EFFICIENCY OF TETRAPHENYLIMIDO DIPHOSPHATE AS AN EXTRACTANT

Oldřich NAVRÁTIL[a] and Eckhard HERRMANN[b]

[a] *Department of Chemistry, Military University, 682 03 Vyškov, Czechoslovakia*
[b] *Chemistry Section, Martin Luther University, 4010 Halle-Wittenberg, Germany*

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Tetraphenylimido diphosphate (HA) and five other bidentate reagents containing PO and CO groups in a close vicinity to phenyl or phenoxy groups were examined as reagents for solvent extraction of some metals. Hafnium, scandium and rare earth compounds were found to easily pass from weakly acid aqueous solutions into benzene solutions of HA, whereas the other reagents investigated mostly lack this extracting power. The causes of this effect are discussed.

Bidentate extractants, particularly phosphorus-containing ones, have gained a firm position in separation processes in nuclear technology[1]. They can be divided into neutral and acid reagents, or into homofunctional and heterofunctional reagents.

Previously[2-5] we concerned ourselves with the application of tetraphenylimido diphosphate, $[(PhO)_2P(O)]_2NH$ (henceforth HA), as an extractant for the separation of some metals, fission products in particular. In order to verify the separation efficiency of this reagent, we compared it in the present work with that of other bidentate reagents containing PO and CO groups in a close vicinity to phenyl (Ph) or phenoxy (OPh) groups. The metals on which the efficiency was tested included silver, zinc, scandium, europium, thulium, and hafnium; benzene served as the organic solvent.

EXPERIMENTAL

Chemicals and Apparatus

The following bidentate acidic reagents were used: $PhCOCH_2COPh$ (*I*), PhCONHCOPh (*II*), $(PhO)_2PONHCOPh$ (*III*), $(PhO)_2POCH_2COPh$ (*IV*), $(PhO)_2POCH_2PO(OPh)_2$ (*V*), and $(PhO)_2PONHPO(OPh)_2$ (*VI*). Their synthesis and purity checking have been described[3,6,7]. The other chemicals used were of reagent grade purity.

The radioactive isotopes ^{46}Sc, ^{65}Zn, ^{110m}Ag, $^{152+154}$Eu, ^{170}Tm, and $^{175+181}$Hf (Poland and C.I.S.) were used in their solutions in 0.1M-HCl (2M-HCl for Hf) or in 0.1M-HNO_3 (Ag). Their specific activities (in kBq cm^{-3}) and concentrations (in μmol l^{-1}) in the working solutions were as follows: Sc 10 – 500, 0.2 – 1.1; Zn 2, 160; Ag 1, 2.5; Eu 2.5, 0.1 – 0.3; Tm 3, 340; and Hf 5, 1.7, respectively.

The gamma activity of the solutions was measured with a Nuclear Chicago 1185 Automatic Gamma Counting System (U.S.A.).

Procedure

Benzene and water (5 ml each) were shaken on a rotary shaking machine at 20 ± 1 °C for 2 h ; this time was sufficient for the extraction equilibrium to establish. After phase separation, 2 ml of each phase were pipetted into glass ampoules and their gamma activity was measured. The relative standard deviation of the individual measurements did not exceed 2%. The aqueous phase contained HCl in a concentration of 0.1 mol l^{-1} (2 mol l^{-1} for Hf), or HNO$_3$ in the former concentration (for Ag).

RESULTS AND DISCUSSION

For the metal distribution study, the initial concentration of the reagents *I* through *VI* in benzene was 2 . 10^{-3} mol l^{-1}. The logarithms of the distribution ratios, log D, are given in Table I. They indicate that in the above conditions, complexes of the metals are extracted only with those reagents containing two (PhO)$_2$PO– functional groups. The PhCO– group plays virtually no role. Scandium with reagent *IV* is an exception; this element has a special position due to its cation radius. No doubt is raised that all the reagents employed function as bidentate reagents, i.e., coordination of the CO group to the central atom exists. Six-membered chelate rings with the reagent in the enol form are invariably involved. Reagents *I* through *IV*, however, cannot compete with reagents *V* and *VI* with their double PO coordination. In the two-phase system, the stability of the complexes extracted will depend on the dissociation constants of the reagents in the aqueous phase (e.g., for reagents *I* and *VI* at an ionic strength of 0.1, pK = 9.35 (ref.[8]) and 4.11 (ref.[3]), respectively); the distributions constants $K_{D,HA}$ and dimerization constants in the organic phase of the reagents as well as the stability constants of the complexes in the aqueous phase and their distribution constants will also contribute.

TABLE I
Logarithms of metal distribution ratios, log D, for systems comprising solutions of reagents *I* – *VI* (2 mmol l^{-1}) in benzene and 0.1M-HCl or HNO$_3$ aqueous phases

Metal	*I*	*II*	*III*	*IV*	*V*	*VI*
Ag	-3.35	-3.05	-3.30	-2.55	-1.55	-1.80
Zn	< -4.0	*a*	< -4.0	< -4.0	*a*	-2.77
Sc	-3.30	-3.20	-4.0	-0.60	1.37	> 3.5
Tm	< -4.0	< -4.0	< -4.0	< -4.0	-2.75	1.60
Eu	< -4.0	< -4.0	< -4.0	-4.0	-2.10	0.90
Hf^b	< -4.0	*a*	< -4.0	-1.02	*a*	1.16

^{a} Not determined; ^{b} c(HCl) = 2 mol l^{-1}.

The dependence of the metal distribution ratio (*D*) on the starting reagent concentration in benzene was also examined for the last two reagents. The dependences for Sc, Eu, Tm, Ag and Hf are shown in Fig. 1. Their slope analysis indicates that with reagent *VI* (HA), the MeA_3 complexes (Me = Sc, Tm, Eu) and AgA are extracted. Scandium is extracted very efficiently, its extraction constant is 10^{14} at an aqueous phase ionic strength of 0.1. Thus, this reagent can be applied with advantage to the extraction of lanthanoids or actinoids, as has also been demonstrated previously[3].

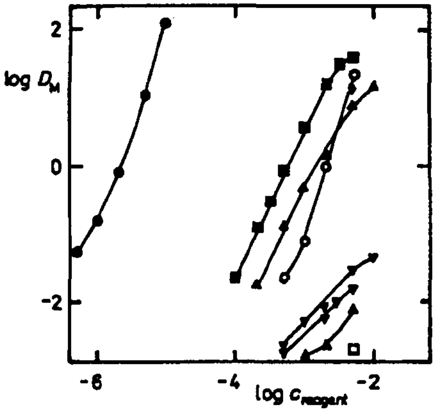

FIG. 1

Distribution of metals between solutions of reagents *V* (open marks) and *VI* (full marks) in benzene and aqueous phase of 0.1M-HCl (2M-HCl for Hf) or 0.1M-HNO_3. ○ Sc, □ Tm, △ Eu, ▽ Ag, ◇ Hf

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