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### Simultaneous determination of Stability Constant and Molar Absorptivity Coefficient of the Charge-transfer complexes of Metal – Alizarin Red S

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#### Abstract

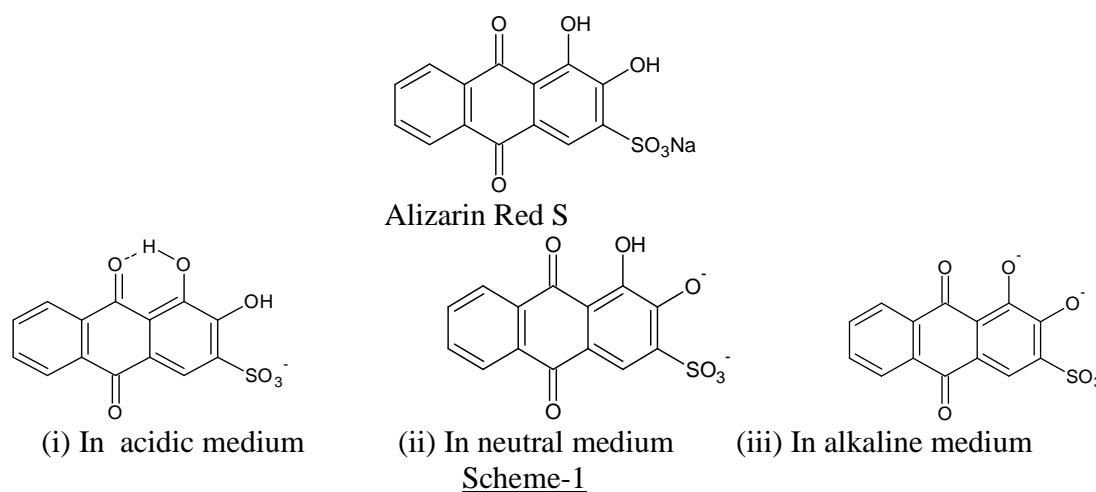
Anthraquinone dye, alizarin red S, has several important analytical applications. Its charge transfer complexes with metal ions will be a key for their applicatory uses. For that their various complexes with metal ions, viz., Cr(III), Cu(II), Pb(II), Th(IV) and UO<sub>2</sub> (II) were studied spectrophotometrically with the help of a novel graphical method in which stability constants(logK) and molar absorptivity coefficient ( $\epsilon_0$ ) of these complexes were determined simultaneously. Standard free energy( $\Delta G^o$ ), oscillator strength (f), energy of interaction(Ect) and resonance energy (RN) of the charge transfer complexes were also calculated.

**Key words:** Alizarin red S, charge transfer spectra, chelation, stability constant, molar absorptivity.

#### INTRODUCTION

Among the anthraquinone dyes, Alizarin and its derivatives are well known colorimetric reagents. Alizarin Red S (ARS; 1:2 dihydroxy 3-anthraquinone sulphonic acid ) has found application in the micro determination of a number of metals[1]. The presence of a quinoid oxygen, with two hydroxyl groups at  $\alpha$ - and  $\beta$ - positions in ARS, makes it very suitable for chelation. Coordination bonding of metal to dye molecule occurs when phenolic group of dye is partly oxidized and partly ionized and metal gets bound. Oxidized quinonic oxygen begins to form a coordination with the same metal and thus chelate is formed which facilitates the charge transfer(CT) from ligand to metal ion, which is responsible for its chromophoric properties. This property has been exploited in the detection and

determination of a number of transition metals[2]. The staining of bone, cartilage and connective tissue *in vitro* has been achieved through ARS oxidation. The electrochemical behavior of ARS has been also studied in connection with voltametric determination of metals like Ca, Sc and Al[3-5]. The staining of gel with ARS has been reported in which stained gel was washed and washing was monitored using spectrophotometry[6]. The presence of sulphonate group in the molecule adds further reactivity to the molecule. The sodium salt of the dye has structure (i) (Scheme-1) which takes different forms in different media- (ii-iv) (Scheme-1):



