



SYNTHESIS AND CHARACTERIZATION OF SOME ALKALINE EARTH METAL ION COMPLEXES WITH ACID YELLOW-42 AND DYEING PERFORMANCE OF WOOL

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ABSTRACT

Novel binary complexes of alkaline earth metal ion (Mg^{+2} , Ca^{+2} , Ba^{+2} , Sr^{+2}) has been synthesized using acid yellow-42 [1,1'-Biphenyl]-2,2'-disulfonic acid, 4,4'-bis[(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl) azo]¹⁻² ligand capable of forming stable chelate. After syntheses the complexes were characterized by chemical as well as instrumental methods. Like elemental, IR and TGA analyses, UV-visible absorption spectra and magnetic moment. Their dyeing performance as acid dyes has been assessed on wool.

Key words: Acid yellow-42, Alkaline earth metal ion, Chelate, IR, Dyeing performance.

INTRODUCTION

Acid dye is a member of a class of dye that is applied from an acidic solution. In the home or art studio, the acid used in the dyebath is often vinegar (acetic acid) or citric acid. The uptake rate of the dye is controlled with the use of sodium chloride³.

In textiles, acid dyes are effective on protein fibers, i.e. animal hair fibers like wool, alpaca and mohair. They are also effective on silk. They are effective in dyeing the synthetic fiber nylon but of minimal interest in dyeing any other synthetic fibers.

Acid dyes are thought to fix to fibers by hydrogen bonding, Vander Waals forces and ionic bonding. They are normally sold as the sodium salt therefore they are in solution anionic. Animal protein fibers and synthetic nylon fibers contain many cationic sites therefore there is an attraction of anionic dye molecule to a cationic site on the fiber. The

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strength (fastness) of this bond is related to the desire/chemistry of the dye to remain dissolved in water over fixation to the fiber². Various dyes of alkaline earth metal ion complexes with acid yellow-42 system have been reported to be useful on natural and man-made fibres, showed high affinity and good dyeing performance⁴⁻⁵. This process of dyeing is simple and cheap. It gives the brightness of the shade.

EXPERIMENTAL

1 : 1 mole ratio of metal perchlorate {Ca(ClO₄)₂, Mg(ClO₄)₂, Sr(ClO₄)₂, Ba(ClO₄)₂} and dye were taken in the form of aqueous solutions, after mixing, this mixture was refluxed with water condensor for 2 hours at 150°C temperature, until the mixture remains ¼ part. After doing this process the solutions were cooled and the binary complexes isolated from the mixture, it was cooled, filtered and washed with pure water and alcohol to remove impurities soluble in those solvents, then they were characterized by different methods.

Dyeing process of acid yellow-42

The woolen samples were dyed with acid dyes before and after the enzymatic treatment. The dyeing with acid dyes was performed using 1% stock solution of the dyes. Dyeing was carried out according to procedure given by Shenai and Saraf⁶⁻⁷.

Dyeing of compounds on wool fabric

Weight of wool fabric : 2 gm weight of dye under study : 40 mg M : L : 1 : 50.

Dye bath was prepared using the stock solution of the dye, acetic acid and water to maintain the liquor ratio 1 : 50. The fabric was introduced at 55°C. The temperature was raised to 70-75°C within 30 minutes. Stirring was continued to ensure uniform distribution of dye 2% acetic acid (10% solution) was added and dyeing was continued for another 15 minutes. After dyeing, samples were taken out from the dye bath rinsed thoroughly with water and soap.

RESULTS AND DISCUSSION

Elemental analysis of the binary complexes isolated in the present study is given in Table 1.

The important infrared absorption bands and spectra of dyes and its metal complexes using Perkin elmer spectrophotometer; Frequency range: 4000 – 500 cm⁻¹ (KBr disc.) are shown in Table 2.

