# POLYFUNCTIONAL DERIVATIVES OF IMIDODIPHOSPHORIC ACID AS EXTRACTANTS

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The distribution of calcium, strontium, barium and scandium between aqueous and organic phases was studied using 0.1 M $HNO_3$ or 0.01 to 0.1 M HCl as the aqueous phase and solutions of selected derivatives of organophosphoric reagents containing the conventional =P(O)NHP(O)= bifunctional group or the analogous trifunctional or tetrafunctional group in various organic solvents as the organic phase. The effect of substitution of one ester group by an OH or $NH_2$ group was examined. While for the alkaline earth metals the distribution ratio increases if the bifunctional group is replaced by a higher-functional group, the reverse is true for scandium. The extraction efficiency is improved by the presence of OH or $NH_2$ substituent groups. The composition of the extracted species was inferred by logarithmic analysis and the corresponding extraction constants were calculated.

**Key words:** Calcium; Strontium; Barium; Scandium; Solvent extraction; Polyfunctional analogs of imidodiphosphoric acid.

Polydentate μ-imido organophosphoric compounds, in particular bidentate aryl esters of imidodiphosphoric acid, $(RO)_2P(O)NHP(O)(OR)_2$ (henceforth HA), serve as efficient extractants for the separation of many metals by solvent extraction[1–6]. In general, trivalent and polyvalent metals, particularly scandium and rare earth elements, are extracted selectively if oxygen derivatives are employed.

So far, little attention has been paid to tridentate and polydentate derivatives. Examination of such reagents and comparison of the extraction efficiency for some metals were the objectives of the present work.

## EXPERIMENTAL

### Chemicals and Apparatus

The following compounds were synthesized by applying procedures published previously[7,8]: $(PhO)_2P(O)NHP(O)(OPh)_2$ (**1a**); $(PhO)_2P(O)NHP(O)(OPh)NHP(O)(OPh)_2$ (**2a**); $(p\text{-Me–PhO})_2P(O)NHP(O)(p\text{-Me–OPh})NHP(O)(p\text{-Me–OPh})_2$ (**2b**); $(PhO)_2P(O)NHP(O)(OPh)NHP(O)(OPh)(OH)$ (**3a**);

$(PhO)_2P(O)NHP(O)(OPh)(NH_2)$ (**4a**); ($m$-Me–PhO)$_2$P(O)NHP(O)($m$-Me–OPh)(NH$_2$) (**4b**); $(PhO)_2P(O)NHP(O)(OPh)NHP(O)(OPh)(NH_2)$ (**4c**); $(PhO)_2P(O)NHP(O)(OPh)NHP(O)(NH_2)NHP(O)(OPh)_2$ (**4d**).

Their purity was checked by $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy[7]. Stock solutions were prepared by diluting the substances in benzene, chloroform, or a 1,1,2,2-tetrachloroethane–chloroform 1 : 1 mixture, as appropriate with respect to the solubility of the particular reagent in question. All chemicals were of reagent grade purity (Lachema, Brno, Czech Republic, and VEB Apolda, Germany).

Radioactive tracers (Poland) were added to the aqueous phases in the form of chlorides or nitrates. Their concentrations (in nmol $l^{-1}$) and specific activities (in kBq $ml^{-1}$) in the working solutions were as follows: $^{45}$Ca: 65, 9; $^{46}$Sc: 10–200, 50; $^{85}$Sr: 16, 3; $^{133}$Ba 12, 1.5. Their gamma activities were measured with an NA 3601 Gamaautomat (TESLA, Liberec, Czech Republic) equipped with an NaI(Tl) well-type detector. The beta activity of calcium was measured by using a pulse counter interfaced to a high-voltage supply (Military Institute 010, Vyskov, Czech Republic), an NKQ 323 probe, and an SPF 35 beta scintillator (both TESLA, Premysleni, Czech Republic). The pH of the aqueous phase was measured by means of an OP-208/I pH-meter fitted with an OP-0808P combined glass electrode (Radelkis, Hungary). Phthalate and citrate buffers were used for calibration. The NMR spectra were measured on an WP 80 SY spectrometer (Bruker, Germany).