Hu *et. al.* used ARS for capturing chemiluminescence emission for binding proteins and metal ions under appropriate conditions[7]. According to them, because of structure of ARS, some functional group could form a hexahydric ring complexes with metal ions. The ARS part of the complex could bind the proteins when the solution pH is below the isoelectric part of the protein. Wang *et. al.* applied direct chemiluminescence methods in which the metal ARS complex is used for labeling the protein[8]. Cordeiro *et al.* have studied ARS as a coordination ligand electrode surface to facilitate Cu (II) preconcentration process by absorptive stripping voltametry[9]. In pharmaceutical formulations, ARS was applied in the determination of some drugs[10]. The use of oxidants should promote the staining ability which is quite selective and the process proceeds through complex formation, especially when regulating the staining[11].

The spectrophotometric determination of metal ions using ARS and other anthraquinone derivatives continued to hold interest of scientists[12,13]. It is well known that the ease of formation of a complex with dye, thus stability of the complex decides its applicatory importance. Moreover, the intensity of the colour is decided by its CT spectra as mentioned above. The dyes of hydroxyl phenyl group (e.g., ARS) give coloured chelates with metal ions in solution and the pronounced chelating properties of these dyes must be due to the presence of donor groups like  $-\text{COOH}$ ,  $-\text{OH}$  and  $-\text{O}$ . In the present work, the complexes formed by ARS with five metal ion Pb (II), Cr (III), Cu (II), Th (IV), U(VI) were studied spectrophotometrically. The stability constants of these complexes along with standard free energy change, oscillator

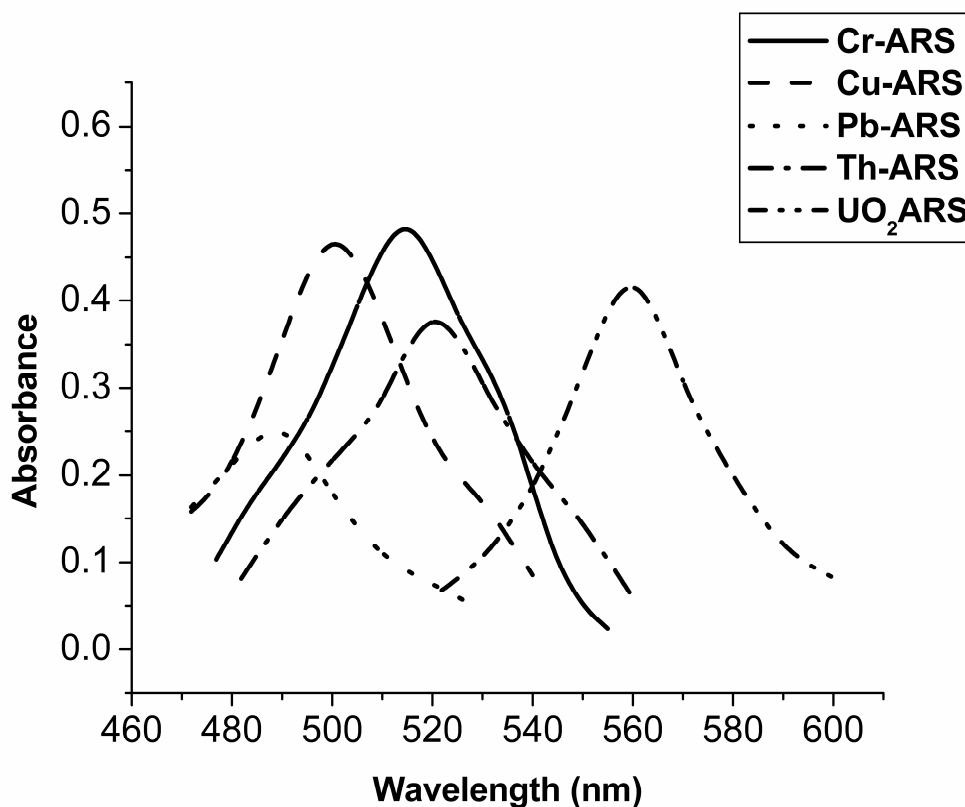
frequency, energy of interaction and resonance energy of charge transfer complexes formed in these systems were determined

