

ANION-EXCHANGE BEHAVIOUR OF 12 ELEMENTS IN H₂SO₄ AND HF-H₂SO₄ MEDIUM

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Anion-exchange data have been obtained for the elements As, Hf, Mo, Nb, Pa, Re, Sb, Sn, Ta, Tc, W, and Zr in 0.1 to 10M H₂SO₄ and in HF-H₂SO₄ mixtures of combination extending from 0.1 to 10M HF and from 0.1 to 10M H₂SO₄. The distribution ratios for mixed solutions are presented in form of adsorption contour lines.

Introduction

Available data on the anion exchange distribution coefficients of elements in sulfuric acid and sulfuric acid-hydrofluoric acid solutions is, as compared with other mineral acids and their mixtures, incomplete. This is especially true for easily hydrolyzable elements which tend to form polynuclear species and/or hydroxidic precipitates at low concentration of sulfuric acid in the absence of some other strong complexing agents.

The adsorption of some fission products and actinides in the system Dowex-2 and 0.1-36N H₂SO₄ was studied by BUNNEY et al.¹ DANIELSSON² has reported the anion-exchange behaviour of 26 elements on Dowex-1 in 0.05-10N H₂SO₄. The refractory metals Nb, Ta and W were not included in this study because they easily form hydrolytic precipitates at the applied concentration (about 10⁻³M) in the absence of suitable complex agents. KURODA et al.³ have investigated the adsorption characteristics of 20 elements on weakly basic resin Amberlite CG-4B in sulfuric acid varying from 0.005 to 2M, whereby the hydrolytic reactions of several elements were prevented by addition of hydrogen peroxide. Finally, anion-exchange behaviour of 52 elements on Bio-Rad AG1X8 was studied by STRELOW and BOTHMA⁴ in 0.01 to 4N H₂SO₄. The distribution coefficients for elements strongly tending to hydrolysis were measured in the presence of H₂O₂, too.

Much less data are available for anion exchange in the mixture HF-H₂SO₄. This

system was investigated only by DANIELSSON,⁵ who reported distribution data of 27 elements on Dowex-1X8 for two concentrations, i.e., of 0.1 and 1N of both acids.

Sulfuric acid, either alone or in a mixture with other inorganic acids, is an important decomposition reagent for many metals, and ceramic, geological and biological samples. The medium HF-H₂SO₄ is often used for the separation of many elements, especially of Hf, Nb, Ta, Th, U and Zr by extraction.⁶⁻¹¹ Due to its high boiling point, sulfuric acid can hardly be removed from the solute by evaporation. Therefore, knowledge about the influence of this acid as accompanying medium component on the ion exchange of the elements is of great practical importance. In our previous paper, the adsorption behaviour of some elements on Dowex-1X8 in HF-HNO₃,¹² HF-HCl¹³ and HF-NH₄F¹⁴ was described. Continuing this series, in this work, the adsorption behaviour of 12 elements on Dowex-1X8 in 0.1 to 10M H₂SO₄ and 10 elements in HF-H₂SO₄ mixtures at concentration combinations covering the range between 0.1 to 10M for both acids was studied. The results obtained for-niobium and tantalum in HF-H₂SO₄ medium were published recently.¹⁵

Experimental

The resin used (Dowex-1X8) was converted to the sulfate form by pretreatment with 1M H₂SO₄, then it was washed thoroughly with deionized water and dried at 60 °C overnight. The distribution ratios were measured under static conditions (batch method) by means of the radiotracer ⁷⁶As, ¹⁸¹Hf, ⁹⁹Mo, ⁹⁵Nb, ²³³Pa, ¹⁸⁸Re, ¹²⁴Sb, ¹¹³Sn, ¹⁸²Ta, ^{99m}Tc, ¹⁸⁷W and ⁹⁵Zr. With exception of Pa and Tc, for each element studied, the solution contained 0.1–1 μg of inactive carrier per ml. The solutions of the radiotracers were prepared in 10M H₂SO₄ and diluted with water 1:9 shortly before use. All other experimental conditions were the same as reported earlier.¹³

Results and discussion

Distribution in sulfuric acid solutions

The distribution ratios obtained are given in Figs 1a and 1b. Elements for which only a very weak or no adsorption in sulfuric acid solutions could be expected² were not included in this study. The data obtained for elements easily hydrolyzable at lower H₂SO₄ concentrations deviated largely from the published results, first of all from that by DANIELSSON² using the same resin. This discrepancy can be caused

by two factors: the concentration of the studied elements in the solution, and/or the pre-history of the solution.

