THE DETERMINATION OF THE STABILITY CONSTANTS BINARY COMPLEXES OF ALIZARIN WITH Mg (II) and Al(III) BY POTENTIOMETRIC AND SPECTROPHOTOMETRIC METHODS

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ABSTRACT

Alizarin, which consists of 1,2 dihydroxyanthraquinone, is the common madder of anthraquinoid pigment group. It has been used for textiles, food and medicine. The colour of alizarin is light brown and dissociates low in water. It is in the root of *Rubia tinctorum* plant. The plant is 50-80 cm high and its trunk is cornered, hard and thorny.

In the present study a potentiometric titration and spectrophotometric method has been used to determine stability constants for Mg(II) and Al(III) with alizarin. Stability constants of binary system have been evaluated by the method suggested by Irving –Rossotti procedure.

The protonation and acid constants at 25 °C have been found as follows:

$LogK_1 = pK_2 = 8,09$ $LogK_2 = pK_1 = 5,91$

The conditional formation constants of the formed complexes were calculated and pH ranges through which the complexation occurs were found.

Magnesium (II)-Alizarin: $LogK_1 = 4,96$; $K_1 = 9,12.\ 10^4$
Aluminium(II)-Alizarin: $LogK_1 = 10,88$; $K_1 = 7,586.\ 10^{10}$ $LogK_2 = 10,31$; $K_2 = 2,042.\ 10^{10}$

In addition, the conditional constants were calculated as a function of pH. The maximum values of the conditional formation constants were found to be in accordance with the metal ligand complexes formation constants in a given pH region. The mole fraction of complexes was calculated by means of formation constants. The values of stability constants of metal ligand complexes at 25°C are as follows:

The ionic strength was kept constant at I= 0,01 with $NaClO_4$. Additionally Mg(II)-Alizarin and Al(III)-Alizarin complex formation was examined by spectrophotometric method.

Keywords: Alizarin,anthraquinone, binary complex, stability constants

INTRODUCTION

Common madder (*Rubai tinctorum)* produces anthraquinone pigments in its roots, one of them being alizarin(1,2 dihydroxy anthraquinone) which has been used for dyeing textiles since 2000 B. C /1/. These pigments produce useful colours which have distinctive heat and light resistant properties /2/. The alizarin component became the first natural dye to be synthetically duplicated in 1868 when the German chemists Carl Graebe and Carl Liebermann /3/ found a way to produce it from anthracene. Its molecular structure is shown below:

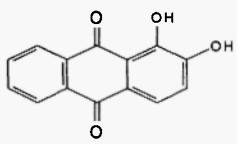


Fig. 1: Alizarin

Textiles are articles of prime necessity with a greater or lesser degree of skin proximity and regulations have been legislated which seek to avoid risks to the textile end user. On the other hand textile dyeing is characterised by high environmental pollution and by high health risk to personal handling harmful substances. Many colorants from synthetic sources can be harmful and cause allergies in humans, therefore interest in natural dyes has increased considerably during the last few years /4,5/. A number of dye crops were stil grown in the Mediterranean area and in Italy specifically, up to the Second World War. These vegetal species were mostly native to the Mediterranean region, or naturalised more or less, throughout the area.

Antioxidants are used to preserve foods by retarding discoloration, rancidity, or deterioration due to autoxidation. However synthetic antioxidants have been reported to be carcinogenic /6/. Hence several attempts to replace synthetic antioxidants with natural antioxidants have been developed /7/. The synthetic alizarin could be produced at less than half the cost of the natural product and the market for madder collapsed virtually overnight.

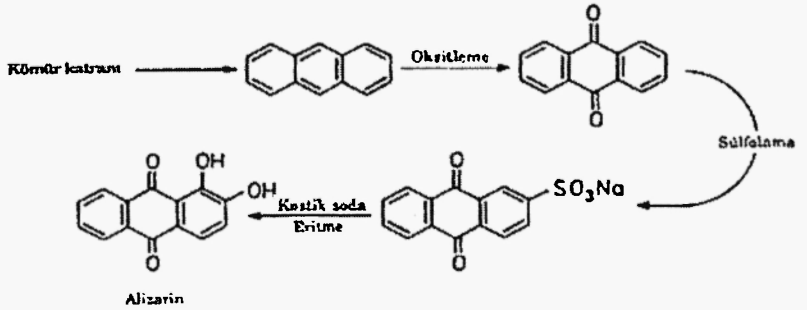


Fig. 2: The synthesis of alizarin

In the present paper the method of Irving-Rossotti /8,9/ and Calvin-Wilson /10 / was applied to study the acid constants of alizarin as ligand whose Ca(II) and Zn(II) complexes were examined in our previous paper /11/ and then the condition of complex formation with Mg(II) and Al(III) was investigated.

