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Interaction of Divalent Metal Acids with Pentyl Alcohol and Isopentyl Acetate

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Extraction of monobasic divalent metal bromo acids in pentyl alcohol-benzene and isopentyl acetate-benzene mixtures was studied at room temperature (25 °C). Three molecules of pentyl alcohol ae well as of isopentyl acetate were associated with each metal acid molecule of cobalt and copper in the organic phase. Zinc, cadmium, and mercury acids take up two molecules of pentyl alcohol and one molecule of isopentyl acetate. Metal acids studied here mostly exist as monomer in the organic phase. In pentyl alcohol, however, copper acid is monomeric only at lower concentrations (4×10^{-5} to 2×10^{-4}M) and dimeric at higher concentrations (3.3×10^{-4} to 1.4×10^{-3}M).

It has long been known that aqueous $HClO_4$, $HReO_4$, and HBr are extracted by tributyl phosphate[1] (TBP) in xylene or CCl_4 as $H_3O^+\cdot 3TBP\cdot yH_2O\cdot X^-$, where $0\leqslant y\leqslant 3$, and X^- is the respective anion. A number of mineral and complex metal acids were later extracted in trioctylphosphine oxide[2] (TOPO) in organic solvents.

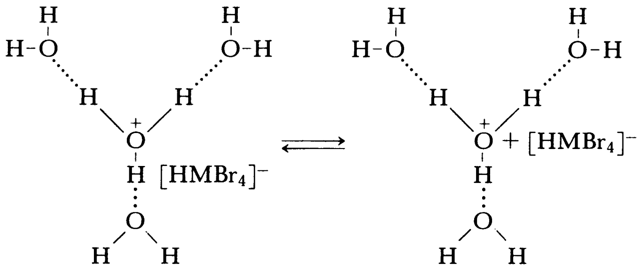
The extraction studies for metal acids made so far, are mostly limited to species of the type HMX_4. Several polyvalent transition[3] and nontransition[4] metal salts have been extracted with various extractants and solvents. It was thus thought worthwhile to study the extraction of dibasic metal acids,[5–9] $H_2[CoBr_4]$, $H_2[CuBr_4]$, $H_2[ZnBr_4]$, $H_2[CdBr_4]$, and $H_2[HgBr_4]$ which are practically monobasic in pentyl alcohol and isopentyl acetate mixture using benzene as diluent and seek a relation between the acidity of extracted acids and basicity of the solvents.

Experimental

For extraction studies, 3.0 ml aqueous metal acid solution obtained by adding the respective metal bromide in concentrated HBr was shaken with 25.0 ml benzene-pentyl alcohol (1—10%) or isopentyl acetate (8 to 15%) mixture for 1 h and there after allowed to stand for about 10 h. Polymerization studies were, however, made in 10% pentyl alcohol (or 10% isopentyl acetate)-benzene mixture. Metal content in either phase was determined by titrating it against EDTA using indicator (Xylenol Orange for cobalt, PAN for copper, and Erichrome Black T for zinc, cadmium, and mercury). Metal content in the organic phase was determined after evaporating off the solvent completely and digesting the residue in distilled water. Aqueous phase was also evaporated and digested in distilled water before titration.

Extraction Equilibria

In concentrated aqueous HBr, bromides of cobalt, copper, zinc, cadmium, and mercury exist[5–9] as H_2MBr_4, M being surrounded tetrahedrally with Br. As in aqueous phase, the proton is further hydrated through hydrogen bonding[10] and the dissociation constant of $[HMBr_4]^+$ species being negligible, the metal acid species in the aqueous phase may be represented[1,2e] as follows:



When aqueous metal acid is shaken with the organic phase, some acid passes into the organic phase. In this process, the hydrogen bonded water of the proton is partly or completely replaced by the organic ligand.[2e] Since, pentyl alcohol as well as isopentyl acetate are less basic than water, they do not interact with the second proton, to which even water is inert. In low dielectric constant solvents like benzene (D=2.3) the metal acid anion, $[HMBr_4]^+$ forms the ion pair $H_3O^+\cdot 3AA\cdot [HMBr_4]^-$.