The concentration of the elements in this work was at least by a factor of 100 lower than that applied by DANIELSSON.² In the case of molybdenum, he reported an increase of the distribution coefficient with increasing total concentration of the metal.

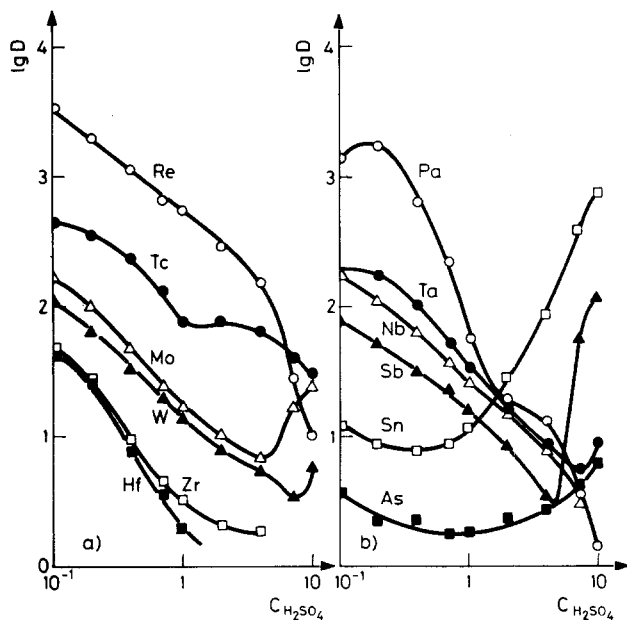


Fig. 1. Adsorption of elements on DOWEX-1X8 in sulfuric acid solutions; D – distribution ratio; $C_{H_2SO_4}$ – molar concentration of sulfuric acid

The pre-history of the solutions can also play an important role. In this work, the stock solutions were 10M with sulfuric acid, leading to a quantitative dehydrolysis of all elements studied. Only low acidic or even basic stock solutions were applied by other authors, in which, in many cases, the formation of hydrolytic species can be expected. As a result of the hydrolysis, polynuclear ions and/or neutral hydroxidic species are adsorbed instead of simple anions. These phenomena have already been discussed by STRELOW and BOTHMA.⁵ Both of these effects have to be taken into account in separations of the elements Hf, Mo, Nb, Ta, W and Zr under dynamic conditions.

As is evident from Fig. 1b, protactinium tends to form species with relatively high distribution ratios. Nearly the same adsorption behaviour was observed also in sulfuric acid medium on cation exchangers and silica gel.^{16,17} The retention of an

element on such different sorbents (anion exchanger, cation exchanger and neutral silica gel) can take place only on the assumption that an adsorption mechanism different from that of ion exchange is actual. Based on this it seems very doubtful that anionic sulfato complexes of protactinium are retained in this case; the molecular adsorption of neutral complexes is more probable for all above mentioned sorbents. This assumption is also based on the similarities of the adsorption isotherms. A saddle-like plot was also obtained for the adsorption of protactinium on silica gel in sulfuric acid.¹⁷ The saddle point on the Pa-curve in 2–7M H₂SO₄ might be connected with the presence of bisulfate ions in this concentration region of H₂SO₄ solutions.¹⁸

Figure 1 shows that the elements Hf, Nb, Ta and Zr are adsorbed much weaker than protactinium. The adsorption of hydrolytic species can also be assumed here, because these elements are retained predominantly in dilute solutions of sulfuric acid. It is known that the complete dehydrolysis of these elements takes place only at high acidities.

A peculiar behaviour was observed in the adsorption of antimony(V), tin(IV) and arsenic(V). At the beginning, the distribution ratio decreases with increasing H₂SO₄-concentration and then it reaches a minimum being sharp for antimony (at about 6M), and rather broad and flat for tin (at about 0.5M) and arsenic (at about 1M). With further increase of the H₂SO₄-concentration, the distribution ratio strongly increases (only moderate increase in the case of arsenic). This effect of sulfuric acid can be explained by dehydrolysis of the elements in the descending part of the curves and by formation of the anions Sn(HSO₄)₅⁻ and Sb(HSO₄)₆⁻ in more concentrated sulfuric acid solutions (ascending part of the curves). In concentrated solutions of sulfuric acid, the complexation by HSO₄⁻ might be more probable than that by bivalent SO₄²⁻ ions. The steep slope of the antimony curve as well as the comparison with adsorption behaviour of these elements in hydrochloric acid solutions¹³ support this assumption.

