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Spectrophotometric Studies on Galium (III) Complexes With Some Azoxine S Dyes

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SUMMARY

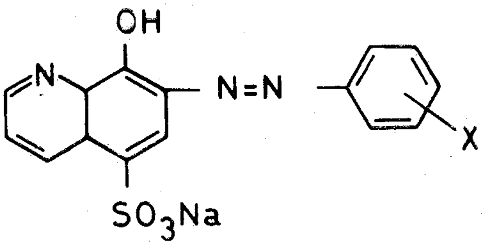
A new rapid and accurate method for the spectrophotometric microdetermination of Ga (III) ion using 7-(phenylazo) -8- hydroxy-quinoline -5- sulphonic acid and five halogen substituents is given. The optimum conditions favouring the formation of the complexes are extensively investigated. The molecular structure of the complexes and their obeyence to Beer's law, as well as, their stabilities are studied. A spectrophotometric titration method for Ga (III) with EDTA using four of these reagents as indicators is also given.

INTRODUCTION

Azoxine s dyes, 7-(arylazo)-8- hydroxyquinoline -5- sulphonic acid are used as metallochromic indicators.(1,4) The complexes of several bivalent metal ions with azoxine s dyes were studied using photometric and potentiomeric methods(5–7). Tetravalent vanadium was determined spectrophotometrically using some azoxine s dyes.(8) The acid dissociation constants of several azoxine s dyes were determined; the ionization constants of the strong -SO_3H groups were determined potentiometrically while those of the -OH group were determined spectrophotometrically.(9)

In the present investigation the reactions of Ga (III) ions with six azoxine s dyes is investigated spectrophotometrically.

The dyes used are formula



X = H,(I); o-Cl,(II); m-Cl,(III); p-Cl,(IV);
p-Br,(V) and p-I,(VI).

EXPERIMENTAL

The chemicals used in this investigation were of the highest purity available. The water used was always twice distilled from all glass equipment. The absorption spectra were recorded using a PYE UNICAM SP 1750 spectrophotometer. The 0.001 M solution of Ga^{3+} was prepared by diluting a previously standardized 0.05 M stock solution.(10)

A solution of 0.001 M EDTA was prepared by diluting 0.05 M standard EDTA solution.(10) Acetate and modified Britton and Robinson universal buffers were prepared as recommended.(11) The dyes used in the present investigation were prepared and purified by the method of Uusitalo(5) and the purity was confirmed by elemental analysis and potentiometric titration against standard sodium hydroxide solution to be more than 99.5 %. The 0.001 M dyes solutions were prepared by dissolving the accurate weight of each dye in doubly-distilled water containing the requisite amount of sodium hydroxide to affect solution.

Procedure for micro determination of Ga^{3+} ions:

To a solution containing not more than 35 μg Ga^{3+} add, 2 ml of 0.001 M dye and 6 ml acetate buffer (universal buffer in case of Ga-V) of the recommended pH value, and the solution mixture is made up to 10 ml with water. The absorbances of these solutions are then measured at 405, 400, 400, 405, 375 and 390 nm for Ga-I-VI complexes respectively, against a blank containing the same species except the metal ions.

The concentration of Ga^{3+} is computed from a standard calibration curve obtained in a similar manner.

This method affords a new fairly accurate and highly precise means for the rapid spectrophotometric microdetermination of Ga^{3+} in pure solutions as well as in presence of a variety of cations and anions which do not interfere with such determinations. The standard deviation in determining 3.5 μg Ga^{3+} amounts to 0.005 - 0.008 on the average (10 determinations).

RESULTS AND DISCUSSION

As to the effect of pH, the studies showed that acetate buffers of pH volues 3.5, 4.0, 3.5, 3.0 and 3.0 are the most suitable for developing the Ga-I, Ga-II, Ga-III, Ga-IV and Ga-VI complexes respectively; whereas universal buffer of pH 7.0 is recommended for Ga-V complex.

The absorption spectra of the dyes and their complexes measured at the optimum pH and ionic strength of 0.1, against water and ligand showed that the complexes of galium have bands, at shorter wavelengths compared with the main band of the ligand. Representative curves are shown in Figs. (1 and 2).