A home-made shaking machine and test tubes with ground-in stoppers were used for the extraction.

### Procedure

The organic and aqueous phases (5 ml each) were mixed and agitated at 20 ± 1 °C for 60 min. This time was sufficient for the extraction equilibrium to establish, as verified by tentative experiments. After phase separation, 2 ml aliquots of either phase were taken. For Sr, Ba, and Sc, the aliquots were added to a glass ampoule and their gamma activity was directly measured, whereas for Ca, the solution was pipetted onto a Petri dish 50 mm in diameter, evaporated to dryness, and measured under the beta scintillator. The activity was such that the relative mean square deviation of each measurement did not exceed 2%.

## RESULTS AND DISCUSSION

### *Alkaline Earth Complexes*

The dependences of the distribution ratio of the alkaline earth metals on the analytical concentration of the reagents **1a** and **2a** in benzene (Fig. 1) demonstrate that the extractability is unambiguously higher with the reagent **2a** than with **1a**, the atomic number of the alkaline earth playing no role in this. Slope analysis of curves in Fig. 1 gives values of 2.0 ± 0.2. Since the dependences of the logarithm of the metal distribution ratio on pH (Fig. 2) also give slopes of 2.0 ± 0.1, the equilibrium can be described by Eq. (*A*):

$$M^{2+} + 2\,(HA)_0 \rightleftharpoons (MA_2)_0 + 2\,H^+ \qquad (A)$$

with the extraction constant

$$K_{ex} = \frac{[MA_2]_0\,[H^+]^2}{[HA]_0^2\,[M^{2+}]}\ , \qquad (1)$$

where M = Ca, Sr, Ba. The $K_{ex}$ values are given in Table I.

Figure 3 shows the dependences of the metal distribution ratio on the analytical concentration of reagent (in logarithmic coordinates) for reagents involving the OH and $NH_2$ functional groups as substituents, *viz.* **3a** (in chloroform), **4b** (in benzene), and **4c** (in chloroform). As mentioned above, chloroform was resorted to where the reagent solubility in benzene was insufficient. Logarithmic analysis of curves in Figs 2 and 3 follows more complex patterns. While all of the pH-dependences possess slopes of 2.0 ± 0.2, the dependences on the reagent concentration display slopes of 2.0 ± 0.2 only for the reagents **3a** and **4b** with Ca and Sr, whereas for the reagents **3a** with Ba, **4b** with Ba, and **4c** with Ca, Sr, and Ba, the slopes are 3.0 ± 0.3. This suggests that both the $MA_2$ and $MA_2(HA)$ type complexes are extracted. The calculated $K_{ex}$ values are also included in Table I. As to the extraction efficiency, Fig. 3 documents that the extractability with the reagent **3a**, possessing the OH functional group, is appreciable and increases in order Ba < Sr < Ca, which, however, does not apply to the reagents **4b** and **4c** possessing the $NH_2$ functional group.

### *Scandium Complexes*

The dependences of the distribution ratio of scandium on the concentration of the reagents in benzene solutions are shown in Fig. 4 (in logarithmic coordinates). In contrast to the alkaline earth metals, the extraction of scandium proceeds better in the presence

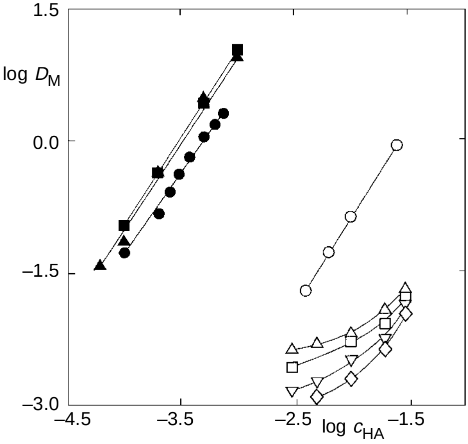

Fig. 1

Effect of analytical concentration of reagent **1a** (open symbols) or **2a** (full symbols) on the distribution of alkaline earth metals between aqueous 0.01 M HCl and benzene or toluene solution of reagent. Metal: ❍ Ca, Δ ∇ Sr, ❐ ✧ Ba; solvent: ∇ ✧ toluene, otherwise benzene

