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Adsorption of a Number of Elements from Sulphuric Acid Solutions by Anion Exchange

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Studies of ion exchange separations in some mixed acid systems and their application to the analysis of metals and alloys are in progress at the Swedish Institute for Metal Research. Necessary systematic anion exchange data for elements in sulphuric acid solutions are lacking. In this paper the anion exchange characteristics of 26 metal ions in various H_2SO_4 solutions are reported. Molybdenum(VI) and zirconium(IV) are adsorbed strongly whereas most other metals show negligible adsorption. The effect of hydrogen peroxide on the adsorption of Ti(IV), V(V), Mo(VI) and Fe(III) in H_2SO_4 solutions has also been studied.

Anion exchange data for metals in mixtures of HF and HCl, first presented by Kraus and Nelson,[1,2] have been of great importance for the development of separation methods in the chemical analysis of metals and alloys. It was thought that adsorption from other mixed acid systems such as $HF-H_2SO_4$ and $HF-HNO_3$ would differ appreciably from the system HF—HCl and thus give rise to new separation methods.

An investigation of the pure acid systems involved is, however, highly valuable as the basis of a study of the adsorption in mixed acids. The adsorption of metals from HNO_3 solutions by the strongly basic anion exchange resin Dowex 1 has recently been studied in detail [3,4] and data are also available for HF solutions.[5] A similiar systematic investigation for H_2SO_4 solutions is lacking.

In this paper adsorption data for a number of elements from H_2SO_4 solutions by Dowex 1 are reported. The study has been confined to elements of interest in the analysis of metallurgical products. For this reason U(VI) and Th(IV) which have received most attention in this medium, have been omitted.

EXPERIMENTAL

Resin. The resin used was Dowex 1X8, 100—200 mesh, supplied in the chloride form. Before use it was treated in a column alternately with 1 N HCl and 1 N NaOH and converted completely to the sulphate form with 1 N H_2SO_4 and finally with water until the effluent was free from sulphate and almost neutral (pH 5). For the column experiments the coarsest and finest particles were removed. The resin was dried to constant weight in a vacuum desiccator over the system $Na_2Cr_2O_7 \cdot 2H_2O$ + saturated solution (rel. humidity 52 % at 20°C).

The water content of this "wet" resin was found to be 21.3 % (range ± 0.3 %) by heating samples to constant weight at 110°C. This value was used for the calculation of distribution coefficients. Later some thermogravimetric measurements in vacuum at 70°C indicated this result to be about 0.5 % too low.

The capacity was 3.45 mequiv./g dry resin, both for the sulphate and chloride forms determined after column elution with *ca.* 3 N NaOH.

Reagents and solutions. All chemicals were of reagent grade quality. Standard solutions were prepared from chemically or spectrographically pure metals, oxides or sulphates. For the solutions of V, Mo, As and Sb(V) the alkali salts of the corresponding acids were used.

Neutralization with alkali was avoided. In the case of free acid in the metal sulphates correction was made in the added amounts of sulphuric acid.

Procedure. The distribution coefficients were determined by the batch equilibrium method and the column elution method.[1]

In the *batch method* 1 g portions of resin (21.3 % H_2O) were equilibrated for 16 h in a mechanical shaker with 20 ml of 5×10^{-3} M solutions of the metal at different H_2SO_4 concentrations. The solutions were then filtered through sintered glass filters of medium porosity and analysed.

Lower metal concentrations were used for Bi (10^{-4} M), Fe(III) and Ti(IV) (10^{-3} M) and Sb(V) (5×10^{-4} M) at the lowest acid concentrations in order to minimize the risk of hydrolytic precipitation. For the same reason Sn(IV) and Sb(III) (5×10^{-4} M) were studied only in H_2SO_4 not less than 1 N.

All elements (except Sn(IV) and Sb(III)) were tested separately at the following initial normalities of H_2SO_4: 0.1, 0.3, 1.0, 3.0, and 10.0. For many elements intermediate normalities were also investigated. All determinations were made at least in duplicate.

