SULFUR ANALOGS OF IMIDODIPHOSPHORIC ACID AS EXTRACTANTS

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The distribution of Ag, Zn, Cd, Sc, Eu, Hg, and Hf between mineral acids (HNO_3, HCl) and benzene solutions of selected sulfur derivatives of organophosphoric reagents containing the P(X)NHP(X) or $(RO_3)PS$ group (X = O, S) was examined. The effect of the organic solvent was also investigated for Hg and some of the reagents. The composition of the complexes extracted was identified, and the corresponding extraction constants were calculated.
Key words: Solvent extraction; Sulfur analogs of imidodiphosphoric acid.

Polydentate μ-imido organophosphoric compounds, in particular alkyl and aryl esters of imidodiphosphoric acid and their sulfur analogs, $(RO)_2P(X)NHP(X)(OR)_2$ where X = O, S (henceforth HA), are employed as efficient reagents for the separation of many metals by solvent extraction[1–7]. As a rule, trivalent and multivalent metals, particularly scandium and rare earth elements, are extracted selectively with the oxygen derivatives, whereas metals such as platinum, silver, and mercury are extracted with the sulfur derivatives. Since the sulfur derivatives have not been mutually compared in detail, such comparison is presented in this paper. Special attention is paid to the distribution of mercury, which finds use as a detector in the determination of some chemical warfare agents[8].

EXPERIMENTAL

Chemicals and Apparatus

The following compounds were synthesized by procedures published recently[9–12]: $(PhO)_2P(S)NHP(S)(OPh)_2$ (**1a**), $(PhO)_2P(S)NHP(S)(p\text{-}Me\text{-}PhO)_2$ (**1b**), $(p\text{-}Me\text{-}PhO)_2P(S)NHP(S)(p\text{-}Me\text{-}PhO)_2$ (**1c**), $Ph_2P(S)NHP(S)Ph_2$ (**1d**), $(PhO)_3PS$ (**1e**), $(p\text{-}Me\text{-}PhO)_3PS$ (**1f**), $(PhO)_2P(S)OP(S)(OPh)_2$ (**1g**), $Ph_2P(S)NHP(S)(Ph)NHP(S)(Ph)_2$ (**1h**), $Ph_2P(S)NHP(S)(OH)NHP(S)(Ph)_2$ (**1i**), $\{[(PhO)_2PSS]^-,[NH_2(i\text{-}Bu)_2]^+\}$ (**1j**), $(PhO)_2P(O)NHP(S)(PhO)_2$ (**2a**), $(o\text{-}Me\text{-}PhO)_2P(O)NHP(S)(o\text{-}Me\text{-}PhO)_2$ (**2b**), $(m\text{-}Me\text{-}PhO)_2P(O)NHP(S)\text{-}(m\text{-}Me\text{-}PhO)_2$ (**2c**), $(p\text{-}Me\text{-}PhO)_2P(O)NHP(S)(p\text{-}Me\text{-}PhO)_2$ (**2d**), $(PhO)_2P(O)NHP(O)(PhO)_2$ (**3a**).

Their purity was checked by ^1H, ^{13}C, and ^{31}P NMR spectroscopy[10]. The stock solutions were prepared by dissolving weighed amounts of the reagents in the solvent of choice, *viz.* benzene, heptane, 1,1,2,2-tetrachloroethane, or chloroform. All chemicals were of reagent grade purity (Lachema, Brno, Czech Republic and VEB Apolda, Germany).

Radioactive isotopes (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: ^{46}Sc: 10–200, 50; ^{65}Zn: 2 000, 2; ^{60}Co: 9, 1; ^{110m}Ag: 500, 1; ^{115m}Cd: 200, 1; ^{155}Eu: 0.3, 0.8; ^{203}Hg: 38, 50.

The gamma activity of the solutions was measured on an NA 3601 Gamaautomat (Tesla, Liberec, Czech Republic) equipped with a well-type NaI(Tl) detector. The pH of the aqueous phase was measured with an OP-208/I pH-meter in conjunction with an OP-0808P combined glass electrode (Radelkis, Hungary), calibrated by means of phthalate and citrate buffers. The NMR spectra were scanned on a WP 80 SY instrument (Bruker, Germany).

