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On the Sorption of *d*-Metal Ions on Mixed Phosphates of the 4-th Group Elements

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Mixed titanium–zirconium, tin–zirconium, and tin-titanium phosphates containing different amounts of the 4-th group elements were synthesized and their ion-exchange properties towards Cu^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+} ions were studied. The values of the equilibrium costants of the ion-exchange reactions of the *d*-metal sorptions from acetate and chloride solutions were calculated. It was found that the sorbents affinity to the transitional metal ions greatly depended on their chemical composition; enriching of tin-containing samples with Zr and, especially, with Ti increases the affinity to Co^{2+} ions; enrichment of titanium–zirconium containing ionites with Zr increases their affinity to Cu^{2+} ions, etc. It is suggested that the observed changes in the selectivity of the inorganic ion-exchangers are connected with the possibility of creating in their structure adsorption centers with different geometrical parameters depending on the dimensions of the 4-th group elements.

High selectivity towards certain ions is one of the main advantages of inorganic ionites over synthetic ion-exchange resins, which makes the former promising materials in various technological processes.[1–3] The sources and mechanisms of the selective ion-exchange sorption on inorganic adsorbents based on the amorphous phosphates of the 4-th group elements have been studied in previous works[4,5] It was revealed that geometrical conformity of the size of an ion to the parameters of sorptive centers (zeolite-like cavities formed with oxygen atoms of P=O, P–OH, P–O–M^{IV}, and other functional groups) provides the main effect on sorption selectivity. On the basis of this observation there was offered a method of a specific formation of ionites with the desired properties.[6,7] According to this method, all stages of the adsorbent synthesis (precipitation, washing, drying, and thermal treatment) are carried out in the presence of ions, towards which an ionite selectivity has to be achieved. Thus, synthesized ionites "remember" the parent ion and then can selectively adsorb such ions from complex solutions. Among them, samples of titanium and zirconium phosphates selective towards Cs^+, K^+, Na^+ and some alkaline-earth metal ions were synthesized. However, this method turned out to be insufficient for the monitoring of the adsorbents selectivity towards transitional metal ions.

In this connection, we suggest the synthesis of mixed phosphates of 4-th group elements to be a promising method for the desired alteration of the sorptive properties of ionites. As the structure of such materials contains atoms (elements) of various radii, e.g. titanium (R=1.48 Å), zirconium (R=1.60 Å), and tin (R=1.58 Å), their sorptive centers will alter those occuring in individual phosphates of titanium (TP), zirconium (ZP), and tin (SP).

In this paper, we present the results of the investigation of the sorption of some *d*-metal ions on mixed phosphates of titanium and zirconium (TZP), tin and zirconium (SZP), and titanium and tin (TSP), which contain various amounts (from 0 to 100 mol %) of the 4-th group elements.

Experimental

Reagents. $ZrOCl_2\cdot 8H_2O$, $TiCl_4$, $SnCl_4$, and H_3PO_4 ("chemically pure" grade) were used for the synthesis of mixed ion-exchangers. All other chemicals were of analytical grade.

Apparatus. An EV-74 Ionomer (USSR) was used for the pH measurements. A "Saturn" atomic absorption spectrophotometer (USSR) was used for the *d*-metal ions determination. An electric temperature-controller shaker LPAN-340 (Poland) was used for shaking.

Synthesis. Individual and mixed phosphates of the 4-th group elements were synthesized accoroding to gel technology.[8] Formalin, glycerol, and hexamethylenetetramine were used as complex forming agents in the synthesis of titanium, zirconium, and tin phosphates, respectively. Working solutions (5 mol dm^{-3} solution of H_3PO_4 and 1 mol dm^{-3} solution of a salt mixture of the 4-th group elements) were mixed in a mole ratio of P : M^{IV}=2 : 1. The obtained spherical granules of a sorbent hydrogel were washed with a 0.5 mol dm^{-3} solution of HNO_3 and then with water to remove excess acid. After that, the product was dried in air to achieve a residual humidity of 40—45%.

