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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Selective Extraction of Fe^{3+} Ions from Fe^{3+}–Zn^{2+} Mixture with Phosphate Sorbents

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Abstract—The absorption of Fe^{3+} ions from Fe^{3+}–Zn^{2+} mixture with zinc and calcium phosphates was studied.

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Presently, a variety of natural and synthetic materials, from modified filings to most recent synthetic ion-exchangers, products of complex organic synthesis, has been proposed for recovery of nonferrous metals from solutions. At the same time, only few of them are selective. The extraction and concentration of metal ions from solutions with nonselective ion-exchangers or the use of chemical precipitants (mainly, of hydroxides) results in the new problems including burial or treatment of the obtained concentrates and waste, which are necessary to remove valuable nonferrous metals and recover them into technological process.

For processing of the solutions containing multiple-charged ions, the chemisorption technologies using heterogeneous chemical reactions with phosphates of double-charged metal ions are promising [1, 2]. First, the amount of heavy and nonferrous metals recovered in the above processes is as high as 12 mmol g^{-1}, i.e., exceeds by an order of magnitude the values for common synthetic and natural ion-exchangers. Second, the use of chemisorption procedures for selective absorption of ions from mixtures has been suggested and confirmed in practice of [3, 4]. It was shown that selective chemisorption can be realized by monitoring the ratio between the weight of chemisorbent and the volume of a liquid phase. If in the course of chemical reaction the sorbent may form less soluble compounds with all cations, then all these cations will be sorbed. In the case, when its mass is insufficient, only a cation forming less soluble compound with the sorbent will be sorbed.

This work continues the early study concerned with the possibility of separating the Fe^{3+}–Zn^{2+} mixture with phosphate sorbents.

EXPERIMENTAL

Double-substituted calcium phosphate $CaHPO_4 \cdot 2H_2O$ from Polilkhim Ltd Research and Production Enterprise and zinc phosphate $Zn_3(PO_4)_2 \cdot 4H_2O$ synthesized by the method [5] were sorbents.

Sorption of metal ions from solutions of their nitrate salts was studied under static conditions at room temperature at varied ratio between the amounts of sorbent and metal ions displaced into the solution.

Test solutions were prepared form crystal hydrates of chemical purity grade $Fe(NO_3)_3 \cdot 6H_2O$ and analytical purity grade $Zn(NO_3)_3 \cdot 6H_2O$; 50 ml of a solution of varied concentration was added to 0.2 g of the sorbent (sifted fraction 0.075–0.125 mm), and this mixture was kept for 1 day at intermittent stirring. Then, the solid phase was filtered off and the concentration of metal ions in the liquid phase was determined. The amount of sorbed and released ions, the degree of metal recovery from solution, and the molar ratios between the amounts of sorbed ions and ions released into the solution during heterogeneous reaction were calculated from the difference of the concentrations of iron and zinc ions in initial and equilibrium solutions after reaction.

The concentration of Fe^{3+} ions was measured photocolorimetrically [6] on a KFK-2MP colorimeter.

The concentration of Zn^{2+} ions and the total concentration of Fe^{3+} and Zn^{2+} ions, while present simultaneously, were determined by complexometric titration with Trilon B (acetate buffer solution, xylenol orange indicator). The pH variation of the initial and equilibrium solutions was monitored on an EV-74 pH meter.

It has been shown previously [3] that for separation of mixture constituted by two metal cations, a metal phosphate whose solubility is higher is suitable. Experimentally, the solubility of iron phosphate is lower than that of zinc phosphate. The contact of zinc phosphate with the solution leads to heterogeneous substitution with formation of less soluble iron phosphate.

Preliminary information about the character of the interaction of zinc phosphate with iron(II) ions was obtained in a study of one-component solution of iron(II) nitrate. Table 2 lists the results of analysis of the initial and equilibrium solutions in the $Zn_3(PO_4)_2 \cdot 4H_2O$–$Fe(NO_3)_3$ system and calculated values of amount of sorbed A (mmol g^{-1}) and released B (mmol g^{-1}) ions, molal ratio of sorbed and released ions, degree of Fe^{3+} recovery α (%), and degree of Zn^{2+} ions displaced into the solution.

