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EXTRACTION WITH THE PARTICIPATION OF TWO COMPLEX-FORMING AGENTS

(Presented by Academician I. V. Tananaev on 7 March 1960)

An improvement in the extractability of chelate compounds of metals has been observed in a number of cases upon the addition of certain polar substances (alcohols, amines, etc.) (1-3), substances similar in structure to the chelate-forming agent (1), and also in the presence of a sufficient excess of the corresponding chelate-forming reagent (4, 5). It was noted (1) that sometimes the presence of very small amounts of the indicated additives is sufficient for a sharp increase in the distribution coefficient to occur. Such phenomena were explained by hydrophobization of the chelate molecules with a simultaneous increase in oleophilicity due to replacement of coordinated water molecules by molecules of the organic additives (1, 3), and also by shielding of regions of the chelate molecule with increased charge density.

We investigated the influence of a second complex-forming agent on the extractability of chelate complexes under conditions where one or each of the two complex-forming agents, taken separately, is insufficient for extraction of the given metal. The following were used as complex-forming agents: pyridine (I), 3,5-dimethylpyrazole (II), 4,5-dimethylimidazole (III), ethylenediamine (IV), 2,2′-dipyridyl (V), 1,10-phenanthroline (VI), 5,5′-dimethyl-3,3′-dipyridazyl (VII), 1-(2-pyridyl)-3,5-dimethylpyrazole (VIII), pentachlorophenol (IX), 8-hydroxyquinoline (X), 2-methyl-8-hydroxyquinoline (XI), 5-methyl-8-hydroxyquinoline (XII), 5,7-dichloro-8-hydroxyquinoline (XIII), *N*-nitrosophenylhydroxylamine (XIV), *N*-benzoyl-*p*-tolylhydroxylamine (XV), acetylacetone (XVI), 8-*p*-toluenesulfonylaminoquinoline (XVII), sodium diethyldithiocarbamate (XVIII), 2,2′-dioxyazobenzene (XIX), 4-nitro-2,2′-dioxy-5′-methylazobenzene (XX), 5-nitro-2,2′-dioxy-5′-methylazobenzene (XXI), 4-nitro-2,2′-dioxy-4′-methyl-5′-isopropylazobenzene (XXII), 5-chloro-2,2′-dioxybenzene-(1-azo-1′)-naphthalene (XXIII), 2-hydroxy-4-methyl-3,5-diisopropylazobenzene-2′-arsonic acid (XXIV), benzene-(1-azo-1′)-2′-naphthol-2-arsonic acid (XXV), 2-naphthol-(1-azo-1′)-4′-methylbenzene-2′-sulfonic acid (XXVI), 2-naphthol-(1-azo-1′)-4′-nitrobenzene-2′-sulfonic acid (XXVII), 2-hydroxy-(1-azo-2′)-naphthalene-1′-sulfonic acid (XXVIII), 2-hydroxy-(1-azo-1′)-naphthalene-8′-sulfonic acid (XXIX), and 2-hydroxy-(1-azo-1′)-naphthalene-2′-sulfonic acid (XXX).

For each of the selected cations, in the pH range from 1 to 13, the change in color of the organic phase during extraction was studied in the following systems: 1) reagent No. 1; 2) reagent No. 1 + cation; 3) reagent No. 1 + reagent No. 2; 4) reagent No. 1 + reagent No. 2 + cation; 5) reagent No. 2 + cation; 6) reagent No. 2. More detailed study was made of those cases in which, in systems of type 4, colors appeared that differed sharply from the colors in the other control systems.

All tests were carried out with extraction by chloroform. In some cases, carbon tetrachloride, benzene, isoamyl alcohol, and dibutyl ether were also used as extractants.

For combinations of reagents of types I–VIII with reagents of types XIX–XXX, the greatest number of cases of color effects caused by the simultaneous presence of two complexing agents was observed for copper, cobalt, and nickel. This phenomenon is somewhat less characteristic of zinc, cadmium, lead, mercury(II), silver, and thallium(I).

The combination of reagents of types X–XVIII with reagents of types XIX–XXV in some cases makes it possible to observe these effects in the extraction of beryllium, magnesium, calcium, strontium, manganese(II), scandium, yttrium, lanthanum, and trivalent rare-earth elements. Color effects are observed more rarely for barium, aluminum, zirconium, hafnium, thorium, and uranium(VI). Sometimes it is possible to find conditions for high selectivity of reactions based on extraction involving two reagents. Some interesting cases of selectivity of the phenomenon under investigation are given below.

Copper(II): reagents of types I–VIII in combination with IX at pH 6.0–8.0 (especially the combination VIII + IX), and also in combination with reagents XXVI–XXX (especially in combination with XXX) at pH 8–13, in the presence of very many cations.

Zinc: reagents XX–XXII in combination with III at pH 4.5–7.5 in the presence of cadmium, mercury(I, II), and lead.

Cadmium: reagents XX–XXII in combination with V–VIII at pH 8–11, in the presence of zinc, lead, and mercury.

Calcium: reagent XVII in combination with XX or XXII at pH 8–13 (especially in extraction with carbon tetrachloride), in the presence of beryllium, strontium, barium, and small amounts of magnesium.

Scandium: reagents X–XIII in combination with XIX–XXIII at pH 7.5–12, in the presence of aluminum, yttrium, lanthanum, rare earths, thorium, uranium, zirconium, etc.

Yttrium, lanthanum, and rare-earth elements (trivalent): reagents XIV, XVI, XVIII in combination with XIX–XXII at pH 8–12 and combinations of XIV with XXIV and XXV at pH 12–13, in the presence of aluminum, scandium, thorium, zirconium, uranium, etc.

Thorium: reagents XX–XXII in combination with XV at pH 5.0–7.5, in the presence of aluminum, scandium, yttrium, rare earths, zirconium, uranium, etc.

The appearance of unusual colors during extraction involving two complexing agents is most likely to be explained by the extraction of neutral mixed chelate complexes. Some cases of extraction of mixed chelate compounds have been mentioned in the literature (6–11). However, the possibility is not excluded that, in the cases we observed, simple or mixed chelate formation is combined with the effects mentioned at the beginning of the article.

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