Chemical Composition. For the determination of the chemical composition of mixed 4-th group elements phosphates, 0.10 g of sorbent was dissolved in hot concentrated H_2SO_4 (if necessary with preliminary addition of HF). 4-th Group elements and phosphorus were determined by the extraction-spectrophotometric method according to the literature.[9]

Chemical analysis showed the same mole ratio of the 4-th group elements both in a sorbent phase and in a working solution. Chemical composition and some sorptive parameters of mixed phosphates are summarized in Table 1.

Sorption Experiments. The sorption of *d*-metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+}) on mixed phosphates of 4-th group elements was studied in 0.01 mol dm^{-3} solutions of appropriate chlorides or acetates under static conditions. The solid to liquid phase ratio was varied from 1 : 10 to 1 : 1000 (g : ml). Mixtures (3 parallel experiments) were shaken for 5—6 d at an ambient temperature. Sorbent grading was

Table 1. Composition and Properties of Mixed 4-th Group Element Phosphates

N	Sorbent	Composition/mol%			Maximum adsorption capacity/mmol g^{-1}			
		Zr	Ti	Sn	Cu^{2+}	Co^{2+}	Ni^{2+}	Cr^{3+}
1	ZP	100	—	—	1.8	0.8	0.8	
2	TZP-80	80	20	—	1.7	0.5	0.25	
3	TZP-60	60	40	—	1.5	0.8	0.5	
4	TZP-40	40	60	—	1.6	0.75	0.7	
5	TZP-20	20	80	—	3.2	0.5	1.0	
6	TP	—	100	—	3.3	0.8	0.7	
7	TSP-25	—	75	25	3.3	1.4	1.5	0.8
8	TSP-50	—	50	50	3.4	1.7	1.45	0.45
9	TSP-75	—	25	75	2.7	1.2	1.0	0.4
10	SP	—	—	100	1.8	0.8	0.33	0.17
11	SZP-75	25	—	75	1.8	0.8	0.5	0.18
12	SZP-50	50	—	50	3.3	1.8	1.35	1.2
13	SZP-25	75	—	25	3.0	1.4	1.2	0.65

0.25—0.31 mm.

The amount of *d*-metal ions left in the solution was then determined by the atomic absorption method. The mean values of capacity were used for the calculation of the concentration equilibrium constants (K_c). The deviation of K_c did not exceed 5—10%.

Results and Discussion

Sorption study of various $m:V$ ratios with a constant initial concentration of a solution enabled us to plot sorption isotherms in capacity (A) versus equilibrium concentration (C_e) for relatively diluted solutions ($C<0.01$ mol dm^{-3}), which is of certain practical interest (e.g. for purification of industrial solutions and sewage).

Isotherms of *d*-metal ions sorption on a sample of SZP-25 are plotted in Fig. 1 as a) A against C_e and b) $\overline{x}$ (equivalent fraction of the ion in a sorbent phase) against x (equivalent fraction of the ion in a solution). The former type of isotherms makes the magnitudes of ionites sorption capacity obvious and the latter allows us to present ion adsorption in dimensionless coordinates and estimate the character of sorption selectivity. Thus, if sorption isotherm is situated above the 0,0-1,1 diagonal, an adsorbent will predominantly adsorb metal ions, otherwise it will prefer protons.

Since the experiments were carried out in dilute solutions with a small ionic strength ($I \ll 0.1$), in which the activity coefficients of ions were approximately unity, we tried estimate quantitatively the affinity of mixed phosphates for *d*-metal ions.