2. EXPERIMENTAL

2. 1. Material and Methods

All chemicals used in the experiments were of analytical purity grade from Merck. The stock solution of alizarin was prepared by dissolving in dioxan-water. The stock solutions of metal ions were prepared from nitrate salts. Solutions were made up under N_2 atmosphere in H_2O which was decarbonated. A Metrohm 654 digital pH meter,with a combined glass electrode assembly was used for pH measurements. The concentration of Mg(II) and Al(III) ions in the solution was typically kept 2,5. 10^{-4}M and determined accurately by titration with standard ethylenediamine tetraacetic acid (EDTA). Computer calculations were performed on the pH-metric data.

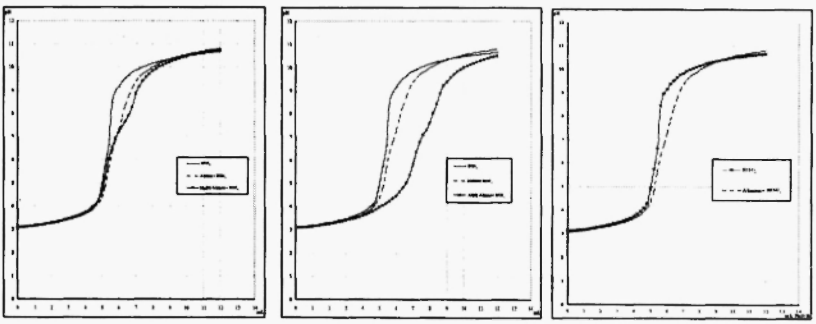
A Shimadzu UV-160 double beam UV-visible spectrophotometer was used for spectrophotometric measurements.

THE DETERMINATION OF STABILITY CONSTANTS

In order to determine the stability constants of binary ligand complexes, the solutions including 0. 01M $HclO_4$: ($HclO_4$+L) : ($HclO_4$+L+M) solutions were titrated potentiometrically using NaOH solutions (0,01N) at 25°C. Alizarin was dissolved in dioxan- water (1+1,v/v)

The average n_A values were calculated from the titration curves. The following equation was used for this calculation:

$$n_A = y + \frac{(V_1 - V_2)(N + E^o)}{(V^o + V_1)T^o{}_L}$$



Alizarin + $HClO_4$ | Alizarin + $HClO_4$ + Mg(II) | Alizarin + $HClO_4$ + Al(III)

Fig. 3: Potentiometric titration curves of Mg(II) and Al(III) with Alizarin

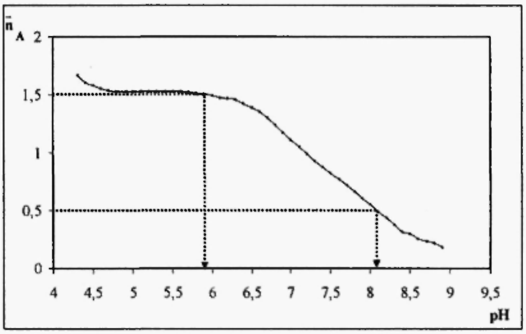


Fig. 4: pH-n_A curve for Alizarin

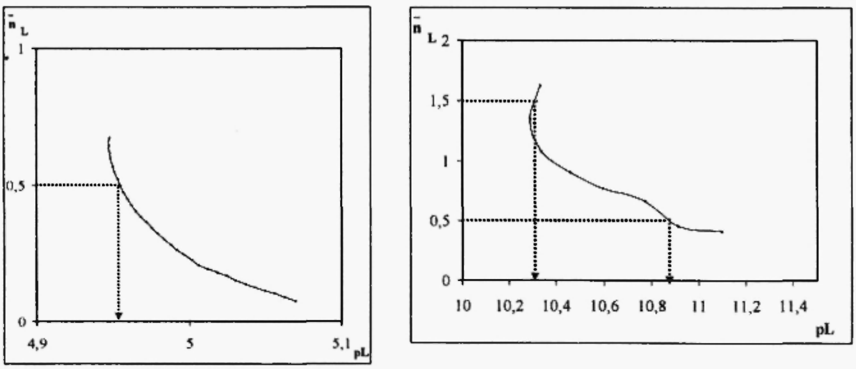


Fig. 5: $n_L = f(p_L)$ curves Mg(II) - Alizarin and Al(III) - Alizarin

where

V^o = volume at the beginning	: 50,00ml
N = normality of base	: 0,0100N
T^o_L =total ligand concentration	: 5. 10^{-5} M
E^o = concentration of acid	: 0,0012M
y = the number of protons given for alizarin	: 2
T^o_M = total molar metal concentration	: 5. 10^{-5} M

The mixtures which also contain metal ions were titrated with 0,0100N NaOH solution potentiometrically and the titration curves were plotted in Fig. 3. The n_A values corresponding to several pH values for ligands were calculated by the use of V_1 and V_2 volumes from Fig. 3. The figure of n_A

=f(pH) was plotted by using the values obtained. The protonation constants for the corresponding acid constants were found. Using the potentiometric titration data of the solutions, the metal ligand average formation numbers n_L at various were calculated.