Assuming that metal acid is extracted into the organic phase as one single species, having J metal ion, the extraction equilibrium will be represented by Eq. 1.

$$J[HMBr_4]^-_w + J\,H_3\overset{+}{O}_w + nAA_o \rightleftharpoons nAA.\ J(H_3\overset{+}{O}[HMBr_4]^-)_o \tag{1}$$

(secondary solvation of proton is not shown)

AA stands for pentyl alcohol and isopentyl acetate, suffix o and w refer to organic and water phases, respectively. The total metal concentration in the organic phase, $[M^{2+}]_o$, is given by Eq. 2 in terms of metal concentration in the aqueous phase and extraction equilibrium constant, K,

$$[M^{2+}]_o = KJ[H(MBr_4)^-]^J_w[AA]^n_o[H_3O^+]^J_w, \tag{2}$$

$$\log[M^{2+}]_o - J\log[M^{2+}]_w = n\log[AA]_o + K', \tag{3}$$

where K'=log K+log J+J log$[H_3O^+]_w$ and $[H_3O^+]_w$ is invariant. If J equals unity, Eq. 3 rearranges into Eq. 4.

$$\log D = n\log[AA]_o + K'. \tag{4}$$

D stands for distribution coefficient of metal acid, between organic and aqueous phases. According to Eq. 3, the plot of log $[M^{2+}]_o$ against log $[M^{2+}]_w$ at a constant concentration of extractant (pentyl alcohol or isopentyl acetate in C_6H_6) should yield a straight line, whose slope would measure, J, the degree of polymerization in the organic phase. For the determination of the number of extractant molecules incorporated with metal acid in the organic phase, a plot of log D versus log $[AA]_o$ was drawn.

Results and Discussion

The log $[M^{2+}]_o$ −log $[M^{2+}]_w$ plot in pentyl alcohol-benzene mixture (Fig. 1) yields straight line, whose slopes show that metal acids are extracted as monomer in the organic phase. The behavior of Cu^{2+} is, however, unique in the sense that it is monomer at lower concentrations (4×10^{-5} to 2×10^{-4} M (1 M=1 mol dm^{-3})) and dimer at higher concentrations (3.3×10^{-4} to 1.4×10^{-3} M).

In isopentyl acetate-benzene system, the plots of log $[M^{2+}]_o$ against log $[M^{2+}]_w$ are straight lines (Fig. 2) with unit slopes, showing that metal acids are present

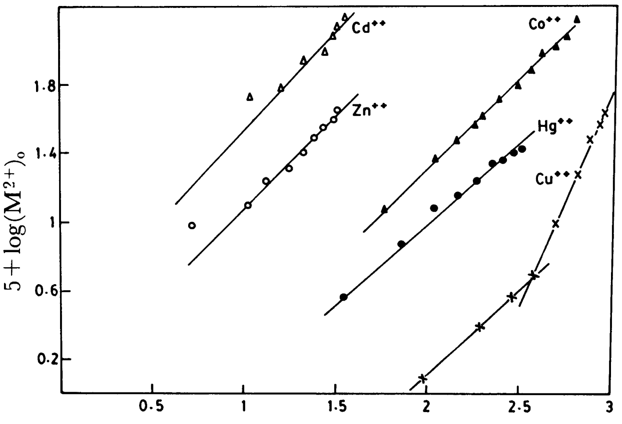


Fig. 1. Log$[M^{2+}]$ versus log$[M^{2+}]_w$ plots, at constant concentration of pentyl alcohol (10% by volume) in benzene at 25 °C.

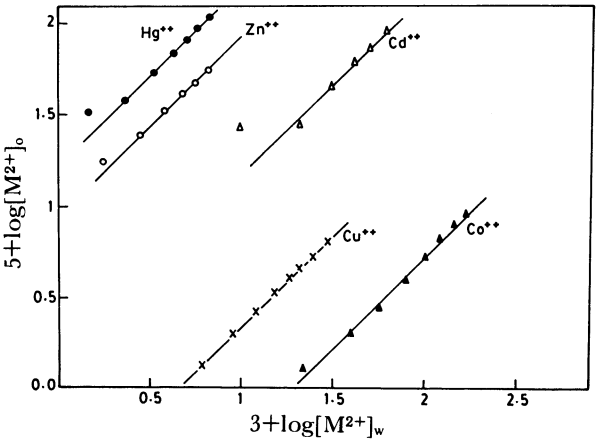


Fig. 2. Log$[M^{2+}]$ versus log$[M^{2+}]_w$ plots, at constant concentration of isopentyl acetate (10% by volume) in benzene at 25 °C.