The elements technetium and rhenium are strongly retained on the resin, especially at low H₂SO₄-concentrations. The decreasing adsorbability with increasing concentration of sulfuric acid indicates that pertechnetate and perhenate ions are significantly involved in the adsorption process. So far, we have no conclusive explanation for the irregularities of the course of both curves.

Distribution in HF–H₂SO₄ solutions

The use of hydrofluoric acid in combinations with other inorganic acids for anion exchange separations offers several advantages. Hydrofluoric acid forms stable complexes with many metals to be separated and, in some cases, it prevents hydrolytic precipitation. Due to the above mentioned complications connected with hydrolysis

in sulfuric acid solutions, the use of hydrofluoric acid as a complexing agent is a very attractive way to prevent hydrolysis. The results obtained for the mixed H_2SO_4 -HF medium are given in Figs 2-11 in form of contour lines. The number on the curves denotes the respective value of the distribution ratio in the corresponding coordinates $\log C_{HF}$ vs. $\log C_{H_2SO_4}$.¹¹

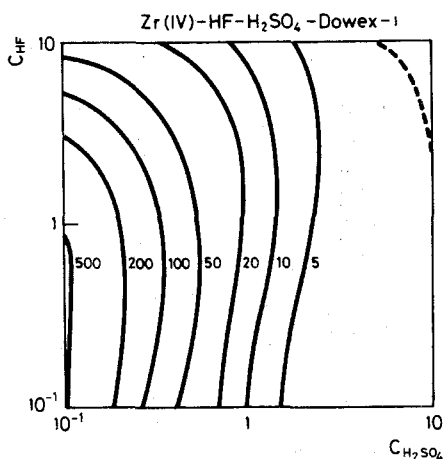


Fig. 2. Figures 2-11 show contour plots of the elements on DOWEX-1×8 in HF-H₂SO₄ medium. The number on the curves denotes the respective value of the distribution ratio. The retention of zirconium

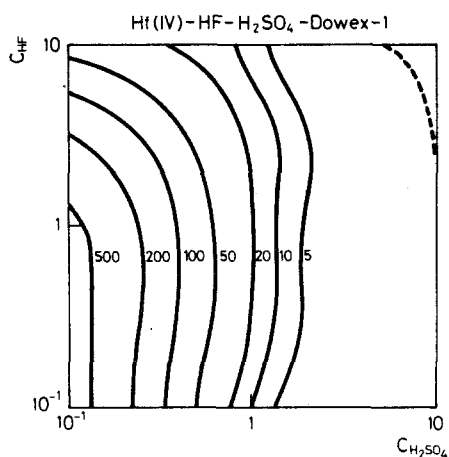


Fig. 3. Retention of hafnium

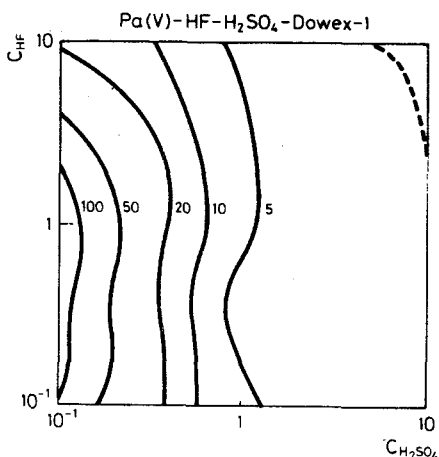


Fig. 4. Retention of protactinium

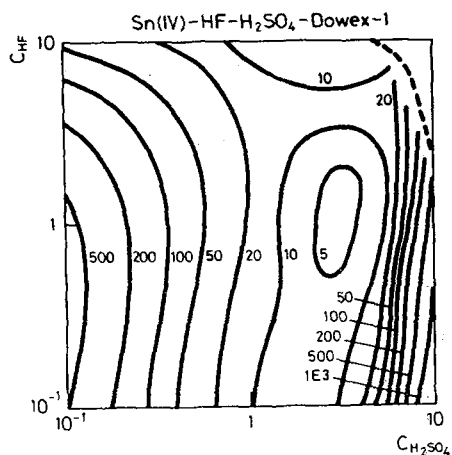


Fig. 5. Retention of tin(IV)