The dissociation constants of alizarin $\log K_1 = 8{,}09$ $\log K_2 = 5{,}91$

$$M + L \longrightarrow ML$$
$$ML + L \longrightarrow ML_2$$

The mixtures consisting of metal and ligands were titrated potentiometrically. The n=f(pL) graphics were plotted using n and pL values which were calculated from titration curves. The separation between ($HClO_4$); ($L+HClO_4$); and ($HClO_4+L+M$), all potentiometric titration curves, showed the formation of a binary compound .

The following equations were used to calculate n_L and p_L values:

$$\bar{n}_L = \frac{(V_3 - V_2)\left(N + E^o + T^o{}_L (y - n_A)\right)}{\left(V^o + V_2\right).n_A.T^o{}_M}$$

$$pL = \log \frac{1 + \beta_1 [H^+] + \beta_2 [H^+]^2}{T^o{}_L - n.T^o{}_M}$$

$\beta_1 = K_1 = 9{,}12.\ 10^4$

$\beta_2 = K_1.\ K_2 = 7{,}586.\ 10^{10}\ .\ 2{,}042.\ 10^{10} = 1{,}60.\ 10^{21}$

n_L f(pL) graphs were plotted using n_L and pL values which were calculated for each metal ligand complex. The formation constants of complexes were found from pL values which corresponded to nL = 0. 5; nL = 1. 5 values. The stability constants of complexes are set out below:

Table 1

The formation constants of binary complexes

	$\log K_1$	$\log K_2$	$\log\beta$
Mg(II)-Alizarin	4,96	-	4,96
Al(III)-Alizarin	10,88	10,31	21,19

In addition the changes in mole fractions of the molecular and ionic species derived from complexes with the pH of solution were calculated.

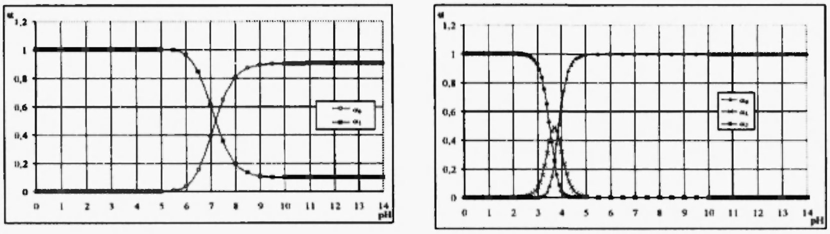


Fig. 6: The relative abundance curve of Mg(II)-alizarin, Al(III)-alizarin complexes depending on the pH

RESULTS AND DISCUSSION

Anthraquinone dyes are among the oldest and the most important dyestuffs used in works of art such as painting, archaeological textiles, and drawings. Alizarin, a major component in the extract of the madder root, was extensively used in Asia and Egypt since ancient times to obtain pink toned pigments in textile materials /12/.

In this paper the solution which has a final ligand concentration of 5. 10^{-5} mol/l and an ionic strength of 0,01 was titrated with 0. 01mol/l NaOH solution. The protonation constant of alizarin was found graphically by using the Irving-Rossotti method. The results are shown in Fig. 4. For finding the stability constants of the complexes of metals with ligand, the solutions which contain Mg(II), Al(III) salts in certain concentrations were titrated with NaOH solution potentiometrically at 25°C. Titration curves were obtained by plotting the pH changes versus the 0. 0100mol/l volumes (Fig. 3). The n_L=f(pL) figures were plotted by using nL values which were calculated by the potentiometric titration curves. The formation constants of the complexes have been read, and they correspond to the n = 0,5 and n = 1,5 values from n_L=f(pL). In the evaluation, the relative abundance of the species in the system is plotted against the pH (Fig. 5). In the analytical applications, it was known that the different ligands in the system have an influence in the formation of complexes. For this reason, they are termed "the conditional formation constants". In addition, the pH range where the conditional formation constant was at the maximum was overlapped with the pH range where the relative abundance of Mg(II)-alizarin and Al(III)-alizarin complexes are at the maximum. The conditional formation constants of the complexes were calculated and they were plotted versus the corresponding pH changes. In calculating the conditional formation constants, it is accepted that the only competitive ligand is the hydronium ion in the reaction medium. The pH ranges in which the complexation occurs, the maximum values of conditional formation constants and the pH values corresponding to these conditional formation constants for 25°C are shown in Table 2 (Figs. 6, 7).