The isotherm of Fe^{3+} sorption from $Fe(NO_3)_3$ solutions with zinc phosphate is plotted in Fig. 1a and the degree of Fe^{3+} recovery from solution as a function the concentration of the initial iron nitrate solution, in Fig. 1b. According to the results obtained, the degree of iron(III) recovery from solution to the concentration $c[Fe(NO_3)_3] \le 0.008$ M is 100%.

As seen from Fig. 1a, the isotherm of iron sorption with zinc phosphate has unusual form: it passes a maximum at $c_{Fe} = 0.012$ M and then sharply descends, i.e., Fe^{3+} absorption sharply decreases, with a plateau corresponding to maximal sorption capacity not attained.

According to the results obtained, anomalous form of the sorption isotherm is due to pH variation of the initial nitrate solutions with increasing concentration. As seen from the data of Table 1, pH of the initial solution with a concentration of more than 0.014 M is less than 2. In such acid solutions the phosphate solubility considerably increases. As a result, the amount of iron(II) ions sorbed from solution sharply decreases.

Table 1. Results of analysis of the initial and equilibrium solutions before and after contact with $Zn_3(PO_4)_2 \cdot 4H_2O$

$c_{Fe\,in}$	$c_{Zn\,in}$	pH_{in}	$c_{Fe\,eq}$	$c_{Zn\,eq}$	pH_{eq}	A_{Fe}	B_{Zn}	$A_{Fe}:B_{Zn}$	α_{Fe}	β_{Zn}
моль·л$^{-1}$			M			mmol g^{-1}			%	
$Fe(NO_3)_3$ solutions										
0.004	–	2.50	0.000	0.009	4.00	0.9	2.1	1.0:2.3	100	–
0.006	–	2.35	0.000	0.015	3.92	1.5	3.6	1.0:2.4	100	–
0.008	–	2.20	0.000	0.018	3.85	1.9	4.5	1.0:2.4	100	–
0.012	–	2.14	0.004	0.019	2.45	2.1	4.6	1.0:2.2	68	–
0.014	–	2.10	0.006	0.022	2.20	1.9	5.4	1.0:2.8	56	–
0.019	–	1.90	0.014	0.023	2.38	1.3	5.6	1.0:4.3	26	–
$Fe(NO_3)_3$+$Zn(NO_3)_2$ solutions										
0.004	0.005	2.65	0.000	0.014	4.61	0.9	2.3	1.0:2.6	100	64
0.006	0.008	2.50	0.000	0.021	4.14	1.4	3.4	1.0:2.4	100	64
0.007	0.010	2.45	0.000	0.026	3.60	1.8	4.1	1.0:2.3	100	63
0.008	0.011	2.40	0.000	0.028	3.30	1.9	4.3	1.0:2.3	100	62
0.010	0.013	2.25	0.002	0.032	2.60	1.8	4.6	1.0:2.6	76	59
0.011	0.015	2.20	0.003	0.033	2.40	1.8	4.5	1.0:2.5	69	55
0.012	0.017	2.30	0.005	0.035	2.35	1.8	4.5	1.0:2.5	61	52
0.015	0.021	2.20	0.008	0.041	2.25	1.9	5.0	1.0:2.6	50	49
0.019	0.026	2.00	0.011	0.048	2.18	1.9	5.6	1.0:2.9	41	47

The exchange interaction of zinc phosphate and iron(III) ions at various pH values can proceed by the following schemes:

$$3Zn_3(PO_4)_2\cdot 4H_2O + 2Fe^{3+} + x_1H^+ \rightarrow 2Fe(H_2PO_4)_3\cdot y_1H_2O + 9Zn^{2+} + z_1H_2O, \quad (1)$$

$$3Zn_3(PO_4)_2\cdot 4H_2O + 4\ Fe^{3+} + x_2H^+ \rightarrow 2Fe_2(HPO_4)_3\cdot y_2H_2O + 9Zn^{2+} + z_2H_2O, \quad (2)$$

$$Zn_3(PO_4)_2\cdot 4H_2O + 2Fe^{3+} + x_3H_2O \rightarrow 2FePO_4\cdot y_3H_2O + 3Zn^{2+}, \quad (3)$$

$$Zn_3(PO_4)_2\cdot 4H_2O + 3\ Fe^{3+} + x_4OH^- \rightarrow 2\ FePO_4\cdot y_3H_2O + Fe(OH)_3 + 3Zn^{2+}. \quad (4)$$

