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Abstract

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Extraction with the Participation of Three Chelating Agents

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In studying the prevalence of the phenomenon of mixed chelate formation by the extraction method, we discovered interesting cases of extraction of colored compounds caused by the simultaneous presence of three different chelating agents.

The following were used as chelating reagents: 4-nitro-2,2′-dioxy-5-methylazobenzene (I), 4-nitro-2,2′-dioxy-4′-methyl-5′-isopropylazobenzene (II), 8-hydroxyquinoline (III), 2-methyl-8-hydroxyquinoline (IV), 5-methyl-8-hydroxyquinoline (V), mono-*n*-butyl phosphate (VI), di-*n*-butyl phosphate (VII), N-nitrosophenylhydroxylamine (VIII), acetoacetic ester (IX), 2-carbethoxycyclopentanone (X), 2-hydroxyacetophenone (XI), and benzoylsalicylidimethane (XII).

Extraction was carried out with chloroform. The initial concentration of cations in the aqueous phase was at the level of 40 μg/ml. At least four moles of each reagent were added per gram-ion of metal. For comparison, in all cases, control experiments were performed under identical conditions, in which either the cation or, successively, one of the three reagents was absent.

In the following cases, extraction of colored compounds (pink or violet) was observed at pH 10–12 in the simultaneous presence of three reagents (in all control experiments the extracts were colorless): scandium–combinations of reagents II, VII, IX (or X); yttrium and rare-earth elements–combinations I, IV, XII; I (or II), IV (or V), VI; II, III (or IV, or V), VII; II, III (or V), XI (or X); II, VII, IX (or X); thorium–combinations I, V, VIII; I, VII, XI; II, IV, VIII; II, III (or IV, or V), VII; II, VII, IX (or X).

In combinations with II and IX, in the case of the rare-earth elements, and with I and VIII, in the case of scandium, in the presence of 2-methyl-8-hydroxyquinoline (IV), unlike the structurally similar 8-hydroxyquinoline (III) and 5-methyl-8-hydroxyquinoline (V), extraction of colored complexes was not observed. Similar phenomena also occurred in binary combinations with I or II, respectively, of reagents IV, III, and V in the case of thorium. As is known, 2-methyl-8-hydroxyquinoline, unlike 8-hydroxyquinoline, is incapable of precipitating aluminum (^{1}) and of forming an extractable chelate complex with it (2), which is possibly connected with steric hindrance to chelate formation (3). The anomalous behavior of 2-methyl-8-hydroxyquinoline that we observed is probably also due to this cause.

At lower pH values, a transition was sometimes observed from the orange-yellow color of reagents I or II to the orange-red or red color of extractable complexes. For example, yttrium, rare-earth elements, and thorium gave such a transition with combinations of reagents I, III (or IV, or V), VI in the pH range 6–8.

Cases were also found in which the presence of a third chelating agent caused both an increase in the intensity of the color and a certain deepening of it (in comparison with binary combinations). For zirconium this was observed upon adding III or V to the combination II + VIII (at pH 8-12); for thorium, upon adding III or IV or V to the combination II + VIII (pH 6-12); for yttrium and the rare-earth elements, upon adding IX, or X, or XI to the combination I + VII, and III, or IV, or V to the combination II + XI (pH 6-12).

Specially designed experiments established that the ratios of the reagents, especially in the region of relatively low concentrations, substantially affect the extractability of the corresponding colored compounds. Thus, for example, by lowering the concentration of reagent IV in the system of reagents I, IV, and XII at pH 10-12 it was possible to improve significantly the selectivity of extraction of colored compounds of the rare-earth elements. In many other cases it was also possible to find conditions for selective extraction of compounds formed by elements of the same valence and similar in properties. Let us note, for example, that thorium, in contrast to zirconium, forms colored extractable complexes with the combinations of reagents I, VII, XI and II, V, VII, while yttrium and the rare-earth elements, in contrast to scandium, do so with I, VII, IX (or XI) at pH 10-12.

As for the mechanism of extraction, it should be assumed that reagents of types I and II form, under the conditions studied, chelate compounds through at least two donor groups, since the extracts have the color of the deprotonated form of the corresponding reagent. In other words, in the present case there is no coextraction of reagents of types I and II in the form of solvates, which is sometimes observed in the case of other reagents, and predominantly in an acidic medium (4). Taking into account the high pH value, it appears more probable that the other two bidentate reagents involved occupy the corresponding number of coordination sites in the mixed chelate complex and, when in excess, are present in the aqueous phase in the form of anions. Nevertheless, since these additional reagents are colorless or only weakly colored (III-V, XII) and, possibly, form weakly colored incomplete and mixed chelates, the possibility cannot be excluded—especially in the case of trivalent cations—of extraction of compounds with solvating neutral molecules of these reagents. The latter assumption may be especially valid for extraction in the region of lower pH values.

Among the reasons for the observed cases of selective extraction involving three chelating agents, a certain role may possibly be played by an increase in the individuality of the species during stepwise chelate formation of tri- and tetravalent cations.

Such an increase in the individuality of incomplete chelate species can be traced, for example, in the case of acetylacetone (^{5}), 1-nitroso-2-naphthol (^{6}), 2-nitroso-1-naphthol (^{6}), and 8-hydroxyquinoline-5-sulfonic acid (^{7}), where the difference between the logarithms of the second formation constants of chelates of tri- and tetravalent metals is, as a rule, always greater than the corresponding difference for the first formation constants. It may be assumed that the attachment to the ion of a tri- or tetravalent metal of one residue of a chelating reagent leads to such changes in the spatial distribution of electron densities, and to the appearance of such spatial restrictions for the attachment of new species or attack of the central ion by any species, as a result of which the complex species formed behave more individually than the initial ions. Accordingly, it appears probable that upon attachment to an incomplete chelate complex of one more species of another reagent, the individuality of the species formed may increase. Further-

further repetition of this process of changing the character of the particles by adding a new chelating reagent may likewise lead to an increase in selectivity.

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Note: Figure translations are in progress. See original paper for figures.