Extraction of Lanthanides as Mixed Ligand Complexes : A Study of Complex Formation & Distribution Equilibria

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Lanthanide metal ions form intensely red-coloured mixed ligand complexes with 4-(2-pyridylazo)resorcinol (PAR) in the presence of antipyrine and anions like perchlorate, which get readily extracted into nitrobenzene. Quantitative recovery of lanthanides is achieved even in a single extraction into nitrobenzene at pH 6.0-7.5 and in the presence of 30-50-fold PAR, 200-350-fold antipyrine and 90-130-fold perchlorate. The composition of the mixed ligand species extracted indicates a ratio of metal : PAR : antipyrine : perchlorate = 1:1:1:1. The distribution coefficient of PAR and antipyrine between nitrobenzene and water, the stepwise ionisation constants of PAR and the overall extraction equilibrium constants of the mixed ligand complexes have been determined. The trend in the variation of the extraction constants with the atomic number of lanthanide metal ions and the mechanism of extraction are discussed.

THE reagent, 4-(2-pyridylazo) resorcinol (PAR) forms intensely red-coloured water-soluble complexes with lanthanides in aqueous solution at pH 6 to 8 and several authors[1-6] have proposed this reaction for the photometric estimation of lanthanides. Chang Tiau-Hsu et al.[7] investigated this reaction potentiometrically in 1:1 dioxan-water mixture and determined the stability constants. However the extraction of lanthanide-PAR complexes has so far not been reported in the literature. Lanthanides form mixed ligand complexes with PAR in the presence of antipyrine and an anion like perchlorate, which get readily extracted into oxygenated solvents. In our earlier communication[8] we proposed a sensitive and selective photometric method for the estimation of lanthanides based on extraction. The present paper deals with the results of our investigations on the extraction equilibria and mechanism of extraction of the lanthanide mixed ligand complexes.

Materials and Methods

CZ spectrophotometer and Toshniwal Digital pH meter were used. Stock solutions of lanthanides, PAR, antipyrine and sodium perchlorate were prepared and standardised as reported earlier[8]. Other reagents used were of AR grade. Freshly distilled solvents and deionised water were employed. All the distribution experiments were carried out at an ionic strength of 0.20 ± 0.01 (sodium perchlorate or sodium sulphate) and $28° \pm 1$ °C.

General extraction procedure and calculation of distribution ratio → An aliquot of lanthanide metal ion was mixed with requisite amounts of PAR, antipyrine and perchlorate, diluted to 15 ml, the pH adjusted to the appropriate value and equilibrated with an equa volume of nitrobenzene for 1 min. The organic phase after separation was dried over

anhydrous sodium sulphate and its absorbance measured at 520 or 530 nm against reagent blank. The distribution ratio of the metal (q) was calculated from the absorbance values using Eq. (1)

$$q = A_{obs}/(A_{max} - A_{obs}) \qquad ..(1)$$

where A_{obs} is the absorbance of the complex; A_{max} is the absorbance when all the metal is assumed to be complexed and extracted and corresponds to the absorbance of the metal in presence of large excess of reagent under optimum conditions. The value of q compared satisfactorily with the value obtained by estimating the lanthanide metal content present in aqueous and organic phase after back extraction (twice with 0.05 N HCl) with Arsenazo III[9].

The distribution ratio (D) of PAR between nitrobenzene and water was determined in the presence of antipyrine and perchlorate at various pH values by equilibrating known amount of PAR and estimating the amount of PAR present in the aqueous phase.

The partition coefficient (P) of antipyrine between nitrobenzene and water was determined by equilibrating known amount of antipyrine and estimating the amount of antipyrine present in the aqueous phase by an iodometric method[10].

The composition of the extracting species in all the systems was determined by the method of slope analysis.

Results and Discussion

The optimum conditions for the extraction of lanthanide-PAR-antipyrine-perchlorate mixed ligand complexes, given in Table 1, indicate that quantitative recovery of lanthanides can be achieved even in a single extraction with only 1 min equilibration time at pH 6.5 and in presence of 30-50-fold PAR, 200-350-fold antipyrine and 90-130-fold excess of perchlorate. Among the various

TABLE 1 — OPTIMUM CONDITIONS AND EXTRACTION EQUILIBRIUM CONSTANTS OF LANTHANIDE-PAR-ANTIPYRINE-PERCHLORATE MIXED LIGAND COMPLEXES

[Ionic strength $= 0.20 \pm 0.01$; temp. $= 28° \pm 1°C$]

