

Sorption of Sc(III) and Fe(III) ions by a cation exchanger from solutions of concentrated acids and organic solvents

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The sorption of Sc(III) and Fe(III) ions by a strongly acidic cation exchanger from concentrated solutions of nitric acid and sulfuric acid in aqueous and mixed media (acetic acid and ethanol) was followed. The increased sorption of Sc(III) and Fe(III) from solutions with a high ionic strength and low permittivity is connected mainly with alterations of ionic solvation, the water activity, activity coefficients of the acids, and the increased interaction of ions in the ion-exchanger phase.

The exchange distribution equilibria of metal ions in solutions containing complexing agents (inorganic and organic acids) and organic solvents have been recently intensively studied [1]. At the distribution of the complexes of metal ions the extraction process [2] accompanying the ion exchange has frequently been observed. The systems with hydrochloric and perchloric acids have often been investigated [3–7]; however, attention has also been paid to concentrated solutions of other electrolytes in order to characterize in detail the exchange reactions and their anomalous course in these media. So far only limited information has been available on the exchange of cations from concentrated solutions of nitric [8] or sulfuric [9] acids. Such a situation might be determined also by a very small number of cations forming complexes in the medium of nitric or sulfuric acids, capable of sorption on an anion exchanger. Furthermore, the chemical stability of ion exchangers in concentrated nitric acid solutions is also limited. The purpose of this work is to provide further information on the selectivity of the cation exchanger in solutions of strong acids and on the influence of an organic solvent upon the anomalous sorption of Sc(III) and Fe(III) ions.

Experimental

Ion exchanger

All the experiments were carried out with a strongly acidic cation-exchange resin (Ostion KSX8; Research Institute of Synthetic Resins and Varnishes, Pardubice); its capacity was 5.10 mval/g of dry exchanger in the H⁺ form, granulation of the swollen resin being 0.3–0.8 mm. The exchanger in the H⁺ form purified by the usual method was air-dried at room temperature (22 ± 1°C) to constant weight and stored in a well-stoppered bottle. Parallel determinations of the water content and the capacity (Czechoslovak Standard 64 0920) of this exchanger were carried out. The total water content

of the exchanger and the moisture coefficient (Czechoslovak Standard 64 0902) were determined by drying a sample of the exchanger at 105–110°C to constant weight. The moisture coefficient is defined as a ratio between the sample weights of the dried and swollen ion exchanger.

Experiments

The prepared cation exchanger (with the known water content) in the H^+ form was weighed (400 ± 1 mg) into a polythene bottle. A solution of acid (10.0 ml) and a solution of Sc(III) or Fe(III) in acid (1.00 ml) of the same concentration were added and the mixture was shaken for 24 hrs at room temperature ($22 \pm 1^\circ C$) [13]. More precise temperature control was not necessary since the temperature gradients of the solution density were only 0.1–0.2% per $1^\circ C$ and the temperature coefficient of swelling of the exchanger was very small [14]. After establishing the equilibrium, the exchanger was separated from the solution and the content of Sc(III) or Fe(III) in the solution was determined by the activity measurements. The calibration curve used for the determination of the cation content was constructed from the results of measurements of a set of reference solutions with known concentrations of Sc(III) or Fe(III) and reagents in the studied range.

The distribution coefficient of Sc(III) and Fe(III) was calculated from the equation

$$D_g = \frac{(\text{imp/min/ml before equil.} - \text{imp/min/ml after equil.})}{(\text{imp/min/ml after equil.})} \frac{V}{G}, \quad (1)$$

where V (in ml) is the volume of the aqueous phase and G (in g) the amount of anhydrous cation exchanger. It was calculated by multiplying the sample weight of the exchanger dried at room temperature by the moisture coefficient.

The used radioactive solutions of ^{46}Sc were prepared from the commercial ScCl_3 (GDR) by evaporation and dissolving in nitric or sulfuric acid. The used radioactive solutions ^{55}Fe and ^{59}Fe were prepared from commercial FeCl_3 (USSR) by the same procedure. The concentration of ^{46}Sc in the prepared solution was 1×10^{-3} M-Sc(III) in 0.1 M acid, the specific activity being 0.114 $\mu\text{Ci/ml}$. The concentration of the solution of ^{55}Fe and ^{59}Fe was 1×10^{-2} M-Fe(III) and its specific activity 2 $\mu\text{Ci/ml}$. γ -Radiation was measured by a probe Tesla NAQ.232 connected with a counter Va-M-15D Vakutronik (GDR).

Solutions of nitric acid and sulfuric acid in mixed media were prepared from the stock solutions, 10 M- HNO_3 and 10 M- H_2SO_4 , by mixing with calculated amount of water and organic solvent (with the known water content).

