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EXTRACTION EQUILIBRIA OF RARE EARTHS BY A NEW REAGENT (2-ETHYLHEXYL-3-PENTADECYLPHENYL) PHOSPHORIC ACID

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Summary—A new reagent (2-ethylhexyl-3-pentadecylphenyl) phosphoric acid (EPPA = HR) was synthesized from cardanol (I, 37300-39-5) and was used to investigate the extraction behaviour of lanthanum(III), europium(III) and lutetium(III) from hydrochloric acid solutions The species extracted were found to be $Ln(HR_2)_3$ (where Ln = La(III) or Eu(III) or Lu(III)) The extraction behaviour of the above lanthanides has also been compared with yttrium and other rare earths It was observed that the extraction increases with increase in atomic number of rare earths In addition, the extraction efficiency of EPPA has also been compared with well known acidic organophosphorus extractants like di-2-ethylhexyl phosphoric acid (DEHPA), 2-ethylhexyl-mono-2-ethylhexyl phosphoric acid (EHEHPA)

Synthesis of novel and specific organic complexing agents often leads to the development of new separation systems for aqueous metal ions. Most of the studies on solvent extraction of rare earths utilize well known commercial acidic organophosphorus extractants like DEHPA[1–5] and EHEHPA.[6–9] There are not many recent reports on the synthesis of newer reagents for the extraction of rare earths. Recently, a variety of octyl phosphonic acid monooctyl esters were synthesized and correlated the structure of these reagents with the extraction of rare earths.[10] The present paper reports the synthesis of new reagent (2-ethyl-hexyl-3-pentadecyl) phenyl phosphoric acid from cardanol. The extraction behaviour of lanthanum(III), europium(III) and lutetium(III) from aqueous chloride solutions using the above reagent in toluene or methylisobutyl ketone (MIBK) as diluents, respectively has been studied with a view to elucidate the nature of complexes extracted into the organic phase. The extraction efficiency of EPPA in comparison with some well-known commercially available acidic organophosphorus extractants has also been systematically investigated

EXPERIMENTAL

Apparatus

IR spectra were recorded in Perkin-Elmer Model 299 B IR spectrometer The ^1H NMR spectra were recorded in a Hitachi 24 B model, 60 HZ NMR spectrometer. The ^{31}P and ^{13}C NMR were recorded in a JEOL FX-90 QFT spectrometer.

A Hitachi 220 double beam microprocessor controlled molecular absorption spectrophotometer was used for measuring the absorbances. An ELICO LI-120 digital pH meter was used for the pH measurements.

Reagents

Stock solutions of the lanthanides were prepared from their oxides (Rare Earth Products, Cheshire, U.K., 99.99%) by dissolving in 2 ml of 1.1 hydrochloric acid and diluting to 100 ml.

Ammonium acetate buffer (pH 7.5) was prepared by dissolving 19.25 g in 250 ml of water and adjusting the pH to 7.5 with HCl or NaOH.

Arsenazo I (Fluka, Switzerland) was prepared by dissolving 25 mg of the reagent in 250 ml of water.

All the other chemicals were of analytical reagent grade and were used without further purification

Cardanol was obtained by double vacuum distillation of cashewnut shell liquid (CNSL-8007-24-7) at 3–4 mm Hg and collecting the fraction distilled at 230–235°C CNSL was purchased from Kerala State Cashew Development Corporation, Quilon. The hydrogenation of cardanol was done in a Parr hydrogenator.

Phosphorus oxychloride was distilled before use 2-ethyl hexanol was dried over calcium oxide and then distilled. Triethylamine was dried over anhydrous KOH and distilled. Benzyl alcohol was dried over anhydrous K_2CO_3 and distilled All the solvents such as hexane, methylene chloride and toluene were dried by following standard methods and then distilled.

Extraction equilibrium procedure

Distribution coefficients were determined by shaking equal volumes of aqueous and organic phases (10 ml) for 5 min in a 60 cm^3 separating funnel at 303 ± 1 K. (Extraction equilibrium was attained in 2 min.) The initial metal ion concentration in the aqueous phase was maintained at $\sim 6 \times 10^{-5} M$ except in the experiments on the role of metal ion concentration. After allowing the phases to settle, a 5 cm^3 aliquot of the aqueous phase was pipetted into a 25 cm^3 beaker and 1 cm^3 of ammonium acetate buffer and 5 cm^3 of Arsenazo I were added for the determination of metal ion. After adjusting the pH to 7.5 ± 0 1, the solutions were transferred to 25 cm^3 volumetric flasks and made up to the mark

