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Abstract

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On Complex Formation in Tartaric-Acid Solutions for Elements of the Middle of the Fourth Period

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It is known that tartaric acid forms complex compounds with many metals, in which metal ions replace hydrogen atoms of both carboxyl and alcoholic groups. Tartrate complexes of the elements have been studied by various methods, but ion exchange has not been used for these purposes. Meanwhile, complex formation in tartaric-acid solutions is beginning to be used for the ion-exchange separation of metals ($^{1-5}$). Since ion exchange is being applied ever more widely as a method for studying the state of metals in acidic media, we undertook a systematic investigation of complex formation in tartaric-acid solutions for elements of the middle of the fourth period. In doing so, the task was set of elucidating new possibilities for the separation of metals by means of ion-exchange chromatography.

Complex formation was investigated for the elements Cr (III), Mn (II), Fe (III), Co (II), Ni (II), Cu (II), and also Ti (IV), in solutions with a tartaric-acid concentration from 0 to 10 N. The distribution coefficients of the elements φ between ion-exchange resins and tartaric-acid solutions, which are a function of complex formation, were determined under static conditions. An accurately weighed portion of air-dry ion exchanger (0.5 g) was shaken with a definite volume of the solution under study (50 ml) until equilibrium was reached; aliquot portions of the solutions were taken, and the amount of the element not sorbed by the resin was determined colorimetrically (^{6}): Ti—in the form $[TiO(H_2O)_2]^{2+}$, Cr—in the form CrO_4^{2-}, Mn—in the form MnO_4^-, Fe and Co—in the form of thiocyanates, Ni—in the form of the dimethylglyoximate, and Cu—in the form of the ammoniate. In all necessary cases the tartrate complexes of the metals were destroyed before colorimetry by boiling with HNO_3 and H_2SO_4. The distribution coefficients of the ele-

Table 1

Distribution coefficients of elements φ in tartaric-acid solutions

Normality of $H_2C_4H_4O_6$ solution	Ti	Cr	Mn	Fe	Co	Ni	Cu
Anion exchanger EDE-10P	**Anion exchanger EDE-10P**	**Anion exchanger EDE-10P**	**Anion exchanger EDE-10P**	**Anion exchanger EDE-10P**	**Anion exchanger EDE-10P**	**Anion exchanger EDE-10P**	**Anion exchanger EDE-10P**
0.1	150.10	195.00	0	17.55	0	0	54.77
0.5	395.20	60.25	0	18.44	26.65	4.71	20.68
1	232.20	52.01	0	15.22	8.88	31.92	20.68
2	232.20	2.84	0	15.22	5.00	0	10.43
4	149.20	0	30.85	10.70	0	0	0
6	148.60	0	5.94	7.13	0	0	0
8	99.30	0	5.94	4.14	0	0	0
10	42.50	0	0	4.14	0	0	0
Cation exchanger KU-2	**Cation exchanger KU-2**	**Cation exchanger KU-2**	**Cation exchanger KU-2**	**Cation exchanger KU-2**	**Cation exchanger KU-2**	**Cation exchanger KU-2**	**Cation exchanger KU-2**
0 (water)	0	262.80	11.25	1562.00	5160.70	1586.20	Complete absorption
0.01	168.20	146.30	29.13	3110.00	4979.30	1711.10	Complete absorption
0.1	0	103.70	255.00	2416.20	3325.50	1109.70	Complete absorption
0.5	7.75	10.70	81.74	1592.70	2166.20	811.20	1042.40
1	27.72	26.20	16.34	1505.10	1696.30	811.20	995.20
2	22.30	53.40	0	682.30	1251.40	518.90	227.20
4	9.31	0	0	162.30	7.20	192.80	127.50
6	3.28	0	0	100.20	4.50	66.10	85.20
8	0	0	0	46.70	21.70	20.40	58.86
10	0	0	0	46.70	0	37.50	56.06

ϕ were calculated as described by us earlier ([7], [8]). In addition, the sorption of metals by the resins at equilibrium was determined in milligram-equivalents per 1 g of ion exchanger and as percentages of the initial amounts.