Results and discussion

A comparison of the sorption of Sc(III) and Fe(III) ions shows their different behaviour in nitric acid and sulfuric acid media (Figs. 1–6). In the media with lower concentration of acids (0.5–2 M), a more expressive decrease of the distribution coefficients is seen in solutions of sulfuric than in those of nitric acid. It is connected with the complexing character of the basic electrolyte and with the formation of anionic complexes which are not sorbed on cation exchanger under the given conditions. A more marked penetration of sulfuric or nitric acid into the ion-exchanger phase (Tables 1 and 2) facilitates interactions of cations and anions as well as the extraction of ionic pairs (e.g. $H^+\text{Fe}(\text{SO}_4)_2^-$) from the aqueous into the ion-exchanger phase. It brings about an increase of the distribution coefficients at concentrations above 6 M.

The distribution curves of Sc(III) and Fe(III) ions show a relatively smaller increase of sorption in concentrated solutions of sulfuric or nitric acid (5–10 M) than in solutions of perchloric acid [12]. The water activity does not decrease so considerably in concentrated solutions (5–10 M) of the former acids as in solutions of the latter (Table 3). The degree of dehydration of cations is thus lower and their interactions with $R-SO_3^-$ ions of the exchanger are weaker. It results in a small rise of the distribution coefficients.

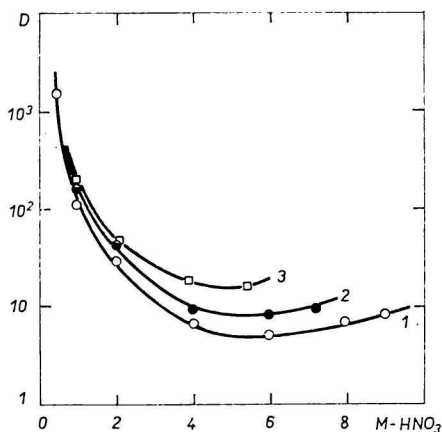


Fig. 1. Dependence of the distribution coefficient of Sc(III) on the concentration of nitric acid.

1. 0%; 2. 20%; 3. 40% acetic acid.

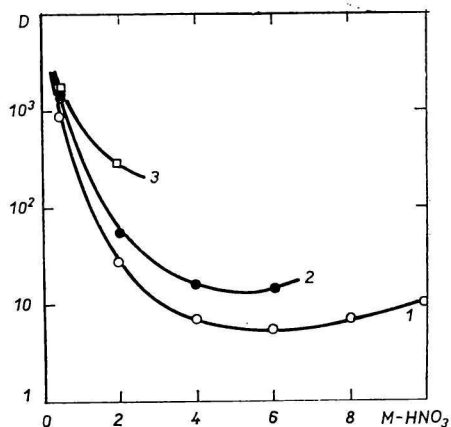


Fig. 2. Dependence of the distribution coefficient of Fe(III) on the concentration of nitric acid.

1. 0%; 2. 40%; 3. 80% acetic acid.

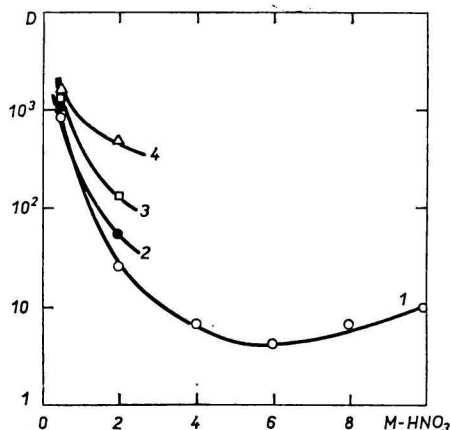


Fig. 3. Dependence of the distribution coefficient of Fe(III) on the concentration of nitric acid.

1. 0%; 2. 20%; 3. 40%; 4. 80% ethanol.

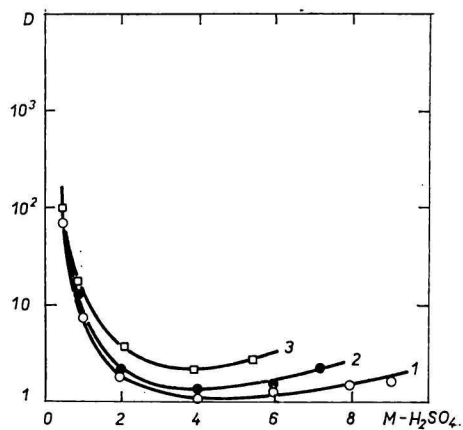


Fig. 4. Dependence of the distribution coefficient of Sc(III) on the concentration of sulfuric acid.

1. 0%; 2. 20%; 3. 40% acetic acid.

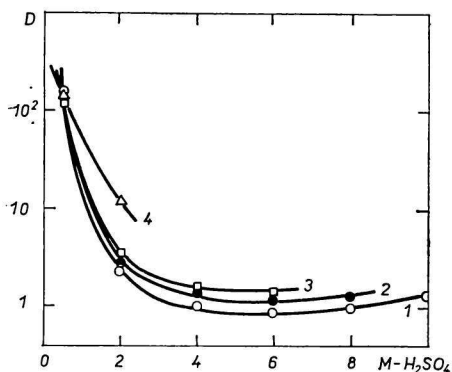


Fig. 5. Dependence of the distribution coefficient of Fe(III) on the concentration of sulfuric acid.

1. 0%; 2. 20%; 3. 40%; 4. 80% acetic acid.