Metal M^{3+}	pH	[PAR] (M)	[Antipyrine] (M)	[Perchlorate] (M)	Av. % recovery	log K_E^H	log K_E
La	5.5-7.0	40	200	110	98.9	4.08	16.38
Ce	6.0-7.5	40	250	130	99.3	4.41	16.71
Pr	6.0-7.5	40	300	110	99.4	4.72	17.02
Nd	6.0-7.4	30	250	90	98.9	4.76	17.06
Sm	6.0-7.5	30	250	90	98.6	4.99	17.29
Eu	6.0-7.5	40	350	130	99.3	4.19	16.48
Gd	6.0-7.5	50	300	110	99.4	4.11	16.41
Tb	6.0-7.5	40	200	130	99.5	4.60	16.90
Dy	6.0-7.5	30	250	110	98.8	4.70	17.00
Ho	6.4-7.5	30	200	130	99.2	4.82	17.12
Er	6.4-8.0	40	250	130	98.8	4.91	17.21
Tm	6.0-7.5	30	250	130	99.3	4.83	17.13
Yb	6.0-7.5	50	350	110	99.5	4.66	16.96
Lu	6.0-7.5	50	300	110	98.7	4.57	16.87

solvents studied, nitrobenzene is found to be the most efficient solvent for the quantitative recovery of lanthanides.

Chloride, bromide, nitrate, acetate, sulphate, thiocyanate and cyanide do not interfere with the extraction even when present in 1000-fold amounts. Fluoride, pyrophosphate, thiosulphate, citrate, tartrate and oxalate do not interfere when present in 100-fold amounts. However, EDTA and phosphate interfere seriously even when present in amounts equal to that of lanthanides. Al(III), Be(II), Mo(VI), Ca(II), Mg(II) and Tl(III) in 100-fold amounts do not interfere with the extraction. Zr(IV) does not interfere with the extraction provided the reagent (PAR) is present in sufficient excess. Zn(II), Co(II), Ni(II), Cd(II), Fe(III), Cu(II), Th(IV) and U(VI) interfere with the extraction by forming extractable complexes. However, their interference can be effectively eliminated by prior extraction of these metal ions with sodium diethyldithiocarbamate[11] into chloroform-acetone (5:2) at pH 3.0.

The distribution ratio (D) of PAR can be represented as

$$D = \frac{[H_2R]_{org}}{[H_3R^+]_{aq} + [H_2R]_{aq} + [HR^-]_{aq} + [R^{2-}]_{aq}}$$

$$= \frac{K_{DR}}{\dfrac{[H^+]}{K_{a1}} + 1 + \dfrac{K_{a2}}{[H^+]} + \dfrac{K_{a2}.K_{a3}}{[H^+]^2}} \quad ..(2)$$

where K_{a1}, K_{a2}, K_{a3} are the ionisation constants of H_3R^+, H_2R and HR^- respectively and K_{DR} is the distribution coefficient of PAR. The values of K_{a1}, K_{a2}, K_{a3} and K_{DR} obtained from a plot of log D versus $2 pH$ (Fig. 1) were in good agreement with those reported earlier in the literature by other methods[12,13].

The partition coefficient (P) of antipyrine between nitrobenzene and water was found to be 3.20 which was in agreement with the previously reported value of Rao et al.[14]
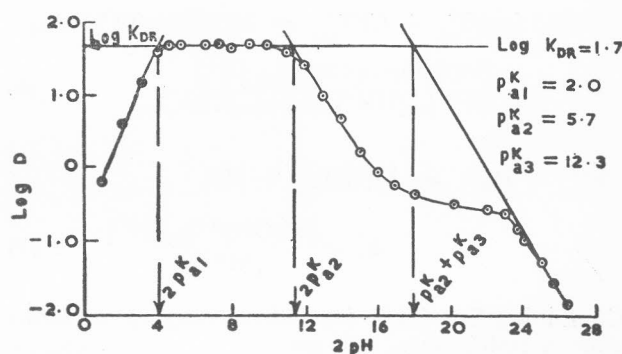

Fig. 1 — pH dependence on the distribution of PAR [5.0 ml of 1×10^{-2} M PAR + 2.0 ml of 1×10^{-1} M antipyrine + 1.0 ml of 3.0 M sodium perchlorate + x ml of $HClO_4$ and/or NaOH Aqueous phase diluted to 25 ml and equilibrated with 25 ml nitrobenzene].