The absorbances of the formed complexes were found to be stable for about 48 hours. However, in the case of Ga-III complex, it was only stable for about 2 hr. It was noted that the temperature range 20-50°C. has no effect.

Limits of obeyence to Beer's law and molar absorptivities with different dyes are given in table (1).

Nature and Composition of the Complexes:

The nature and composition of the formed complexes were investigated using some recommended methods, e.g. the molar ratio(12) continuous variation(13), and slope ratio(14) methods. The results indicate that 1:2 and 1:3 Ga:I; 1:2 Ga-II and Ga-V and 1:3 Ga-III, Ga-IV and Ga-VI (Metal: reagent) complexes were formed, representative figures are shown (Fig. 3 and 4). The existence of these species in solution was confirmed by applying coleman graphical method(15) for determining the

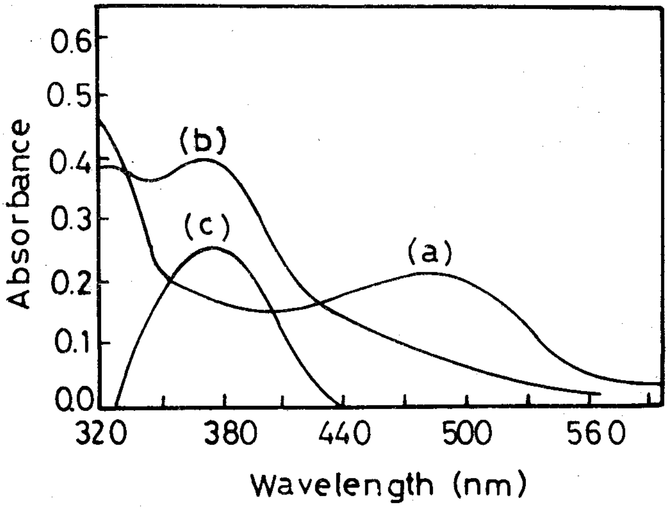


Fig. (1). Absorption spectra of Ga-V complex.
a) 6 x 10^{-5}M Vwater as blank,
b) 3 x 10^{-5}M Ga-V complex water as blank,
c) 3 x 10^{-5} Ga-V complex, 6x10^{-5}M as blank.

the number of absorbing species to the results of the molar ratio method. The results were in agreement with those already obtained.

The stability constants were calculated using the above mentioned methods(12–14) and the results are given in table (2).

Effect of foreign ions:

The interference due to several anions and cations was studied in detail. The study showed that up to 20 fold of Li, Na, K, Pb (II), Zn (II), Zn (II), Mn(II), Ca (II), Ba (II), Sr (II), Cr (III), Zr (IV), Th, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, CH_3COO^-, SO_4^{2-} and phthamate do not interfere, while Tl^+, Co (II), Ni (II), Cu (II), UO_2^{2+}, Fe (II), Fe (III), Bi (III), Al (III). In (III), F^-, CN^-, citrate, tartrate, oxalate, EDTA and CDTA interfered.

Spectrophotometric titration of Ga^{3+} with EDTA using I, IV, V and VI as indicators:

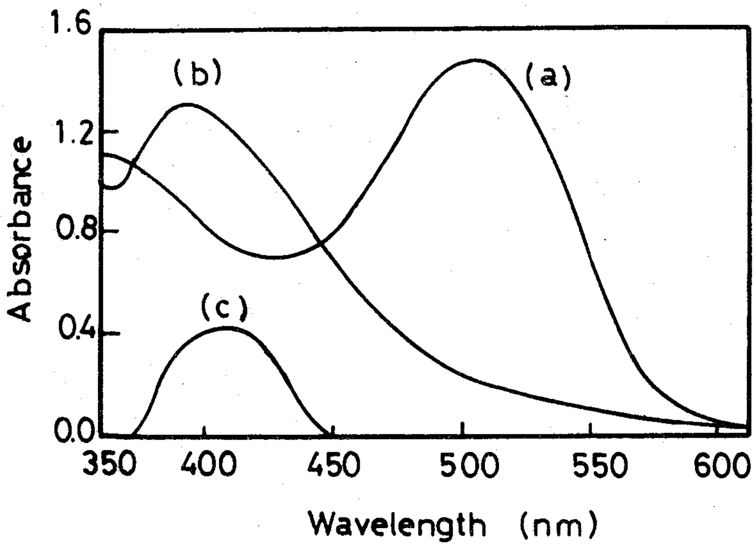


Fig. (2). Absorption spectra of Ga-VI complex.
a) 1 x 10^{-4}M VI water as blank,
b) 5 x 10^{-5}M Ga-VI complex water as blank,
c) 5 x 10^{-5}M Ga-VI complex, 1 x 10^{-4}M VI as blank.

