Asian Journal of Chemistry Vol. 2, No. 3 (1990), 239–244

Spectrophotometric Determination of Praseodymium(III) After Extraction with 8-Quinolinol and its Halogen Derivatives into Molten Naphthalene

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The sensitive method "solid-liquid separation after liquid-liquid extraction" has been employed for collecting traces of Pr(III) from aqueous solution by precipitation with 8-quinolinol, 5-chloro-8-quinolinol and 5-chloro-7-iodo-8-quinolinol into molten naphthalene. The extraction behaviour of praseodymium(III) complexes with these reagents have been discussed in terms of various parameters like molar absorptivities, linear calibration ranges for Beer's law, Sandell sensitivities and standard mean deviations.

INTRODUCTION

8-Quinolinol (HQ) and its halogen substituted derivatives have been used for the extractive determination of lanthanides by several workers[1-3]. Investigations of the complexation in lanthanone—HQ system have revealed that except lanthanum other lanthanides form self-adduct chelates[4,5] of the composition $LnQ_3 \cdot 2HQ$ and $LnQ_3 \cdot 3HQ$, and are difficultily extractable into common organic solvents at room temperature. It has been found that these self-adduct chelates are easily extractable into molten naphthalene and can be determined spectrophotometrically using the technique "solid-liquid separation after liquid-liquid extraction"[6-8].

In the present communication the fundamental conditions for the spectrophotometric determination of microgram quantities of Pr(III) after its precipitation with 8-quinolinol, 5-chloro-8-quinolinol and 5-chloro-7-iodo-8-quinolinol from the aqueous solution and their subsequent extraction into molten naphthalene has been described.

EXPERIMENTAL

Stock solutions of Pr(III) was prepared by dissolving its oxide (E. Merck, Darmstadt) in nitric acid and diluting with deionized water and standardised complexometrically using EDTA and xylenol orange[9]. 0.01M solutions of 8-quinolinol, 5-chloro-8-quinolinol and 5-chloro-7-iodo-8-quinolinol (recrystallized from ethanol) were prepared by dissolving weighed quantities in ethanol. Dilute aqueous ammonia solution was used for controlling pH. N,N-Dimethylformamide (DMF) and naphthalene were tested for impurities before further use.

Procedure

An aliquot of standard metal solution containing 40 μg Pr(III) was transferred to a tightly stoppered Erlenmeyer flask and diluted with water to 35 ml. 4 ml of 0.01M of chelating reagent was added to it. After adjusting the pH of the reaction mixture with dilute aqueous ammonia solution, the solution was warmed to 60°C in a water bath. 2 gm solid naphthalene was added and heating continued till naphthalene melted (81–85°C). After that the mixture was stirred vigorously until naphthalene solidified forming very fine crystals. Naphthalene was remelted, stirred and allowed to stand at room temperature. The solid naphthalene containing coloured complex was separated by filtration, dried and dissolved in DMF. The solution is made exactly 10 ml in a volumetric flask. A portion of it was taken in a 1 cm cell and absorbance measured against reagent blank.

RESULTS AND DISCUSSION

Absorption spectra of 8-quinolinol, 5-chloro-8-quinolinol and 5-chloro-7-iodo-8-quinolinol in naphthalene and DMF were recorded. Pr(III) chelates with these reagents were recorded against reagent blank. Absorption maxima of the complexes have been observed at 390–400 nm, 400–410 nm and 410–420 nm respectively as shown in Fig. 1.