Procedure

The mixtures of the organic and aqueous phases (5 ml + 5 ml), accommodated in test tubes with glass stoppers, were agitated on a home-made rotary shaking machine at 20 ± 1 °C for 60 min. (Preliminary experiments gave evidence that this period of time was sufficient for the extraction equilibrium to establish.) After phase separation, 2 ml aliquots of either phase were collected, and their gamma activity was measured in glass vials. The activity in the well-type detector was chosen so that the mean square error of measurement never exceeded 2%.

RESULTS AND DISCUSSION

Silver Complexes

The distribution ratios of silver between 0.1 M HNO_3 and benzene solutions of the reagents are plotted in Fig. 1 in dependence on the starting concentrations of the reagents (logarithmic scale). The plots show that the efficiency of extraction increases in
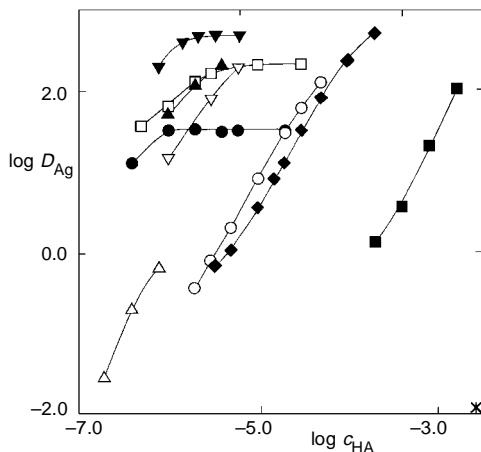

FIG. 1

Effect of the analytical concentration of reagent on the distribution of silver between aqueous 0.1 M HNO_3 and benzene. Reagent: **1a** (□), **1c** (●), **1d** (▼), **1f** (▽), **1g** (■), **1i** (▲), **1j** (△), **2a** (◆), **2b** (○), **3a** (✶)

order $3a < 1g < 2a = 2c = 2d < 2b < 1j < 1f < 1i < 1c < 1d = 1a$ (the curves for **2c** and **2d** are identical with that for **2a** and are not included in Fig. 1). The slopes of the ascending segments of the curves are 2.0 ± 0.2; this is not quite well demonstrable for the reagents **1c**, **1d**, and **1a**, which are so efficient extractants that the complexes pass into the organic phase even if the reagents are present in a very slight excess over the metal. The above series demonstrates that silver ions are not extracted with the oxygen derivatives of HA (**3a**), are poorly extracted with catena-dithiodiphosphoric acid esters (**1g**) which contain no acid hydrogen, and are moderately extracted with derivatives which involve the $=P(S)NHP(O)=$ grouping. The best results were achieved by using the reagents **1c**, **1d**, and **1a**. These findings are in line with the well-known fact[13] that silver ions are reluctantly coordinated by ligands containing oxygen donor atoms, but no conclusion can be made concerning the spatial arrangement of the complexes extracted (X-ray data are unavailable); so, assuming the coordination number 2 and the associated linearity of the complex structures, univalency of the ligands is involved.

As to the dependence of the logarithm of the silver distribution ratio on the logarithm of hydrogen ion concentration (pH) in the aqueous phase, the slope is 1.0 ± 0.2 for the acid HA reagent. This implies that silver passes into the organic phase following the scheme

$$Ag^+ + 2\,(HA)_0 \rightleftharpoons \quad [AgA(HA)]_0 + H^+ \qquad (A)$$

with the extraction constant

$$K_{ex} = \frac{[AgA(HA)]_0[H^+]}{[Ag^+][HA]_0^2} = 10^{0.05}\, D_{Ag}\, [H^+]\, /\, [HA]_0^2 \;, \qquad (1)$$

whose values, for ionic strength 0.1, are given in Table I. The correction term on the right-hand side of Eq. (*1*) corresponds to the stability constants of silver nitrate complexes[14].