## MATERIALS AND METHODS

### *Reagents and chemicals*

All experiments involving absorbance measurements have been performed at fixed hydrogen-ion concentrations, because the chelates are found to change their colour with variations in pH of the medium. The ionic strength has also been kept constant, wherever cited, by the addition of suitable inert electrolytes,  $\text{NaClO}_4$

Standard solution of Alizarin Red S (E. Merck), Copper Sulphate, Chromium Chloride, Lead Nitrate, Thorium Chloride and Uranyl Sulphate, (all from BDH) were prepared in double distilled water. Freshly prepared solutions were, always used, and care was taken to exclude carbon dioxide from the double distilled water used for preparing the same.



**Fig. 1. Spectra showing absorption maxima of metal – ARS complexes.**

### *Apparatus*

The pH measurement were carried out using Orion Research Microprocessor Ionalyzer/901 and spectrophotometric data were obtained using a digital UV-Visible spectrophotometer (Systronic) with 10 mm quartz cuvettes. The work was carried out at room temperature of  $30 \pm 2^\circ\text{C}$ .

*Determination of Wavelength of Maximum Absorption:*

A solution was prepared by mixing 10 mL of  $2.5 \times 10^{-4}$  mol dm<sup>-3</sup> solution Alizarin Red S (ARS) and 10 mL of  $2.5 \times 10^{-4}$  mol dm<sup>-3</sup> different metal solutions, viz. Pb (II), Cr (III), Cu (II), Th (IV), U(VI) followed by diluting the solution to 50 mL. The colour appeared instantaneously. The absorption spectra of each solution were measured in the wavelength range 400-750 nm taking water as blank. It was found that value of absorbance does not change even after a long time. The composite spectra of metal – ARS is shown in figure 1.

*Composition of the complexes:*

The composition of the complexes formed by above metal ions with ARS was determined by Job's method of continuous variations[14] using spectrophotometric data at suitable pH value. In all cases, it was observed that the composition of complexes was found to be 1:1.

**RESULTS AND DISCUSSION**

A number of graphical methods have been developed for determination of stability constants of metal complexes using spectrophotometric data. Ramette, Nash and McBryde have reviewed some of these methods[15-18]. Seal et. al. have also discussed some modifications of previous methods[19-20]. Hazizadeh et al[6] have determined the equilibrium constant formed by phynyl boronic acid(PBA) with ARS by a graphical method in which the concentration of PBA was much larger than the experimental concentration of ARS and thus neglected the concentration of complex in order to formulate a linear relationship. However, in present study we have developed a novel graphical method which does not require omission of any concentration or term and at the same time allows simultaneous determination of molar absorptivity and stability constants of the chelate. The method adopted in this work has been described below.

Consider the formation of 1:1 species according to the equation (1)



for which the stability constant can be expressed as equation (2),

$$K = \frac{[ML]}{([M^0] - [ML])[L^0] - [ML]} \quad (2)$$

$M^0$  and  $L^0$  are the analytical concentration of metal ion and ligand respectively. If metal ion, ligand and complex absorb light in the region of study the absorbance for unit path length can be expressed as equation (3),

(3)

Where,  $\epsilon_M$ ,  $\epsilon_L$  and  $\epsilon_C$  are the molar extinction coefficient of the species M, L and ML respectively.

$$A = \{[M^0] - [ML]\}\epsilon_M + \{[L^0] - [ML]\}\epsilon_L + [ML]\epsilon_C$$

Combining equations (2) and (3) and rearranging we get equation (4),

$$\frac{M^0 L^0}{A - \epsilon} + \frac{A - \epsilon}{\epsilon_0^2} = \frac{M^0 + L^0}{\epsilon_0} + \frac{1}{K\epsilon_0} \quad (4)$$