Owing to the reaction

$$SO_4^{2-}{}_{(resin)} + 2H^+ + SO_4^{2-} \rightleftharpoons 2HSO_4^-{}_{(resin)}$$

and some electrolyte invasion the acidity of the solutions decreased on equilibration (Table 1). This has been considered in the presentation of the results.

The distribution coefficients were calculated after equilibrium as

$$D = \frac{\text{mmoles metal on resin per g dry resin}}{\text{mmoles metal in solution per ml solution}}$$

In the *elution method* glass columns (internal diameter 0.95 cm) were used, containing w = 2.5—2.7 g (dry weight) of resin equilibrated with the appropriate acid solution. A small amount of metal (usually 0.2 ml of 0.1 M solution) was moved through the column at a flow rate of 0.4—0.5 cm/min and eluted with the appropriate acid. Fractions of 0.2—0.5 ml were collected and analysed.

Table 1. Normalities of H_2SO_4 before and after equilibration of 20 ml of H_2SO_4 solution with 1 g of "wet" resin in the batch procedure.

Before equil. (N)	0.100	0.200	0.300	0.500	1.00	3.00
After equil. (N)	0.052	0.129	0.216	0.400	0.89	2.91

For a certain acid concentration the maximum concentration of metal appeared after $v_{\max}$ ml. The distribution coefficient is given by

$$D = \frac{v_{\max}\ (\text{ml}) - i\ (\text{ml})}{w\ (\text{g})}$$

where i is the interstitial volume of the column.

The interstitial volume i was determined by elution of Ni with 0.1—0.5 N H_2SO_4. ($D_{\text{Ni}} = 0$ by the batch method).

The column elution method was used for elements with low values of D especially when difficulties from partial precipitation in the batch method were apprehended (*cf.* Fig. 1). The shape of the elution curve showed whether or not the operation was satisfactory.

Analytical methods. Most elements were determined colorimetrically by well established methods according to Sandell [6] or by complexometric titration according to Schwarzenbach.[7] X-Ray fluorescence analysis was used for Ag and La in the batch method and for several elements in the column elution experiments.

Zr was determined according to Young *et al.*,[8] Ti according to Sommer [9] and Mo essentially according to Kapron and Hehman.[10] The Beckman B and Elko II instruments were used for the colorimetric measurements.

The total metal concentration, irrespective of species, was determined. Thus analysis of solutions of V(V), partially reduced by the resin, was done after reoxidation. Elements very sensitive to reduction or oxidation such as Cr(VI), Mn(VII), Ce(IV), and Sn(II) were not investigated.

RESULTS AND DISCUSSION

Distribution coefficients were determined for 26 elements including different valency states in 0.05—10 N H_2SO_4. At appreciably higher concentrations degradation of the resin took place. Among the elements of special interest in the analysis of metallurgical products Ca, Pb, Nb, Ta, and W have been omitted; Ca and Pb form difficultly soluble sulphates, whilst, Nb, Ta, and W easily form hydrolytic precipitates in the absence of suitable complexing agents.

The investigated elements may be divided into three groups with regard to their adsorption characteristics: *A* No adsorption, *B* Adsorption only from H_2SO_4 below 1 N and *C* Strong adsorption.

A. No adsorption

This constitutes the main group. It contains elements with distribution coefficients $D \leq 1$ in 0.1—10 N H_2SO_4. It includes Be, Mg, La, Ce(III), V(IV), Mn(II), Fe(II), Co, Ni, Cu, Ag, Zn, Cd, Al, As(III), and Sb(V). Also Sn(IV) and Sb(III) have been placed here although they were studied only in H_2SO_4 1—10 N.

All these elements (except Sn(IV) and Sb(III)) showed insignificant adsorption in the batch experiments in $H_2SO_4 \geq 0.22$ N but a slight adsorption was observed at lower concentation of H_2SO_4 for La, Ce(III), V(IV), Ag, As(III), and Sb(V). In 0.10 N H_2SO_4 the elution method gave $D = 0.4$ for Ag and $D = 0.8$ for La and Ce.