Analogously, the scheme

$$Ag^+ + NO_3^- + 2\,(HA)_0 \rightleftharpoons \quad [Ag(NO_3)(HA)_2]_0 \qquad (B)$$

can be set up for the reagents **1f** and **1g**, the corresponding extraction constant being

$$K_{ex} = \frac{[Ag(NO_3)(HA)_2]_0}{[Ag^+][NO_3^-][HA]_0^2} \;. \qquad (2)$$

Mercury Complexes

The dependence of the mercury distribution ratio on the starting reagent concentration, on the logarithmic scale, is shown in Fig. 2 for 1 M HCl as the aqueous phase and benzene as the organic phase. The relatively high aqueous phase acidity was resorted to in view of the non-negligible solubility of $HgCl_2$ itself in pure organic solvents[5] at low starting HCl concentrations. The extraction efficiency increases in order **3a** < **1e** < **2a** < **1g** < **1f** < **1b** < **1a** < **1i** < **1h** < **1d** < **1j;** hence, mercury(II) ions remain virtually unextracted with oxygen derivatives of HA (**3a**) and are poorly extracted with trialkylthiophosphates (**1e**, **1f**), imidothiodiphosphoric acid esters (**2a**), and catena-di-thiodiphosphoric acid esters (**1g**). The best extraction efficiency is achieved by using diphenyldithiophosphoric acid **1j** (which is consistent with published data[15]) and imi-dotetraphenyldithiophosphoric acid **1d**.

TABLE I
Logarithms of extraction constants of metal complexes with the reagents[a]

Reagent	Metal				
	Ag	Hg	Sc[b]	Zn	Cd
1a	13.3	25.5	5.4	−1.6	2.8
1b		25.3			
1c	13.0				
1d	13.3	27.7		−0.1	4.0
1e		17.1			
1f	12.2	21.2			
1g	6.3	19.1			
1h		26.1			
1i	12.8	25.9			
1j	11.1	28.2			
2a	9.7	18.1	8.8		
2b	9.9				
2c	9.7				1.0
2d	9.7				
3a	0.6	15.3	15.5	0.9	1.3

[a] Organic phase: benzene, ionic strength 0.1 (for Hg 1.0); [b] ref.[6].

The slopes of the linear segments are 2.0 ± 0.2 for all curves in Fig. 2, irrespective of whether acid or neutral reagents are involved. This suggests that the composition of all of the extracted complexes is 1 : 2.

Noteworthy is the fact that the presence of an additional (third) P=S functional group in the reagent **1h** brings about decrease in mercury extractability (**1h** < **1d**), this being unaffected by replacement of the central Ph group by an OH group (**1i** = **1h**). This implies that divalent mercury reacts with the bidentate system but not with the tridentate system, and that the previously described formation of chelates of metals with the terminal N–P–S groups of the reagent **1a** (not the –S–P–N–P–S– groups, as given above) concerns palladium[9] only as an exception, this in the solid state. The former statement is borne out by the distribution of europium and cobalt in the presence of mercury, as shown in Fig. 3, demonstrating an apparent difference in the distribution of mercury on the one hand and europium and cobalt on the other hand using benzene solutions of **1i**, which gives evidence of a marked affinity of mercury for the sulfur-containing functional groups. The fact should be stressed that the aqueous phase acidity was 0.01 mol l^{-1} HNO_3 for cobalt and europium and 1 mol l^{-1} HCl for mercury. Furthermore, a difference in the behaviour of europium alone was observed when using the reagents **1i** and **1h**, the presence of the OH group bringing about an increase in the extractability by 3 orders of magnitude at least; this is presumably due to the conversion of the bidentate reagent to a tridentate one. Such behaviour is not observed for cobalt. Figure 3 also demonstrates a difference in the behaviour of the 3 metals in the presence of the reagent **1g**, in which the P=S groups are bonded by a oxygen bridge: although this reagent is associated with the lowest extractability of mercury from among all of the bidentate, or multidentate, reagents examined, the extractability of mercury with it exceeds that of cobalt and europium by several orders of magnitude. For the sake of completeness, the distribution of europium between 0.01 M HNO_3 and benzene solutions of the reagent **1a** is included in Fig. 3 as well.
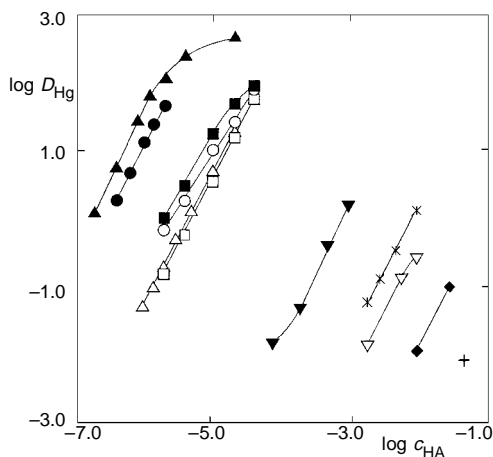