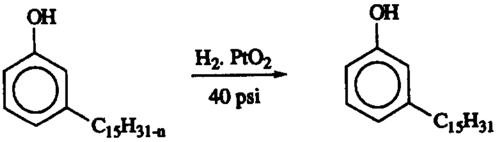
The absorbance of the solutions were measured at 575 nm and the rare earth concentrations were computed from the respective calibration graphs The rare earth concentration in the organic phase was obtained by difference. These concentration values were used to obtain the distribution ratio (D) defined as

$$D = \frac{[\bar{Ln}]}{[Ln]}$$

RESULTS AND DISCUSSION

Synthesis of (2-ethylhexyl 3-pentadecylphenyl) phosphoric acid (EPPA)

Efforts were made to synthesize new extractants EPPA starting from easily available naturally occurring materials like cashewnut shell liquid (CNSL-8007-24-7) which is a byproduct of cashew industry. The major component of CNSL is cardanol (I, 37300-39-5) which is a mixture of 3-pentadecyl phenol with varying degrees of unsaturation. Cardanol was isolated by fractional distillation and the fraction obtained, at 230–235°C at 3–4 mm of Hg, was collected.

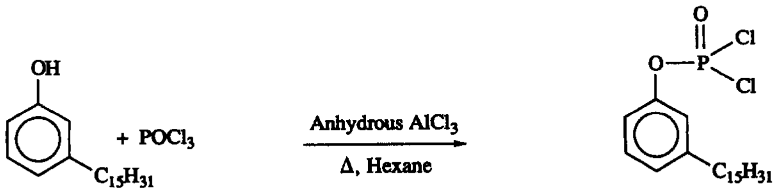


Scheme 1

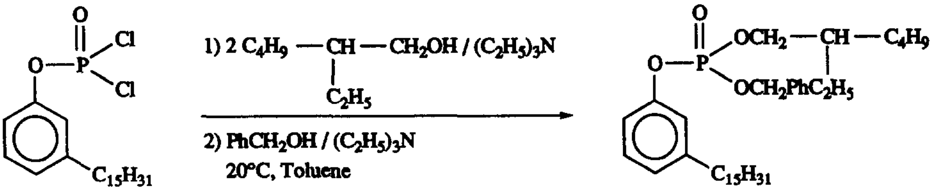
Hydrogenation of cardanol to 3-pentadecylphenol. Cardanol (100 g, 0.33 mol) in methanol (100 ml) was hydrogenated in a parr hydrogenator at 40 psi using platinum oxide (50 mg) at ambient temperature The hydrogenation was complete in 2 hr. The methanolic solution was filtered to remove the catalyst and the solvent was stripped off The residue was distilled under vacuum (4 mm of Hg) to give a white solid. This solid on recrystallization in hexane gave pure 3-pentadecylphenol (M P. = 51°C). IR and NMR of the compound corresponds to the values reported in literature. This reaction is shown in Scheme 1 (yield 70%)

Synthesis of 3-pentadecylphenyl phosphorodichloridate 3-pentadecylphenol (0.33 mol, 100 g) in dry hexane (500 ml) was added dropwise to a refluxing solution of a mixture of phosphorous oxychloride (60 g, 0.39 mol) and anhydrous $AlCl_3$ (1% of phenol, 0.44 g). The reaction was continued for 6 hr. The $AlCl_3$ is filtered off and the excess of $POCl_3$ and hexane were removed to obtain (3-pentadecylphenyl) phosphorodichloridate. The reaction is shown in Scheme 2 (yield = 90%).

Synthesis of (2-ethylhexyl-benzyl-3-pentadecylphenyl) phosphate A mixture of 2-ethyl hexanol (30.9 g, 0.24 mol) and triethylamine (24 g, 0.24 mol) in toluene were added dropwise to a solution of 3-pentadecylphenyl-phosphorodichloridate (100 g, 0 24 mol) in toluene at 20°C followed by the addition of a mixture of



Scheme 2



Scheme 3

benzyl alcohol (25 5 g, 0.24 mol) and triethylamine (24 g, 0.24 mol). The mixture was stirred for 24 hr. The triethylamine hydrochloride was removed by washing with water and solvent stripped off. The pure benzyl ester was isolated by column chromatography (see Scheme 3) (yield = 81%).