During heterogeneous chemical interaction of zinc phosphate with iron(II) ions the solid phase converts to iron phosphate and zinc(II) ions are transferred into the solution. When a reaction proceeds by Eqs. (1)–(4), the molar ratios of the amounts of sorbed iron and released zinc ions are: 2:9 = 1:4.5 (1), 4:9 = 1:2.25 (2), 2:3 = 1:1.5 (3), and 3:3 = 1:1 (4). The experimentally obtained values of the above molar ratios (Table 1) in the studied region of the iron nitrate solution concentrations are from 1:2.3 to 1:2.8. Consequently, the contact of zinc phosphate with iron(III) nitrate solution in the solution concentration range studied, leads to the process described by Eq. (2), i.e., the reaction proceeds with formation of acid iron phosphate.

The characteristics of the iron(III) sorption with zinc phosphate from two- and multicomponent solutions differ only slightly. Results for iron(III) sorption from two-component Fe^{3+}–Zn^{2+} solution with

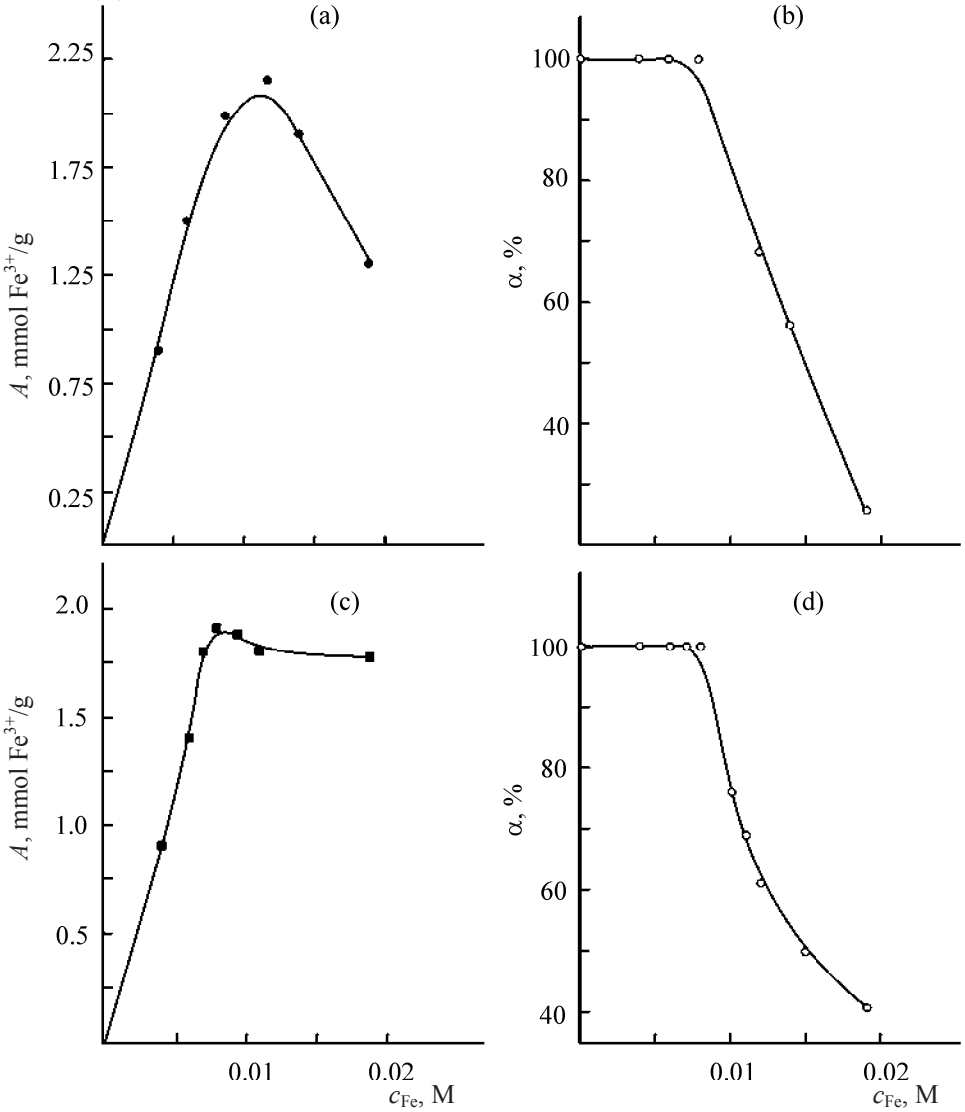

Fig. 1. (a, c) Sorption and (b, d) degree of ion recovery with zinc phosphate vs. the initial concentration of Fe^{3+} ions for (a, b) $Fe(NO_3)_3$ solutions and (c, d) $Fe(NO_3)_3 + Zn(NO_3)_2$ mixture. (*A*) Absorption, (α) degree of Fe^{3+} recovery, and (c_{Fe}) concentration of initial $Fe(NO_3)_3$ solution; the same for Fig. 3.

