

CHROM. 8201

Note

Distribution coefficients for 53 elements in hydrochloric acid (1.2 M)-water-acetone medium on Dowex 50W-X12

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(Received January 20th, 1975)

It is well known that the replacement of part of the aqueous phase by an organic solvent often enhances the ion-exchange affinity of inorganic ions. Very interesting results have been obtained in acetone-mineral acid mixtures¹⁻⁶.

The effect of acetone on the distribution may be due to different factors:

(1) The concentration of water in the resin phase caused by its greater solvation power. Acetone is taken up to a lesser extent⁷⁻⁹.

(2) A liquid-liquid extraction equilibrium superimposed upon the ion-exchange equilibrium. Complete salt extraction into the resin phase, where water is concentrated, is possible¹⁰.

(3) The repression of the dissociation in the liquid phase due to the low dielectric constant.

(4) The stepwise dehydration of the ions and a progressive increase in ion pair formation because of the presence of acetone and the low dielectric constant of the solution^{11,12}.

(5) An increase in chloro-complex formation in hydrochloric acid medium by the addition of acetone.

MEASUREMENT OF DISTRIBUTION COEFFICIENTS

The distribution coefficient, k_d , is defined as the amount of ions per gram of dry resin divided by the amount of ions per millilitre of solution; it is determined by batch experiments at room temperature. Most distribution coefficients were obtained radiometrically and some (lithium, magnesium) by atomic-absorption spectrophotometry.

The appropriate amounts of hydrochloric acid (12 M)-water-radioactive tracer and acetone were mixed in glass bottles with 1 g of dry resin. The volume of the mixture was 50 ml at constant acidity (1.2 M hydrochloric acid) (maximum permissible value for a 1:9 (v/v) mixture of water and acetone). Six different mixtures were used, containing 20, 40, 60, 70, 80 and 90% (v/v) of acetone.

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The bottles were agitated with a mechanical shaker for 20 h. All γ -countings were carried out using a sodium iodide (thallium) 3×3 in. well-type scintillator; some β -countings were performed with a 2π flow counter.

RESULTS

The distribution coefficients for 53 elements in acetone–water–hydrochloric acid (1.2 *M*) on a cationic resin, Dowex 50W-X12, 200–400 mesh, are given in Table I. Numerical values are quoted exponentially, *e.g.* $x \text{ E}y$ means $x \cdot 10^y$. Fig. 1 gives the adsorption functions ($\log k_d$ versus percentage of acetone) plotted in a periodic chart.

DISCUSSION

Three general groups of elements can be distinguished, as discussed below.

Elements for which the distribution coefficient increases with increasing acetone content

For alkali metals, alkaline earth metals, Sc(III), Y(III) and rare earths, k_d increases considerably with regard to water–hydrochloric acid solutions at the same normality; the logarithm of the distribution coefficient varies almost linearly with the percentage of acetone. This behaviour may be due to stepwise dehydration of the ions. As expected, the adsorbabilities at the same acetone content are much higher for trivalent ions than for bivalent ions, the latter being higher than those for monovalent ions.

Elements showing an adsorption maximum

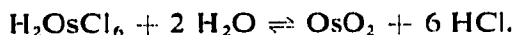
The decrease in k_d beyond a certain acetone content indicates the formation of negatively charged chloro-complexes¹³. The order of stability for the positively charged ions (hydrated ions or positively charged chloro-complexes) in this group is Hf(IV) > Cr(III) > Mn(II) > Ni(II) > Co(II) > Fe(III) > Cu(II) > Ga(III) > In(III) > Te(IV).

Elements with no or very weak adsorption

Most of these elements are known to form negatively charged complexes in hydrochloric acid: Tc(VII) and Re(VII) as TcO_4^- and ReO_4^- ; and Pd(II), Pt(IV), Ag(I), Au(III), Hg(II), Tl(III) and Bi(III) as chloro-complexes. For these elements, there is no retention.

Negatively charged chloro-complexes predominate for Zn(II), Cd(II), Sb(III) and Sb(V). The weak adsorption of Zn(II) can be attributed to the positive complex ZnCl^+ . No adsorption is observed for Cd(II), although in aqueous hydrochloric acid CdCl^+ is more stable than ZnCl^+ . Sb(III) and Sb(V) can form some cations: Sb^{3+} , SbO^+ and Sb^{5+} .