Synthesis of (2-ethylhexyl-3-pentadecylphenyl) phosphoric acid (EPPA). A mixture of benzyl ester (100 g, 0.17 mol) and 10% Pd on activated charcoal (7.8 g) in acetic acid (100 cm^3) was hydrogenated at ambient temperature and atmospheric pressure for 1 hr. The activated charcoal was filtered off. Acetic acid was removed by washing with water and the solvent was stripped off. The pure EPPA was recovered. The reaction is shown in Scheme 4 (yield 1 = 100%).

The above product was characterized by IR, ^{1}H NMR and ^{31}P NMR.

IR.

2950 cm^{-1} P—OH, 3000 —C—H aromatic
2920 cm^{-1} C—H aliphatic, 1630 cm^{-1} (C═C aromatic)
1250 cm^{-1} P═O, 1150 cm^{-1} (P—O—C aryl)
980 cm^{-1} (P—O—C aryl).

^{1}H NMR.

δ 0.9 (m, 3 H, CH_3), δ 1.2 (m, 26 H $(CH_2)_{13}$),
δ 2.5 (m, 2 H, Ar—CH_2), δ 3.8 (m, 2 H, —OCH_2),
δ 6.8 (m, 4 H, Ar—H), δ 12.2 (S, 1 H, P—OH).

^{31}P NMR:

−6.2 ppm

C—H analysis (%) Found C 69.93 H 10.29

The reaction scheme is as shown in Schemes 1–4

Extraction studies of the rare earths using (2-ethylhexyl-3-pentadecylphenyl) phosphoric acid (EPPA)

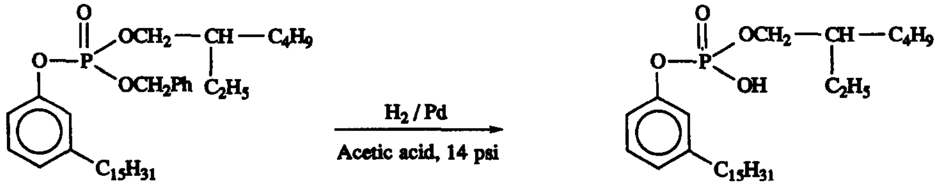
Distribution of acid. The association of EPPA in toluene and MIBK was ascertained by IR absorption spectra. No band for the —OH in the vicinity of 2900–3550 cm^{-1} was observed. The absence of OH indicated hydrogen bonding which may be due to the association of EPPA molecules The nature of aggregation was also confirmed by vapour pressure osmometry as it showed a molecular weight of 990 in toluene. This indicates that EPPA exists as dimer in toluene and MIBK.

Extraction mechanism. The general mechanism of extraction of lanthanides by an acidic organophosphorous extractant, may be represented by the following general expression[11]

$$Ln^{3+} + 3\,\overline{(HR)_2} \rightleftharpoons \overline{Ln(HR_2)_3} + 3\,H^+$$

where Ln stands for rare earth element and $\overline{(HR)_2}$ refers to the dimer of the extractant in the organic phase.

Effect of EPPA. The dependence of the extraction of lanthanum(III), europium(III) and lutetium(III) (representative of light, middle and heavy rare earths) from 0 1*M* of HCl solutions into toluene and MIBK was investigated as a function of EPPA concentration (0.0015–0 002*M* for Lu(III), 0.01–0.03*M* for Eu(III) and 0.03–0 08*M* for La(III) in toluene and 0.018–0.028*M* for Lu(III), 0.076–0.14*M* for Eu(III) and 0.12–0 22*M* for La(III) in MIBK, respectively) In both diluents, the extraction



Scheme 4

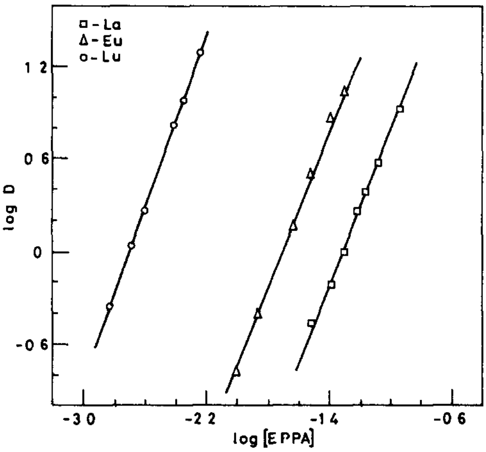


Fig 1 Plot of log D *vs* log [EPPA] during the extraction of La(III), Eu(III) and Lu(III) in presence of 0 1M HCl into toluene

increases with increase in reagent concentration for all rare earths. The plot of log D *vs* log (EPPA) is linear (Figs 1 and 2 for toluene and MIBK as diluents, respectively) with slopes equal to 2.9 ± 0.3 and 3.2 ± 0.2 suggesting that three molecules of the reagent are involved in the extracted species.