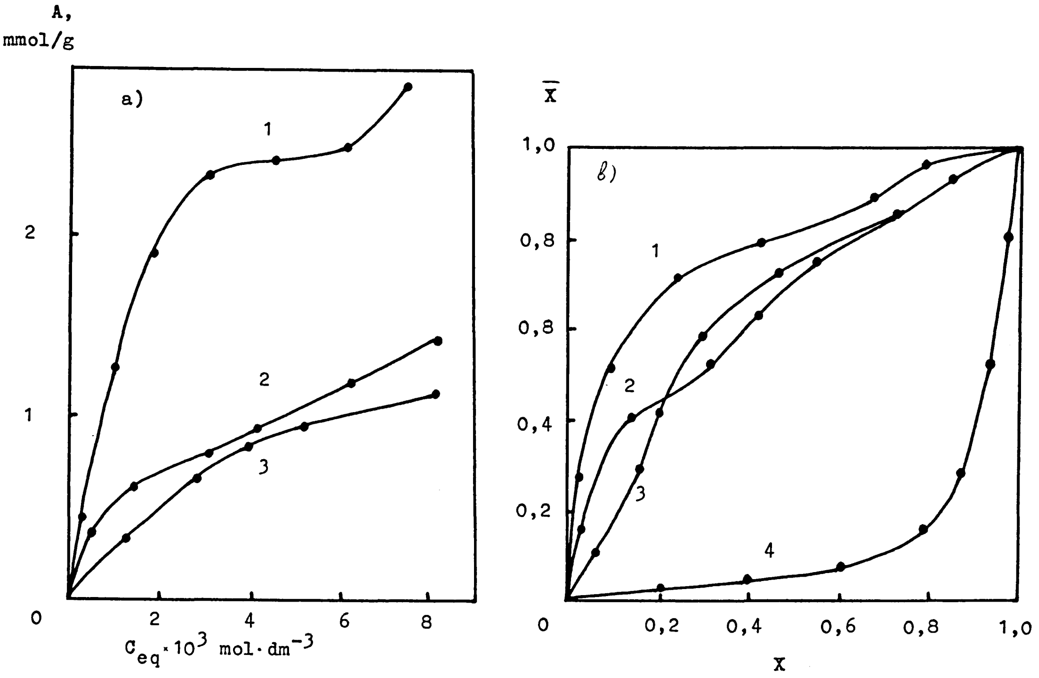

Fig. 1. Adsorption isotherms of Cu^{2+} (1), Co^{2+} (2), Ni^{2+} (3), and Cr^{3+} (4) ions from acetate solutions on SZP-25.

Since the ion-exchange reaction

$$n\,\overline{\mathrm{R{-}H}} + \mathrm{M}^{n+} \rightleftarrows \overline{\mathrm{R}_n\mathrm{M}^{n+}} + n\,\mathrm{H}^+$$

is a reversible process, the thermodynamic equilibrium constant (K) may be calculated by applying the law of mass action

$$K=\frac{[\overline{a_1}]^{n_2}[a_2]^{n_1}}{[\overline{a_2}]^{n_1}[a_1]^{n_2}}$$

(where $\overline{a}_1$, $\overline{a}_2$ and a_1, a_2 are the activities of the exchanging ions in sorbent phase and solution, respectively and n_1, n_2 are the valencies of these ions).

Direct calculation according to this formula fails because of the lack of experimental data on the sorbent phase activity coefficients. However, the thermodynamic exchange constants are shown[10,11] to be calculated using concentration exchange constants according to the formula:

$$\ln K=\int_0^1 \ln K_\mathrm{c}\, \mathrm{d}\overline{x}_\mathrm{A},$$

where

$$K_\mathrm{c}=\frac{M_\mathrm{B}\,\overline{x}_\mathrm{A}}{M_\mathrm{A}\,\overline{x}_\mathrm{B}}\;\frac{f_\mathrm{B}}{f_\mathrm{A}}$$

(M_A, M_B: equivalent concentrations of ions in a solution; (f_A, f_B: activity coefficients for these ions in a solution).

The absolute value of K_c is affected by the magnitude of sorbent capacity. The ionite exchange capacity in turn is not constant and depends on a few factors, cation nature and conditions of adsorption, being among them.

Therefore, in further calculations of K_c, the capacity values of the exchanging ions only are used. Limiting magnitudes of the sorption capacity of each pair of the exchanging ions are determined under static conditions in 0.01 mol dm^{-3} solutions of appropriate metal acetates ($m:V=1:1000$) and checked in 0.1 mol dm^{-3} solution of chlorides ($m:V=1:100$).