The unexpected adsorption of Os(IV) probably arises from entrapment of colloidal oxide inside the solid phase owing to the reversible reaction



Mo(VI) and W(VI) probably give complex oxy-anions with variable degrees

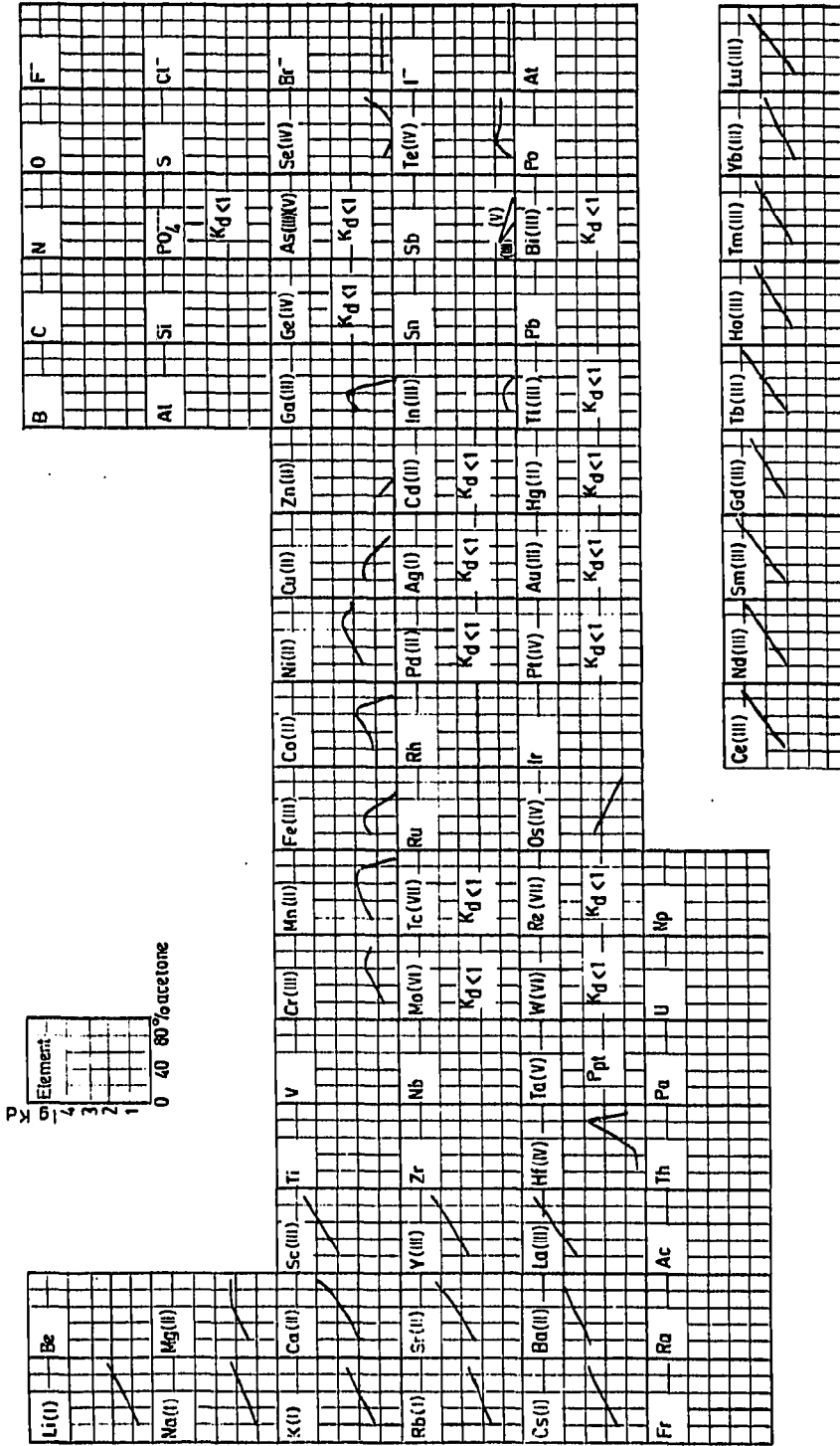


Fig. 1. Adsorption functions of elements on Dowex 50W-X12 cation-exchange resin, 200-400 mesh, in hydrochloric acid (1.2 M)-water-acetone.

of condensation. Ge(IV), As(III) and As(V) never form cations. For Se(IV), neutral complexes such as SeCl_4 and SeOCl_2 could explain the weak retention on cationic resins¹⁴.

Our results agree with those found by Peterson *et al.*⁶, who used acetone-water-hydrochloric acid (0.3 *M*) mixtures. An increase in hydrochloric acid concentration from 0.3 to 1.2 *M* gives a considerable change in the distribution coefficients to lower values; this change becomes more pronounced as the ability of the elements to form negatively charged ions increases (chiefly negative chloro-complexes). On the contrary alkali metals, alkaline earth metals and rare earths, which show no ability to form chloro-complexes, retain very high k_d values in comparison with those in 0.3 *M* hydrochloric acid solutions and much greater than those in aqueous solutions of the same hydrochloric acid molarity.

ACKNOWLEDGEMENTS

We are indebted to Professor Dr. G. Duyckaerts for judicious advice and for reading the manuscript. We are grateful to Miss N. Walch for her valuable technical assistance and to the Institut Interuniversitaire des Sciences Nucléaires for financial support for this work.

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