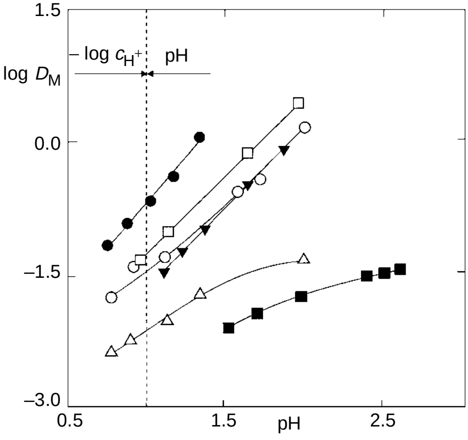

Fig. 2

Effect of aqueous phase acidity on the distribution of calcium and strontium. Reagent, solvent, metal, concentration (mmol $l^{-1}$): **1a**, toluene, ▼ Ca, 50; **2a**, benzene, ❍ Ca, 0.5, ● Sr, 1; **3a**, chloroform, ❐ Ca, 0.1, ■ Sr, 0.25; **4c**, chloroform, Δ Ca, 0.3

TABLE I
Extraction constant logarithms for metal complexes with the reagents[a]

| Reagent | Organic phase | log $D_M$ | | | |
|---|---|---|---|---|---|
| | | Ca | Sr | Ba | Sc |
| **1a** | benzene | –0.8 | –2.6 | –2.7 | 15.2 |
| | toluene | | –2.8 | –3.0 | |
| **2a** | benzene | 2.6 | 3.0 | 3.1 | 10.7[c] |
| **2b** | benzene | | | | 10.0[c] |
| **3a** | chloroform | 4.5 | 2.2 | 5.6[d] | 14.1 |
| **4a** | benzene | | | | 10.9 |
| **4b** | benzene | | 2.1 | 5.7[d] | |
| **4c** | chloroform | 5.3[d] | 5.2[d] | 5.1[d] | 13.7 |
| **4d** | mixture[b] | | | | 12.6 |

[a] Ionic strength 0.1 for Sc, 0.01 for Ca, Sr, Ba; [b] 1,1,2,2-tetrachloroethane–chloroform 1 : 1; [c] assumed organic phase composition: $ScNO_3A_2$, in other cases $ScA_3$; [d] composition: $MA_2(HA)$.

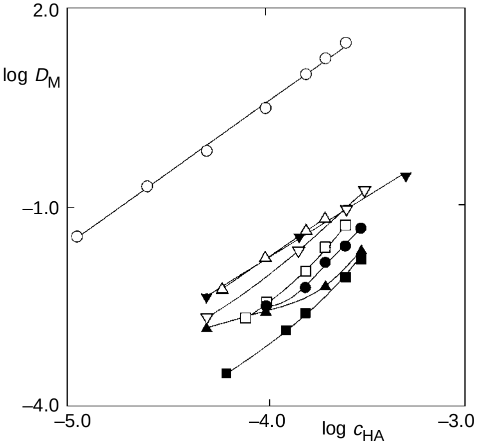

FIG. 3
Effect of analytical concentration of reagent on the distribution of alkaline earth metals between aqueous 0.01 M HCl and reagent solutions in benzene or chloroform. Reagent, solvent, metal: **3a**, chloroform, ❍ Ca, Δ Sr, ❒ Ba; **4b**, benzene, ▼ Sr, ∇ Ba; **4c**, chloroform, ● Ca, ▲ Sr, ■ Ba