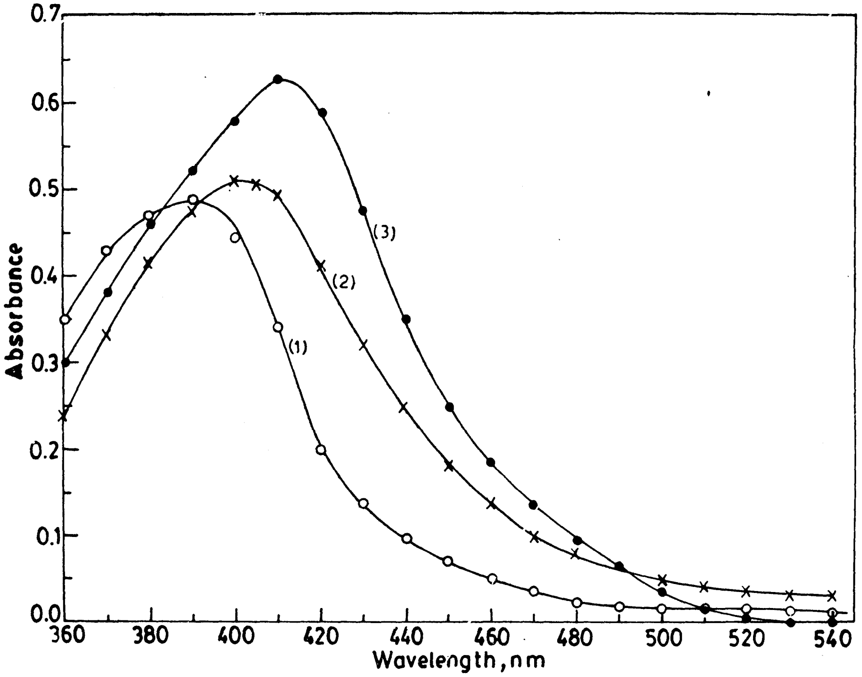

Fig. 1 Absorption spectra of Praseodymium(III) complexes in Naphthalene-N,N-Dimethylformamide solution:
(1) Pr(III) : 40 μg, 0.01 M 8-quinolinol 4 ml (○);
(2) Pr(III) : 40 μg, 0.01 M 5-chloro-8-quinolinol 4 ml (×);
(3) Pr(III) : 40 μg, 0.01 M 5-chloro-7-iodo-8-quinolinol 4 ml (●).

Effect of pH

Extraction was carried out in the pH range 4 to 11 while keeping other conditions constant. Pr(III) was quantitatively extracted over the pH ranges 7.2–8.5, 6.8–8.5 and 6.2–8.3 with 8-quinolinol, 5-chloro-8-quinolinol and 5-chloro-7-iodo-8-quinolinol respectively. Fig. 2 shows that extraction was incomplete beyond these pH ranges.

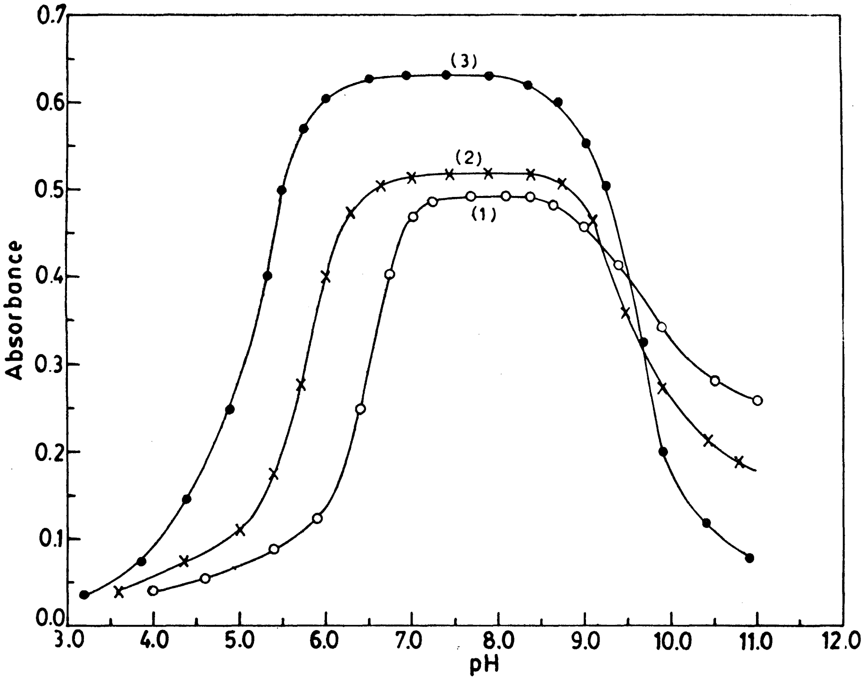

Fig. 2 Effect of pH on absorbance. Pr(III) : 40 μg with:
(1) 8-quinolinol at 390 nm (○);
(2) 5-chloro-8-quinolinol at 400 nm (×);
(3) 5-chloro-7-iodo-8-quinolinol at 415 nm (●).
Reference: reagent blank.

Effect of Reagent Concentration

The amount of chelating reagents in the extractive procedure was varied from 0.5 to 6 ml. Absorbance remained constant when 1.5 to 6 ml of 0.01M solution of reagents used in all the cases. Hence the optimum volume of the reagent was taken to be 4 ml.

Effect of amount of naphthalene

Extractions were carried out by varying the amounts of naphthalene from 0.2 to 4.0 gms at optimum pH. The absorbance remained constant when the amount of naphthalene used was in the range 0.8 gm to 3.5 gm. Extraction was found to be incomplete when less than 0.8 gm of naphthalene was taken while it was difficult to dissolve more than 3.5 gm in the limited quantity of DMF. Therefore 2.0 gm was selected for rapid and complete extraction.

Effect of aqueous phase

Since the amount of naphthalene was small (2.0 gm) as compared to aqueous phase, the effect of the change in volume of water on extraction was investigated. Extraction was quantitative when the volume of the aqueous phase did not exceed 60 ml.