In Fig. 2, $\ln K_\mathrm{c}$ values for *d*-metal ion exchange on a sample of SZP-25 are plotted against the uptake of ions. As a rule, for synthetic ion-exchange resins, $\ln K_\mathrm{c}$ values decrease with uptake increase, thus testifying to the decrease in sorption affinity. Meanwhile, the behavior of inorganic phosphorus-containing cationites is more sophisticated: The plots of $\ln K_\mathrm{c}$ against x may have several minima and maxima. We suggest this to be due to the lack of sorbent swelling as well as to the diverse nature of the sorption centers. As a result, the selectivity of inorganic adsorbents strongly depends on the uptake. In some cases, an inverse affinity series may occur. For example, between Co^{2+} and Ni^{2+}, SZP-25 preferably adsorbs Co^{2+} ions when the uptake is $0<\overline{x}<0.45$, Ni^{2+} ions when $0.45<\overline{x}<0.80$, and Co^{2+} when $\overline{x}>0.80$. Analogous behavior is observed in other mixed phosphates of the 4-th group elements.

On extrapolating $\ln K_\mathrm{c}$ to $\overline{x}=0$, we have determined the values of $\ln K_{\overline{x}\to 0}$ which characterize the exchange process and the affinity of the most active sorptive centers. Then the values of the corresponding thermo-

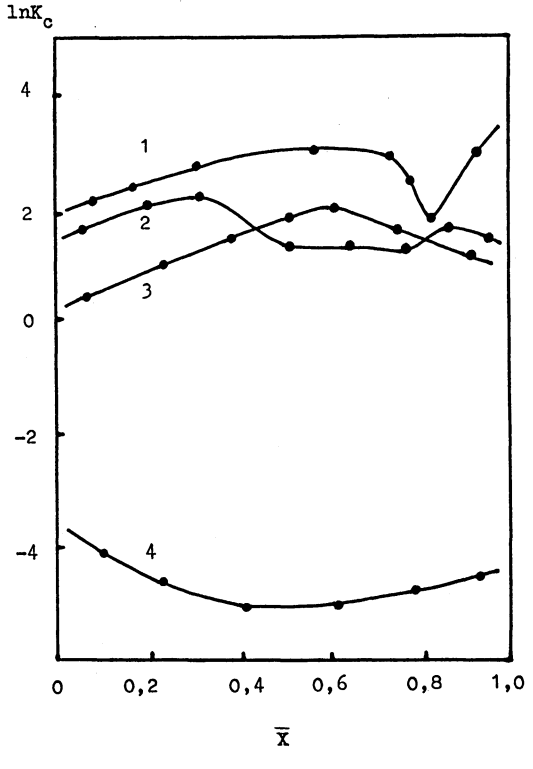

Fig. 2. Plots of $\ln K_\mathrm{c}$ for Cu^{2+} (1), Co^{2+} (2), Ni^{2+} (3), and Cr^{2+} (4) ions vs. $\overline{x}$ on SZP-25.

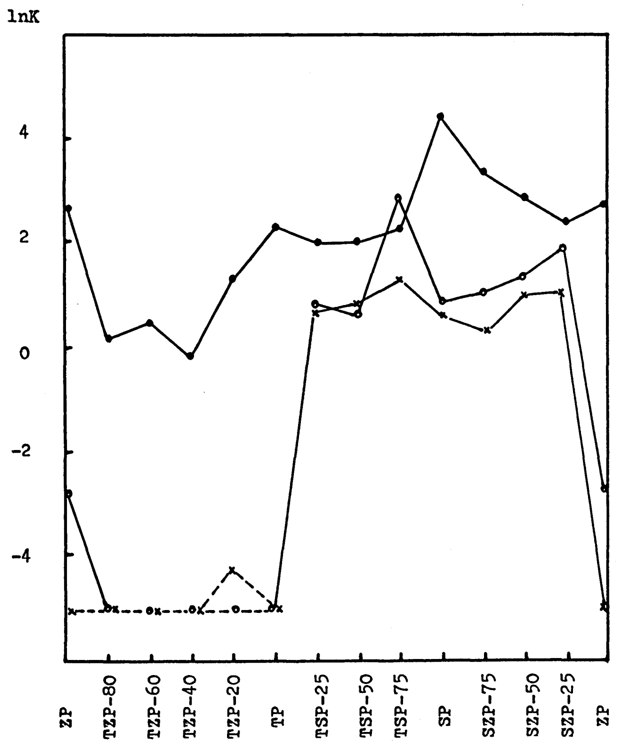

Fig. 3. Values of $\ln K$ for the case of sorption of Cu^{2+} (●), Co^{2+} (○), and Ni^{2+} (×) ions from acetate solutions on mixed phosphates.

