

Introduction

Developments in the field of Coordination Chemistry, which is closely bound up with the study of mixed and mixed polynuclear complexes, have been very extensive in recent years. A study of mixed ligand complex formation is of extreme interest to analytical chemists for the following reasons.

1. Mixed ligand complexes are the most general and probable form of existence of the elements in solution.
2. Studies of mixed ligand complex formation make it possible to estimate the characteristics of the intermediate and final form of the complexes, and therefore to comprehend the mechanism and kinetics of analytical reactions.
3. Certain peculiarities of elements, which are most pronounced in mixed ligand complexes, as well as the physical phenomena accompanying the process of mixed ligand complex formation, open new prospects for the development of selective and sensitive methods for the determination, separation and concentration of elements. The quantitative evaluation of these physical phenomena enables solution of problems of the composition and stability of mixed ligand complexes.
4. The processes of mixed ligand complex formation are closely bound up with one of the most challenging problems in modern analytical Chemistry - the problem of extraction. Hence it becomes clear why the number of publications on experimental study, theoretical generalization and practical use of mixed ligand complexes increases at such speed.

Mixed ligand complexes are characterized by their extreme stability. The chemical individuality of the central atom displays itself clearly, and peculiarities in extraction with organic solvents may be observed. Such properties open new routes to the solution of various theoretical and practical problems in analytical chemistry; true mechanisms and kinetics of analytical reactions can be elucidated and selectivity and sensitivity of analytical methods can be improved. The reasons for the extreme stability of mixed ligand complexes as compared with simple complexes would be much more readily explained if every step of the mixed ligand complex formation could be characterized by complete thermodynamic functions. Unfortunately, at present this question is being solved only by the ratio of stepwise stability constants. It is not yet possible to describe with sufficient certainty, the mechanism of extraction of metal chelates with neutral donors, or to elucidate fully their composition, because reliable data on the interaction of a chelating agent (HA) with neutral donors (B) (MAB , MAB_2 , H_2A_2B , etc.) or with the solvent molecules are not always available. The extraction of a metal with two chelating agents or with the participation of two neutral donors seems to be a very interesting but not sufficiently studied problem, as well as the problem of metal coextraction as mixed polynuclear complexes. Little is as yet known about the thermal stability of mixed chelates, etc.

The specific characteristics of elements in mixed ligand complexes have led to the development of a number of trends in

analytical chemistry. The use of ion associates (triple complexes) in analytical chemistry has become much more frequent in recent years. There are wide possibilities of forming compounds of the ion associate type of various compositions, and the possibilities for their practical application are numerous. The reactions in which ion associates are formed may exhibit higher sensitivity than those with the most sensitive organic reagents. This can be seen from a comparison of the molar extinction coefficients of the solutions of Me-1,10-phenanthroline-Rose Bengal Extra (where Me = Mn, Cu, Cd, Ni etc.) ion associates with the respective metal dithizonates(1). The sharp increase of the molar extinction coefficient on the formation of the mixed ligand complex of niobium with pyrrolidine dithiocarbamate (PDTC) and pyrocatechol (PC) [2].

Solvent extraction methods should be considered the most suitable for the determination of small and ultra-small amount of impurities in highly pure substances; these methods permit the simultaneous separation and concentration of large groups of elements for their subsequent physicochemical determination. The extraction separation of elements as mixed ligand complexes of the ion associate type formed by the anions of acido complexes and cations of organic bases, depends on the difference in the complexing capacity of elements with respect to acido ligands (Cl^- , Br^- , I^- , SCN^- , CN^-). These differences are observed even for elements of similar properties and form the basis of selective method for their separation. From this point of view the reagents of the

pyrazolone class seem to be most promising. Thus, micro- amounts of about 20 elements such as iron, cobalt, copper, zinc, molybdenum, tungsten, tin, titanium, zirconium, hafnium, scandium, uranium, mercury, gallium, indium and others can be extracted with diantipyrinylmethane in the presence of thiocyanate ions from highly pure salts of elements which are not extracted under appropriate conditions (salts of Al, Ni, Cr, Be, Mn, alkali and alkaline earth metals). Micro amounts of tin, zinc, cadmium, bismuth and antimony can be extracted from chloride media, and microamounts of scandium, hafnium and bismuth from nitrate media (3). Hexyldiantipyrinylmethane permits a rapid separation of Zr from Th, U, Sc, Y and the rare-earth elements, in 8-10 M hydrochloric acid, Zr and Hf are extracted with this reagent into dichloroethane and chloroform and many other elements including elements of the scandium subgroup and rare-earth elements remain in the aqueous phase (4). The most selective method for the determination of thorium of those known at present has been developed with the use of methyldiantipyrinylmethane (5), etc.

