STERIC AND HYDROPHOBIC EFFECTS OF SUBSTITUENTS IN EXTRACTION OF METAL COMPLEXES WITH O,O-DIALKYLDITHIOPHOSPHORIC ACIDS

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Summary—The two-phase stability constants (equilibrium constants) of metal complexes MA_n [M^{n+} = Ni(II), Zn(II), Cd(II), Pb(II), Tl(I), In(III)] with a series of O,O-dialkyldithiophosphoric acids in the system water–organic solvent) have been determined. By use of correlation analysis the role of the steric and hydrophobic effects of the substituents at the phosphorus atom on the stability constant β_n and distribution constant P of the complexes has been elucidated. The data obtained are of use for determining the relationships in the influence of structure of a reagent on its extraction properties and on the conditions for practical application of O,O-dialkyldithiophosphoric acids for metal extraction.

A great many organic compounds are suitable for extraction of metals from aqueous solution, but the search for new extractants continues, owing to the growing role of extraction methods in analysis and technology. In this context data on the interrelation between the structure of organic reagents and their extraction properties acquire especial significance.[1]

The O,O-dialkyldithiophosphoric acids (DTPA), first proposed by Busev and Ivaniutin[2] as analytical reagents, have found wide application in various methods of analyses. The availability of a wide variety of dithiophosphoric acid derivatives leads to choice of these compounds as an ideal model system for investigation of the influence of substituents in ligand molecules on the stability and distribution of the corresponding metal chelates. To examine the possibility of applying the principle of linear free-energy change for the quantitative estimation of substituent effects on the extraction properties of DTPA, the extraction of metal ions by a series of DTPA of different structure was investigated.

In extraction in a two-phase system of water and organic solvent there exists the equilibrium:

$$(M^{n+})_{aq} + n(A^-)_{aq} \rightleftharpoons (MA_n)_{org} \qquad (1)$$
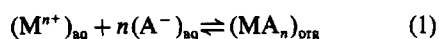
where M = Ni(II), Zn(II), Cd(II), Pb(II), Tl(I), In(III); A^- = anion of DTPA, $(RO)_2P(S)S^-$.

The equilibrium constant (or two-phase stability constant) is equal to the product of the stability constant of the complex MA_n in the aqueous phase, β_n and the distribution constant P:

$$P\beta_n = \frac{[MA_n]_{org}}{[M^{n+}]_{aq}[A^-]^n_{aq}} \qquad (2)$$

When the extraction proceeds in acid solutions, the distribution of DPTA must also be taken into ac-

count:

$$(H^+)_{aq} + (A^-)_{aq} \rightleftharpoons (HA)_{org} \qquad (3)$$
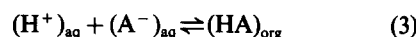
The equilibrium constant of this process (extraction constant of DTPA) is equal to K_d/K_a, where K_d is the distribution constant of HA between the aqueous and organic phases and K_a is the acid dissociation constant of HA in the aqueous phase.

EXPERIMENTAL

Reagents

O,O-Dialkyldithiophosphoric acids were synthesized and purified by a literature method.[3] Heptane, benzene, toluene, carbon tetrachloride and chloroform were used as the solvents.

Procedure

Extraction was performed in test-tubes at constant temperature (25 ± 0.2°) by shaking for 1 hr equal volumes (8 ml) of the aqueous and organic phases, the concentration of metal in the aquous phase being 5×10^{-4}–$10^{-3}M$. The ionic strength and acidity of the solutions were maintained by adding the appropriate amounts of perchloric acid and sodium perchlorate or, in the case of Pb(II) and Cd(II), hydrochloric acid and sodium chloride. The equilibrium concentration of free metal ions in the aqueous phase was determined by complexometric titration or polarographically.

RESULTS AND DISCUSSION

The values of K_d/K_a were obtained by the method of Wingefors.[4] The values of $P\beta_n$ were calculated by using the equation

$$\log D = n \log[A^-] + \log(P\beta_n) \qquad (4)$$

where D is the distribution ratio for the metal.

The dependence of $\log D$ on $\log[A^-]$ is a straight line with slope equal to the charge on the metal ion