Where

$$\epsilon = M^0 \epsilon_M + L^0 \epsilon_L \quad (5)$$

and

$$(6)$$

$$\epsilon_0 = \epsilon_C - \epsilon_M - \epsilon_L$$

If the left hand side of equation (4) is plotted against  $M^0 + L^0$ , one will get a slope as  $1/\epsilon_0$  and intercept as  $1/K\epsilon_0$ . From these one can calculate K. Usually the value of  $\epsilon_C$  is not known initially, nor the value of  $\epsilon_0$ . In such case, a trial value of  $\epsilon_0$  can be taken and approximate values of  $\epsilon_0$  and K calculated. The approximate value of  $\epsilon_0$  can be refined by successive approximations using the method of least squares.

A series of solutions were prepared by mixing said metal ions and dye solutions in 1:1 ratio. The ionic strength was adjusted to 0.1 using sodium perchlorate and the pH was adjusted depending on the value where there is a maximum absorption. The absorbance of each solution was recorded at absorption maxima. The first trial value of  $\epsilon_0$  was taken as  $1 \times 10^4$  and using equation (4), a plot was constructed by the method of least squares. From the slope of linear graph new value of  $\epsilon_0$  was obtained. This fresh value of  $\epsilon_0$  was used as trial in next iteration to get fresh value of  $\epsilon_0$ . It was observed that in second and subsequent iterations the value of  $\epsilon_0$  decreases and K increases. The process was continued till two successive values were the same. The results are summarized in composite table 1.

#### Determination of oscillator strength(f):

From the CT absorption spectra, one can extract oscillator strength. The oscillator strength  $f$  is estimated using formula[21]:

$$f = 4.32 \times 10^{-9} \int \epsilon_{CT} dv$$

where,  $\int \epsilon_{CT} dv$  is the area under the curve of the extinction coefficient of the absorption band in question vs. frequency. To a first approximation:

$$f = 4.32 \times 10^{-9} \epsilon_{\max} \Delta v_{1/2}$$

where  $\epsilon_{\max}$  is the maximum absorption coefficient of the band and  $\Delta v_{1/2}$  is the half-width, i.e., the width of the band at half the maximum extinction. The observed oscillator strengths of CT bands are summarized in Table 2.

*Determination of standard free energy changes ( $\Delta G^0$ ) and energy ( $E_{CT}$ )*

The standard free energy changes of the complexation ( $\Delta G^0$ ) were calculated from the stability constants (association constants) by the following equation derived by Martin et al[22]:

$$\Delta G^0 = -2.303 RT \log K$$

Where  $\Delta G^0$  is the free energy change of the complexes ( $\text{KJmol}^{-1}$ ), R is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}$ ), T is the temperature in Kelvin degrees ( $273+^{\circ}\text{C}$ ) and K is the stability constants of the complexes ( $\text{mol}^{-1}$ ).

Energy of the interaction between donor (ligand) and acceptor (metal ion) is calculated using the following equation derived by G. Briegleb[23]. The calculated values of E are given in Table 2.

$$E = 1243.667 / \lambda_{CT} \text{ nm}$$

Where  $\lambda_{CT}$  is wave length of the CT band.

*Determination of resonance energy ( $R_N$ ):*

Briegleb and Czekalla[24] theoretically derived the relation:

$$\epsilon_{\max} = 7.7 \times 10^{-4} / [h\nu / (R_N) - 3.5],$$

where  $\epsilon_{\max}$  is the molar absorptivity coefficient of the complex at the maximum of the CT absorption,  $\nu$  is the frequency of the peak and  $R_N$  is the resonance energy of the complex at ground state, which obviously is the contributing factor to the stability of the complex. The values of  $R_N$  for the complexes under study have been given in Table 2.

