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SPECTROPHOTOMETRIC MICRODETERMINATION OF TRIVALENT Sc, Y AND La IONS WITH 4-PHENYLAZO-7-(2-ARSONOPHENYLAZO)-CHROMOTROPIC ACID

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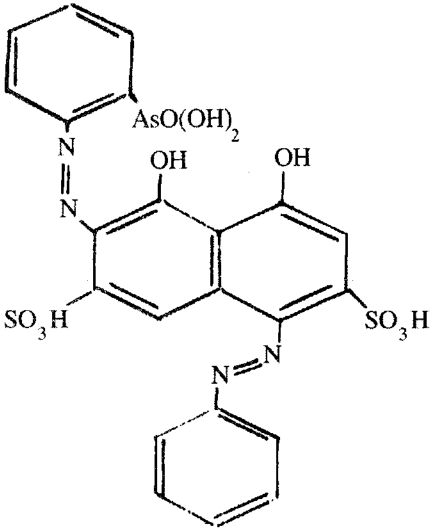
ABSTRACT

Trivalent cationic Sc, Y and La chelates with 4-phenylazo-7-(2-arsonophenylazo)-chromotropic acid ligand have been investigated by spectrophotometric methods. The formed chelates have violet colour. The studies reveal that 1:1, 1:2 and 1:3 metal : ligand (M:L) chelates are formed in solutions. The determination of the three metal ions in $\mu g/cm^3$ range is described. The trivalent Y ion has been successfully determined using spectrophotometric titration with EDTA. The Stability constants of the formed chelates have been determined applying spectrophotometric and potentiometric techniques. The composition of these chelates was confirmed by conductometric titration.

INTRODUCTION

Chromotropic acid is one of the most important reagents to analytical chemists. This is due to its high selectivity, water solubility of both the free ligand and the coloured chelates, exact stoichiometric composition, sensitivity of colour reaction and stability of coloured chelates.(1,2) Not only the mono azo dyes of chromotropic acid have been prepared and studied, but also its bis or diazo dyes.(3-5) These diazo dyes have been investigated spectrophotometrically and potentiometrically,(6,7) in different organic solvents,(8,9) and as complexing agents for several metal ions such as rare earths, alkaline earths and many other elements.(3,10-13) Recently, Sc, Y and La ions were determined spectrophotometrically with some J-acid azo dyes.(14)

The aim of this article is to apply 4-phenylazo-7-(2-arsonophenylazo)-chromotropic acid (L) as chromophoric reagent for the determination of trivalent Sc, Y and La ions.



EXPERIMENTAL

The water used was always twice distilled from all glass equipment. The diazo dye was prepared by coupling diazotized aniline with chromotropic acid in sodium carbonate medium.(15) The coupling process takes place in position (4) which is an α-position. The resulting monoazo dye was used for preparing the di-azo compound (L) by further coupling with diazotized o-arsenilic acid in sodium hydroxide medium.(16) The coupling process, this time, takes place in position 7 in which position 5 is, sterically hindered. The diazo dye prepared was crystallized according to Mehta(17) and was confirmed by H^1- NMR, IR and elemental analysis to more than 99.7% pure The H^1- NMR spectroscopic data of ligand (L) is given by:

$\delta_{7.21-8.13}$ ppm (m,11 H, aromatic protons).
$\delta_{8.43}$ ppm (S, 1 H, OH, D_20 exchangeable).
$\delta_{10.72}$ ppm(S, 1H, ASO $(OH)_2$, D_20 exchangeable).
$\delta_{12.50}$ ppm (S,lH, SO_3H, D_20 exchangeable).

A 10^{-3} M solution of (L) was prepared by dissolving the accurate weight in water. Scandium and lanthanum oxides (BDH) were dissolved in perchloric acid to prepare 0.01 M solutions. The 0.01 M solution of yttrium was prepared from a nitrate sample. The elements were standardized by recommended methods,(18) and 0.001 M solutions were prepared by accurate dilution. Hexamine buffers(19) were used to control pH and NaCl to control the ionic strength in potentiometry. The pH values were measured by means of a pH meter, (Lseibold, Austria). Shimadzu UVVisible recording spectrophotometer UV-240, Japan was used to obtain the absorption spectra. The stability constants were determined spectrophotometrically(20-21) and potentiometrically.(22) The titrations were carried out three times to test the reproducibility of the results. The average number of protons associated with the ligand at different pH values (nA), the average number of ligand attached to a metal ion (n) and the free ligand exponent (pL) were calculated using the equations given by Sarin and Munshi.(23) Conductometric measurements were performed using a D-812 conductivity meter model LBR at a frequency of 3 kHz.

