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Abstract

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On the Stability of Chloride Acido-Complexes in Elements of the Fourth Period

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Much attention is being paid to the study of the state of elements in hydrochloric-acid solutions by means of anion exchange, since the sorption even of elements similar in properties may differ because of the unequal strength of chloride acido-complexes ([1]). There are, however, very few data on the anion-exchange properties of chloride complexes of the elements of the fourth period ([2–4]).

In carrying out a systematic study of the state of the elements of the middle of the fourth period in hydrochloric-acid solutions ([5]), we set ourselves the goal of studying in detail the stability of chloride complexes in these elements by means of anion exchange.

The behavior of the elements Ti(IV), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) was investigated in solutions with hydrochloric acid concentrations from 0.1 to 12 *N*. For this purpose the distribution coefficients of the elements ϕ between anion-exchange resins and hydrochloric-acid solutions were determined: an accurately weighed portion of air-dry anionite (0.5 g) was shaken with a definite volume of the solution under study (50 ml) until equilibrium was reached; aliquot portions of the solution were taken, and the amount of the element not sorbed by the resin was determined by one of the colorimetric methods ([6]). The distribution coefficients of the elements ϕ were calculated by the generally accepted method ([5]). In addition, the sorbability of the elements by the resins at equilibrium was determined as a percentage of the initial amounts.

The initial solutions, prepared in bidistillate from chemically pure reagents, had the following concentrations: Ti 0.1197, Mn 0.2794, Fe 0.1861, Co 0.2947, Ni 0.2935, and Cu 0.4765 mg/ml.

To obtain reliable results, three domestically produced anion-exchange resins were used in the experiments: the strongly basic anionite AV-16, the moderately basic EDE-10P, and the weakly basic anionite AN-2F. In preparation for the study, fractions of all resins with a grain diameter of 0.5–1.0 mm were screened out; the anionites were washed free of impurities, converted into the Cl^- form, and brought to an air-dry state.

The distribution coefficients of the elements between hydrochloric-acid solutions

and the strongly basic anionite AV-16 are shown by the curves in Fig. 1A. Sufficiently clearly expressed absorption of the elements by this anionite occurs from solutions with the following hydrochloric acid concentrations: Fe from 0.5 *N*, Cu from 4 *N*, Co from 6 *N*, Ti from 8 *N*, and Mn from 10 *N* hydrochloric acid solution; Ni was not sorbed by the resin at hydrochloric acid concentrations in the solution from 0.1 to 12 *N*.

From Fig. 1B, C it is evident that the anionite EDE-10P and especially AN-2F generally possess a lower exchange capacity than AV-16. However, the sorbability of the elements by these resins well confirms the regularity found for the behavior of the elements in hydrochloric-acid solutions.

From the factual data we obtained it follows that significant amounts of chloride anionic complexes are formed in Ti approxi-

significantly in 8 *N*, Mn in 10 *N*, Fe in 0.5 *N*, Co in 6 *N*, and Cu in 4 *N* hydrochloric acid. It is obvious that at lower concentrations of hydrochloric acid solutions the chloro complexes of these elements are destroyed. Under the given conditions, a negatively charged nickel complex practically does not exist.

Fig. 1. Dependence of the distribution coefficients of the elements on the concentration of HCl: A—anion exchanger AV-16, —anion exchanger EDE-10P, —anion exchanger AN-2F. 1—Ti, 2—Mn, 3—Fe, 4—Co, 5—Ni, 6—Cu.

Thus, the chloride complexes of the elements of the fourth period that form in solutions with hydrochloric acid concentrations from 0.1 to 12 *N* may be arranged in the following order of decreasing stability:

$$[FeCl_6]^{3-} > [CuCl_4]^{2-} > [CoCl_4]^{2-} > [TiCl_6]^{2-} > [MnCl_4]^{2-}.$$

If, in dilute electrolyte solutions, the sorbability of elements is determined mainly by the magnitudes of the charges or the radii of equivalent hydrated ions, then in the case of chloro complexes there is evidently no such simple dependence. Nevertheless, the strength of the chloride anionic complexes of the elements studied can be related to their position in the periodic system.

A. A. Grinberg showed, as general propositions, that in the long periods the capacity for complex formation is least at the ends and approximately greatest in the center; the maximum capacity for complex formation coincides with the occurrence of the elements in Group VIII, since they have the most labile electron shells with unfilled *d*-cells ([7]). In addition, it is known that ions with 18-electron and incomplete outer shells, other conditions being equal (values of charges and radii), are distinguished by a stronger polarizing action and are more typical complex-formers than 8-electron ions.

The results of determining the stability of chloride acido complexes of the elements of the fourth period are, on the whole, in good agreement with these general propositions. Indeed, the chloro com-

complexes of iron and cobalt, which belong to group VIII. The chloride complex of copper, as an element of the inserted decade adjoining group VIII, is also distinguished by great strength. The stability of the chloride anionic complexes of titanium and manganese is already expressed considerably more weakly. The instability of the negatively charged complex of nickel under the conditions of our experiments may be explained by its conversion into a neutral complex.