Effect of shaking and standing time

Extraction of the chelates in the molten naphthalene (at 81–85°C) was found to be very rapid and no change was observed when the shaking time was varied from 1–3 minutes. Absorbance of the extracts measured at definite time intervals was constant after 24 hrs. of extraction.

Calibration curve

Under the optimum conditions described above, calibration curves are constructed by plotting absorbance versus concentration at 390 nm, 400 nm and 415 nm for Pr(III) chelates with 8-quinolinol, 5-chloro-8-quinolinol and 5-chloro-7-iodo-8-quinolinol respectively. Sandell sensitivities and standard mean deviations have been summed up in Table 1. Aliquots containing 40 μg of Pr(III) gave mean absorbances of 0.49 (390 nm), 0.515 (400 nm) and 0.63 (415 nm) with chelating reagents 8-quinolinol, 5-chloro-8-quinolinol and 5-chloro-7-iodo-8-quinolinol respectively.

TABLE 1

SPECTROPHOTOMETRIC DETERMINATION OF Pr(III) COMPLEXES IN Naphthalene-DMF

Pr(III) complexes	Max. wavelength (nm)	Concentration range (μg/10 ml)	Molar absorptivity $(l \cdot mol^{-1} \cdot cm^{-1})$	Sensitivity (μg/cm^2)	Relative mean deviation (%)
8-quinolinol	390	10–60	1.72×10^4	0.0081	0.81
5-chloro-8-quinolinol	400	5–60	1.81×10^4	0.0077	0.59
5-Chloro-7-iodo-8-quinolinol	415	2–50	2.22×10^4	0.0063	0.32

Effect of diverse ions

Various ions were added individually to a solution containing 40 μg of Pr(III) and the general procedure as described above in determination with 8-quinolinol has been applied. The data given in Table 2 show that among anions EDTA, phosphate, tartrate, citrate and oxalate interfered.

While in case of cations Cu^{+2}, Ni^{+2}, Zn^{+2}, Cr^{+3}, Co^{+2} and Cd^{+2} interfered at relatively higher concentration (>50 μg) but UO_2^{+2} and Fe^{+3} interfered seriously even at lower concentrations.

TABLE 2

EFFECT OF DIVERSE IONS ON EXTRACTION Pr(III) WITH 8-QUINOLINOL

Ion/salt	Amount	Absorbance at 390 nm
—	—	0.49
NaCl	50 mg	0.49
	100 mg	0.49
KI	50 mg	0.49
	100 mg	0.485
NH_4Cl	50 mg	0.49
	100 mg	0.49
KNO_3	50 mg	0.49
	100 mg	0.495
KBr	50 mg	0.49
	100 mg	0.48
KSCN	50 mg	0.485
	100 mg	0.49
CH_3COONa	50 mg	0.49
	100 mg	0.47
Sod. citrate	10 mg	0.485
	50 mg	0.46
	100 mg	0.395
Sod. Pot. tartrate	10 mg	0.49
	50 mg	0.405
	100 mg	0.38
Sod. oxalate	10 mg	0.48
	50 mg	0.42
	100 mg	0.38
EDTA	0.1 mg	0.45
	0.5 mg	0.37
	1.0 mg	0.29
	5.0 mg	0.10
Na_2HPO_4	1.0 mg	0.47
	5.0 mg	
Cu^{+2}	50 μg	0.49
	100 μg	0.42
Ni^{+2}	50 μg	0.49
	100 μg	0.43

TABLE 2 (contd.)

Ion/salt	Amount	Absorbance at 390 nm
Fe^{+3}	10 μg	0.49
	50 μg	0.41
	100 μg	0.24
Zn^{+2}	50 μg	0.49
	100 μg	0.47
Cr^{+3}	50 μg	0.49
	100 μg	0.495
UO_2^{+2}	5 μg	0.485
	10 μg	0.42
	50 μg	0.375
Co^{+2}	50 μg	0.49
	100 μg	0.43
Cd^{+2}	50 μg	0.475
	100 μg	0.415

Experimental observations reported in the present communication suggest that chelates formed by halogen substituted 8-quinolinol molecules are extracted at lower pH. Further due to hydrophobic nature of the halogen substituents, the solubility of the chelate is greatly increased in the organic medium i.e. naphthalene. Therefore in the optimum pH range the order of extractability of Pr(III) chelates formed by the three reagents can be expressed as 5-chloro-7-iodo-8-quinolinol, 5-chloro-8-quinolinol, 8-quinolinol as evident from the data given in Table 1.

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[*Received*: 1 March 1989; *Accepted*: 8 October 1989] AJC–102