Table 2. Results of analysis of the initial and equilibrium solutions of zinc nitrate before and after contact with $CaHPO_4 \cdot 2H_2O$

$c_{Zn\ in}$, M	pH_{in}	$c_{Zn\ eq}$	$c_{Ca\ eq}$	pH_{eq}	A_{Zn}	B_{Ca}	A_{Zn}:B_{Ca}	α_{Zn}, %
		M			mmol g^{-1}			
0.015	5.6	0.003	0.019	4.6	3.1	4.7	1.0:1.5	83
0.025	5.5	0.009	0.023	4.1	4.1	5.6	1.0:1.4	66
0.037	6.0	0.020	0.024	3.8	4.2	5.9	1.0:1.4	46
0.050	5.3	0.033	0.024	3.8	4.2	6.0	1.0:1.4	34
0.070	5.7	0.053	0.027	3.7	4.2	6.7	1.0:1.6	24
0.088	5.8	0.071	0.026	3.4	4.3	6.4	1.0:1.5	19
0.106	5.0	0.089	0.026	3.4	4.4	6.5	1.0:1.5	17

Table 3. Results of analysis of the initial and equilibrium solutions of iron nitrate before and after contact with $CaHPO_4 \cdot 2H_2O$

$c_{Fe\ in}$, M	pH_{in}	$c_{Fe\ eq}$	$c_{Ca\ eq}$	pH_{eq}	A_{Fe}	B_{Ca}	A_{Fe}:B_{Ca}	α_{Fe}, %
		M			mmol g^{-1}			
0.004	2.50	0.000	0.015	5.00	0.9	3.6	1.0:4.0	100
0.009	2.20	0.000	0.027	2.72	2.3	6.6	1.0:2.9	100
0.013	1.98	0.001	–	1.85	3.0	–	–	95
0.014	1.99	0.001	–	1.82	3.2	–	–	93
0.015	2.01	0.008	–	1.75	1.7	–	–	48
0.019	2.10	0.012	–	1.73	1.6	–	–	34
0.022	2.05	0.016	–	1.72	1.4	–	–	26
0.024	2.01	0.018	–	1.70	1.4	–	–	24

Table 4. Results of analysis of the initial and equilibrium $Fe(NO_3)_3$ + $Zn(NO_3)_2$ solutions before and after contact with $CaHPO_4 \cdot 2H_2O$