The linear plots of log q versus log $[PAR]_{total}$, log q versus log $[antipyrine]_{total}$ and log q versus log $[perchlorate]_{total}$ have unit slopes indicating the composition of the extracted species as metal: PAR : antipyrine : perchlorate $= 1 : 1 : 1 : 1$. The variation of distribution ratio of the metal (log q) with pH is linear with a slope of unity indicating the replacement of one hydrogen ion during complexation. Plot of log q versus log [nitrobenzene] is also linear with a slope of two indicating the association of two nitrobenzene solvent molecules with the extracting species.
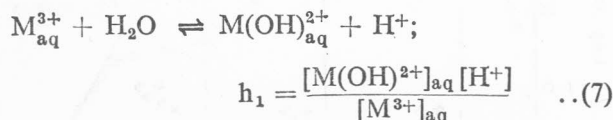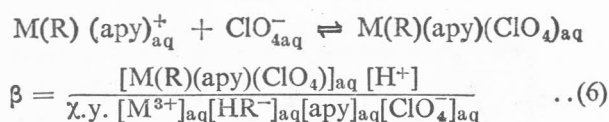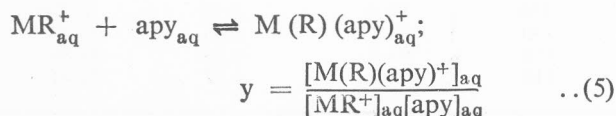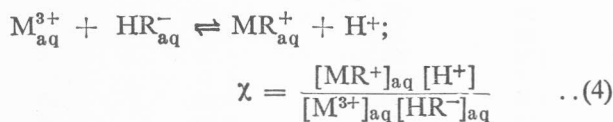
Under the experimental conditions lanthanide metal ions and PAR exists predominantly as M^{3+} and HR^- respectively. The formation and extraction of the lanthanide-PAR-antipyrine-perchlorate complex can therefore be represented as

$$M^{3+}_{aq} + HR^-_{aq} + apy_{aq} + ClO^-_{4aq} \rightleftharpoons$$

$$[M(R)(apy)(ClO_4)]_{aq} + H^+$$

$$\Updownarrow$$
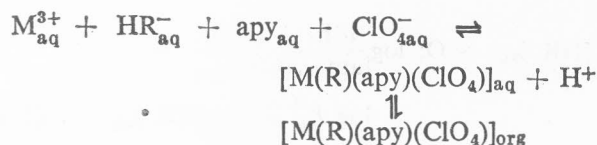
$$[M(R)(apy)(ClO_4)]_{org}$$

the 'acid extraction constant, K_E^H' can be given by Eq. (3)

$$K_E^H = \frac{[M(R)(apy)(ClO_4)]_{org}[H^+]}{[M^{3+}]_{aq}[HR^-]_{aq}[apy]_{aq}[ClO_4^-]_{aq}} \qquad ..(3)$$

considering the following stepwise equilibria (4, 5) and their formation constants

$$M_{aq}^{3+} + HR_{aq}^- \rightleftharpoons MR_{aq}^+ + H^+;$$

$$\chi = \frac{[MR^+]_{aq}[H^+]}{[M^{3+}]_{aq}[HR^-]_{aq}} \qquad ..(4)$$

$$MR_{aq}^+ + apy_{aq} \rightleftharpoons M(R)(apy)_{aq}^+;$$

$$y = \frac{[M(R)(apy)^+]_{aq}}{[MR^+]_{aq}[apy]_{aq}} \qquad ..(5)$$

$$M(R)(apy)_{aq}^+ + ClO_{4aq}^- \rightleftharpoons M(R)(apy)(ClO_4)_{aq}$$

$$\beta = \frac{[M(R)(apy)(ClO_4)]_{aq}[H^+]}{\chi.y.[M^{3+}]_{aq}[HR^-]_{aq}[apy]_{aq}[ClO_4^-]_{aq}} \qquad ..(6)$$

$$M_{aq}^{3+} + H_2O \rightleftharpoons M(OH)_{aq}^{2+} + H^+;$$

$$h_1 = \frac{[M(OH)^{2+}]_{aq}[H^+]}{[M^{3+}]_{aq}} \qquad ..(7)$$

Combining Eqs (3) to (6) and rearranging the terms after simplification, we get

$$K_E^H = \lambda . \chi . y . \beta \qquad ..(8)$$

where λ is the partition coefficient of the mixed ligand complex between nitrobenzene and water.

In the absence of any predominant side reactions except that of the first stage of the hydrolysis of the lanthanides, the distribution ratio (q) of the metal may be represented as

$$q = \frac{[M(R)(apy)(ClO_4)]_{org}}{[M^{3+}]_{aq}+[MR^+]_{aq}+[M(OH)^{2+}]_{aq}} \qquad ..(9)$$