Table 1: Analytical data and some physical properties of the metal complexes

Compound molecular formula	Colour	Formula weight	Analysis (%) calculated / (Found)				m.p. °C
			C	H	N	M	
[(Acid yellow -42) · H ₂ O] · 2H ₂ O C ₃₂ H ₃₂ N ₈ O ₁₁ S ₂	Dark yellow	762.74	50.34 (49.77)	4.19 (3.69)	14.68 (13.89)	-	>300
[Mg- (Acid yellow -42) · H ₂ O] · 4H ₂ O C ₃₂ H ₃₅ N ₈ O ₁₃ S ₂ Mg	Yellow	818.04	46.94 (46.58)	4.27 (4.11)	13.69 (13.38)	2.97 (2.73)	>300
[Ca- (Acid yellow -42) · H ₂ O] · 2H ₂ O C ₃₂ H ₃₁ N ₈ O ₁₁ S ₂ Ca	Light yellow	801.81	47.89 (46.93)	3.86 (3.63)	13.96 (13.71)	4.99 (4.40)	>300
[Sr- (Acid yellow -42) · H ₂ O] · 5H ₂ O C ₃₂ H ₃₇ N ₈ O ₁₄ S ₂ Sr	Light yellow	897.36	42.79 (41.73)	4.12 (3.26)	12.48 (11.83)	9.76 (8.98)	>300
[Ba - Acid yellow -42] · 4H ₂ O C ₃₂ H ₃₃ N ₈ O ₁₂ S ₂ Ba	Yellow	915.07	41.96 (39.89)	3.60 (3.21)	12.23 (12.89)	15.01 (14.41)	>300

Table 2: Infrared spectroscopy of the metal complexes of acid yellow-42 ($\bar{\nu}$ values in cm^{-1})

Compound	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$	$\bar{\nu}$
	(O-H) Str.	[Ar (C-H)] Str.	N(-OH) Str.	(-SO ₃ H) Str.	(C=N) Str.	(C-O) Str.	(S=O) Str.	(C-S) Str.	(M-N) Str.	(N=N) Str.	(M-OH ₂) Str.	(M-OH ₂) Str.
[(A.Y. - 42) · H ₂ O] · 2H ₂ O	3510	1040		2849	1649	-	1339	-	-	2276	-	-
		755			1553		1040					
[Mg - (A.Y. - 42) · H ₂ O] · 4H ₂ O	3392	1040		-	1649	1219	1340	671	725	-	-	543
		755			1545		1040					
[Ca - (A.Y. - 42) · H ₂ O] · 2H ₂ O	3396	1040		-	1656	1220	1340	671	725	2366	543	
		755			1545		1041					
[Sr - (A.Y. - 42) · H ₂ O] · 5H ₂ O	3409	1041		-	1655	1220	1340	671	725	2365	543	
		741			1546		1041					
[Ba - A.Y. - 42] · 4H ₂ O	3405	1027		-	1655	1219	1339	671	725	-	-	508
		757			1545		1082					

N.B.: Ar (C-H) = Aromatic C-H stretching, (-SO₃H) = O-H stretching band of -SO₃H,
(A.Y. - 42) = Acid Yellow - 42, Str. = Stretching

The functional groups present in the current dye and metal complex were identified with their characteristic vibrational frequencies, nature and magnitude of intensity of the absorption bands. Normally N-H stretching bands and O-H stretching bands occur in the region $3500\text{-}3100\text{ cm}^{-1}$. Such strong bands occur at $\sim 3396.3\text{ cm}^{-1}$ in metal complex and 3150 cm^{-1} in dye⁸.

Dye spectra shows an intense band at 2849 cm^{-1} for -OH stretching of -SO₃H group but this band not shown in any metal complexes spectra⁹.

Two bands which are strong and are of medium intensity in range of $624\text{-}590$ and $783\text{-}800\text{ cm}^{-1}$ in studied metal complex. These can be M-N and M-N = C stretching respectively. A sharp and strong band obtained $\sim 480\text{ cm}^{-1}$ in metal complex are attributed to M-N stretching⁹⁻¹⁰.

Sharp and medium intensity bands are observed at $\sim 500\text{ cm}^{-1}$ in IR spectra of all metal complexes which represent M-OH₂ stretching¹¹⁻¹².

The thermogravimetric analysis of the ligand sample and their metal chelates was carried out in air. All the metal chelates were Cumulative % Weight loss data of metal complexes at various temperatures (°C) shown in Table 4.

Thermogravimetric analysis of the complexes have been carried out using Du-point Thermal Analyzer at a $10^{\circ}\text{C min}^{-1}$ heating rate. It has been observed that M (II) chelates show loss in weight corresponding to two water in the dye acid yellow-42 (Table 3). This shows that there are water molecules present in each metal chelate.