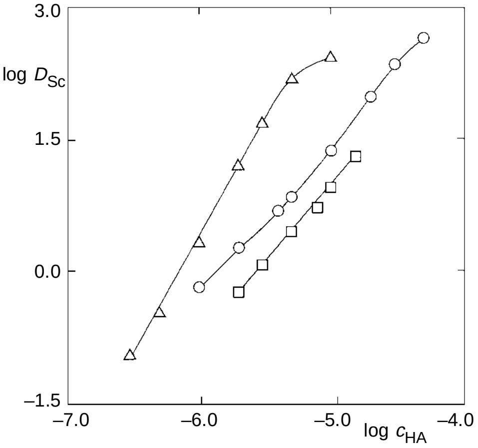

FIG. 4
Effect of analytical concentration of reagent on the distribution of scandium between aqueous 0.1 M $HNO_3$ and benzene solutions of reagents: Δ **1a**, ❍ **2a**, ❒ **2b**

of the bifunctional reagent **1a** than in the presence of the trifunctional reagents **2a** or **2b**. This astonishing fact is presumably due to the small scandium cation interacting better with a bifunctional group than with a trifunctional group, provided that the –OPh or –OPh–Me groups are only present. Slope analysis for the reagent **1a** indicates that the extractable complex is $ScA_3$. For the reagents **2a** and **2b** the maximum slope of the extraction curves in Fig. 1 is 2.0 ± 0.1, suggesting that the composition of the extractable complex is $ScNO_3A_2$. This problem was not studied in more detail within this work.

The situation is different with reagents where the ester groups are substituted. Figure 5 shows that, on the one hand, the scandium distribution ratio decreases considerably if the OPh group is substituted by an $NH_2$ group (**4a** *vs* **1a**) and, on the other hand, the distribution ratio increases slightly if the OPh group is substituted by OH or $NH_2$ groups; this, however, is true for the reagents **3a**, **4c** but not for the reagents **4a**, **4d** *vs* **2a**. (The fact that the organic phase composition is not identical in all cases was taken into account.) We can refer to the above reasoning concerning the interaction of the bifunctional and trifunctional groups, but support of this concept can only be gained through an X-ray study of the complexes in the solid state or by a spectroscopic study of the liquid phases.

Slope analysis of the curves in Fig. 5 leads to maximum slope values of 2.8 to 3.0. The fact that the pH-dependences of logarithms of the scandium distribution ratio for the reagents **1a**, **3a**, **4a**, and **4c** possess maximum slopes of 3.0 ± 0.2 suggests that the extractable complexes are $ScA_3$, formed by the pathway

$$Sc^{3+} + 3\,(HA)_0 \rightleftharpoons (ScA_3)_0 + 3\,H^+ \qquad (B)$$

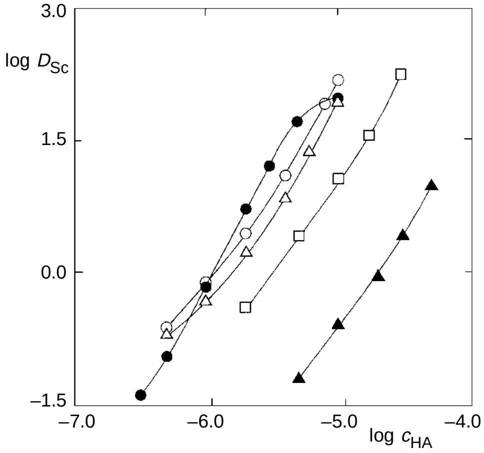

FIG. 5
Effect of analytical concentration of reagent on the distribution of scandium between aqueous 0.1 M $HNO_3$ and solutions of reagents in organic solvent. Solvent, reagent: benzene, ● **1a**, ▲ **4a**; chloroform, ❍ **3a**, Δ **4c**; 1,1,2,2-tetrachloroethane–chloroform mixture, ❐ **4d**

with the extraction constant

$$K_{ex} = \frac{[ScA_3]_0\,[H^+]^3}{[Sc^{3+}]\,[HA]_0^3}\ , \qquad (2)$$

whose values are included in Table I.

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