Asian Journal of Chemsitry Vol. 8, No. 4 (1996), 731–735

Spectrophotometric Determination of Gallium(III) and Indium(III) with Some Hydroxy Naphthoic Acid Azo Dyes

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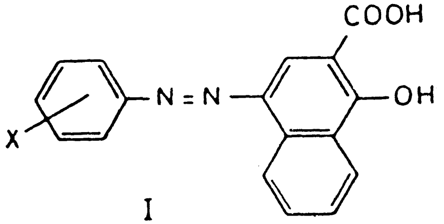
A rapid and sensitive spectrophotometric method for the determination of Ga(III) and In(III) has been reported using some hydroxy naphthoic acid azo dyes as reagents. The metal ions react with the mentioned reagents to form 1 : 1, 1 : 2 and 1 : 3 (M : L) complexes. The molecular ratios and the stability constants of the formed complexes are given. The interferences of several ions are reported.

INTRODUCTION

The complexes of several metal ions with hydroxy naphthoic acid azo dyes were studied by Pant and Aitta[1, 2]. Trace amounts of In(III) were determined spectrophotometrically[3, 4]. The molecular structure of Ga(III) and In(III) complexes with azoxine S dyes, their uses for the spectrophotometric determination, obeyence of Beer's law and stability constants were determined[6]. The spectral properties of In(III) complexes with salicylfluorene in presence of surfactant were studied[6].

Potentiometric, conductometric, IR, NMR and TG studies were carried out on lanthanide complexes with some azo derivatives of 3-hydroxy-2-naphthoic acid[7]. Ga(III) and In(III) were determined spectrophotometrically[8] by measuring the absorbance of their complexes with some chromotropic acid diazo dyes at 635 and 685 mm, respectively. The optimum pH ranges of formation, molar absorptivities, ranges of Beer's law obeyence, molecular ratios and the stability constants were determined.

The present investigation is a systematic study on the complexes of Ga(III) and In(III) with 4-(arylazo)-1-hydroxy-2-naphthoic acid dyes (Ia–e). The azo dyes under investigation are represented as follows:



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4-(arylazo)-1-hydroxy-2-naphthoic acid.

where X = H(a), 2-OH, 5-SO_3H(b), *o*-NO_2(c), *o*-COOH(d) and *o*-OCH_3(e).

EXPERIMENTAL

The water used in this investigation was always twice distilled from all glass equipment. The azo dyes under investigation were prepared in the usual way[9]. The melting points of the resulting products were concordant with those previously reported[10].

Solutions

0.001 M solutions of Ia–e were prepared by dissolving the accurately weighed amounts in the requisite volume of spectrally pure ethanol or DMF except Ib which was dissolved in water. 0.001 M Ga(III) solution was prepared by dissolving Ga_2O_3 in the least amount of concentrated hot hydrochloric acid, then the volume is completed to the required volume with twice distilled water. 0.001 M In(III) solution was prepared from indium sulphate. The metal ion solutions were stadardized by EDTA[11].

Solutions containing 1 mg/mL of metal ions to investigate their interference effect were prepared as usual. The buffers used were the modified Britton and Robinson universal series (pH 2–12) and acetate buffer solutions (pH 0.65–5.70)[12]. The pH values of the buffer solutions were checked by the aid of Seibold pH-meter C-103 (Austria). A Pye Unicam SP 1750 spectrophotometer was used for the spectral measurements. Conductometric titrations of Ga(III) and In(III) with Ia–e were performed using a D 812 conductivity meter model LBR at frequency of 3 kHz/s.

Procedure

To solutions containing 0.35–5.58 or 0.57–8.04 $\mu g\ mL^{-1}$ of Ga^{3+} or In^{3+}, respectively, add the appropriate amounts of Ia–e (Table-1). The solutions were completed to 10 cm^3 with the recommended buffer solution. The absorbances of the resulting solutions are measured at their respective λ_{max} *i.e.* 388, 556, 388, 410 and 395 mn for Ga^{3+}- (Ia–e), respectively. In the determination of In^{3+}, the absorbances were measured at 553 and 404 nm using Ib and Id, respectively. The concentration thus can be determined for a calibration curve constructed in the same manner.

RESULTS AND DISCUSSION

The present work affords a new rapid spectrophotometric method for the determination of Ga(III) and In(III) with the help of the azo dyes under investigation. The optimum pH values for developing the coloured complexes were in the pH range 5.5–11.7 (Table-1).

The maximm absorbance of the formed complexes in comparison with that of the free ligand is shifted towards shorter wavelength with the exception of Ga and In with Ib which are shifted towards longer wavelength. The effects of time and temperature on the formation of Ga(III) and In(III) complexes were studied in details. The colour of Ga(III) and In(III) complexes is formed instantaneously in all cases. The complexes are stable up to 20 min, 24 h, 30 min, 24 h and 15 min. for Ga-(Ia–e) complexes, respectively and 24 h for In-(Ib and Id) complexes.

Rasing the temperature up to 70°C has no effect on the colour intensity of these complexes. Trials for the use of polyvinyl alcohol and gum arabic as a surfactant in case of trivalent Ga and In complexes to increase the stability of the complexes were unsuccessful.