Table 1 gives data on the sorbability of elements by anion exchangers from hydrochloric-acid solutions, in percent. They make it possible to see that the uptake by resins of the elements under study increases with increasing acidity of the solutions and, even under static conditions, reaches appreciable values. Obviously, it can be used in practice, especially since under dynamic conditions (column chromatography) the effectiveness of the anion exchangers increases still more.

Table 1

Sorbability of elements by anion exchangers from hydrochloric-acid solutions

Anion exchanger	Normality of HCl	Fe	Cu	Co	Ti	Mn	Ni
Anion exchanger AB-16	0,1	0	0	0	0	0	0
Anion exchanger AB-16	0,5	6,23	0	0	0	0	0
Anion exchanger AB-16	1	6,66	0	0	0	0	0
Anion exchanger AB-16	2	8,81	0	0	0	0	0

Anion exchanger	Normality of HCl	Fe	Cu	Co	Ti	Mn	Ni
Anion exchanger AB-16	4	11,23	8,91	0	0	0	0
Anion exchanger AB-16	6	19,98	12,05	5,83	0	0	0
Anion exchanger AB-16	8	29,60	26,41	11,67	6,18	0	0
Anion exchanger AB-16	10	32,61	32,79	26,67	24,17	3,34	0
Anion exchanger AB-16	12	24,94	46,39	24,46	30,57	20,12	0
Anion exchanger EDE-10 P	0,1	0	0	0	0	0	0
Anion exchanger EDE-10 P	0,5	3,00	0	0	0	0	0
Anion exchanger EDE-10 P	1	3,33	0	0	0	0	0

Anion ex-changer	Normality of HCl	Fe	Cu	Co	Ti	Mn	Ni
Anion ex-changer EDE-10 P	2	3,33	0	0	0	0	0
Anion ex-changer EDE-10 P	4	4,19	4,46	0	0	0	0
Anion ex-changer EDE-10 P	6	6,66	15,83	5,02	0	0	0
Anion ex-changer EDE-10 P	8	11,87	17,43	9,16	9,42	0	0
Anion ex-changer EDE-10 P	10	18,75	24,21	17,23	25,58	3,64	0
Anion ex-changer EDE-10 P	12	16,61	21,12	26,39	35,57	17,03	0
Anion ex-changer AN-2F	0,1	0	0	0	0	0	0
Anion ex-changer AN-2F	0,5	0	0	0	0	0	0

Anion exchanger	Normality of HCl	Fe	Cu	Co	Ti	Mn	Ni
Anion exchanger AN-2F	1	4,62	0	0	0	0	0
Anion exchanger AN-2F	2	5,05	0	0	0	0	0
Anion exchanger AN-2F	4	5,85	5,57	0	0	0	0
Anion exchanger AN-2F	6	11,28	11,67	6,67	0	0	0
Anion exchanger AN-2F	8	19,61	19,20	9,46	4,76	0	0
Anion exchanger AN-2F	10	23,75	21,65	11,67	20,55	5,02	0
Anion exchanger AN-2F	12	30,84	17,78	17,57	37,51	18,71	0

The different stability of the chloride anionic complexes of the elements may serve as a basis for separating them on anion-exchange resins. If the uptake of elements by anion exchangers in hydrochloric-acid solutions is due to the formation of chloride anionic complexes, then by lowering the concentration of hydrochloric acid in the solution washing the column it may be possible

to achieve successive destruction of these complexes and, consequently, desorption of the elements. By repeated washing of the anion-exchange column with hydrochloric-acid solutions of ever lower concentration, chromatographic separation of a mixture of elements can be carried out. Thus, the domestic anion-exchange resins AB-16, EDE-10P, and AN-2F can be used to one degree or another for separating elements of the fourth period, just as some of the elements of this period were separated with the aid of the anion exchanger Dowex-1 ([2]). In addition, separation on anion exchangers of pairs of elements of the fourth period in various combinations appears possible.

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CITED LITERATURE

[1] K. Kraus, F. Nelson, in: *Chemistry of Nuclear Fuel*, Moscow, 1956.
[2] K. Kraus, G. Moore, *J. Am. Chem. Soc.*, **75**, No. 3, 1460 (1953).
[3] M. N. Zvereva, V. N. Shibarov, *Vestn. Leningr. Univ.*, No. 4, 145 (1959).
[4] V. V. Strepin, V. I. Ponosov, E. V. Silaeva, *Zav. Lab.*, **24**, issue 8, 934 (1958).
[5] I. K. Tsyitovich, *DAN*, **128**, No. 5, 970 (1959).
[6] A. K. Babko, A. T. Pilipenko, *Colorimetric Analysis*, Moscow, 1951.
[7] A. A. Grinberg, *Introduction to the Chemistry of Complex Compounds*, Moscow –Leningrad, 1951.

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