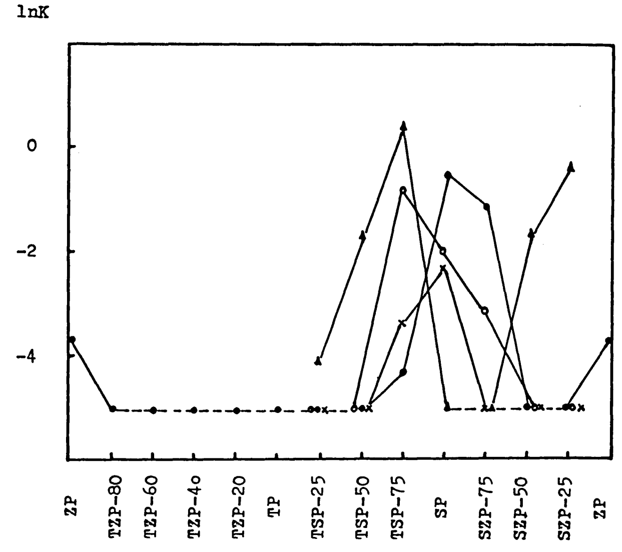

Fig. 4. Values of $\ln K$ for the case of sorption of Cu^{2+} (●), Co^{2+} (○), Ni^{2+} (×), and Cr^{3+} (▲) ions from chloride solutions on mixed phosphates.

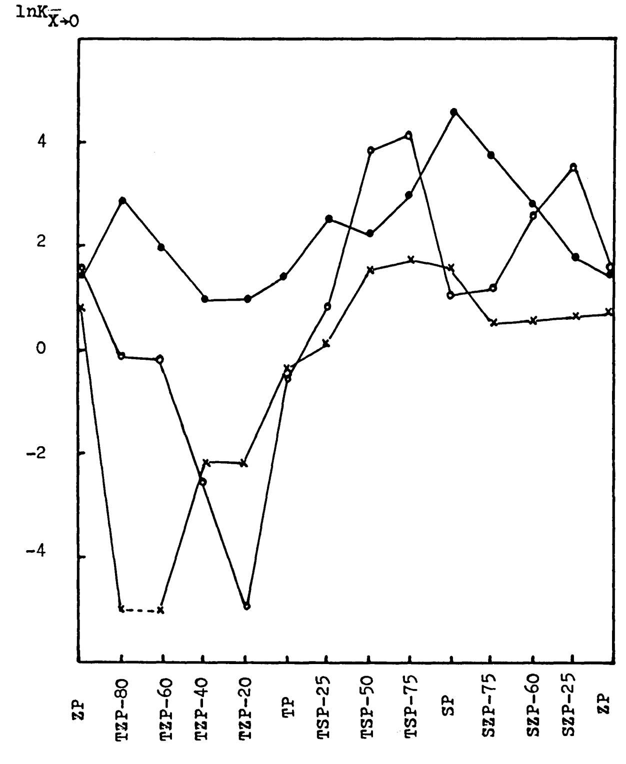

Fig. 5. Values of $\ln K_{\bar{x}\to 0}$ for the case of sorption of Cu^{2+} (●), Co^{2+} (○), and Ni^{2+} (×) ions from acetate solutions on mixed phosphates.

dynamic exchange constants K were calculated by integrating areas under $\ln K_c$ versus $\bar{x}$ curves. Analysis of $\ln K_{\bar{x}\to 0}$ and $\ln K$ values represented in Figs. 3—6 resulted in a series of conclusions about the character of the selectivity of mixed phosphates of the 4-th group elements and the effects of solution acidity, uptake, and chemical composition of a sorbent. It is clear that the sorbent affinity for d-metal ions increases with the solution pH evaluation (the equilibrium values of pH are 3.5—4.5 for the sorption from acetate solutions and pH=2.0—3.0 for chloride solutions). Positive values of $\ln K$ for acetate solutions testify to the possible spontaneous direct ion-exchange reaction resulting in the appropriate salt forms of ionites. The values of $\ln K$ are, as a rule, negative for the sorption from chloride solutions.