The accuracy of the batch method at very low values of D is not entirely satisfactory and the results do not eliminate slight adsorption also of other elements in this region. Since these low adsorption levels are of limited interest for analytical purposes, they were not studied further.

Several of the elements in this group form strongly adsorbable chloride complexes,[1] indicating that large differences between HF—HCl and HF—H_2SO_4 solutions may be expected. In HNO_3 solutions adsorption has been reported only for La, Ce(III), and Sn(IV).[4]

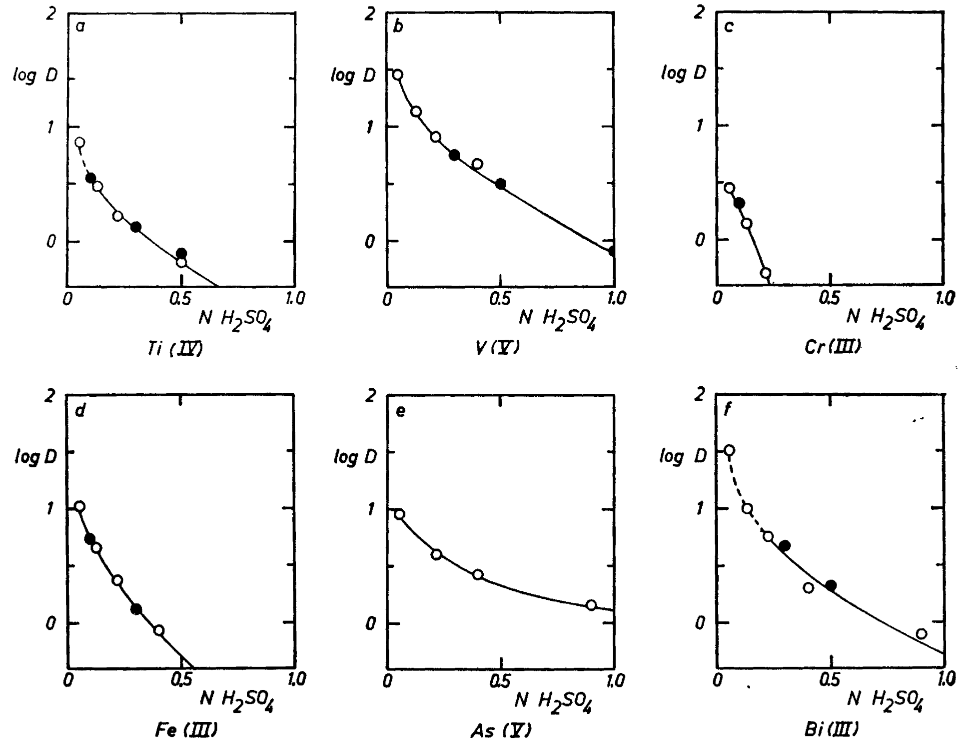

Fig. 1. Adsorption of Ti(IV), V(V), Cr(III), Fe(III), As(V), and Bi(III) by Dowex 1 from 0.05—1 N H_2SO_4. Batch method O, column method ●. Dashed line indicates region with less reliable results. (*Cf.* text Bi).

B. Adsorption only in H_2SO_4 below 1 N (Fig. 1)

To this group belong Ti(IV), V(V), Cr(III), Fe(III), As(V), and Bi(III). In all cases the adsorption increased with decreasing H_2SO_4 concentration. At the lowest acid concentrations, where the distribution coefficients rise to useful levels, analytical use is rendered difficult by the low metal solubilities encountered.

Titanium(IV) has been readily eluted with 0.1 N H_2SO_4 from a similar type of resin (Amberlite IRA-400).[11] In this study however, $D \geq 1$ was found for H_2SO_4 below *ca.* 0.4 N. No adsorption has been reported in low concentrations of HCl or HNO_3.

Vanadium(V) is rather strongly adsorbed in contrast to V(IV). Solutions of ammonium vanadate were used. Newly prepared solutions showed two maxima in the column elution experiments indicating two species not in rapid equilibrium. No adsorption from HCl and HNO_3 solutions has been reported at low acidities. In the presence of H_2O_2 the adsorption is increased markedly (Fig. 5).