$c_{Fe\ in}$	$c_{Zn\ in}$	pH_{in}	$c_{Fe\ eq}$	$c_{Zn\ eq}$	pH_{eq}	A_{Fe}	A_{Zn}	α_{Fe}	α_{Zn}
M			M			mmol g^{-1}		%	
0.002	0.003	2.70	0.000	0.001	5.25	0.4	0.5	100	80
0.003	0.005	2.45	0.000	0.002	4.80	0.8	0.8	100	67
0.005	0.007	2.35	0.000	0.005	4.50	1.2	0.5	100	31
0.006	0.009	2.30	0.000	0.008	4.05	1.6	0.1	100	6
0.008	0.011	2.19	0.000	0.010	3.65	1.9	0.1	100	5
0.012	0.016	2.04	0.000	0.016	2.05	3.0	0.0	100	0
0.013	0.018	2.05	0.000	0.018	1.85	3.3	0.1	98	3
0.014	0.019	2.04	0.001	0.019	1.75	3.3	0.0	93	0
0.015	0.021	1.95	0.010	0.021	1.65	1.3	0.0	35	0
0.019	0.026	1.85	0.014	0.026	1.50	1.1	0.0	23	0

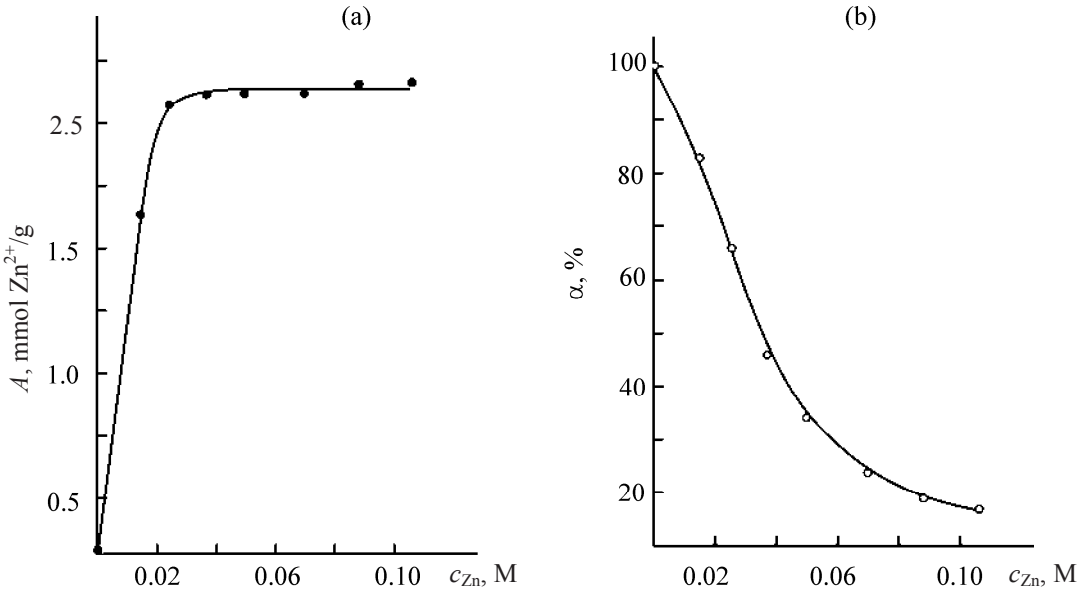

Fig. 2. (a) Sorption isotherms and (b) the degree of Zn^{2+} recovery with calcium phosphate vs. the initial concentration of $Zn(NO_3)_2$. (A) Absorption, (α) degree of Zn^{2+} recovery from solution, and (c_{Zn}) concentration of initial $Zn(NO_3)_2$ solution.

zinc phosphate are given in Fig. 1c, 1d and in Table 2. The ratios of the amounts of iron sorbed and zinc passed into the solution are close to values obtained in multicomponent solution and vary from 1:2.5 to 1:2.9 as the concentration of the initial two-component nitrate solution increases from 0.004 to 0.015 M.

The isotherm of iron sorption from two-component solution has no anomalous inflections, contrary to the case of sorption from multicomponent solution (Fig. 1a). This is because the pH values of the initial two-component solutions at all the points considered are larger than 2.