Table (1)

Obeyence of Beer's law and absorbtivities of the complexes

Complex	λ nm max.	up to (ppm)	ε
Ga-I	405	4.88	22.400
Ga-II	400	4.18	22.200
Ga-III	400	4.88	22.300
Ga-IV	405	2.79	36.300
Ga-V	375	4.18	23.600
Ga-VI	390	2.09	53.100

Galium was successfully titrated with EDTA up to 48.79, 55.76, 55.76 and 34.85 ug using I, IV, V and VI respectively, as indicators.

It is clear from the titration curves Fig. (5), that the phenyl-and p-halophenyl-azo-8-quinolinol -5- sulphonic acid derivatives are the most suitable as indicators for the determination of Ga (III), Table (3). The sharp end point can be explained by comparing the values of the

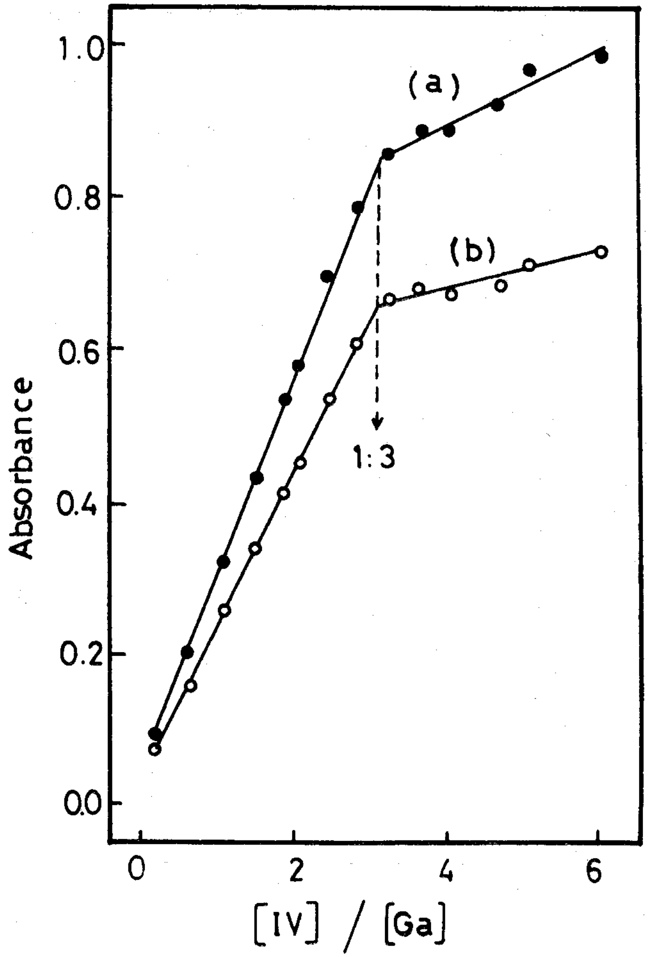


Fig. (3). Molar ratio method for Ga-IV complexes.
a) λ = 405 nm, b) λ = 430 nm, (Ga) = 5 x 10^{-5}M.

stability constants of Ga-EDTA complex⁽¹⁰⁾, (log k = 20.3) as well as Ga-I, -IVIV, -V and - VI as computed in the present work (Table 2), comparison shows that there is a remarkable difference between log k_1 of EDTA complex and log K_n of azoxine S complexes, where n is the maximum number of ligand molecules per one Ga^{3+} ion.