Some important observations have been made. It has been observed that all the M (II) chelate show loss in weight corresponding to two water crystallize molecules and one water of coordination molecule in acid yellow-42 dye. Five crystallized water molecules and one coordination water molecules in Sr (II), four crystallized water molecules in Ba (II), two crystallized water molecules and one water coordination molecules in Ca (II), four crystallized and one coordination water molecules in the Mg (II) complex.

In general the water of hydration may be considered as either the crystallization water or coordination water. According to Nikolaev et al.¹³ water eliminating below 15°C can be considered as the water of crystallized and water eliminated above 15°C may be due to its coordination in the metal complex.

Table 3: Water content at 25°C and cumulative weight loss data of the metal chelate at 50°C, 100°C and 150°C

Complex	50°C		100°C		150°C	
	g	%	g	%	g	%
[(Acid yellow - 42) · H ₂ O] · 2H ₂ O	0.714	0.1	42.84	6.0	49.98	7.0
[Mg- (Acid yellow - 42) · H ₂ O] · 4H ₂ O	0.736	0.1	73.55	9.99	88.35	12.0
[Ca- (Acid yellow - 42) · H ₂ O] · 2H ₂ O	0.75	0.1	45.124	6.0	60.166	8.0
[Sr- (Acid yellow - 42) · H ₂ O] · 5H ₂ O	0.800	0.1	79.981	9.99	96.074	12.0
[Ba - Acid yellow - 42] · 4H ₂ O	0.85	0.1	67.17	7.9	72.278	8.5

Table 4: Cummulative % weight loss data of metal complexes at various temperatures (°C)

Complex	50 (°C)	100 (°C)	150 (°C)	200 (°C)	250 (°C)	300 (°C)	350 (°C)	400 (°C)	450 (°C)	500 (°C)	550 (°C)	600 (°C)
[(Acid yellow - 42) · H ₂ O] · 2H ₂ O	0.1	6.0	7.0	7.9	8.3	15.9	20.0	27.5	32.0	42.0	44.0	45.0
[Mg- (Acid yellow - 42) · H ₂ O] · 4H ₂ O	0.1	9.99	12.0	13.5	14.0	20.0	24.0	28.0	36.0	46.0	48.0	52.0
[Ca- (Acid yellow - 42) · H ₂ O] · 2H ₂ O	0.1	6.0	8.0	8.5	9.0	16.0	19.6	23.7	31.0	44.0	47.0	49.0
[Sr- (Acid yellow - 42) · H ₂ O] · 5H ₂ O	0.1	9.99	12.0	12.4	14.0	21.8	27.7	29.0	37.0	46.0	49.8	50.2
[Ba - Acid yellow - 42] · 4H ₂ O	0.1	7.9	8.5	10.0	12.0	19.0	23.7	27.0	36.0	44.0	47.0	48.0

Absorption spectral data and magnetic moment of the metal complexes shown in Table 5 the chelates of Ca²⁺, Mg²⁺, Sr²⁺ and Ba²⁺ are analysed for UV-visible absorption

spectra and magnetic moment. This group has a usual characteristic of absence of d-d transitions because no space for excited electron is present in the d-orbital, which is completely filled in these ions. The results indicate diamagnetic nature of these chelates with ligand to metal charge transfer bands¹⁴⁻¹⁵.

Table 5: Absorption spectral data and magnetic moment of the metal complexes

Metal complexes	Transitions cm ⁻¹	μ_{eff} (B.M.)
[Mg- (Acid yellow -42) ·H ₂ O]·4H ₂ O	19531 22883	Diamagnetic
[Ca- (Acid yellow -42) ·H ₂ O] ·2H ₂ O	19342 20964	Diamagnetic
[Sr- (Acid yellow -42) ·H ₂ O] ·5H ₂ O	19920 26881	Diamagnetic
[Ba - Acid yellow -42] ·4H ₂ O	20940 29239	Diamagnetic

The shade of Mg complex is lemon yellow where as the other complexes as well as dye itself impart slight turmeric yellow shade on the fabric. The shade of Ca complex is darkest among all other shades including the dye itself. Thus complexation with Ca seems to enhance the yellow shade towards the turmeric yellow. In contrast the Mg complex reduces the colour intensity compared to the dye. Remaining all complexes do not show major change of dyeing on complex formation.

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