

Anion-Exchange Study

I. Adsorption of Some Elements in HBr-Solutions

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The anion exchange behaviour of some elements with 18-electron configuration and of Al, Re, Th, Pa, and U was studied in HBr-solutions. Negligible adsorption was shown by Al(III) and Th(IV). Zn(II), Ga(III), Ge(IV), Re(VII), Pa(V), and U(VI) were adsorbed less from HBr-solutions than from HCl-solutions contrary to Cd(II), Hg(II), In(III), Tl(III), Sn(IV), Pb(II), and Sb(III). Improved separation methods are offered for groups of these elements in comparison to earlier HCl-methods.

Recently anion exchange has obtained a widespread application in analytical and nuclear chemistry for separations of the chemical elements. Kraus and Nelson¹ have presented a comprehensive study of the adsorption of the elements by strong base anion resin as a function of the HCl-concentration. Anion exchange data were reported for a number of metals in HF² and in mixtures of HCl-HF^{3,4}. Less attention has been paid to the application of HBr. Herber and Irvine⁵ studied the behaviour of bromide anion complexes of zinc, cobalt, nickel, copper, and gallium; successful separations of these elements were obtained. They indicated that the study of the bromide anion complexes could not be extended beyond ~ 7 N HBr due to the chemical interaction between the resin and the acid.

Cations with 18-electron configuration have a tendency to form bromo complexes rather than chloro and fluoro complexes⁶. Bromide ions are tied more strongly than chloride ions to the anion exchange resin used, Dowex 1.

In this study a comparison between the adsorption of some elements to a base anion exchange resin from HBr and HCl solutions was carried out in order to improve some of the separation methods using HCl-solutions as elutrient.

EXPERIMENTAL

The resin used was 8 % crosslinked Dowex 1, 200-400 mesh, with a capacity of 3.4 mequiv/g dry resin, in the chloride form. The resin was washed thoroughly with

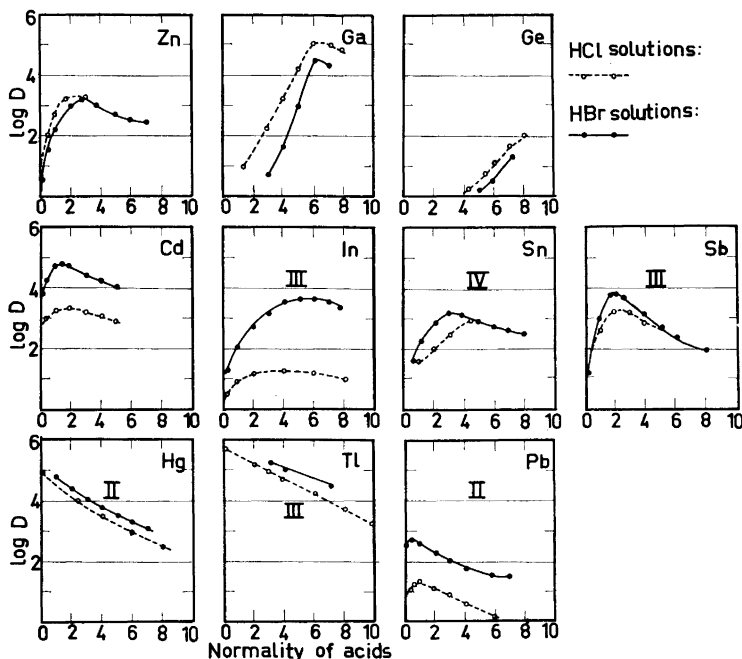


Fig. 1. Adsorption of some elements with 18 electron configuration and of Sb(III), Pb(II) from HBr and HCl solutions.

distilled water and dried at 110°C. In the HBr-investigations the resin was previously converted with HBr.

Adsorbabilities were measured by equilibration methods or column elution as described by Kraus and Nelson³. Usually 0.1–0.5 g resin and 5–10 ml liquid were applied. Equilibration was obtained after shaking for 18–20 h. In the case of tin 48 h, of lead 4 h, and of thallium 4 days shaking were applied.

The weight distribution coefficient, D , was calculated from radiometric analysis of the liquid phase before and after equilibration.

$$D = \frac{\text{m.equiv. metal on resin/g dry resin}}{\text{m.equiv. metal. in solution/ml solution}}$$

The volume distribution coefficient, D_v , was determined by the column elution method.

$$D_v = (V/Ad) - i$$

V = total effluent volume necessary to obtain elution peak maximum.

A = cross-sectional area of the column.

d = height of the column.

i = interstitial volume (about 0.4).

The relation between D_v and D is $D_v = D \cdot \rho$, where ρ is the bed density (about 0.45 kg/l).