Effect of H^+ *concentration.* Increase of H^+ concentration at a constant strength of Cl^- from a mixture of HCl + LiCl solutions decreases the extraction of rare earths into EPPA in toluene. The EPPA concentrations used were 0.08M for La(III), 0.025M for Eu(III) and 0.01M for Lu(III) in toluene. The plot of log D *vs* log [H^+] has slope of −2.9 ± 0.2 (Fig. 3) suggesting that the release of three H^+ ions during extraction with EPPA. This confirms the cation exchange mechanism as represented above. Similar results and conclusions were drawn using MIBK as diluent.

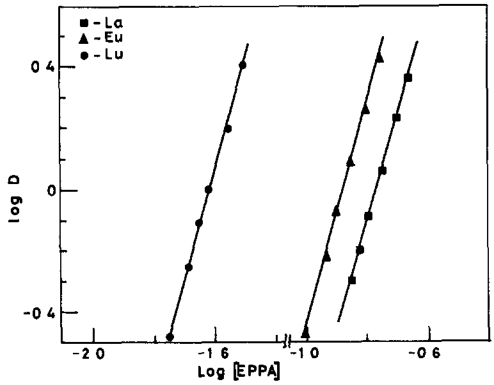


Fig 2 Plot of log D *vs* log [EPPA] during the extraction of La(III), Eu(III) and Lu(III) in presence of 0 1M HCl into MIBK

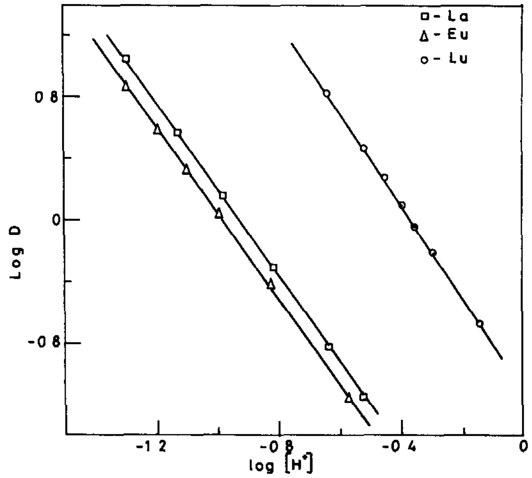


Fig 3 Plot of log D *vs* log [H^+] during the extraction of La(III), Eu(III) and Lu(III) with 0 08, 0 025 and 0 01M EPPA in toluene using HCl + LiCl mixtures

Effect of metal ion concentration. The effect of varying the metal ion concentration on the extraction of La(III), Eu(III) and Lu(III) from 0.1M HCl solutions by 0.05, 0.015 and 0 0015M EPPA, respectively in toluene has been studied. The log–log plot (Fig 4) of equilibrium organic phase metal concentration against the equilibrium aqueous phase metal concentration is linear with a slope of nearly equal to 0.87 ± 0 1 indicating the extraction of mononuclear metal complexes Similarly, the effect of metal ion concentration on the extraction of La(III), Eu(III) and Lu(III) from 0.1M HCl solutions into EPPA in MIBK as diluent has also been studied. Similar conclusions were drawn using MIBK as diluent (cf. Fig 5) as in the case of toluene.

Extraction behaviour of other rare earths. The extraction behaviour of other rare earths including yttrium has been studied at two different

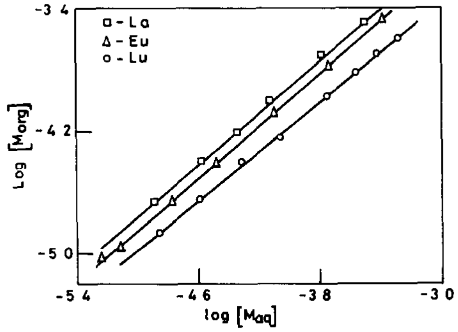


Fig 4 Effect of metal ion concentration on the extraction of La(III), Eu(III) and Lu(III) from 0 1M HCl medium by EPPA (0 05M for La(III), 0 02M for Eu(III) and 0 002M for Lu(III) in toluene

