*Asian Journal of Chemistry* Vol. 4, No. 2 (1992), 402–404

*NOTE*

# Mixed Ligand Complexes of Praseodymium(III) with 8-Quinolinol and 1,10-Phenanthroline or 2,2′-Bipyridyl into Molten Naphthalene

V. P. MITTAL* AND P. C. VYAS

*Department of Chemistry, University of Rajasthan,*
*Jaipur-324 004, India*

The solid-liquid extraction of mixed ligand complexes of praseodymium(III) with 8-quinolinol and 1,10-phenanthroline or 2,2-bipyridyl has been investigated in molten naphthalene-DMF. Traces of metal extracted are determined spectrophotometrically. The extraction of the mixed ligand complexes has been discussed in terms of various parameters, like Beer's law, range of concentration, molar absorptivity and Sandell's sensitivity. The results are compared with the equilibrium extraction behaviour of praseodymium(III) complexed with 8-quinolinol alone. An enhancement in extractability of praseodymium(III) due to the formation of mixed ligand complexes has been noticed.

The liquid-liquid extraction of mixed ligand complexes of a series of tervalent lanthanide metal ions with 8-quinolinol (8-HQ) and nitrogen containing bases like 1,10-phenanthroline (phen) and tetraalkyl ammonium salts ($R_4N^+$) reported by Freiser *et al.*[1,2] These investigations revealed that lanthanons are extracted as the ternary complexes having composition $LnQ_3$. 2HQ Phen. Tervalent lanthanide ions usually have coordination number greater than six, these can be expected to form coordinately unsaturated chelates. The advantage of mixed ligand extraction has been recognized in the improved separation and extraction capabilities. The analysis by solid-liquid extraction continues to be a valuable tool for the separation and preconcentration of metals from aqueous solutions[3–5]. Use of 8-HQ and its halogen derivatives for preconcentration of Pr(III) into molten naphthalene has been reported earlier[6]. The present communication reports the extractive spectrophotometric determinations of mixed ligand complexes of Pr(III) with 8-HQ and Phen or 2,2′-bipyridyl (Bipy) into molten naphthalene. The comparative studies of equilibrium extraction behaviour of binary and ternary complexes of Pr(III) in naphthalene have also been reported.

A stock solution of Pr(III) was prepared from its oxide (E. merck) and standardised complexometrically. The stock solution (0.01M) of 8-quinolinol (E. merck), 1,10-phenanthroline (SDS) and 2,2-bipyridyl (SDS) all of analytical reagent grade were prepared in absolute ethanol. Naphthalene

---

*B-11, Prathvi-Enclave, Sukhdham, Civil-Lines, Kota-324,001, India.

and N,N-dimethyl formamide (DMF) were purified before use and tested for impurities spectrophotometrically.

An aliquot containing 40 μg of Pr(III) was transferred in a tightly stoppered Erlenmeyer flask (100 ml) and was adjusted to 7.5 with few drops of aqueous ammonia solution followed by the addition of 4.0 ml of 8-HQ and 2.0 ml of Phen/Bipy reagent solutions. The reaction mixture was warmed to 60°C and allowed to stand at room temperature for 30 minutes. A 2.0 gm portion of solid naphthalene was added and the sample solution was heated to 81–85°C. As soon as the solid naphthalene melted completely, the contents were stirred vigorously for few minutes and the yellow coloured solid mass obtained was filtered, dried and dissolved in 10 ml DMF. Absorption spectra of the resultant solutions were recorded against the reagent blank solutions.

The absorption spectra of DMF solutions of ternary complexes of Pr(III) with 8-HQ and Phen or Bipy were observed in the visible region from 360 to 500 nm. The absorption maxima were obtained at 380–390 nm. Extractions were carried out in the pH range 4.0 to 10.0, it was found that extractions were quantitative in the pH range 6.8–8.5 and 7.1–8.7 for Pr(III) : 8-HQ : Phen and Pr(III) : 8-HQ : Bipy complexes respectively.

At optimum pH, extractions were carried out by varying the concentration of both the reagents individually. It was observed that maximum extractions were achieved when 70 to 200 fold molar excess of primary reagent (8–HQ) was available. A 65–70 fold molar excess of the auxiliary reagent (Phen/Bipy) was sufficient for maximum extractions. Under optimum experimental condition, calibration curves were plotted at 388 nm in each case. Beer's law holds in the concentration range 5.0–65 μg of Pr(III) : 8–HQ : Phen and Pr(III) : 8–HQ : Bipy respectively.

A comparative statement of the concentration range, mean absorbance, molar absorptivity and Sandell's sensitivity data for the mixed ligand complexes and binary complexes with 8–HQ alone have been summarized in Table 1. The data clearly indicate the increased inten-

TABLE 1

SPECTROPHOTOMERIC DETERMINATION OF BINARY AND TERNARY COMPLEXES OF Pr(III) IN NAPHTHALENE—DMF

| Pr(III) complexes | Max. wave-length (nm) | Mean absorbance | Concentration range (μg/10 ml) | Molar absorptivity (l.mol.$^{-1}$ cm$^{-1}$) | Sensitivity (μg/cm$^2$) |
|---|---|---|---|---|---|
| Pr(III) : 8–HQ | 390 | 0.491 | 10–60 | $1.7265\times10^4$ | $8.1\times10^{-3}$ |
| Pr(III) : 8–HQ : Phen | 388 | 0.561 | 5–65 | $1.9732\times10^4$ | $7.2\times10^{-3}$ |
| Pr(III) : 8–HQ : Bipy | 388 | 0.505 | 7–70 | $1.7794\times10^4$ | $7.0\times10^{-3}$ |

sities of spectral absorptions of ternary complexes. The order of extractability of binary and ternary complexes can be expressed as follows:

$$8\text{–HQ : Phen} > 8\text{–HQ : Bipy} > 8\text{–HQ}$$

## REFERENCES

1. T. Hori, M. Kawashima, H. Freiser, *Sep. Sci. Technol.*, **15**, 52, 861, 1772 (1980).
2. M. Kawashima and H. Freiser, *Anal. Chem.*, **53**, 874 (1981).
3. T. Fujinaga, M. Satake and M. Shimiju, *Bunseki Kagaku* (*Jpn.*), **25**, 313 (1976).
4. M. Satake and Y. Takagi, *Bunseki Kagaku* (*Jpn.*), **26**, 386 (1977).
5. M. Satake, Y. Matsumura and M. C. Mehra, *Microchim. Acta*, **1(5-6)**, 455 (1980).
6. P. C. Vyas and V. P. Mittal, *Asian J. Chem.*, **2**, 239 (1990).

(*Received*: 30 March 1991; *Accepted*: 30 April 1991) AJC–290