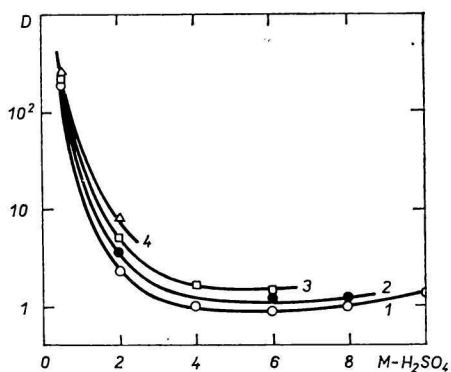


Fig. 6. Dependence of the distribution coefficient of Fe(III) on the concentration of sulfuric acid.

1. 0%; 2. 20%; 3. 40%; 4. 80% ethanol.

Table 1

Dependence of the molality of nitric acid sorbed in the cation-exchanger phase on the composition of the external solution (M-HNO₃, % org.) [10]

Concentration	0% HAc	20% HAc	40% HAc	60% HAc
1	0.20	0.20	0.20	0.25
2	0.59	0.54	0.64	0.90
4	1.90	1.70	2.10	2.72
6	4.00	3.61	4.25	
8	6.75	6.33		
10	10.6			

Table 2

Dependence of the molality of sulfuric acid sorbed in the cation-exchanger phase on the composition of the external solution (M-H₂SO₄, % org.) [11]

Concentration	0% HAc	20% HAc	40% HAc	60% HAc
1	0.17	0.14	0.19	0.23
2	0.48	0.43	0.45	0.67
4	1.70	1.43	1.59	2.03
6	3.80	3.25	3.65	
8	7.30	5.90		
10	11.9			

Table 3

Activity of water in solutions of acids ($a_{\text{H}_2\text{O}}$) [12]

Concentration	HClO ₄	HNO ₃	H ₂ SO ₄
0.1	0.997	0.997	0.996
0.5	0.982	0.983	0.981
1.0	0.961	0.964	0.960
2.0	0.905	0.920	0.903
4.0	0.724	0.808	0.721
6.0	0.456	0.681	0.479
8.0	0.191	0.555	0.258
10.0	0.046	0.436	0.108

A good relation was found between the course of the distribution curves of Sc(III) and Fe(III) in concentrated nitric or sulfuric acid solutions and the mean activity coefficients of these acids (Table 4). The exchange of ions in concentrated solutions represents specific problems which are not encountered in diluted aqueous solutions. A change of the ratio of the activity coefficients of the exchanged ions in the external solution may be negligible at high dilution but it becomes an important factor at higher concentrations of the basic electrolyte.

Table 4

Mean activity coefficients of acids (γ_{\pm}) [12]

Concentration	HNO ₃	H ₂ SO ₄
0.1	0.790	0.265
0.5	0.720	0.155
1.0	0.725	0.131
2.0	0.809	0.129
4.0	1.157	0.199
6.0	1.607	0.389
8.0	2.08	0.802
10.0	2.52	1.610

The main characteristic of the ion exchange in concentrated solutions of acids is a partial destruction of the water structure and a change from the aqueous solvation of ions to the formation of complexes with co-ions of the basic electrolyte or $\text{R}-\text{SO}_3^-$ ions of the ion exchanger. In comparison with diluted solutions of acids, the ion-exchange equilibria may therefore deviate from the course determined by the mass-action law. If association of cations and anions or the more usual complex formation occur, the course of the exchange equilibrium



depends strongly on the nature of the electrolyte and its concentration in the external solution. It is owing to the competitive equilibria, e.g.



The presence of an organic solvent (ethanol, acetic acid) increases the distribution coefficients of Sc(III) and Fe(III) in solutions of both nitric and sulfuric acids. This effect is quite common at high concentrations (5–10 M) of the basic electrolyte. At lower concentrations (0.5–2 M) it occurs only when the formation of anionic complexes of metal ions with the basic electrolyte does not predominate over the interactions of cations with the functional groups of the ion exchanger. Contrary to expectation the sorption of Fe(III) in the mixed medium of nitric acid and acetic acid is not higher than that in the medium of nitric acid and ethanol, but is lower or equal. It might indicate that the influence of the chemical nature of the solvent and its solvation ability upon the distribution equilibria of Fe(III) have to be considered beside the permittivity of the medium. Solutions with acetic acid have lower permittivity than those with ethanol at equal concentrations.

The degree of dissociation of the dissolved electrolyte in the mixed medium decreases with the increasing concentration of the organic component. If the state is reached where the Donnan potential (affecting only ions) does not determine the exclusion of co-ions in the diluted solutions either, the penetration of the basic electrolyte into the ion-exchanger phase becomes more important than the stoichiometric exchange of ions (Tables 1 and 2). Under these conditions the exchange process can be considered as a distribution of the solute (H_2SO_4 , $\text{H}^+\text{Fe}(\text{SO}_4)_2^-$) between the phase of the swollen ion exchanger and the external solution.

The generally known increase of selectivity with decreasing swelling of the ion exchanger appears to be valid also in the mixed media of nitric and sulfuric acids.

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