Chromium(III) is adsorbed very weakly in the green as well as in the violet modification and differs only slightly from the elements in group A. Elution with 0.1 N H_2SO_4 gave $D = 2.1$.

Iron(III) was found to have the same adsorption characteristics as Ti(IV). Kraus and Nelson,[12] observed adsorption in H_2SO_4 of less than 0.1 M, the values of D increasing with decreasing concentration of H_2SO_4 to $D =$ *ca.* 100 in 0.001 M H_2SO_4. Fe(III) is not adsorbed from HNO_3 and only from HCl > 1 N.

Bismuth(III) is significantly adsorbed. The column experiments gave symmetrical elution curves and results in reasonable agreement with the batch experiments. Reproducible experimental data were obtained in the batch experiments also in the most dilute H_2SO_4 solutions. However, these results may be less reliable due to hydrolytic precipitation or, at the low level of Bi used (10^{-4} M solution), the formation of strongly adsorbed chloride complexes ($D > 10^5$) from trace amounts of chloride in the resin (*cf.* Fig. 1, dashed line).

Rapid elution of large amounts of Bi in sulphate solutions at pH 1—1.5 has been reported.[13] No quantitative data were presented and high concentrations of sulphate from neutralization of sulphuric acid were used.

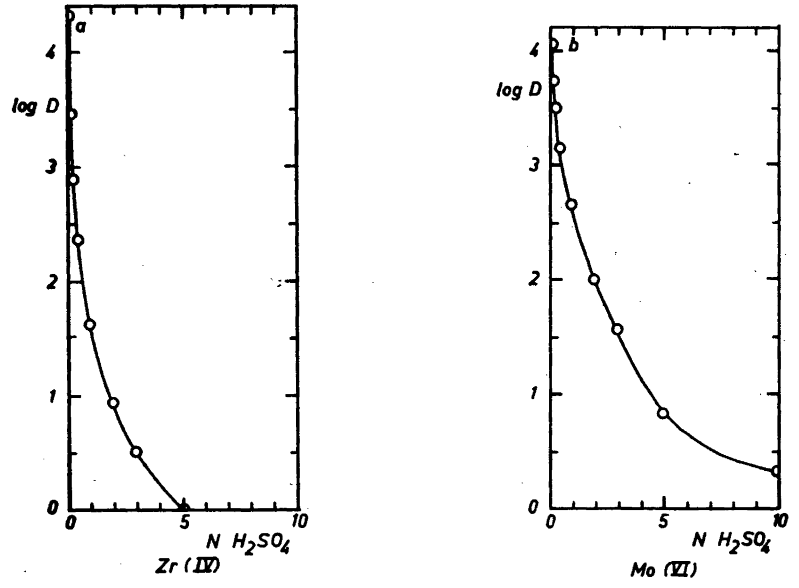

Fig. 2. Adsorption of Zr(IV) and Mo(VI) by Dowex 1 from 0.05—10 N H_2SO_4. Batch method.

C. Strong adsorption (Fig. 2)

This group contains only Zr(IV) and Mo(VI) of the elements investigated. The two curves have the same general shape. The distribution coefficients decrease rapidly from $D > 10^4$ in 0.05 N H_2SO_4 with increasing H_2SO_4 concentrations.

Bunney *et al.*[14] have reported strong adsorption of these elements and also of Nb by the Dowex 2 resin in various concentrations of H_2SO_4.

Zirconium(IV) solutions were prepared from spectrographically pure zirconium sulphate (Johnson, Matthey & Co.) with a certified content of hafnium less than 0.01 %.

If a charge of -2 is assumed for the adsorbed ions the loading was somewhat less than 7 % at the highest values of D. Loading is defined as the per cent of resin sites occupied by the adsorbed ions. A few experiments were made at 50 % less loading but no effects were observed. The analytical method used [8] did not permit accurate determinations of still lower amounts of Zr.