In the formation of mixed complexes of the ion associate type, very interesting properties are exhibited by the thiocyanate complexes $[Me(SCN)_n^{(m-n)}]$. The absorption bands of such mixed ligand complexes are charge transfer bands and have very high molar extinction coefficients: For example, the niobium - pyrrolidine - dithiocarbamate - thiocyanate complex has $\epsilon_M = 36000$ (6). The variety of compounds used for the separation and extraction -

photometric determination of elements as mixed ligand complexes of the ion associate type is continuously widening. Among recent systems, the extraction of metals as ion associates of their positively charged chelates (with 1,10-phenanthroline or 2,2'-bipyridine) with anions of organic acids (7) should be mentioned. The use of coloured positively charged iron(II) complexes or 1,10-phenanthroline makes it possible to carry out the extraction and photometric determination of colourless anions such as CdI_4^{2-} (8). A large number of dyes, in particular anabasine dyes, luminescent dyes and others, can be used for similar purposes (9,10). Several papers have dealt with the study of aliphatic and heterocyclic amines as organic bases (11,12). The variety of the available so-called 'onium' bases has been widened, and bases such as $\text{R}(\text{CH}_3)_4^+$ (ammonium, phosphonium, arsonium, stibonium), $\text{R}(\text{CH}_3)_3^+$ (sulphonium, telluronium), $\text{[(C}_6\text{H}_5)_4\text{M}]^+$ (tetraphenyl arsonium, tetraphenylstibonium), etc., have been examined (13). The determination of 10^{-6} per cent of tantalum in a sample of niobium pentoxide irradiated by neutrons has been carried out by the extraction of the $\text{[(C}_6\text{H}_5)_4\text{As}]\text{TaF}_6$ ion associate complex (14).

Synergic phenomena with mixed complexes is considerably important. A particularly interesting trend which has been broadly reflected in analytical chemistry, is the study of mixed complexes formed by coordinately unsaturated chelates with donor molecules. Many synergic phenomena have been observed in solvent extraction.

Factors determining the positive and negative effects of synergy have been studied : the nature of the central atom, the nature of the ligands taking part in the formation of the adduct, the neutral effect of chelating and donor ligands, spatial effects, etc. But the complexity of this problem should be particularly emphasized. It should be recognized that many questions remain to be solved, and that the generalizations that have been suggested are not without exceptions. More references are also found in the text book of Morrison (15) and De (16) and Ph.D. thesis of Paria (17).

References

1. Bailey, B.W., Dagnall, R.M., and West, T.S., Talanta, 1966, 13, 753.
2. Gibalo, I.M., Alimarin, I.P., and Eremina, G.V., Zh. Analit. Khim. 1968, 23, 1822.
3. Zhivopistsev, V.P., Petrov, B.I., Selezneva, E.A., and Sibiriyakov, I.F., "Proceeding of the Commission for Analytical Chemistry," USSR Academy of Sciences 1968, 16, 80.
4. Zhivopistsev, V.P. and Petrov, B.I. Transactions of the Perm. State University, 1966, 159, 248.
5. Zhivopistsev, V.P., and Pyatosin, L.P. Zh. Analit. Khim. 1967, 22, 70.
6. Gibalo, I.M., Alimarin, I.P., and Eremina, G.V., Doklady Akad. Nauk SSSR, 1967, 176, 1300.
7. Kuznetsov, V.I. The Chemical Foundations of Extraction - Photometric Methods of Analysis. Gosgeal-tekhizdat, Moscow, 1963.
8. Keija, K., Bull. Chem. Soc. Japan 1965, 38, 986.
9. Talipov, Sh. T. and Dzhijanbaeva, R.K., Summary of the report at the All-Union Conference on the use of Organic Reagents in Analytical Chemistry, Saratov, 1966, p. 60.
10. Blyum, I.A. & Pavlova, N.N., Zavod. Lab. 1963, 29, 1407.
11. Ivanova, S.I., Gindin, L.M., and Mironova, L. Y., Izv. Akad.

Nauk. S.S.S.R. No. 7. Vypusk 2. 1964, 35.

12. Borbat, V.F., Bobikov, P.I., and Kouba, E.F., Zh. Analit. Khim., 1965, 20, 192.
13. Alimarin, I.P. and Makarova, S.V., Zh. Analit. Khim. 1964, 19, 90, 564, 847.
14. Alimarin, I.P., Bilimovich, G.N., and Yakovlev, Y.V., Zavod. Lab. 1967, 33, 145.
15. Morrison, G.H., and Freiser, H. Solvent Extraction in Analytical Chemistry, John Wiley & Sons, 1962.
16. De, A.K., Rhopkar, S.M. & Chalmers, R.A. Solvent Extraction of Metals, London, 1970.
17. Paria, P.K., Ph.D. Thesis, North Bengal University, 1975.

NORTH BENGAL
UNIVERSITY LIBRARY
RAJA RAMMOHUNPUR

85928
6 JUN 1984