Combining Eqs (6) to (9), we get

$$q = \frac{K_E^H[HR^-]_{aq}[apy]_{aq}[ClO_4^-]_{aq}}{[H^+]\{1 + \chi[HR^-]_{aq}[H^+]^{-1} + h_1[H^+]^{-1}\}} \qquad ..(10)$$
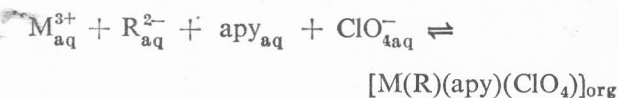
The distribution curve of $\log q$ versus $\log[HR^-]_{aq}$ will have two assymptotes[15], namely

$$[HR^-]_{aq} \rightarrow 0; \log\frac{q\{h_1 + [H^+]\}}{[apy]_{aq}[ClO_4^-]_{aq}} =$$

$$\log K_E^H + \log[HR^-]_{aq} \qquad ..(11)$$

and

$$[HR^-]_{aq} \longrightarrow \infty ; \log q = \log \lambda \qquad ..(12)$$

The 'extraction constant (K_E)' of the mixed ligand complex which represents the equilibrium reaction

$$M_{aq}^{3+} + R_{aq}^{2-} + apy_{aq} + ClO_{4aq}^- \rightleftharpoons$$

$$[M(R)(apy)(ClO_4)]_{org}$$

is related to the 'acid extraction constant (K_E^H)' by the Eq (13)

$$\log K_E = \log K_E^H + pK_{a3} \qquad ..(13)$$

The equilibrium concentrations of $[HR^-]_{aq}$, $[apy]_{aq}$ and $[ClO_4^-]_{aq}$ have been calculated using the mass balance Eqs (14) to (16).

$$[HR^-]_{aq} = \frac{[PAR]_{total}-[M(R)(apy)(ClO_4)]_{org}}{1 + \frac{K_{a3}}{[H^+]} + \frac{[H^+]}{K_{a2}}\left(1 + K_{DR} + \frac{[H^+]}{K_{a1}}\right)} \qquad ..(14)$$

$$[apy]_{aq} = \frac{[apy]_{total}-[M(R)(apy)(ClO_4)]_{org}}{(1 + P)} \qquad ..(15)$$

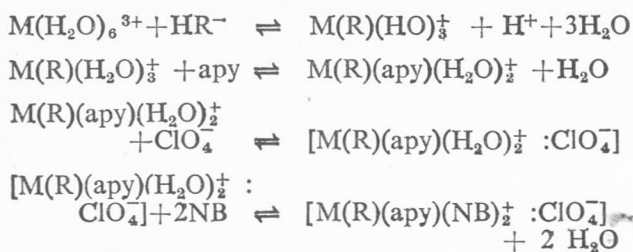$$[ClO_4^-]_{aq} = [ClO_4^-]_{total} - [M(R)(apy)(ClO_4)]_{org} \qquad ..(16)$$

The acid extraction constants of the mixed ligand complexes have been obtained from the intercepts of the plots of $\log\dfrac{q\{h_1 + [H^+]\}}{[apy]_{aq}[ClO_4^-]_{aq}}$ versus $\log[HR^-]_{aq}$ as per Eq. (11). The extraction constants of the complexes (K_E) have been evaluated from Eq. (13) and the values are incorporated in Table 1.

The variation of $\log K_E$ with atomic number (Z) of lanthanides indicates a more or less regular increase of K_E with atomic number in the case of lighter lanthanides, a break at Gd^{3+} and almost constancy for the heavier lanthanides. This is in agreement with the behaviour of lanthanide metal ions with a number of chelating agents such as acetylacetone[16], diglycolic acid[17], dipicolinic acid[18], etc. It appears reasonable to interpret the gadolinium break on the basis of the half-filled electronic configuration for the terpositive lanthanide metal ions[19].

Based on the experimental evidence the mechanism outlined in Scheme 1 is proposed for the formation and extraction of lanthanide-PAR mixed ligand complexes into nitrobenzene

$$M(H_2O)_6{}^{3+} + HR^- \rightleftharpoons M(R)(HO)_3^{\ddagger} + H^+ + 3H_2O$$

$$M(R)(H_2O)_3^{\ddagger} + apy \rightleftharpoons M(R)(apy)(H_2O)_2^{\ddagger} + H_2O$$

$$M(R)(apy)(H_2O)_2^{\ddagger} + ClO_4^- \rightleftharpoons [M(R)(apy)(H_2O)_2^{\ddagger} :ClO_4^-]$$

$$[M(R)(apy)(H_2O)_2^{\ddagger} : ClO_4^-] + 2NB \rightleftharpoons [M(R)(apy)(NB)_2^{\ddagger} :ClO_4^-] + 2\ H_2O$$

Scheme 1

It is believed that an ion association type of mixed ligand complex of lanthanide-PAR-antipyrine with perchlorate is initially formed in solution which is hydrophilic because of the presence of two water molecules in the coordination sphere. Nitrobenzene being a weak oxygen donor[20,21] enters into the coordination sphere of the lanthanides and replaces the water of hydration rendering the species hydrophobic and thus facilitating quantitative extraction.

Acknowledgement

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