Spectrophotometric Study on the Stability Constant of Complex Al³⁺-Arsenazo-III

SHARMILA POKHARNA, K.D. GUPTA*, RITURAJ MAHLA and CHANDNI KIRPALANI

Department of Chemistry, Malaviya National Institute of Technology Jaipur-302 015, India

The interaction of aluminium ion (Al³⁺) with arsenazo-III has been investigated by spectrophotometric technique. Al³⁺ ion forms a light purple water-soluble complex with arsenazo-III having 1:1 metal to ligand ratio with maximum absorbance at 560 nm. The pH range of constant maximum absorbance is between 4 and 5. Their stability constants have been determined by applying mole ratio method, Job's method of continuous variation and Dey and coworkers' method. The value of log K for Al³⁺ was found to be 5.03.The analytical applications of the colour reaction have also been investigated.

Key Words: Al3+, Chelate, Arsenazo-III, Stability constant.

INTRODUCTION

From the survey of literature¹⁻⁹, it has been found that there are very few references regarding spectrophotometric studies on the stability of Al³⁺-Arsenazo-III complex. As no data are available in the literature on the above complex, the nature and composition of the complex have been determined spectrophotometrically. In this communication the composition and stability of the chelate formed by arsenazo-III, with Al³⁺ have been reported.

EXPERIMENTAL

An ECIL made PC based double beam UV-Vis spectrophotometer UV 5704 SS was used for absorbance measurement using matched quartz cells. Arsenazo-III and AlCl₃ were obtained from BDH. All the other reagents were of analytical grade. The solutions were prepared in doubly distilled water. pH was measured on EC made L 1612 microprocessor based pH-meter. All the experiments were performed at $25 \pm 0.1^{\circ}$ C. The total volume of the mixture prepared for the measurement was kept at 25 mL. The requisite amounts of buffer solutions were added to maintain the desired pH.

The methods applied for determination of stability constant are Job's method of continuous varition¹⁰, Dey and coworkers'¹¹ method and mole ratio method¹². The method of Vosburgh and Cooper¹³ was employed to determine the nature of the complexes formed in the solution.

RESULTS AND DISCUSSION

In view of the observation of Dey and Coworkers¹¹, the organic chelating agents behave as colloidal electrolytes; dilute solutions of 10⁻⁴ M and 10⁻⁵ M of arsenazo-III were employed to avoid complications in absoptiometric measurements. With variation in hydrogen ion concentration arsenazo-III changes its colour and its region of maximum absorption is found to shift. From Table-1 it is concluded that arsenazo-III exists in two different forms depending upon the pH of the solution.

TABLE-1 SHIFT OF λ_{max} WITH CHANGE IN pH

pН	Region of maximum absorption (nm)	
2–9	530	
above 9	550	

The method of Vosburgh and Cooper¹³ was employed to determine the nature of the complex formed in solution. The reagent alone showed a maximum absorption at 530 nm at pH 4.5, but mixtures containing varying proportions of metal (Al³⁺) and arsenazo-III (0:1.0, 1:0.5, 1:1, 1:2, 1:3, 1:4) had λ_{max} at 560 nm, indicated under the condition of study.

TABLE-2 MOLE RATIO METHOD: COMPOSITION OF THE Al³⁺-ARSENAZO-III CHELATE

Total Vol.= 25 n

	AlCl ₃	
Figure		1
Curve	Α	В
Concentration of the Arsenazo-III in 10 ⁻⁵ M	4	3.33

TABLE-3
METHOD OF CONTINUOUS VARIATION: COMPOSITION
OF THE Al³⁺-ARSENAZO-III CHELATE

Total Vol. = 25 mL

	Al	Cl ₃
Figure	2	
Curve	Α	В
Concentration of the Arsenazo-III in 10 ⁻⁵ M		2
Wavelength (nm)	560	
Volume of Al at peak (mL)	12.5	
mposition of the chelate Al : arsenazo-III 1:1		: 1

TABLE-4 JOB'S METHOD OF NON-EQUIMOLAR CONCENTRATION COMPOSITION OF THE Al³⁺-ARSENAZO-III CHELATE

Total Vol. = 25 mL				
	Concentration of re	eagent in 10 ⁻⁵ M		
Figure	3			
Curve	Α	В		
Value of p	Arsenazo-III	AlCl ₃		
0.5	2	4		
2	4	2		

The colour formation is instantaneous and the absorbance values remain constant up to 72 h. No significant change occurs when the order of addition of the reaction of the reactants is altered.

For determining the empirical formula of the chelate formed under the experimental conditions, mole ratio method (Fig. 1) (Table-2), method of continuous varition (Fig. 2) (Table-3) and Job's method of non-equimolar concentration (Fig. 3) (Table-4) were used. It was found that the combining ratio of Al-arsenazo-III was 1:1 at 4.5 pH suggesting the formation of M (arsenazo-III).

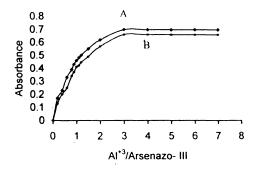


Fig. 1. Composition of Al-arsenazo-III complex by mole ratio method

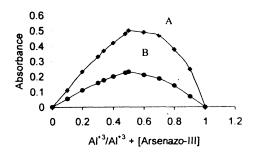


Fig. 2. Composition of Al-arsenazo-III complex by method of continuous variation

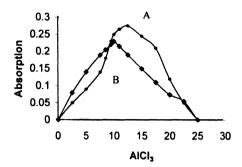


Fig. 3. Composition of Al-arsenazo-III complex by method of Job's non-equimolar concentration

The apparent stability constants were calculated by three different methods. Values of log K are reported in Table-5.

TABLE-5 VALUES OF log K

Method	Al-arsenazo-III
Mole ratio	5.09
Continuous variation	4.85
Non-equimolar concentration	5.15

The maximum colour formation is only attained when the mixture contains a four-fold concentration of the reagent with the metal ion. The effective pH range for the determination of Al³⁺ using arsenazo- III as a spectrophotometric reagent and where the result is reproducible is 4–5, which is shown by the constancy of both wavelength and absorbance of the chelate within this range of pH.

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