Most of the radioactive tracers were obtained by irradiation of the metals or oxides in the Danish Atomic Energy reactor DR 2. ^{210}Pb was supplied by the Radiochemical Center, Amersham UK. The radioactive tracers were: ^{65}Zn (245 d), ^{115}Cd – ^{115}In (54 h–4.5 h), ^{197}Hg (65 h), ^{72}Ga (14.1 h), ^{114}In (49 d), ^{204}Tl (4.1 y), ^{113}Sn – ^{113}In (119 d–1.73 h),

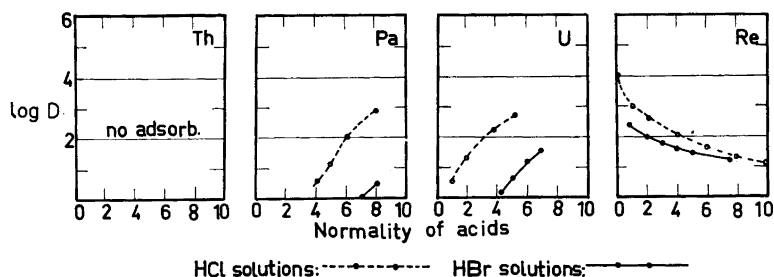


Fig. 2. Adsorption of thorium, protactinium, uranium, and rhenium from HBr and HCl solutions.

^{124}Sb (60 d), and ^{186}Re (91 h). ^{210}Pb was separated from ^{210}Bi by ion exchange ¹, and ^{234}Th (24.1 d) from uranium ⁹. ^{233}Pa (27 d), formed by neutron irradiation of thorium, was purified by ion exchange ¹.

All tracers were converted to bromide form with HBr. Aluminium was dissolved in HBr, germanium dioxide in 2 N NaOH. Uranium nitrate was converted to UO_3 and dissolved in HBr.

^{204}Tl , which is a pure β -emitter, was determined by evaporating aliquots of the liquid phase on polyethylene plates and counted with an endwindow G-M counter. The relative amounts of the other radioactive tracers were determined by a well type scintillation counter. Aluminium was detected with alizarinsulphonic acid ⁷, germanium with benzidine ⁸. Uranium was detected by the yellow colour of the UO_2^{++} -ions.

RESULTS

The logarithms of the distribution coefficients are presented in Figs. 1–2 as a function of hydrobromic acid or hydrochloric acid normality.

Zn(II), Cd(II), Hg(II)

The adsorption of Zn(II) is less in HBr-solutions than in HCl-solutions contrary to Cd(II) and Hg(II). Zn shows significant adsorption at concentrations $> 10^{-1}\text{N}$, while Cd is adsorbed at very small concentrations ($< 10^{-3}\text{N}$ HBr). Mercury is strongly adsorbed in HBr as well as in HCl-solutions in the concentration range 1–7 N acid.

Separation of Zn–Cd and Zn–Hg is possible on Dowex 1 with HBr as elutriant.

Zn–Cd: Approximately 0.1 ml 2 N HBr containing ^{65}Zn and ^{115}Cd — ^{115}In tracers was passed into a 5 cm column with a cross-section of 1 mm². Zn was eluted with 0.1 N HBr; Cd was eluted with 4 N HNO_3 as it could not be removed successfully with very dilute HBr-solutions.

Al(III), Ga(III), In(III), Tl(III)

Cations with rare gas electron configuration prefer to form fluoride anion complexes to chloride and bromide complexes ⁶. Kraus *et al.*¹⁰ have reported that the alkali metals, the alkaline earths and Al, Y, La, and Yb of group III show no adsorption in HCl.

As a representative of these elements Al showed no adsorption in HBr. The elution constant $E = Ax_d/V = (i + D_v)^{-1}$ was 2.2–2.3 in the concentration range 1–7 N HBr. Ax_d is the column volume, V the total effluent volume to reach elution peak maximum. $E = 2.2$ –2.5 indicates no adsorption. Herber and Irvine⁵ reported that Ga(III) chloride anion complexes are formed at lower halid concentration than bromide anion complexes. Ga(III) is adsorbed in 1 N HCl, but shows no adsorption in HBr-solutions at concentrations lower than 3 N.

In(III) is adsorbed strongly in HBr-solutions contrary to HCl-solutions. The adsorption function of In(III) in HBr rises rapidly with increasing acid concentration.

Thallium was investigated only in the valence state (III). Contrary to Horne¹¹ Kraus *et al.*^{4,10} have shown that Tl(I) is not adsorbed in HCl solution. Reduction of Tl(III) was prevented by addition of bromine or chlorine to the batch samples. It is difficult to obtain exact results on account of the high distribution coefficients, $\sim 10^5$. According to Horne¹¹ the bromine anion complexes are tied more strongly to the resin than the chloride anion complexes.