Proceducres

Spectrophotometric Determination of Sc, Y and La Ions

To solutions containing up to 15.7 μg, 35.6 μg and 34.7 μg of Sc, Y and La ions, 2 cm^3, 10^{-3} M (L), 6 cm^3 hexamine buffer of the required pH (5, 6 and 3, respectively) and distilled water up to 10 cm^3 were added. The absorbance values were then measured at 610, 615 and 715 nm for Sc-L, Y-L and La-L chelates respectively, against blank solutions containing the same ingredients except the metal ion. Standard calibration curves were thus constructed. Analytical application and statistical treatment of the results were also given.

Spectrophotometric Titration of Y

1 or 2 cm^3 of 10^{-3} M (L), 0.3-0.7 cm^3 10^{-3} M yttrium solution and 6 cm^3 hexamine buffer of pH 6 were pipetted into each standard measuring flask, and successive volumes (0.05, 0.1, 0.15, 0.2,0.2 cm^3 etc.) of 10^{-3} M EDTA (ethylenediaminetetraacetic acid, disodium salt) were added. These solutions were made up to the mark with water, then the absorbances were measured at 615 nm using the same volume of (L) as blank. The absorbance against cm^3 EDTA plot was two straight lines intersecting exactly at the equilibrium point.

RESULTS AND DISCUSSION

On adding the dark red 4-phenylazo-7-(2-arsonophenylazo)-chromotropic acid to the metal ions (Sc, Y and La), a blue-violet colour is observed as a result of complex formation. The absorption spectra of the chelates were recorded at different pH values using hexamine buffer. The optimum pH values for developing the colours of Sc-L, Y-L and La-L chelates were found to be 5.2, 6.1 and 3.3, respectively.

The absorbances of the chelates show very low values in strong acidic solutions which may be due to the competition between the H^+ ions and the metal ions. In otherwords, the chelates absorb maximally in slightly acidic medim, as seen before, above which the absorbance values decrease sharply due to the formation of more stable hydroxy chelates and decomposition of metal chelates.

The absorption spectra of the ligand against water and the metal chelate against the ligand show that these chelates absorb maximally at 610, 615 and 715 nm for the above mentioned chelates, respectively. Fig. (1) represents the absorption spectra of La-L from 800-330 nm as a representative one. It was noticed that in all cases the blue-violet colour formed instantaneously and remains stable for more than 48 hours.

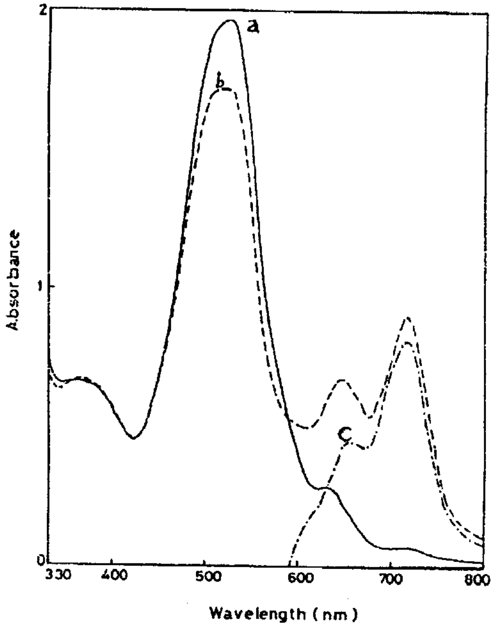


Fig. 1. Absorption spectra of La-L Complex at pH 3. a) Ligand VS. water blank; b) Complex VS. water blank; c) Complex VS. ligand blank.

The stoichiometry of the chelates formed was studied by standard spectrophotometric methods such as the molar ratio(24) and the continuous variation(25) methods. The results listed in Table (1) indicate the formation of 1:1 , 1:2; 1:2 and 1:3 for Sc-L, Y-L and La-L chelates, respectively.