The strong adsorption of Zr(IV) from dilute H_2SO_4 solutions by strongly basic anion exchange resins has been used for separations in analytical chemistry.[11,15] Fig. 2 shows that elution from Dowex 1 may be achieved with 5 N

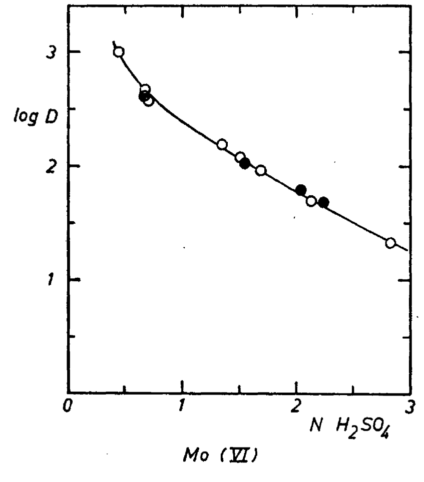

Fig. 3. Adsorption of Mo(VI) determined by the normal batch procedure ○, and by reversible experiments ●.

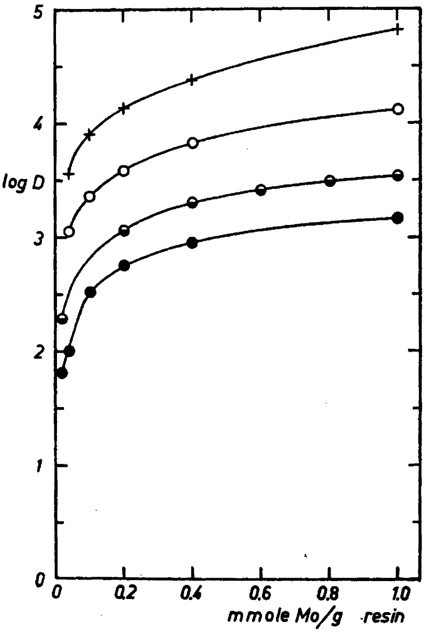

Fig. 4. Effect of the total amount of Mo per g of "wet" resin on the adsorption of Mo at different concentrations of H_2SO_4. Batch procedure. + 0.05 N, ○ 0.22 N, ◒ 0.50 N, ● 0.90 N H_2SO_4.

or higher concentrations of H_2SO_4. Only weak adsorption of Zr takes place from HNO_3 by Dowex 1 [4] and the adsorption is negligible in HCl below 6 N.[1]

Molybdenum(VI) is adsorbed throughout the region of H_2SO_4 concentrations investigated. Extremely high values of D were found contrary to the slight adsorption by Dowex 1 reported in very dilute HCl and HNO_3 solutions.[16,4] It seems reasonable to assume that the species adsorbed from H_2SO_4 differs from those adsorbed from HCl and HNO_3.

Some additional experiments were performed using solutions prepared from $Na_2MoO_4 \cdot 2H_2O$ and a different batch of Dowex 1X8, 100—200 mesh. Using the ordinary batch procedure equilibrium was reached within 2 h in 0.66 N H_2SO_4 and the adsorption remained at a constant value during the