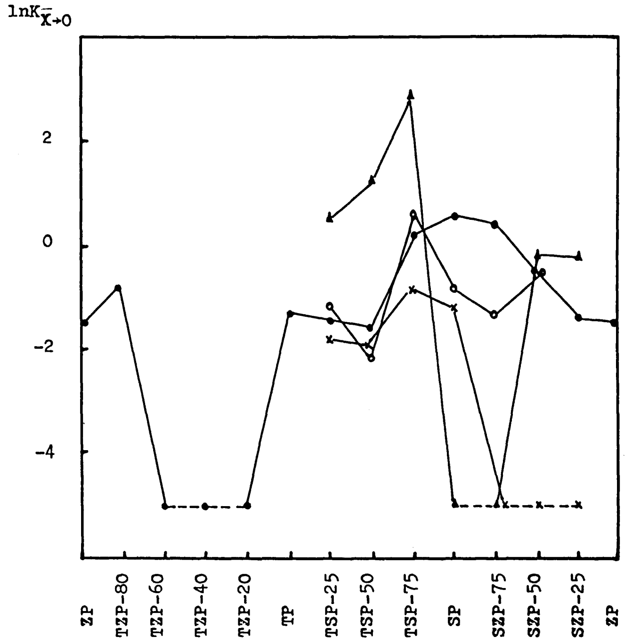

Fig. 6. Values of $\ln K_{\bar{x}\to 0}$ for the case of sorption of Cu^{2+} (●), Co^{2+} (○), Ni^{2+} (×), and Cr^{3+} (▲) ions from chloride solutions on mixed phosphates.

Chemical composition of an ionite matrix has a more complicated effect on the ionite selectivity. Thus, TP and ZP have the following typical affinity series for transition metal ions:

$$\mathrm{Cr^{3+} > Cu^{2+} > Co^{2+} > Ni^{2+}} \text{ (in chloride solutions)}$$

and

$$\mathrm{Cu^{2+} > Co^{2+} > Ni^{2+}} \text{ (in acetate solutions)}$$

In the case of mixed titanium-zirconium adsorbents, enrichment of an ionite structure with zirconium atoms increases the selectivity towards Cu^{2+} ions (the maximum effect is observed with TZP-80), whereas the increase in titanium content leads to a higher affinity for nickel: A sample of TZP-20 will prefer Ni^{2+} ions to Cu^{2+} ions.

Analysis of the analogous information on tin-containing samples shows that SP has a suprisingly low selectivity towards Cr^{3+} ions and its affinity series is Cu^{2+}>Co^{2+}>Ni^{2+}>Cr^{3+}. The affinity of tin-containing adsorbents for Cr^{3+} and Co^{2+} ions increases on enriching these materials with zirconium and especially titanium atoms. For example, in acetate solutions the samples of TSP-25, TSP-50, and SZP-25 have a maximum affinity for cobalt rather than for copper. Their affinity series are as follows: $Co^{2+}>Cu^{2+}>Ni^{2+}$ (at the low uptake). Such sorbents can be used in the processes of sorptive separation of nickel and cobalt, for deep purification of nickel salts.

We must also uderline that among the studied adsorbents mixed phosphates of tin and titanium have the maximum affinity for the transitional metal ions.

Conclusion

The investigation of the sorption of *d*-metal ions on mixed phosphates of the 4-th group elements shows that the sorbent selectivity is governed by the chemical composition of a sorbent matrix. This means that the offered assumption about the possible monitoring of the sorptive properties of ionites on varying the parameters of their sorptive centers by introducing atoms of various dimensions in their structure, turns out to be correct even in the case of amorphous ionites.

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