Table 1. Molecular Ratios (M:L) and Determination of Log β of Trivalent Sc, Y and La.

Metal	**Conductometric**	**Spectrophotometric**					**Potentiometric**		
Ion	**Titration**	**M.R.M.**	**C.V.M.**	**Log β_1**	**Log β_2**	**Log β_3**	**Log β_1**	**Log β_2**	**Log β_3**
Sc	1:1	1:1	1:1	8.20	19.90	32.20	10.90	2070	2800
	1:2	1:2	1:2						
Y	1:1	1:2	1:2	8.10	20.10	32.30	10.80	20.70	29.00
	1:2	1:3	1:3						
La	1:1	1:3	1:3	9.70	21.60	33.50	11.30	21.80	30.72
	1:2								
	1:3								

M.R.M. = Molar Ratio Method

C.V.M. = Continuous Variation Method

The apparent stability constants of the chelates of the scandium group metal ions with (L) were calculated using the equation(20):

$$npH + n \log C_{HL} = \log A/A_m\text{-}A + npK - \log \beta$$

Thus, log β can be determined from absorbance -pH spectra by plotting log A/A_m-A versus pH of the medium.

Beer's law was verified by applying the least squares method(26) and found to be satisfactorily obeyed up to 1.57, 3.57 and 3.47 $\mu g/cm^3$ of Sc, Y and La, respectively. The molar absorptivity (e), specific absorptivity (a)(27) and Sandell Sensitivity (S)(28) were calculated. Their values listed in Table (2) indicate that the method is sensitive. The statistical results applying the least squares method are listed in Table (3).

Table 2. Molar Absorptivitiy, Specific Absorptivity and Sandell Sensitivity of M-L Complexes

Metal Ion	$\varepsilon \times 10^{-4}$	a	$S \times 10^{3}$
Sc	3.60	0.801	1.23
Y	2.20	0.250	4.00
La	1.80	0.130	7.70

ε = Molar Absoptivity (L mol^{-1} cm^{-1}).
a = Specific Absorptivity (Lg^{-1} cm^{-1}).
S = Sandell Sensitivity (μg cm^{-1}).

Table 3. Statistical Results Applying Least Squares Method

Metal Ions	Slope	Intercept	S.D.	C. C.
Sc	0.6630	0.089	0.0010	0.995
Y	0.0132	0.019	0.0200	0.984
La	0.0463	0.039	0.0003	1.001

S.D. = Standard Deviation
C.C. = Correlation Coefficient.

Table 4. Weight Taken, Weight Found, Relative Error, Percentage Recovery, standart Deviation and Statistical t-Values.

M3+	Weight Taken $\mu g/cm^3$	Weight Found $\mu g/cm^3$	Relative Error %	% Recovery	S.D.	t*
Sc	2.70	2.65	1.85	98.15	0.040	2.50
Y	16.00	15.98	0.16	99.84	0.096	0.52
La	12.68	12.79	0.85	100.85	0.120	1.83

* Compared with Fritz method.(29)

In order to test the reproducibility of the results, the standard deviation for six replicates was derived as well as mean recovery, relative error, percentage recovery and t-test values compared with Fritz rnethod.(29) c.f Table (4). The values indicate that the procedure used for obtaining the calibration curves is extremely reliable as applied for the determination of the investigated ions. The regression equations for Sc, Y and La may be expressed as:

$$Y = a + bx$$

The values of a and b are listed in Table (3) and the standard deviation was determined applying the least squares method.

The interference effect up to 20 folds due to several anions and cations was studied quantitatively. The data led to the conclusion that monovalent cations Ag, Li, Na, K, Rb, Cs, TI, divalent cations Mg, Ca, Co, Ni, Zn, Cd, Hg, Mn, Pd, monovalent anions Cl, I, $N0_3$, CN and divalent sulfate do not interfere. On the other hand, divalent Cu, trivalent Fe, Al, Ga, In, Bi, Ce, tetravalent Th, V, hexavalent uranium, tartrate and EDTA interfere and must be excluded.