Table 1 Distribution ratios of Ln(III)–HCl–EPPA

	Distribution ratios									
Reagent	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
0.1*M* HCl 0.002*M* EPPA in toluene	<0.01	<0.01	<0.01	0.07	0.03	0.06	0.08	0.58	1.0	0.10
0.1*M* HCl 0.025*M* EPPA in toluene	0.18	0.63	0.85	1.76	2.40	2.52	57.82	>99.99	>99.99	54.56
0.1*M* HCl 0.04*M* EPPA in MIBK	<0.01	<0.01	<0.01	<0.01	0.04	0.04	0.12	4.67	7.16	0.23
0.1*M* HCl 0.1*M* EPPA in MIBK	<0.01	0.14	0.25	0.29	0.33	0.51	5.94	32.99	43.50	21.00

Table 2 Comparison of extraction efficiency of EPPA with D2EHPA and EHEHPA

	Distribution ratios					
	0.002*M* extractant			0.025*M* extractant		
Reagent	La	Eu	Lu	La	Eu	Lu
(a) Toluene as diluent						
EPPA	<0.01	0.03	1.0	0.18	2.40	>99.99
D2EHPA	<0.01	<0.01	0.05	<0.01	<0.03	<39.82
EHEHPA	<0.01	<0.01	<0.01	<0.01	<0.01	0.24
	0.04*M* extractant			0.1*M* extractant		
(b) MIBK as diluent						
EPPA	<0.01	0.05	7.16	<0.01	0.33	23.50
D2EHPA	<0.01	<0.01	1.72	<0.01	0.01	48.02
EHEHPA	<0.01	<0.01	0.34	<0.01	<0.01	8.80

concentrations of EPPA (0.002 and 0.025*M* in case of toluene as diluent and 0.04*M* and 0.1*M* in case of MIBK as diluent) and the results obtained are shown in Table 1. It is clearly seen from Table 1 that EPPA is a selective extractant for heavy rare earths (especially for Yb and Lu) when compared to lighter and middle rare earths.

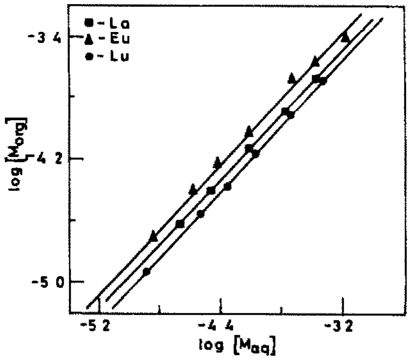


Fig 5 Effect of metal ion concentration on the extraction of La(III), Eu(III) and Lu(III) from 0.1*M* HCl medium by EPPA (0.18*M* for La(III), 0.15*M* for Eu(III) and 0.025*M* for Lu(III)) in MIBK

Comparison with other acidic organophosphorous extractants. The extraction efficiency of EPPA has been compared with well known commercially available acidic organophosphorous extractants like DEHPA and EHEHPA for the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1*M* HCl solutions. The comparison has been made at different extractant concentrations in toluene and MIBK (see Table 2). In all the cases EPPA was found to be a better extractant for heavy rare earths especially ytterbium and lutetium than DEHPA and EHEHPA.

REFERENCES

1 A T Kandil and K Farah, *J Inorg Nucl Chem*, 1980, **42**, 277
2 P R Daneshi, E P Horwitz and P Rickert, *Sep Sci Technol*, 1982, **17**, 1183
3 G W Mason, D N Metta and D F Peppard, *J Inorg Nucl Chem*, 1976, **38**, 2077
4 N E Thomas and L E Burkhart, *J Inorg Nucl Chem*, 1974, **36**, 1369
5 T C Owens and M Smutz, *J Inorg Nucl Chem*, 1968, **30**, 1617

6 Y Mori, H Ohya, H One and W Eguchi, *J Chem Engng Japan*, 1981, **21**, 86

7 P B Santhi, M L P Reddy, T R Ramamohan and A D Damodaran, *J Chem Engng Japan*, 1991, **24**, 542

8 T Sato, *Hydrometallurgy*, 1989, **22**, 121

9 B J Ballint, *J Rare Earths*, 1991, **1**, 386

10 C Yuan, H Long, E Ma, W Cheng and X Yan, *Proc of Int Conf on Rare Earth Development and Applications*, 1985, **1**, 457

11 D F Peppard, G W Mason and S W Moline, *J Inorg Nucl Chem*, 1957, **5**, 141