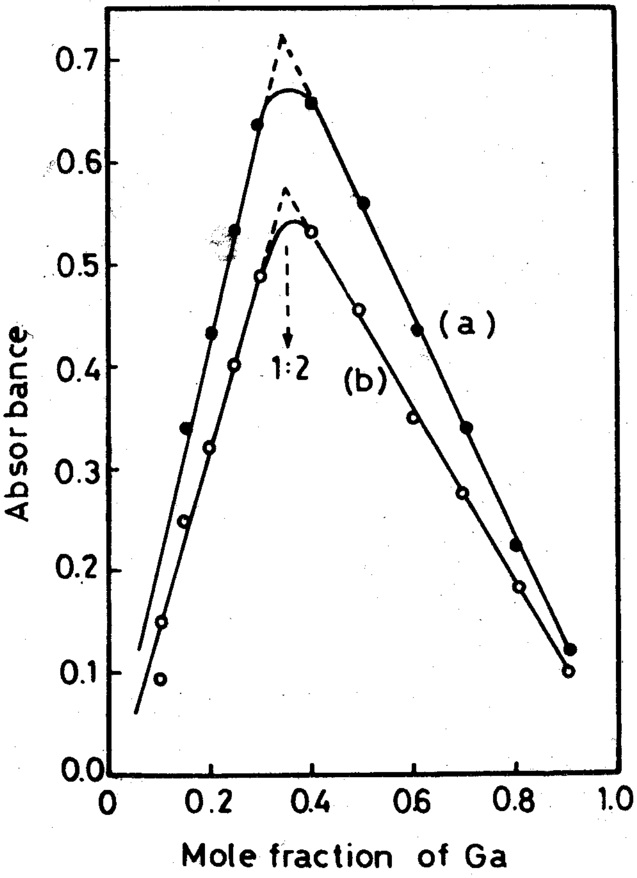


Fig. (4). Continuous variation method for Ga-II complex.
a) λ = 400 nm, b) λ = 420 nm.

Table (2)
The apparent stability constants of Ga-I, Ga-II, Ga-III, Ga-IV, Ga-V and Ga-VI complexes.

Complex	pH	n	log K
Ga-I	3.5	2	8.19
		3	16.28
Ga-II	4.0	2	7.36
Ga-III	3.5	3	13.76
Ga-IV	3.0	3	12.84
Ga-V	7.0x	2	7.74
Ga-VI	3.0	3	15.27

x Universal buffer

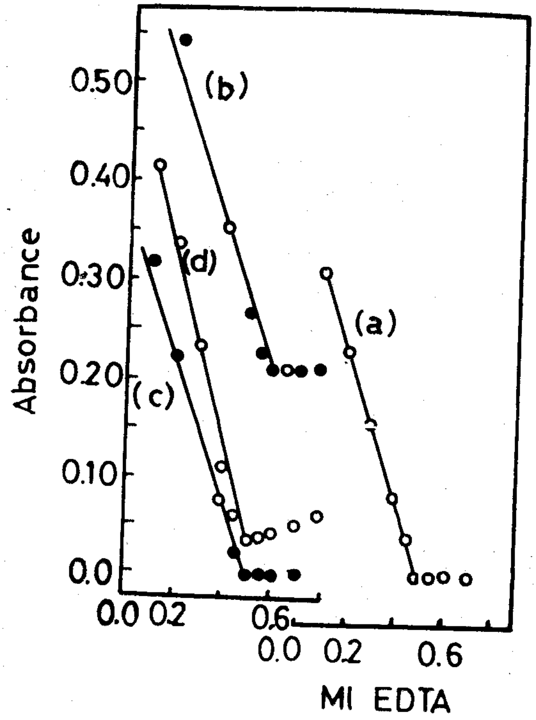


Fig. (5). Spectrophotometric titration of 10^{-3}M Ga^{3+} with 10^{-3}M EDTA using I (a), IV (b), V (c) and VI (d) as indicators.

Table (3)

Spectrophotometric titration of gallium with EDTA using I, IV, V and VI as indicators.

Dye	λ_{max} nm	pH	ug Ga/10 ml	
			Taken	Found
I	400	3.5	34.85	34.84
			48.79	48.80
IV	405	3.0	41.82	41.82
			55.76	55.76
V	375	7.0*	34.85	34.85
			48.79	48.79
VI	405	3.0	13.94	13.94
			34.85	34.85
			20.91	20.90

* Universal buffer

Caption of figures:

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