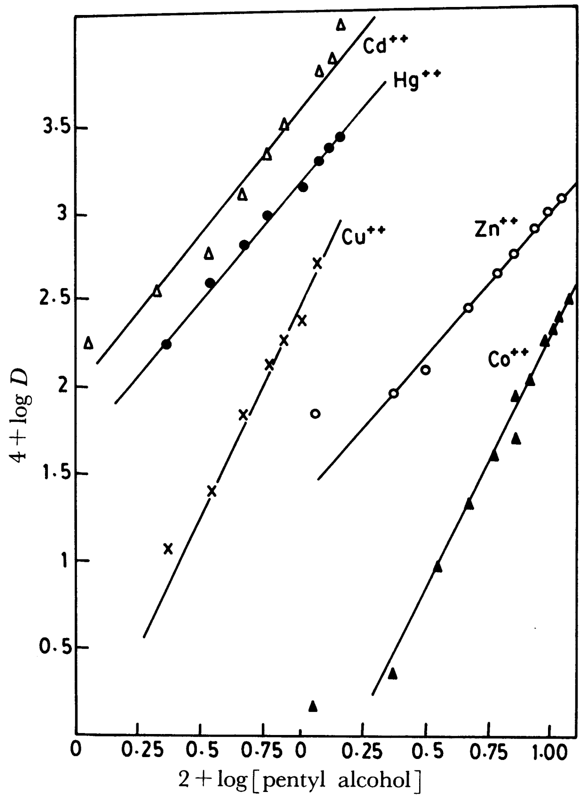


Fig. 3. Log$D$ versus log [pentyl alcohol] plots, for five metal acid. X: 1.1×10^{-2}, ▲: 1.5×10^{-2}, O: 5.0×10^{-3}, Δ: 7.0×10^{-3}, O: 5.0×10^{-3} mol dm^{-3} at 25 °C.

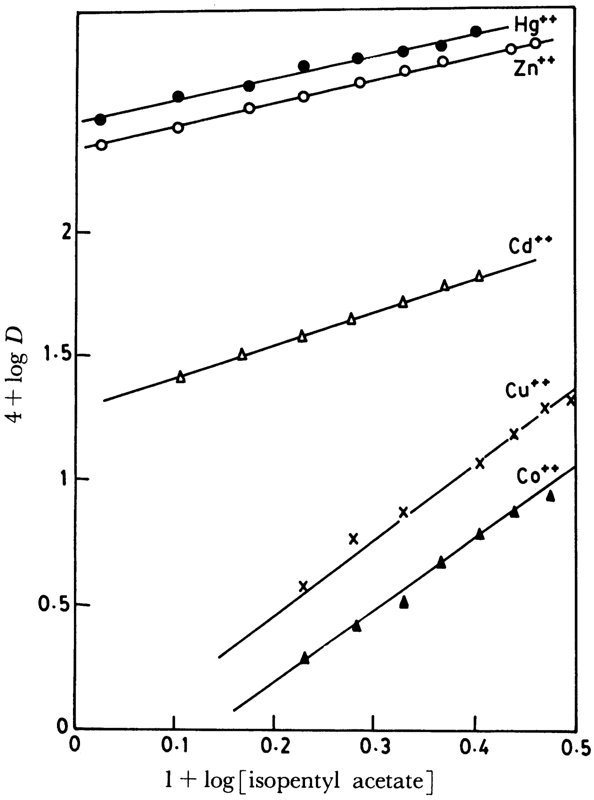


Fig. 4. Log$D$ versus log [isopentyl acetate] plots, for five metal acid. X: 2.0×10^{-4}, ▲: 3.5×10^{-4}, O: 1.2×10^{-2}, Δ: 1.1×10^{-2}, ●: 1.3×10^{-2} mol dm^{-3} at 25 °C.

as monomer in the organic phase in this system as well.

Because of proportionately higher transport of HBr from aqueous into the organic phase at lower metal acid concentrations, the slopes (Figs. 1 and 2) become progressively less than unity. As metal acids compete with HBr (present in excess) for coordination with extracts in the organic phase, the extraction of metal acids at their lower metal concentration decreases significantly because excessive flow of HBr into the organic phase reduces the availability of the extracts to metal acids. This becomes distinct in the case of zinc and cadmium. Similar behavior has also been observed[11] in the extraction of tetraalkylammonium hydroxide in different alcohols.

The log plots of distribution coefficient versus concentration of pentyl alcohol in benzene (Fig. 3) at constant metal ion concentration are straight lines for Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}, having slopes of 2.8, 2.7, 2.1, 2.3, and 2.3 respectively. Thus, the number of pentyl alcohol molecules, incorporated with metal acids, are assumed to be three for cobalt and copper and two each for the rest.

Again, the log plots of distribution coefficient versus concentration of isopentyl acetate in benzene for the five species of metal ions at constant metal ion concentration are straight lines (Fig. 4) with the slopes showing three incorporated isopentyl acetate molecules each for cobalt and copper and one each for zinc, cadmium, and mercury.

The transition metal (cobalt and copper) acids are comparatively more acidic than those of the zinc family members which have more pronounced covalent character. Hence metal acids of zinc, cadmium, and mercury give more strongly bound ion pairs, whereas those of cobalt and copper give weakly bound ones. Thus in case of cobalt and copper, each cation (hydrated proton) of the ion pair incorporates three extractant molecules (pentyl alcohol or isopentyl acetate) whereas zinc, cadmium, and mercury acid anions being more closely held to the proton accommodate only two pentyl alcohol molecules. Further, due to steric hindrance and crowding, only one isopentyl acetate molecule could be bound with the cation of the ion pair in the zinc family.

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