FIG. 2

Effect of the analytical concentration of reagent on the distribution of mercury between aqueous 1 M HCl and benzene. Reagent: **1a** (△), **1b** (☐), **1d** (●), **1e** (◆), **1f** (▼), **1g** (✶), **1h** (■), **1i** (○), **1j** (▲), **2a** (▽), **3a** (✚)

Figure 4 shows the dependence of the distribution of mercury on the aqueous phase acidity for the reagents **1a** and **1d** at an ionic strength of $I = 1.0$, adjusted with HCl and NaCl. The slope of the plot is 2.0 ± 0.1; hence, the acid reagents extract mercury following the scheme

$$Hg^{2+} + 2\,(HA)_0 \;\rightleftharpoons\; (HgA_2)_0 + 2\,H^+ \qquad (C)$$
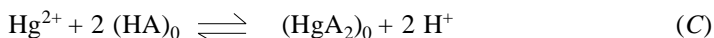
with the extraction constant

$$K_{ex} = \frac{[HgA_2]_0[H^+]^2}{[Hg^{2+}][HA]_0^2} \;, \qquad (3)$$

whose values are included in Table I. When calculating the extraction constant, the fact should be taken into account that D_{Hg} encompasses not only the Hg^{2+} ions but also the corresponding chloro complexes. Then we have for the aqueous phase

$$
\begin{aligned}
c_{Hg,w} &= [Hg^{2+}] + [HgCl^+] + [HgCl_2] + [HgCl_3^-] + [HgCl_4^{2-}] = \\
&= [Hg^{2+}]\,(1 + \sum_{i=1}^{i=4} \beta_i[Cl^-]^i) \;,
\end{aligned}
\qquad (4)
$$

where β_i are the cumulative constants of the mercury chloro complexes, taken into account in the calculation of K_{ex}. Based on data in stability constant tables[16], the $(1 + \beta_i[Cl^-]^i)$ value is $10^{14.81}$ for 1 M HCl; hence,

$$K_{ex} = 10^{14.81}\,D_{Hg}\,[H^+]^2/[HA]_0^2 \;. \qquad (5)$$

Since uncharged complexes only can pass into the organic phase, we suggest that the extraction of mercury by using the neutral reagents **1e**, **1f**, and **1g** (which involve no
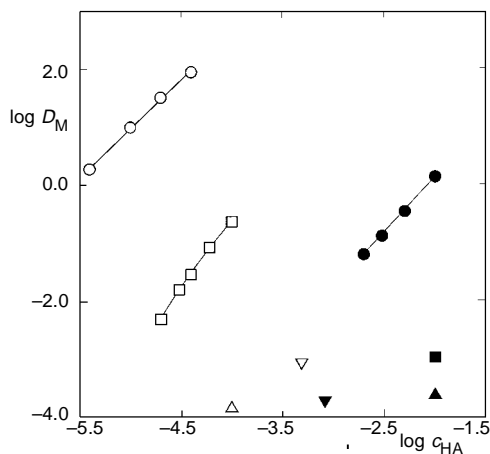