The initial solutions, prepared with bidistilled water from chemically pure reagents, had the following concentrations: Ti 0.1197, Cr 0.1734, Mn 0.2794,

Fig. 1

Figure 1: Fig. 1

Fe 0.1861, Co 0.2947, Ni 0.2935, and Cu 0.3177 mg/ml. To eliminate the influence of different ions, all salts were taken as sulfates (Ti—in the form of $TiCl_4$). In the experiments, domestically produced ion-exchange resins were used: the medium-basic anion exchanger EDE-10P and the strongly acidic monofunctional cation exchanger KU-2. In preparing for the study, fractions of the ion exchangers with grain diameters of 0.5–1.0 mm were sieved out; the resins were washed free of impurities; the anion exchanger was converted to the tartrate form, and the cation exchanger to the H-form. The sorbents were then brought to an air-dry state.

Fig. 1. Dependence of the sorption of elements by the anion exchanger EDE-10P on the concentration of $H_2C_4H_4O_6$ solutions: 1—Fe, 2—Ti, 3—Cu, 4—Cr, 5—Ni, 6—Mn, 7—Co

The distribution coefficients of the elements ϕ are given in Table 1. The sorption of metals by the EDE-10P anion exchanger at tartaric acid concentrations below 0.1 *N* is not shown in it because, in solutions close to neutral, formation by the elements of atypical solid complexes with this resin is possible ([9]). From the data in Table 1 it is seen that only Ti and Fe are sorbed by the anion exchanger at all the tested concentrations of tartaric acid. The remaining elements are absorbed by the anion exchanger only at some of its concentrations. Nevertheless, it is evident that tartrate anionic complexes with tartaric acid are formed by all the elements studied.

The curves in Fig. 1 clearly show that tartrate anionic complexes of individual elements are present in solutions with the following concentrations of tartaric acid: for Ti and Fe, from 0.1 to 10 *N*; for Cr, from 0.1 to 4 *N*; for Mn, from 2 to 10 *N*; for Co, from 0.1 to 4 *N*; for Ni, from 0.5 to 4 *N*; and for Cu, from 0.1 to 4 *N*. These differences open new possibilities for separating the metals studied by means of anion-exchange columns in tartaric-acid media, just as the different stability of complex anions was used for the purpose of separating elements from citric-acid ([10]) or hydrochloric-acid ([11]) solutions. For example, in principle Ti can be separated from Cr, Mn, Co, Ni, and Cu with the aid of the EDE-10P anion exchanger from tartaric-acid solutions.

Tartrate anionic complexes are in equilibrium with simple metal cations, which are absorbed from solutions by the KU-2 cation exchanger. The curves in Fig. 2 make it possible to see that the sorption of simple cations of all of metals gradually decreases as the concentration of tartaric acid is increased. The sorption curves by the cation exchanger for the elements Ti, Cr, Cu, and Ni deserve special attention. After the absorption of the simple cations of these

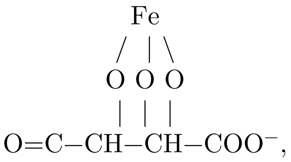
Fig. 2. Dependence of the sorption of elements by the KU-2 cation exchanger

Fig. 2. Dependence of the sorption of elements by the KU-2 cation exchanger on the concentration of $H_2C_4H_4O_6$ solutions. Designations as in Fig. 1

Figure 2: Fig. 2. Dependence of the sorption of elements by the KU-2 cation exchanger on the concentration of $H_2C_4H_4O_6$ solutions. Designations as in Fig. 1

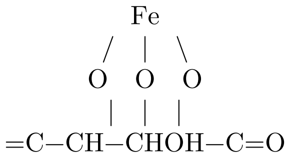
on the concentration of $H_2C_4H_4O_6$ solutions. Designations as in Fig. 1.