Complete recovery of iron(III) ions from solution and, correspondingly, separation of Fe^{3+}–Zn^{2+} mixture is reached in the region of concentrations of the initial two-component solution to c_{Fe} = 0.008 M. The reaction causes solid phase to convert to iron phosphate and two-component solution to transform into multicomponent solution of zinc(II) nitrate. In this case, the concentration of zinc(II) ions in the equilibrium solutions is 2.5–3.5 times higher than in the initial two-component solutions.

Phosphates containing none of the cations being recovered can be also used for selective recovery of ions from mixture. This is especially important in the case when synthesis of metal phosphate is made difficult.

As known from the literature [1, 7–8], calcium phosphate excellently recovers iron(II) and zinc(II) ions from solution. Its solubility product exceeds by many orders of magnitude the solubility products of iron and zinc phosphates. Therefore, calcium hydrophosphate $CaHPO_4{\cdot}2H_2O$ was used to study separation of Fe^{3+}–Zn^{2+} mixture.

Tables 2–4 list the results of analysis of the initial and equilibrium solutions in the systems $CaHPO_4{\cdot}2H_2O$–$Zn(NO_3)_2$, $Ca{\times}HPO_4{\cdot}2H_2O$–$Fe(NO_3)_3$, and $CaHPO_4{\cdot}2H_2O$–$Fe(NO_3)_3$+$Zn(NO_3)_2$.

Figures 2a, 3a present the isotherms of zinc(II) and iron(III) absorption from one-component solutions of $Zn(NO_3)_2$ and $Fe(NO_3)_3$ and Fig. 3c, isotherm of iron (III) absorption from two-component $Fe(NO_3)_3$+$Zn(NO_3)_2$ solution. Variation of the recovery degree of the above ions from one- and two-component solutions are shown in Figs. 2b, 3b.

The isotherm of zinc(II) absorption with calcium phosphate has a traditional form, i.e., no anomalies are present, and it passes a horizontal plateau at A_{Zn} = 4.3 mmol g^{-1} (Fig. 2a). The isotherms of iron(III) sorption with calcium phosphate in one- and two-component solutions have the same run (Fig.3a,c) as those in the considered system $Zn_3{\times}(PO_4)_2{\cdot}4H_2O$–$Fe(NO_3)_3$ solutions (Fig. 1a), i.e., pass a maximum.

The comparison of the dependences of zinc(II) and iron(III) recovery on the concentration of initial two-component solution (Fig. 4) shows that the degree of iron recovery with calcium phosphate reaches 100%