Fig. 3

Effect of the analytical concentration of reagent on the distribution of mercury, cobalt, and europium between aqueous 1 M HCl (Hg) or 0.01 M HNO$_3$ (Co, Eu) and benzene. Metal: Hg ($\bigcirc$), Co ($\triangle$), Eu ($\square$); full symbols: reagent **1g**, open symbols: reagent **1i**; europium + **1a** ($\triangledown$), europium + **1h** ($\blacktriangledown$)

acid hydrogen and therefore will be denoted R) is based on the solvation mechanism of ion pair formation:

$$Hg^{2+} + 2\ Cl^- + 2\ R_0 \quad \rightleftharpoons \quad [HgR_2^{2+};\ 2\ Cl^-]_0 \qquad (D)$$

with the extraction constant

$$K_{ex} = \frac{[HgR_2^{2+};\ 2\ Cl^-]_0}{[Hg^{2+}][Cl^-]^2[R]_0^2} = 10^{14.81} D_{Hg}/[Cl^-]^2[R]_0^2\ . \qquad (6)$$

To investigate the effect of the organic solvent on the distribution of mercury between 1 M HCl and solutions of the reagents **1a** and **1d**, we examined the dependence for the following solvents: heptane, benzene, 1,1,2,2-tetrachloroethane, and chloroform. The extractability of mercury decreases in this order (Fig. 5), *i.e.* in the order of increasing permittivities of the solvents.

Hafnium Complexes

The examination of hafnium was stimulated by its resemblance to zirconium, an important fission product, for which no suitable radioactive indicator is available. The dependence of the hafnium distribution ratio on the starting reagent concentration, using 1 M HNO$_3$ as the aqueous phase, is shown in Fig. 6 (in logarithmic coordinates). The use of so high an acidity was necessary in view of the hazard of hydrolysis at lower acid concentrations (this applies to hafnium as well as to zirconium). On the other hand, the fact then should be taken into account that the extraction mechanism may not be based on ion exchange solely, the transfer of combined complexes[17,18] of the type of Hf(NO$_3$)$_x$A$_{4-x}$(HA)$_y$ into the organic phase being conceivable. Figure 6 demonstrates that the extractability of hafnium increases in order **2a** < **1a** <
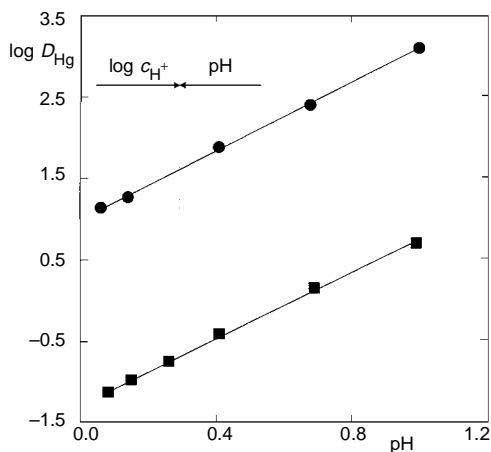

FIG. 4
Effect of aqueous phase acidity on the distribution of mercury between 1 M (H$^+$, Na$^+$)Cl and benzene solutions of the reagents **1a** (■) and **1d** (●)

1c < **3a** < **1d**; hence, neither oxygen-containing nor sulfur-containing HA reagents are preferred by hafnium when using 1 M HNO_3 as the aqueous phase. The reagent **1d**, which possesses the =P(S)NHP(S)= group and whose four phenyl groups are directly bonded to phosphorus, seems to be an exception. Logarithmic analysis of the curves in Fig. 6 suggests that the $Hf(NO_3)_2A_2$ complexes ($Hf(NO_3)A_3$ for the reagent **1c**) pass into the organic phase. Further research is necessary to obtain conclusive results.

