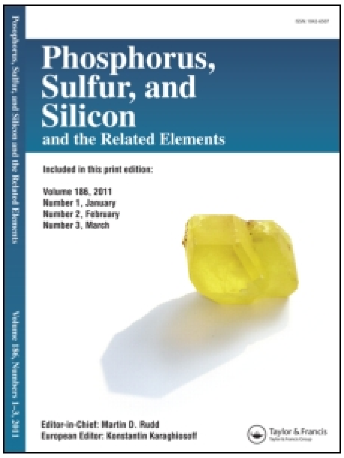

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# Acidic Phosphorus Esters, Synthesis and Structure-Reactivity Studies as Ligands

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# ACIDIC PHOSPHORUS ESTERS, SYNTHESIS AND STRUCTURE-REACTIVITY STUDIES AS LIGANDS

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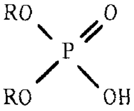
Abstract Methods for the synthesis of five types of acidic phosphates, phosphonates as well as phosphinates have been described. The mechanism of extraction of various metals by these compounds is examined. A free energy relationship existed in plotting equilibrium constants against either pKa or $\Sigma\sigma$ values of the acidic organophosphorus compounds under investigation. Steric effects, which is closely related to the configuration of the coordination compounds play an important role in these extraction systems as expected. A trial on estimation of Es values in extraction reaction was proposed.

## INTRODUCTION

Di (2-ethylhexyl) phosphoric acid (D2EHPA) has been extensively studied for the extractive separation of metal ions. The wider applications of D2EHPA are, however, limited by some disadvantages arised from its insufficient large capacity in extraction, difficult stripping and comparatively higher acidity of aqueous phase required for extraction. Various efforts have been made for the development of more powerful extractants. The appearance and industrial application of 2-ethylhexylphosphonic acid mono-2-ethylhexylester (IIa) in lanthanides and cobalt/nickel separation show great potentialities in this respects. The structure-reactivity study is considered to be one of the effectual routes to design valuable ligands.

Acidic phosphates or phosphonates may be regarded as products of partial or complete replacement or esterification of hydroxyl function in the molecule of phosphoric acid by alkyl groups. They may be classified as monobasic (I,II,III) or dibasic (IV,V) phosphates, phosphonates or phosphinates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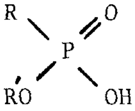
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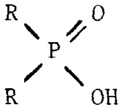
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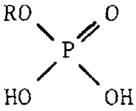
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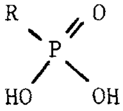
V

Ia $R=iC_8H_{17}$(1);Ib $R=sC_8H_{17}$(2);IIa $R=R'=iC_8H_{17}$(3);
IIb $R=iC_8H_{17}$, $R'=sC_8H_{17}$(4);IIc $R=sC_8H_{17}$, $R'=iC_8H_{17}$(5);
IId $R=cC_6H_{11}$, $R'=nC_8H_{17}$(6);IIe $R=cC_6H_{11}$, $R'=iC_8H_{17}$;(7);
IIf $R=cC_6H_{11}$, $R'=sC_8H_{17}$(8);IIg $R=CH_3$, $R'=iC_{18}H_{37}$(10);
IIh $R=iC_3H_7$, $R'=iC_{14}H_{35}$(9);IIi $R=C_6H_5$, $R'=nC_8H_{17}$(11);
IIj $R=C_6H_5$, $R'=iC_8H_{17}$(12);IIk $R=C_6H_5$, $R'=SC_8H_{17}$(13);
IIl $R=O\text{-}CH_3C_6H_4$, $R'=nC_8H_{17}$(14);IIm $R=O\text{-}CH_3C_6H_4$, $R'=iC_8H_{17}$(15);
IIIa $R=iC_8H_{17}$(17);IIIb $R=nC_8H_{17}$(16);IVa $R=iC_8H_{17}$(18);
IVb $R=iC_{18}H_{37}$(19);Va $R=iC_8H_{17}$(20);Vb $R=iC_{18}H_{37}$(21);

This paper describes the methods for the synthesis of five types of acidic organophosphorus acids with various substituents. The structure-reactivity studies of these compounds in extraction of cobalt and nickel as well as lanthanides were discussed in terms of reactivity of coordinating group and steric effect of ligand in the coordination process.

## SYNTHETIC STUDIES

The extraction behaviour of acidic phosphorus esters is closely related to the purity of these compounds. Negligible amount of neutral esters usually causes significant variation on the extraction performance of acidic phosphorus ligand due to synergistic effect. The purification method based on the recrystallization of the copper complex of acidic phosphorus ester was reported by our Laboratory as early as 1964. It was considered as a simple

& effective method for the purification phosphoates and phosphonates.

## STRUCTURE-REACTIVITY STUDIES

The distribution ratio(D) of rare earths as well as cobalt and nickel in extraction with mono-basic organophosphorus acids was investigated as a function of hydrogen ion concentration [H] in the aqueous phase and ligand concentration [HL] in the organic layer.

The D value for a given lanthanides or cobalt and nickel was found to be inversely third or second power dependent upon the [H] respectively and directly third or second power dependent upon the [HL]. The extraction constant (Kex) was thus calculated in the usual manner.

### Reactivity of the Coordinating Atom or Group

In extraction with organophosphorus acids, grouping >P(O)OH acts as coordinating group, in which the reactivity of ionizable hydrogen can be measured quantitatively by pKa value. As indicated in our previous reports both Kex for Nd, Sm, Y and Yb and D for Co are increased, as the acidity of ligand is enhanced.

For the quantitative studies, the influence of summation of Taft constants ($\Sigma\sigma$ *) of substituents and pKa of five different types of acidic phosphorus-based ligand with some alkyl groups Ia, IIa, IIIa, IVa and Va on their extraction behaviour for rare earths has been investigated.

The extraction constants of such elements by various acidic organophosphorus compounds are governed cheifly by the charge density of hydroxyl oxygen atom (HOMO) in group >P(O)OH in HMO calculation. The plot of Kex versus q OH (HOMO) values of these compounds gives straight line as anticipated, owing to the direct influence of qOH value on the pKa of ligand. A quantitative relationship also exists between the $\Sigma\lambda$i and $\Sigma\sigma\phi$ value of acidic phosphorus ligands. i.e.

$$\Sigma\sigma\phi = -4.12 + 0.166\ \Sigma\lambda i$$

## Steric effect of the Ligand

The steric effect in extraction was also illustrated by us that log Kex, ß is correlates linearly with Z/r value of metal ions in extraction by acidic organophosphorus ligands. On the basis of experimental data an empirical formula was deduced for extraction reaction

$$\log \mathrm{Kex},\ \beta = \alpha \mathrm{pKa} + \beta - \gamma\Sigma\ \mathrm{Es}$$

A series of steric constants for rare earth extraction ($E_s^{RE}$) of various substituents were estimated.

Various degree of steric effect was observed in extracting metals with the formation of different composition of extracted complex even with similar size of atomic radius. For exemple, the steric requirements of ligands for complex with square planar (i.e. $Cu^{2+}$, $Ni^{2+}$ with coordinated water molecule) is quite different from those with tetrahedron ($Co^{2+}$) or octahedron ($Ln^{3+}$) configuration.

It was also found by us that there is quantitative relationship between the separation factor (log $\beta$ ) and steric parameter ($\Delta$ Es) of ligand in extractive separation of cobalt and nickel by monobasic organophosphorus acids.

$$\log \beta = 1.0034\ \Delta \mathrm{Es} + 0.5486, \quad r = 0.997$$

On this theoretical basis some new organophosphorus based ligands were designed and synthesized.

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