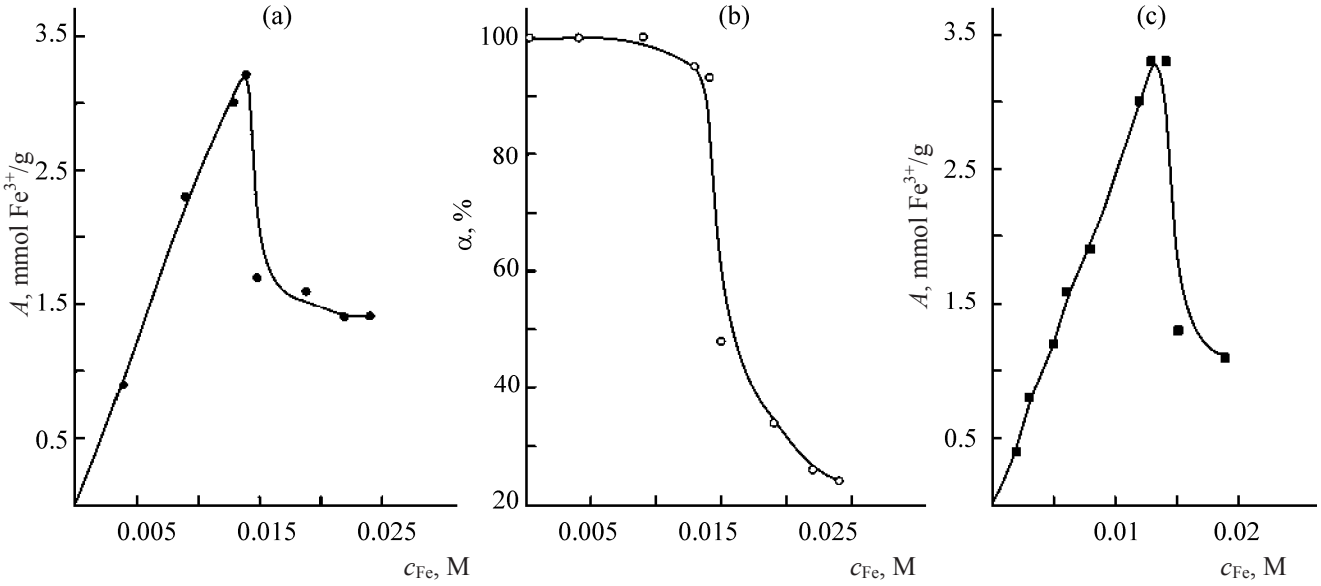

Fig. 3. (a, c) Sorption isotherms and (b) the degree of ion recovery with calcium phosphate vs. the initial concentration of Fe^{3+} ions for (a, b) $Fe(NO_3)_3$ solutions and (c) $Fe(NO_3)_3 + Zn(NO_3)_2$ mixture.

and the degree of zinc(II) recovery is nearly zero within a pronounced region at $c_{\Sigma(Fe+Zn)}$ = 0.014–0.031 M. This region corresponds to selective recovery of iron(III) ions and (at $m_{sor}:V_{sol}$ = 1:250) should be used for selective recovery of iron(III) ions from a mixture with zinc(II).

It should be mentioned that the sorption of nonferrous metals with calcium phosphate is due to heterogeneous substitution with displacement of calcium(II) ions into the solution by the reaction (1)–(4). Hence, the solution obtained after iron(III) recovery is a mixture of zinc(II) and calcium(II) ions. Separation of mixture constituted by nonferrous and alkaline-earth metal ions is not difficult. First, zinc may be removed by the same way as iron, i.e., by addition of new calcium phosphate sample. Second, similar mixtures can be easily separated by the precipitation of zinc(II) in the form of hydroxide at pH 6–8, with calcium hydroxide not precipitated.

The results obtained can be used in processing electrolytic zinc plating baths for iron parts. After removal of iron(III) from spent solutions, zinc electrolyte may recycled.

CONCLUSIONS

Zinc and calcium phosphates, when brought in contact with the solution containing Fe^{3+} and Zn^{2+} ions (the ratio $m_{sor}:V_{sol}$ = 1:250, where m is the weight of sorbent and V, the volume of solution) at the ion concentration in solution $c_{\Sigma(Fe+Zn)}$ = 0.014–0.031 M are selective sorbents for iron(III) ions and can be used for quantitative separation of Fe^{3+}–Zn^{2+} mixture.

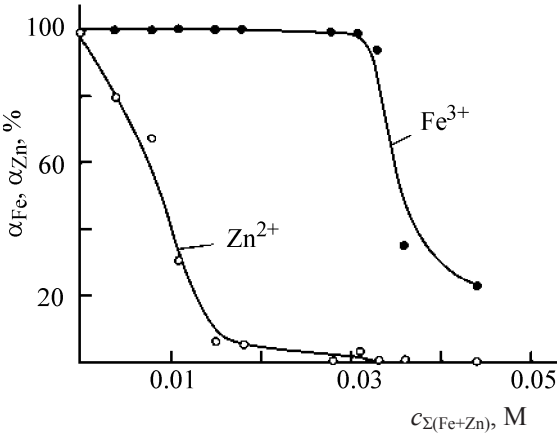

Fig. 4. Degree of Fe^{3+} (α_{Fe}) and Zn^{2+} (α_{Zn}) recovery from solution with calcium phosphate vs. the initial total concentration of ions $c_{\Sigma(Fe+Zn)}$ in $Fe(NO_3)_3 + Zn(NO_3)_2$ mixture.

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