Scandium Complexes

The dependence of the scandium distribution ratio on the starting reagent concentration, using 0.1 M HNO_3 as the aqueous phase and benzene as the organic phase, is shown in Fig. 7 (in logarithmic coordinates). The extractability of scandium is
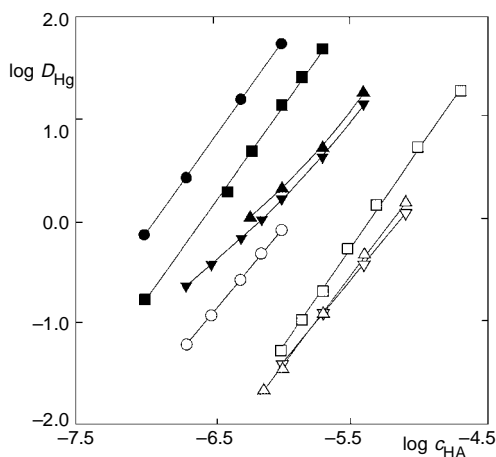
FIG. 5
Effect of the analytical concentration of reagent (**1a**, open symbols, and **1d**, full symbols) on the distribution of mercury between 1 M HCl and the organic phase, *viz.* heptane ($\bigcirc$), benzene ($\square$), 1,1,2,2-tetrachloroethane ($\triangle$), and $CHCl_3$ (∇)
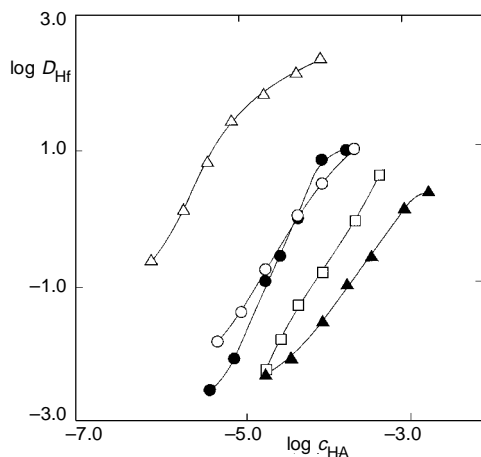

FIG. 6
Effect of the analytical concentration of reagent on the distribution of hafnium between aqueous 1 M HNO_3 and benzene. Reagent: **1a** ($\square$), **1c** ($\bullet$), **1d** ($\triangle$), **2a** ($\blacktriangle$), **3a** ($\bigcirc$)

clearly seen to increase in order **1a** < **2a** << **3a** in agreement with the data mentioned in the introduction. In contrast to hafnium, the reagent **1d** is no exception with scandium.

As found by us previously[6], the complexes passing into the organic phase are ScA_3. Their extraction constants are consistent with the sequence above.

Some differences in the reactivity of reagents in group **2**, associated with steric effects, are likely and call for a more detailed investigation.

Zinc and Cadmium Complexes

The dependences of the zinc and cadmium distribution ratios on the starting reagent concentrations, using 0.01 M HCl as the aqueous phase and benzene as the organic phase, are shown in Figs 8 and 9, respectively (in logarithmic coordinates). The lower acidity than in the cases above is associated with the fact that the extractability of the two metals involved is generally lower. The plots of the logarithms of the distribution ratios of the two metals in dependence on pH for the reagents **1a**, **1d**, and **3a** give straight lines with slopes of 2.0 ± 0.2, which, along with the result of slope analysis of the dependences in Fig. 8, suggests that the ZnA_2 complexes are extracted into the organic phase. On the other hand, the use of reagents containing the =P(O)NHP(S)= group, *i.e.* **2a**, **2b**, **2c**, and **2d**, leads to a slope of 1, suggesting that only the ZnClA complexes, *i.e.* ion-associates, are extracted. This assumption, however, is not well grounded in a sufficient volume of experiments, and so it lacks the necessary likelihood; still, it is a fact that such behaviour is only exhibited by the above reagents containing the functional group mentioned, involving both sulfur and oxygen atoms.
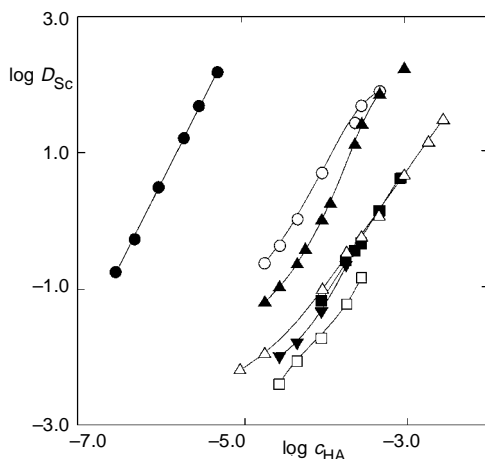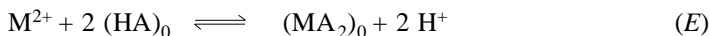

