillate. Inert fillers for improving the flow-through capacity of the sorbents were not introduced into the columns. The sorbability of cations was expressed in milligram-equivalents per 1 g of ion exchanger. In addition, the sorption series of cations for each ion exchanger were determined by the generally accepted method.

Data on the sorbability of cations (arranged in order of increasing radii) are given in Table 1. For comparison, the same table includes the sorbability values of ions by titanium hydroxide and chromatographic alumina oxide ([6]).

It is evident from the data in Table 1 that all sparingly soluble titanium compounds (except oxineholinate) have a higher exchange capacity than chromatographic alumina oxide. The exchange capacity of titanyl arsenate and chromate, as well as potassium metatitanate, proved to be higher than that of titanium hydroxide. Cations of the transition elements of the fourth period are best sorbed by potassium metatitanate, which had never previously been tested as an ion exchanger.

A quite definite dependence has been established between the sorbability of equivalent (divalent) cations by mineral ion exchangers and the position of the elements in the periodic system (Fig. 1). The minimum of sorbability occurs, as in our previous studies ([6]), for the nickel cation, which has the smallest radius (0.78 Å) and, consequently, the greatest hydration and the poorest incorporation into the sorbent. The maxima of absorption occur for the cations of divalent iron and copper.

Fig. 1. Change in the sorbability of equivalent (divalent) cations as a function of the atomic number of the element: 1 —on titanyl "wolframate"; 2 —on titanyl "molybdate"; 3 —on metatitanic acid; 4 —on potassium metatitanate; 5 —on titanyl arsenate; 6 —on titanyl hydrophosphate; 7 —on titanyl dihydrophosphate; 8 —on titanyl chromate.

Fig. 1. Change in the sorbability of equivalent (divalent) cations as a function of the atomic number of the element: 1 —on titanyl "wolframate" ; 2 —on titanyl "molybdate" ; 3 —on metatitanic acid; 4 —on potassium metatitanate; 5 —on titanyl arsenate; 6 —on titanyl hydrophosphate; 7 —on titanyl dihydrophosphate; 8 —on titanyl chromate

Figure 1: Fig. 1. Change in the sorbability of equivalent (divalent) cations as a function of the atomic number of the element: 1 —on titanyl "wolframate" ; 2 —on titanyl "molybdate" ; 3 —on metatitanic acid; 4 —on potassium metatitanate; 5 —on titanyl arsenate; 6 —on titanyl hydrophosphate; 7 —on titanyl dihydrophosphate; 8 —on titanyl chromate

Study of the filtrates showed that, upon absorption of all cations by titanyl arsenate, chromate, hydrophosphate, dihydrophosphate, "molybdate," and "wolframate," as well as by potassium metatitanate, potassium ions absorbed from solutions by the sorbents during their preparation pass into the filtrate. Since NH_4OH was used in the preparation of metatitanic acid, all cations displaced ammonium ions from this sorbent into the filtrate.

Of interest are the sorption series of cations established by us for titanium-based ion exchangers. Thus, the sorption series of cations on titanyl hydrophosphate is

$$Fe^{3+} > Cu^{2+} > Mn^{2+} > Zn^{2+} > Cr^{3+} > Fe^{2+} > Co^{2+} > Ni^{2+}$$

differs substantially from the sorption series of the same cations on titanyl dihydrogen phosphate:

$$Fe^{3+} = Cu^{2+} > Fe^{2+} > Mn^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+} > Ni^{2+}.$$

This undoubtedly indicates a different quantitative composition of the sorbents we obtained.

Table 1

Comparative sorbability (in mg-eq/g) of cations by mineral ionites on a titanium basis

Sorbent	Cr^{3+}	Fe^{3+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	Mn^{2+}
Titanium hydroxide	1.59	2.25	0.90	1.69	1.59	1.24	1.76	1.46

Sorbent	Cr^{3+}	Fe^{3+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	Mn^{2+}
Titanyl hydrophosphate	0.23	1.05	0.30	1.44	1.79	0.68	1.73	1.35
Titanyl dihydrogen phosphate	1.69	2.76	1.07	1.70	1.58	1.53	1.81	1.73
Titanyl hydroarsenate	3.04	2.23	1.53	2.52	2.90	2.45	2.70	2.04
Titanyl chromate	1.69	4.58	0.92	1.95	2.39	2.03	2.12	2.18
Pertitanic acid	0.29	1.27	0.81	1.27	1.35	0.97	2.77	1.20
Potassium pertitanate	5.89	4.55	2.29	3.35	2.79	2.08	7.01	2.11
Titanyl molybdate	1.36	2.43	1.16	1.41	1.54	1.10	2.06	1.32
Titanyl tungstate	1.53	2.30	0.82	1.19	1.22	1.15	1.68	1.20
Titanyl oxyquinolinate	0	0	0	0	0	0	0	0
Chromatographic alumina	0.35	0.48	0.24	0.31	0.35	0.26	0.25	0.25