**Table 1 Experimental data and results; temperature : Cr(III)-, Cu(II)-, Pb(II)- Th(IV)- and UO<sub>2</sub>-ARS at 30 °C**

System	Concentration Range $\times 10^5$ (M)	pH $\pm 0.2$	Ionic Strength (M)	$\lambda_{\max}$ (nm)	$\epsilon_0 \times 10^{-4}$ ( $\text{L.M}^{-1}.\text{cm}^{-1}$ )	Log $K_1$
Cr(VI)-ARS	2.50-6.25	5.6	0.1	515	4.370	4.36
Cu(II)-ARS	2.50-6.25	4.4	0.1	500	4.193	4.38
Pb(II)-ARS	2.00-5.00	5.0	0.1	490	2.498	4.60
Th(IV)-ARS	2.00-5.00	3.9	0.1	520	1.030	4.96
UO <sub>2</sub> (II)-ARS	2.50-6.25	4.1	0.1	560	2.164	4.66

**Table 2 - Values of oscillator strength, free energy, energy and resonance energy of complexes of Cr(III) -, Cu(II) -, Pb(II) -, Th(IV)- and UO<sub>2</sub> - ARS**

System	Oscillator strength $f \times 10^3$	Free energy $-\Delta G_0 \times 10^{-3}$	Energy $E_{CT}$	$\lambda_{max}$ (nm)	Resonance energy $R_N$
Cr(VI)-ARS	8.87	25.28	2.41	515	$1.37 \times 10^4$
Cu(II)-ARS	7.97	25.40	2.48	500	$1.35 \times 10^4$
Pb(II)-ARS	5.61	26.68	2.53	490	$8.21 \times 10^3$
Th(IV)-ARS	2.49	28.77	2.39	520	$3.20 \times 10^3$
UO <sub>2</sub> (II)-ARS	3.93	27.08	2.22	560	$6.20 \times 10^3$

From the stability constant and molar absorptivity determinations, it is seen that the dye form stable chelates with transition and inner transition metals. Moreover, it can be assumed in the case of metal - dye chelates, there are two alternative positions of the chelate ring. The metal ion may be co-ordinated either between (i) the quinoid oxygen and the adjacent oxygen of the carboxylic group or (ii) the phenolic oxygen and the adjacent carboxylic oxygen. On the basis of the decrease in the pH when hydrogen ions are liberated as a result of the chelation, as in the case of normal group elements, the hydroxyl oxygen participates in the chelation. On the other hand, no change in pH occurs in the reaction with the transition and rare earth elements. In such cases chelation appears to occur between the quinoid oxygen and the adjacent carboxylic oxygen. Generally in low oxidation states, an element tends to be soft but in higher oxidation states, an element is most stable when combined with harder bases like O<sup>2-</sup> and OH<sup>-</sup>. In hard - hard interactions lowest unoccupied molecular orbital (LUMO) of the acid lie far above the highest occupied molecular orbital (HOMO) of the base and relatively little change in the orbital energies on adduct formation. A soft-soft interaction involves HOMO & LUMO energies that are much closer and give a large change in orbital energies on adduct formation. In the above complexes, charge transfer transition indicate that the transition results in an electron transfer from the HOMO of the donor to the LUMO of the acceptor. Oscillator strength in charge transfer complexes is due to these transitions. The binding of the donor produces an increase in oscillator strength. The availability of 'd' orbitals in transition metal ions increases the ease of binding sites which reflected in the higher oscillator strength in the case of Cr and Cu Charge transfer complexes. Higher resonance energy of these complexes also supports the above said facts. With inner transition metal ion, low oscillator strength reflected the inferior binding ability of these ions. The value lies in between in the case of Pb, a normal representative metal ion.

The novel graphical method used here has three clear advantages: no term is omitted, since equimolar amounts of metal and ligand has been taken hence there is no possibility of the formation of higher complexes and lastly the most important advantage of this method is that stability constant and molar absorptivity can be determined simultaneously.



## CONCLUSIONS

A novel graphical method is used to study some metal – ARS complexes spectrophotometrically. With the help of this method, we have simultaneously determined the stability constant and molar absorptivity coefficient of the said complexes successfully. The proposed method offers good selectivity for the determination of metal – dye complexes because of a number of advantages. Moreover the behavior of charge transfer complexes were also studied on the basis of their oscillator strengths and resonance energies.

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