TABLE-1

MOLAR ABSORPTIVITY (ε), SPECIFIC ABSORPTIVITY (a), SANDELL INDEX (S) AND OBEYENCE RANGE FOR Ga AND In-(Ia–e) COMPLEXES

Ligand	Metal ion	pH	λ_{max} 1	2	$\varepsilon \times 10^{-3}$	a	$S \times 10^2$	Beer's law obeyed up to (μg/mL)	Ringbom range μg/mL	
Ia	Ga	11.7	504	388	3.00	0.043	2.32	5.58	2.09	5.58
Ib	Ga	5.7	504	556	23.75	0.341	0.29	3.49	1.39	3.49
	In	5.5	504	553	11.60	0.101	0.90	5.17	1.15	5.17
Ic	Ga	11.25	532	388	3.10	0.044	2.25	3.49	2.44	3.49
Id	Ga	11.25	480	410	8.08	0.116	0.86	4.18	1.04	4.18
	In	10.8	480	404	3.50	0.030	3.28	8.04	3.45	8.04
Ie	Ga	11.7	502	396	2.90	0.042	2.40	4.88	2.79	4.88

* Only values of λ_{max} of 1 : 1 complex are listed. ε : Molar absorptivity (l M^{-1} cm^{-1})

a : Specific absorptivity (mL g^{-1} cm^{-1}) S : Sandell index (μg cm^{-1})

TABLE-2

THE APPARENT STABILITY CONSTANT OF Ga AND In WITH (Ia–e)

Complex	Method	log k_n $n = 1$	log k_n $n = 2$
Ga-Ia	M.R.	5.26	10.97
	C.V.	5.64	
Ga-Ib	M.R.		9.68
	C.V.	5.66	10.07
In-Ib	M.R.*	4.97	9.97
	C.V.	4.85	9.15
Ga-Ic	M.R.	5.52	10.73
	C.V.	4.78	8.89
Ga-Id	M.R.	5.74	10.47
	C.V	5.79	10.09
In-Id	M.R.	5.85	11.49
	C.V.	4.61	9.76
Ga-Ie	M.R.	5.02	9.77
	C.V.	4.76	

*log k_n = 14.13 for $n = 3$

The stoichiometry of the complexes was investigated with the aid of some standard spectrophotometric methods *e.g.* molar ratio[13] and continuous variation methods[14]. The results (Table-2) indicate the formation of 1 : 1 and 1 : 2 (M : L) complexes in most cases, however, in case of (In-Ib) complex, 1 : 3 (M : L) is observed. The apparent formation constants of Ga(III) and In(III) complexes were calculated[15]. Beer's law was verified and found to be satisfactorily obeyed up to 5.58, 3.49, 4.19 and 4.88 μg Ga/mL with Ia–e, respectively, and obeyed up to 5.17 and 8.04 μg/mL of In with Ib and Id, respectively. For more accurate results the Ringbom ranges[16] are 2.09–5.58, 1.39–3.49, 2.44–3.49, 1.05–4.18 and 2.79–4.88 μg/mL for complexes of Ga with Ia–e dyes, respectively, and 1.15–5.17 and 3.45–8.4 μg/mL for complexes of In with Ib and Id, respectively. The results are listed in Table-1.

Effect of foreign ions

Foreign ions such as Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Be^{2+}, PO_4^{3-}, SO_4^{2-}, SCN^-, NO_3^-, CN^-, F^-, Br^-, Cl^-, I^-, oxalate, tartrate, EDTA and CDTA do not interfere. On the other hand, VO^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} seriously interfere and must always be absent during the spectrophotometric determination of trivalent Ga and In ions.

Conductometric titration of Ga(III) and In(III) with Ia–e:

Conductometric titrations of Ga(III) and In(III) with Ia–e were performed to throw more light on the stoichiometric composition of the complexes formed in solutions. The corresponding specific conductance values were determined experimentally, corrected for volume dilution and plotted versus volume of the titrant. The resulting curves are composed of straight lines intersecting at the molecular ratios of the complexes formed, the characteristic curve breaks were observed at molecular ratio (L/M) 1 : 2 confirming the formation of 1 : 1 and 1 : 2 (M : L) complex species.

Conclusions

The azo dyes under investigation are considered to be excellent chromophoric reagents for Ga(III) and In(III). This may be regarded by the difference in the maximum absorbance between the free ligands and the formed metal complexes, amounting to 80 nm on the average. The dyes are soluble in alcohol and stable for long time (up to 24 h). The complexes are also stable for long time. The values of the molar absorptivity (ε) are high. The values of the specific absorptivity (a) and Sandell sensitivity (S) were calculated, the results indicate the sensitivity of the adopted method. The results of the stability constant indicate that such complexes are fairly stable. The 2-OH, 5-SO_3H 4(arylazo)-1-OH-2-naphthoic acid Ic is the most suitable indicator for the spectrophotometric determination of Ga(III) and In(III).

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(*Received*: 12 March 1996; *Accepted*: 1 July 1996) AJC-1124