Spectrophotometric Titration

The application of (L) as an indicator for spectrophotometric titration of trivalent yttrium with EDTA has been ascertained. The titration is applicable up to 62.23 $\mu g/cm^3$ for yttrium, Fig. (2). It was found that, trivalent scandium and lanthanum ions gave constant absorbance with increasing EDTA concentrations which means that, the stability of metalligand is higher than the stability of metal - EDTA. Therefore, Sc^{3+} and La^{3+} can not be determined by this method.

This means that the ligand (L) is very selective indicator for yttrium when titrated with EDTA in presence of Sc^{3+} and La^{3+}.

Conductometric Titration

Conductometric titrations of trivalent Sc, Y and La salts with the ligand (L) were performed as a further insight into the stoichiometric compositions of the chelates formed in solution. In each experiment, 50 cm^3 of $4x10^{-5}$ M solution of the ligand was introduced into the cell. The metal ion was added dropwise with continuous stirring. The corrected specific conductance values were plotted against the molar ratio [L]/[M], Fig. (3) shows a representative graph abtained for Sc^{3+}. The resulting

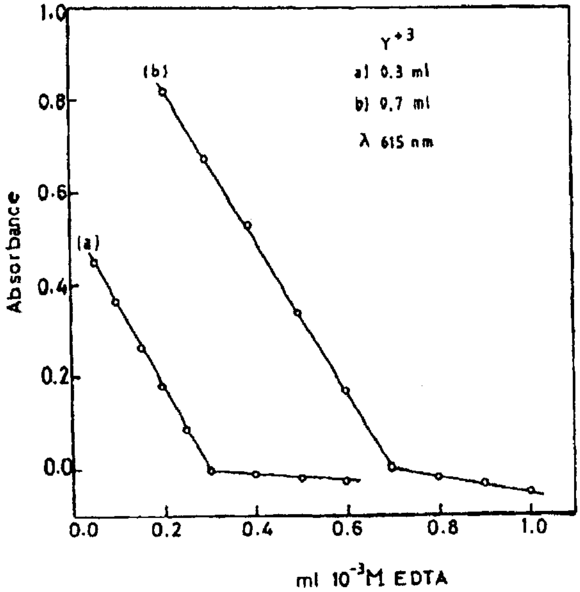


Fig. 2. Spectrophotometric titration of trivalent Y at pH 6 with EDTA using L as indicator.

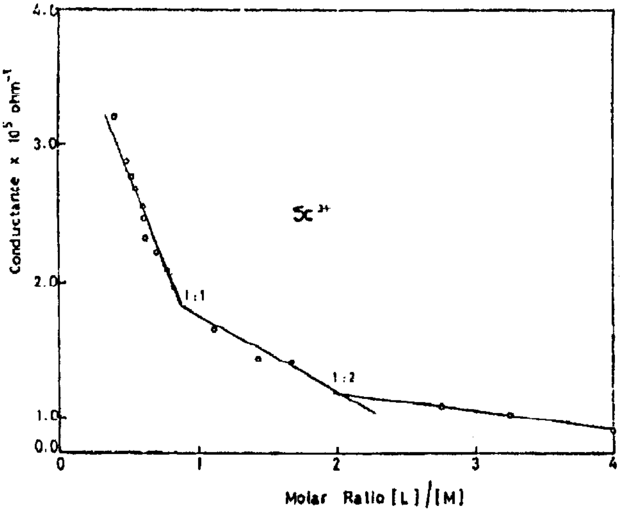


Fig. 3. Conductometric titration curve.

plots were composed of straight line intersecting at the stoichiometric ratio. It was showed that more than one molecular species were formed in solution which confirms the spectral results as indicated in Table (1).

Potentiometric Titration

As a result of potentiomentric titration following the previously mentioned method,$^{(23)}$ the average number of protons associated with the ligand at different pH values (nA) is calculated, then the formation curves relating pH and the corresponding (nA) values were plotted. The ionization constants pK (OH) of the $AsO(OH)_2$ group and the other two (OH) of the ligand were evaluated by the half integral method (i.e. at nA = 0.5, 1.5 and 2.5). The average number of ligands attached to a metal ion (n) and the free ligand exponent (pL) were calculated and then plotted against each other, the formation curves of the metal chelates are thus produced. The stability constants log β_1 log β_2 and log β_3 were calculated. As observed from Table (1), the stability constant increases in the order Sc < Y < La.

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