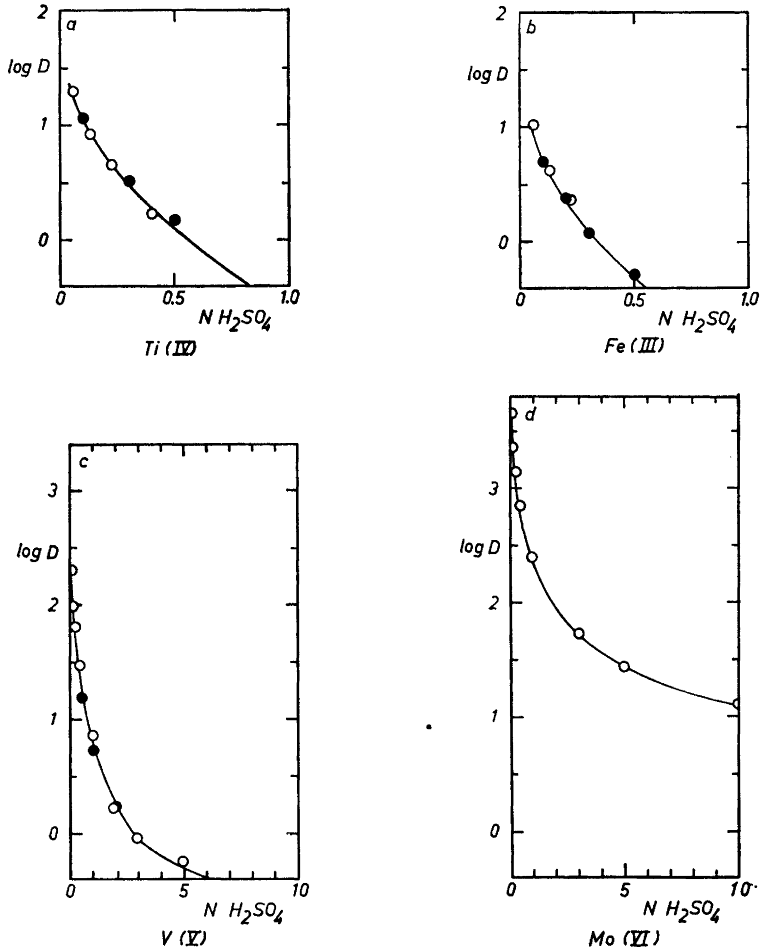

Fig. 5. Adsorption of Ti(IV), Fe(III), V(V), and Mo(VI) by Dowex 1 in the presence of 0.1 M H_2O_2 from various concentrations of H_2SO_4. Batch method ○, column method ●.

next 25 h. As is illustrated in Fig. 3, the adsorption reaction was found to be reversible. In this experiment 10 ml of 10^{-2} M Mo(VI) in 0.2 N H_2SO_4 were shaken with 1 g of resin for 16 h. After that period 10 ml of a more concentrated H_2SO_4 solution were added giving the same total volume and the same total amount of Mo as in the ordinary batch experiments. A new shaking period of 16 h was applied during which a desorption of Mo took place, since the distribution coefficient decreases rapidly with increasing concentration of H_2SO_4.

Batch experiments with varying concentrations of Mo(VI) ($10^{-3}-5 \times 10^{-2}$ M) but all other conditions unchanged were carried out. The total amount of Mo equilibrated with 1 g of "wet" resin ranged from 0.02 to 1.00 mmoles. It was firmly established that the distribution coefficient at a specific concentration of H_2SO_4 increases when the total amount of Mo per g of resin is increased (Fig. 4). Normally a decrease in the distribution coefficient is expected under similar circumstances. Investigations of the ionic species both in the solution and adsorbed by the resin at different concentrations of Mo may lead to an explanation. It is well known that the hydrolytic behaviour of Mo(VI) is complex and that condensed ions are present in weakly acidic solutions.

Analytical application of the strong adsorption of Mo(VI) by Dowex 1 has not been reported. Difficulties may arise in elution. Cooper and Salmon[17] who studied Mo(VI) ions in weakly acidic solutions of HCl used an alkaline solution (N in NaOH) of sodium nitrate (2—3 M) as eluant.

Effect of hydrogen peroxide on the adsorption of Ti, V, Mo, and Fe (Fig. 5)

Adsorption of some elements known to form complexes with hydrogen peroxide was studied at different concentrations of H_2SO_4 using the batch and column methods described earlier. All solutions used contained 0.10 M H_2O_2. Difficulties occurred in the batch procedure due to reactions between H_2O_2 and the resin and presumably also to poor stability of the complexes. Irreproducible results were at first obtained for V(V) but an equilibration period of 4 h gave results in agreement with the column elution method.

Hydrogen peroxide was found to have no effect on the adsorption of Fe(III) and increased only to a small extent the adsorption of Ti(IV). The distribution coefficients for V(V) were increased markedly and $D > 1$ was found in H_2SO_4 below *ca.* 2.5 N. The presence of H_2O_2 lowered the adsorption of Mo(VI) in the most dilute H_2SO_4 solutions but the decrease with increasing concentrations of H_2SO_4 was less rapid and higher values of D were found in H_2SO_4 > 3 N.

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