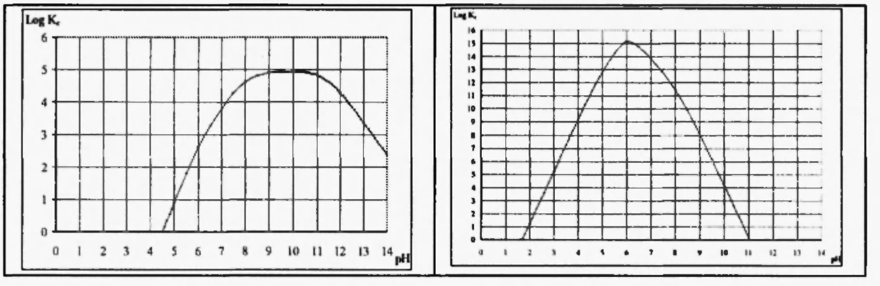


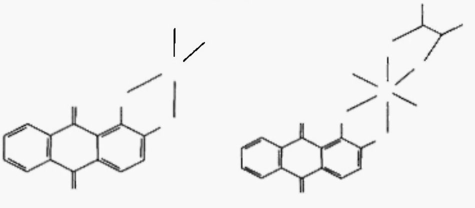
Fig. 7: The conditional formation constants of Mg(II) and Al(III)-Alizarin

Table 2

The conditional formation constants for the metal complex(I=0,01)

Metal-ligand complex	pH range of the metal complexes	pH (Kc is max)	$LogKc_{max}$
Mg(II) - Alizarin	4,5 – 14,0	4,96	4,96
Al(III) - Alizarin	1,5 – 14,0	15	15,15

As a result, the components of metal/ligand complexes are found to be Mg(II) - Alizarin 1:1 Tetrahedral; Al(III) - Alizarin 1:2 Octahedral.



1:1 1:2

Fig. 8: The composition of Mg(II) – alizarinand Al(III) - alizarin complexes

In the spectrophotometric measurements the $HClO_4$ + $NaClO_4$ + metal + ligand were examined in the same position as the mixtures used for the potentiometric titration. After the reaction was completed, no absorption signal originating either from Mg(II) or alizarin was observed. Similar conclusions could be seen from the spectrum of Al(III)-alizarin.

According to spectra of Mg(II), Al(III), alizarin and the complexes of Mg(II) - Alizarin (λ =427,5nm ; A= 0,612), Al(III) -Alizarin (λ=479,5nm; A= 0,682) were examined. The component of binary complex was found.

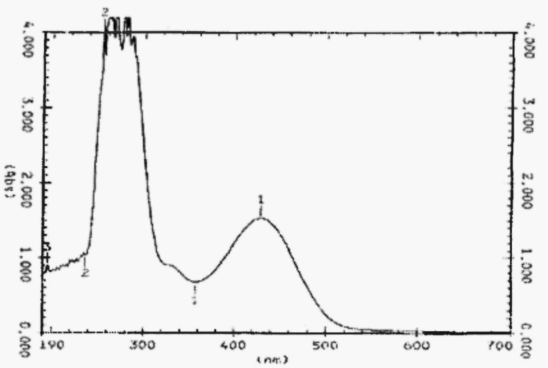


Fig. 9: The absorption spectra of Alizarin

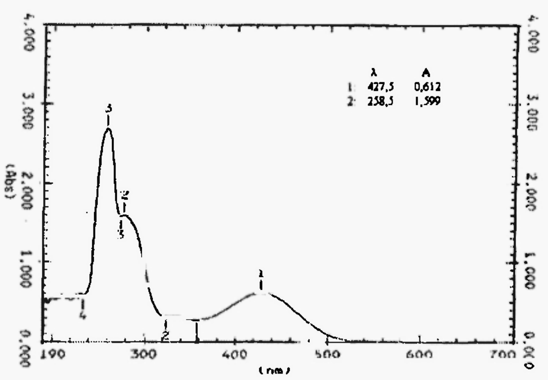


Fig. 10: The absorption spectra of Mg(II)-alizarin and Al(III)-alizarin

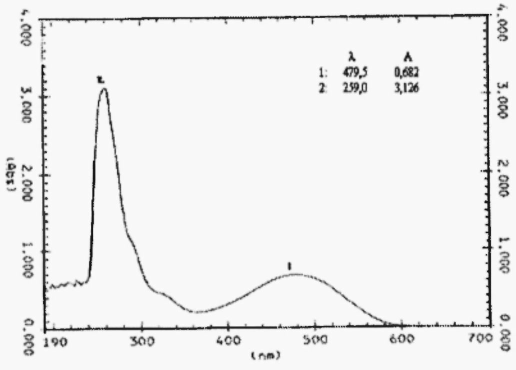


Fig. 10 Contd.: The absorption spectra of Mg(II)-alizarin and Al(III)-alizarin

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