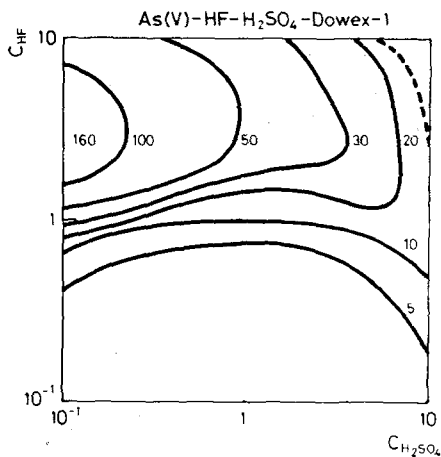


Fig. 6. Retention of arsenic(V)

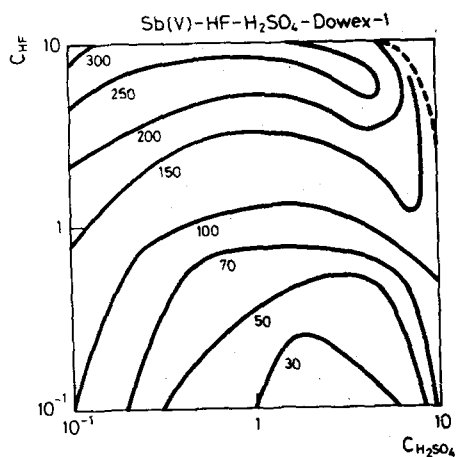


Fig. 7. Retention of antimony(V)

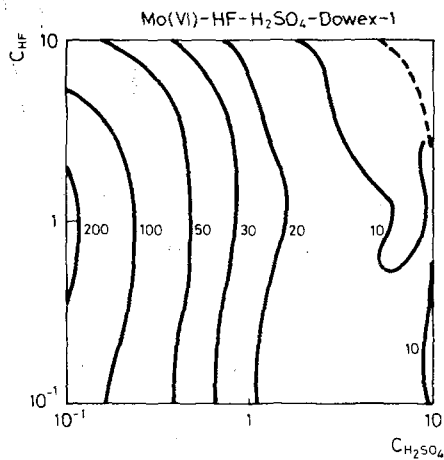


Fig. 8. Retention of molybdenum

Zirconium, hafnium and protactinium. From comparison of the results given in Figs 2–4 with those given earlier for pure hydrofluoric acid solutions,¹² it is evident that the adsorption behaviour of these elements is strongly influenced by sulfuric acid. The respective contour lines run nearly parallel to the C_{HF} -axis. Although in pure sulfuric acid solutions the distribution ratio of protactinium is very high (see Fig. 1b), in mixed HF– H_2SO_4 solutions, the presence of sulfuric acid decreases the adsorbability in the following order: $Hf \approx Zr > Pa$. The form of the contour lines allows to assume that under the given conditions neither sulfates nor fluoro-sulfato complexes are adsorbed

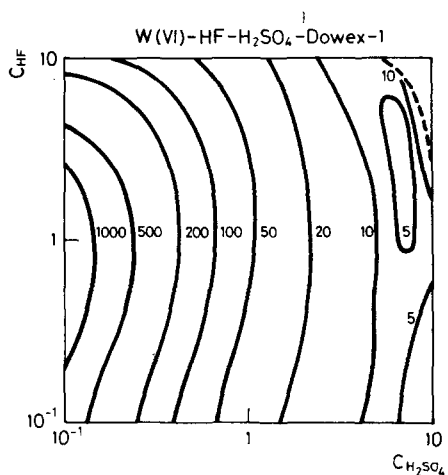


Fig. 9. Retention of tungsten

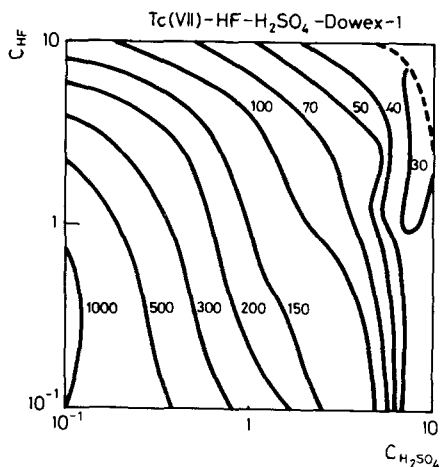


Fig. 10. Retention of technetium(VII)