The sorption series of cations on pertitanic acid also proved to be different:

$$Cr^{3+} > Fe^{3+} > Fe^{2+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Mn^{2+} > Ni^{2+}$$

and on potassium pertitanate:

$$Fe^{2+} > Fe^{3+} > Cr^{3+} > Cu^{2+} > Mn^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}.$$

For titanyl arsenate, a sorption series was obtained that has the following distinctive features:

$$Fe^{3+} = Cu^{2+} > Cr^{3+} > Zn^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+},$$

and for titanyl "molybdate"

$$Fe^{3+} > Cr^{3+} > Cu^{2+} > Fe^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} = Ni^{2+}.$$

Very similar sorption series of cations were obtained on titanyl chromate

$$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Fe^{2+}$$

and on titanyl "tungstate"

$$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Mn^{2+} = Co^{2+} = Ni^{2+} > Fe^{2+}.$$

It is noteworthy that the cation sorbability series on titanium hydroxide and zirconium hydroxide almost completely coincide with the series of cation hydrates arranged in order of increasing values of solubility products (Table 2).

These data make it possible to regard titanium and zirconium hydroxides as sorbents "charged" with hydroxyl ions. In this case, the mechanism of cation uptake by the sorbents is itself represented as a process of formation of the corresponding hydrates, located in the column from top to bottom in the order of increasing values of solubility products.

Investigation of the properties of titanium-based mineral ionites opens new possibilities for selecting sorbents for specific cases of cation separation. In terms of exchange capacity, the most promising among them appear to be potassium pertitanate, titanyl arsenate, and titanyl chromate. For purposes of concentration and analytical separation, it is possible to use

Table 2

Solubility-product values of hydrates and sorption series of cations on
$Ti(OH)_4$ and $Zr(OH)_4$

Hydrates of cation oxides	$Fe(OH)_3$	$Cr(OH)_3$	$Cu(OH)_2$	$Zn(OH)_2$	$Co(OH)_2$	$Fe(OH)_2$	$Ni(OH)_2$	$Mn(OH)_2$
Solubility-product values	$1.1 \cdot 10^{-36}$	$5 \cdot 10^{-31}$	$1.6 \cdot 10^{-19}$	$5 \cdot 10^{-17}$	$1.3 \cdot 10^{-15}$	$5 \cdot 10^{-15}$	$1.1 \cdot 10^{-14}$	$4.0 \cdot 10^{-14}$
Sorption series on $Ti(OH)_4$	$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} = Fe^{2+} > Mn^{2+} > Ni^{2+}$
Sorption series on $Zr(OH)_4$	$Fe^{3+} = Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} = Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} = Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} = Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} = Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} = Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} = Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$	$Fe^{3+} = Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$

as well as the features of the selective absorption of cations by other ion exchangers based on titanium. In addition to the transition elements of the fourth period, it is of interest to study the possibilities for separating alkali and alkaline-earth metals on these sorbents.

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

Received
19 XII 1963

REFERENCES

1. S. E. Bresler, Yu. D. Sinochkin et al., *Radiokhimiya*, **1**, no. 5, 507 (1959).

2. S. S. Rodin, A. K. Lavrukhina, *Radiokhimiya*, **4**, no. 5, 623 (1962).

3. A. K. Lavrukhina, V. V. Malyshev, S. S. Rodin, *Journal of General Chemistry of the USSR*, named after D. I. Mendeleev, **8**, no. 2, 227 (1963).

4. K. A. Kraus, L. S. Johnson, *Nature*, **177**, no. 4520, 1128 (1956).

5. C. B. Amphlett, L. A. McDonald, M. J. Redman, *J. Inorg. and Nucl. Chem.*, **6**, no. 3, 220 (1958).

6. D. I. Ryabchikov, I. K. Tsitovich, M. K. Torpudzhiyan, *Doklady Akademii Nauk SSSR*, **145**, no. 4, 825 (1962).

7. N. G. Polyanskii, *Priroda*, no. 9, 95 (1961).

8. V. I. Spitsyn, E. A. Ippolitova, *Zhurnal analiticheskoi khimii*, **6**, no. 1, 5 (1951).

9. Yu. A. Klyachko, S. A. Shapiro, *Course of Qualitative Chemical Analysis*, Moscow, 1960, p. 680.

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