Separation of Al(III), Ga(III), In(III), and Tl(III)

Kraus *et al.*¹⁰ separated Al–Ga–In–Tl by means of anion exchange and HCl-elution. Using HBr rather than HCl-solutions as elutriant the separation of Al(III), Ga(III), In(III), and Tl(III) is both faster and better, and smaller columns can be used. The complete separation of Ga–In was confirmed by following the decay of ⁷²Ga. Its half-life was found to be $14.1 \text{ h} \pm 0.1 \text{ h}$. Kraus *et al.* eluted thallium with HNO₃ or HClO₄, but these acids do not give a liberation of Tl from the resin in bromide form. However, it is possible to remove thallium from the column with a few column volumes of a 5 % Na₂SO₃-solution (Fig. 3).

Ge(IV), Sn(IV), Pb(II), and Sb(III)

The adsorption of Ge(IV) in HBr occurs at concentrations higher than 5 N, and for HCl at concentrations higher than 3 N. Near 7 N HBr the adsorp-

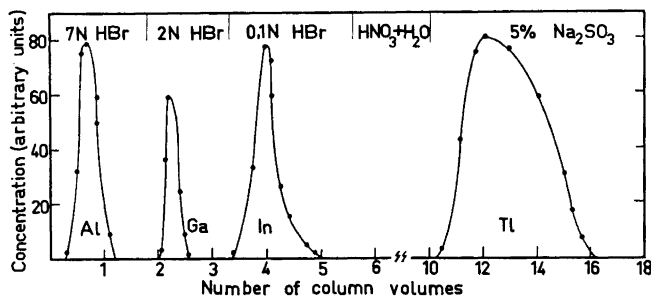


Fig. 3. Separation of Al(III), Ga(III), In(III), and Tl(III) by anion exchange.

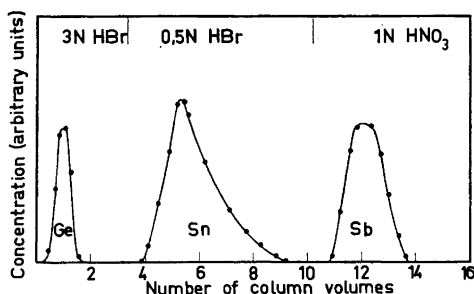


Fig. 4. Separation of Ge(IV), Sn(IV), and Sb(III) by anion exchange.

tion is sufficient to allow separation of germanium from elements which are not adsorbed (*e.g.* aluminium). Tin was only studied in the valence state (IV) because of the oxidation of Sn(II) on the resin. Kraus *et al.*¹² have shown that Sn(IV) is strongly adsorbed in HCl. The authors were not able to reproduce the distribution coefficients given by Kraus; this may be due to different loading of the resin. No investigations were carried out below 0.5 N HBr on account of hydrolysis. Fluoro- and chloro antimony(V) complexes are known, while the existence of antimony(V) bromo complexes is doubtful. Sb(III) shows significant adsorption to the resin in HBr-concentrations > 0.1 N.

Separation of Ge(IV), Sn(IV), and Sb(III) is shown in Fig. 4.

It is possible to separate two or more of the elements: Zn, Cd, Hg, Al, Ga, In, Tl, Ge, Sn, Pb, and Sb using anion exchange resin and HBr-solutions as elutriants, for example Sb(III), In(III), and Cd(II) in Fig. 5.

Th(IV), Pa(V), U(VI), and Re(VII)

Th(IV), Pa(V), and U(VI) show less adsorption to Dowex 1 in HBr- than in HCl-solutions, in agreement with the electron configuration of the ions. Ions with rare gas electron structure prefer to form chloro-complexes rather than bromo-complexes.

The lower adsorbability of Pa(V) agrees well with the lower extractability of this element from HBr than from HCl, as shown by Goble, Golden, and

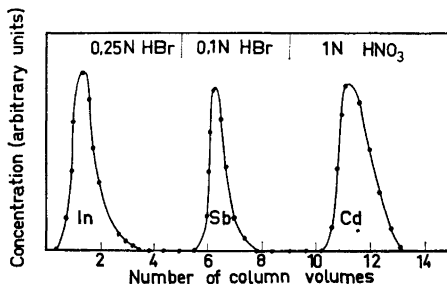


Fig. 5. Separation of Cd(II), In(III), and Sb(III) by anion exchange.

Maddock¹³. Separation of Th—Pa—U is successful with HCl-solutions as elutriant. Only the separation of Th—U and Pa—U is possible with HBr-solutions.

Rhenium shows less adsorption in HBr than in HCl-solutions. Since rhenium (VII) is difficult to remove from the resin with HCl, the application of HBr-solutions as elutriant would be an improvement.

The present results demonstrate that the application of HBr-solutions as elutriant in preference to HCl-solutions can be an advantage in some anion exchange separations. The use of HBr causes less adsorbability of cations with rare gas electron configuration. In the group of cations with 18-electron configuration Cd, Hg, In, Tl, and Sn show greater adsorption from HBr than from HCl solutions contrary to Zn, Ga, and Ge.

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