metals falls to a minimum, a new increase in sorption is observed at higher concentrations of tartaric acid. The appearance of peaks on the sorption curves of these elements suggests the formation of tartrate cationic complexes absorbed by the cation exchanger. For Ti they apparently exist in 0.5-6 N, for Cr in 0.5-2 N, for Co in 6-8 N, and for Ni in 8-10 N tartaric acid solutions. For Fe, tartrate cationic complexes were not found. This is consistent with data of other authors (^{12}), who showed that at pH from 4 to 6 iron forms the complex



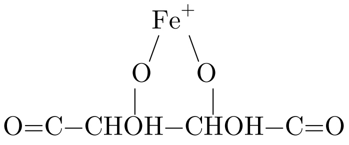
$$\begin{array}{c} \mathrm{Fe} \\ / \quad | \quad \backslash \\ \mathrm{O \quad O \quad O} \\ | \quad | \quad | \\ \mathrm{O{=}C{-}CH{-}CH{-}COO^{-}}, \end{array}$$

anion, although it does not follow from this that under other conditions iron cannot at all form neutral complexes



$$\begin{array}{c} \mathrm{Fe} \\ / \quad | \quad \backslash \\ \mathrm{O \quad O \quad O} \\ | \quad | \quad | \\ \mathrm{{=}C{-}CH{-}CHOH{-}C{=}O} \end{array}$$

or complex cations



$$\begin{array}{c} \mathrm{Fe^{+}} \\ / \qquad \backslash \\ \mathrm{O \qquad O} \\ | \qquad | \\ \mathrm{O{=}C{-}CHOH{-}CHOH{-}C{=}O} \end{array}$$

as occurs with other elements of the fourth period.

Comparison of the distribution coefficients of the elements between the KU-2 cation exchanger and tartaric-acid solutions shows (Table 1) that the sorbability of Fe, Co, Ni, and Cu is tens and hundreds of times higher than that of Ti, Cr, and Mn (from 0.01-2 N solutions). This provides real possibilities for separating metals of the fourth period by means of the KU-2 cation exchanger, analogously to the way in which the different sorbability of elements by cation exchangers from hydrochloric-acid solutions was used (13-15).

The absorption of metals of the middle of the fourth period by the resins EDE-10P and KU-2, as a percentage of the initial amount, is sufficiently large even under

Table 2

Sorbability of elements by ion exchangers from tartaric-acid solutions

Normality of the $H_2C_4H_4O_6$ solution	Ti	Cr	Mn	Fe	Co	Ni	Cu
Anion exchanger EDE-10P							
0.1	60.0	66.1	0	15.0	0	0	35.3
0.5	79.8	37.6	0	15.7	20.5	0	17.1
1	70.0	34.3	0	13.0	7.9	4.4	17.1
2	70.0	3.8	0	13.0	4.9	24.1	9.4
4	60.0	0	23.6	9.8	0	0	0
6	65.0	0	5.7	6.8	0	0	0
8	49.0	0	5.7	4.1	0	0	0
10	29.8	0	0	6.1	0	0	0
Cation exchanger KU-2							
0 (water)	0	72.5	10.1	94.0	98.0	94.0	100.0
0.01	62.7	59.4	22.5	97.0	98.0	94.5	100.0
0.1	0	50.9	71.8	96.0	97.1	92.2	100.0
0.5	7.2	9.7	44.9	94.1	95.6	89.0	91.0
1	21.2	20.8	14.0	93.7	94.5	89.0	91.0
2	18.2	34.8	0	87.2	92.6	83.8	74.0
4	8.5	0	0	61.5	6.7	65.7	56.0
6	3.2	0	0	50.0	4.4	39.7	46.0
8	0	0	0	31.7	17.8	16.8	37.0
10	0	0	0	31.7	0	27.2	36.0

static conditions (Table 2). Under dynamic conditions, i.e., in column chromatography, it increases considerably.

The separation of elements of the fourth period from tartaric-acid solutions by means of cation or anion exchange can be used not only in the analysis of alloys, but also in the determination of trace elements in biological material.

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