Fig. 7
Effect of the analytical concentration of reagent on the distribution of scandium between aqueous 0.1 M HNO_3 and benzene. Reagent: **1a** (□), **1d** (▼), **2a** (△), **2b** (■), **2c** (○), **2d** (▲), **3a** (●)

With cadmium the situation is unambiguous: only the CdA_2 complexes are extracted with the reagents **1a**, **1d**, **2c**, and **3a**. The extraction process can be described as

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

(M = Zn, Cd), with the extraction constant

$$K_{ex} = \frac{[MA_2]_0[H^+]^2}{[M^{2+}][HA]_0^2} = D_{Zn}\,[H^+]^2/[HA]_0^2 = 10^{0.31}\,D_{Cd}\,[H^+]^2[HA]_0^2 \ . \qquad (7)$$

The correction value on the right-hand side of Eq. (7) for Cd is associated with the formation of chloro complexes[14] in 0.01 M HCl, which is negligible for zinc. The K_{ex} values are included in Table I.
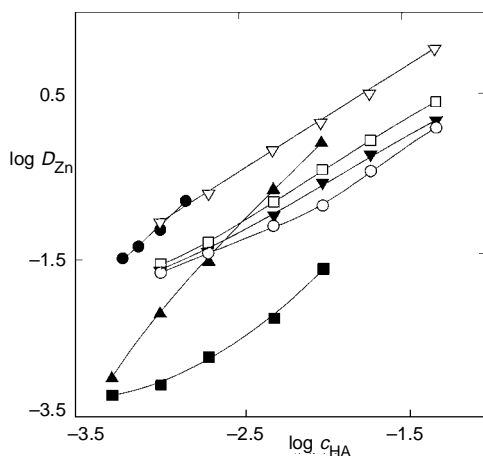

Fig. 8
Effect of the analytical concentration of reagent on the distribution of zinc between aqueous 0.01 M HCl and benzene. Reagent: **1a** (■), **1d** (▲), **2a** (○), **2b** (▽), **2c** (□), **2d** (▼), **3a** (●)
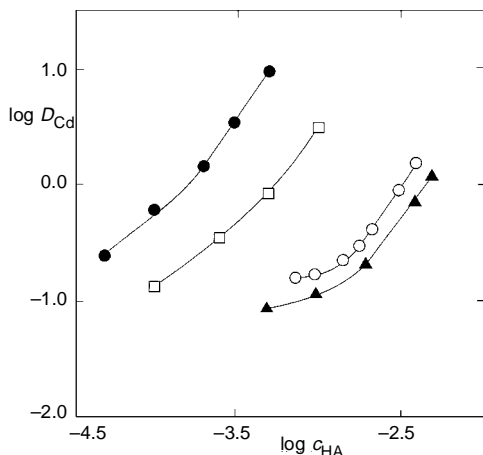

Fig. 9
Effect of the analytical concentration of reagent on the distribution of cadmium between aqueous 0.01 M HCl and benzene. Reagent: **1a** (□), **1d** (●), **2c** (▲), **3a** (○)

Summing up the experimental results, the data confirm the conclusions given in the introduction. Silver and mercury prefer unambiguously the sulfur analogs of imidodiphosphoric acid and diimidotriphosphoric acid, notably the reagents **1a** through **1d**, **1h**, and **1i**. Minor differences in the extractability of the two elements exist (*e.g.*, the reagents **1a**, **1d**), which will allow their mutual separation. The platinum metals will apparently behave likewise. The divalent cations of zinc, cadmium, and cobalt, on the other hand, react reluctantly with those reagents, and the reaction is largely little selective. This is also why the differences between the sulfur and oxygen derivatives are not very marked. Trivalent scandium and rare earth elements prefer the sulfur analogs unambiguously. From among the elements examined, only hafnium does not discriminate clearly between the reagents containing sulfur only or oxygen only when extracted from the aqueous phase into benzene.

Thus, esters of imidodiphosphoric acid and its sulfur analogs appear to be promising reagents, not only with respect to the efficiency of extraction but also in view of their easy preparation.

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