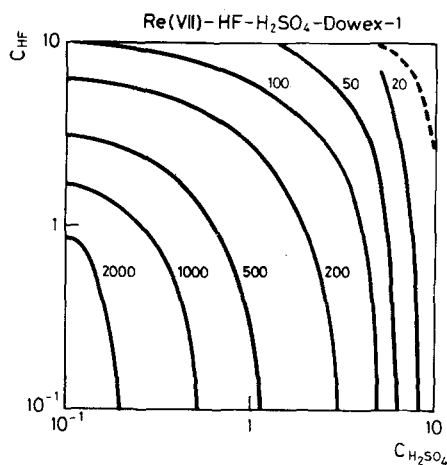


Fig. 11. Retention of rhenium(VII)

on Dowex-1X8. The following factors could cause the decrease of the adsorbability in the presence of sulfuric acid: (a) decrease of the dissociation of hydrofluoric acid with increasing concentration of sulfuric acid, (b) formation of sulfato complexes with low distribution constants, (c) competitive adsorption of sulfate anions on the resin. A quantitative elution of these elements can be expected under dynamic conditions with solutions being 1M or more in sulfuric acid.

Tin(IV). In mixed HF-H₂SO₄ medium, a quite different adsorption behaviour can be observed for tin as compared with the above discussed elements (Fig. 5). This

is caused by the formation of well adsorbable sulfato complexes in solutions with higher concentration of sulfuric acid (see Fig. 1b). The contour lines obtained in solutions with sulfuric acid concentration $< 1\text{M}$ have a similar character to those obtained for zirconium. In solution with H_2SO_4 -concentration $\geq 3\text{M}$, a second adsorption peak occurs, whereby the maximum achievable D-values exceed somewhat those obtained in pure sulfuric acid solutions. These two adsorption peaks are separated by a distinct minimum at 1M HF and 3M H_2SO_4 .

In the case of tin, it can be assumed that the adsorption in mixed hydrofluoric acid solutions with low and high sulfuric acid concentration is realized via the monoligand complexes SnF_5^- and $\text{Sn}(\text{HSO}_4)_5^-$, respectively. The presence of these two acids is advantageous for the dehydrolysis of tin species. Mixed solutions being about 10M with H_2SO_4 and 0.1M with HF are suitable for highly selective separation of tin under dynamic conditions. From this medium, antimony is retained also on the column (see below), but these two elements can be separated from each other by elution of tin with 3M $\text{H}_2\text{SO}_4 + 1\text{M}$ HF.

Arsenic(V) and antimony(V). As arsenic and antimony are more strongly adsorbed at higher concentrations of hydrofluoric acid,¹⁴ the contour lines of these elements (Figs 6 and 7) have a quite different form. In contrary to other elements studied, they show a horizontal course, and the diminishing influence of sulphuric acid on the adsorption of fluoro complexes is weaker as compared with the elements discussed before. The form of the contour lines indicates that, in addition to the monoligand complexes, mixed fluoro-sulfato complexes might also be adsorbed. This makes itself felt especially in the case of antimony (see Fig. 7), where the peak in the upper-left part is probably caused by the adsorption of SbF_6^- species; it passes gradually over to the maximum in the lower-right part, where the adsorption of the complexes $\text{Sb}(\text{HSO}_4)_6^-$ can be assumed. Like in the HF-HCl medium,¹¹ the adsorption of complexes with the central ion SbO^{3+} can be expected at low concentrations of HF and H_2SO_4 .

Molybdenum and tungsten. The adsorption behaviour of these two elements is somewhat similar to that of zirconium and hafnium, however, the decrease of D with increasing concentration of sulfuric acid is weaker. It can be assumed that the formation of monoligand sulfato complexes is suppressed in solutions at concentrations of sulfuric acid lower than 10M . The comparison with results obtained in HF-HCl medium¹³ supports this assumption. The occurrence of the maximum D-value at about 1M HF and low sulfuric acid concentrations is somewhat surprising as in pure hydrofluoric acid, the D-values decrease with increasing HF-concentration.¹⁴ This shift can be explained by dehydrolysis of the ions MeO_2^{2+} to MeO^{4+} which is influenced by the presence of a strong acid. The differences between the behaviour

of Mo and W are relatively small; they offer no possibilities for a meaningful separation of these two elements.

Technetium and rhenium. The adsorption contour lines of the heptavalent elements represent a band of nearly symmetrical hyperbolas with a center in the upper right edge (see Figs 10 and 11). The adsorption of the anions TcO_4^- and ReO_4^- seems to be very probable. Its decrease with increasing concentration of both acids can be explained by competitive retention of fluorides and sulfates. The irregularities observed for technetium in Fig. 10 may be caused by a partial reduction of the pertechnetate ions.

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