

Spectrophotometric studies on the interaction of some triphenylmethane dyes with cationic surfactants

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ABSTRACT

Triphenylmethane dyes are commonly used in the spectrophotometric and complexometric determination of metal ions in solution. The importance of a chromogenic reagent in analytical chemistry is judged by its selectivity and sensitivity. With the development in science and technology and new materials, the importance of sensitive chromogenic reagents has increased. The addition of cationic surfactants to triphenylmethane dyes results in the increase in the sensitivity of these reagents in determination of metal ions by spectrophotometric method. The addition of cationic surfactants to these dyes results in the shifting of maximum absorbance in the alkaline medium towards the acid range by a few units. This shows that the addition of surfactants is causing changes in the dissociation constants of these dyes. The dyes under investigation are Chrome azurol S, Pyrocatechol Violet, Bromopyrogallol Red Xylenol Orange and dissociation constants have been determined at room temperature in presence of cationic surfactants resulting in the early dissociation of the groups present in these dyes. The results have been discussed in the light of different dyes and different surfactants used and because of these properties the simultaneous determination of metal ions is possible.

Keywords: Triphenylmethane dyes complexometric, chromogenic reagents, spectrophotometric method, cationic surfactants.

INTRODUCTION

With the development of science and technology the importance of analytical techniques has increased. Triphenyl methane dyes are commonly used in analytical techniques like spectro-photometric and complexometric determination of metal ions in solution. The importance of a chromogenic reagent in analytical chemistry is judged by its selectivity and sensitivity. In order to use a chromogenic reagent as a chelatochrome indicator the knowledge of dissociation constant is essential. In recent years, the importance of surfactants in spectrophotometric and complexometric methods has been observed. Thus it is necessary to study effect of surfactants on the dissociation of reagents. In the present paper result on the spectrophotometric determination of dissociation constants of a group of triphenyl methane dyes are reported. The dyes under investigation are Chrome Azurol S, Pyrocatechol Violet, Bromopyrogallo Red, Xylenol Orange and Methyl Thymol blue. Dissociation constants have been determined at room temperature in absence and in presence of cationic surfactants and results compared.

The addition of surfactants to these dyes also makes them useful as chelatochrome indicators. Xylenol orange as a chelatochrome indicator has been discussed in detail [1-2] Xylenol Orange as a chelatochrome indicator has been restricted only for the determinations in acidic range. However, the addition of cationic surfactants, permits the extension of its usefulness even in the alkaline range. This enables the determination of more than one metal ion in a mixture. Advantage is taken of this fact and determination of calcium and magnesium in a mixture and in samples of Dolomite has been reported in this paper.

METHODOLOGY

Absorbance measurements were done on a Beckman Model B spectrophotometer and hydrogen ion concentration was adjusted using an Electronic Corporation pH meter provided with combined glass calomel electrode Standard Solutions of Chrome Azurol S (CAS), Methyl Thymol Blue (MTB), Pyrocatechol Violet (PCV), Xylenol Orange (XO) and

Bromopyrogallol Red (BPGR) (B.D.H. England) were prepared by dissolving suitable amounts of reagents in 40 percent ethanol and making up the final volume by distilled water. Solutions of Cetyltrimethyl ammonium bromide (CTAB), Cetyltrimethyl benzyl ammonium chloride (CDBAC), Cetyl pyridinium bromide (CPB), Cetyl pyridinium chloride (CPC) (Fluka, A.G, West Germany) were prepared by dissolving suitable amounts of salts in 20 percent ethanol and the final volume was made up with distilled water.

Previously analysed samples were obtained from Indian Bureau of Mines, Nagpur.

Addition of cationic surfactants to the Triphenyl dyes, in the alkaline range, results in change of wave length of maximum absorbance towards acidic range by a few units, which may be due to the early dissociation of various groups present in these dyes.

Since the application of xylenol orange in the complexometric titration has been studied in detail the effect of surfactants on the dissociation constants of the dye in the presence of different surfactants are discussed in detail. Table.2 gives the dissociation constants of XO in presence of different surfactants.

It can be seen from Table.2 that the quaternary ammonium salts affect the acidity of hydroxyl group and carboxyl group strongly decreasing Pk_2 , Pk_3 , Pk_4 values. In presence of surfactant the solution XO in alkaline range is decolourized, but on addition of different cations, coloured, complexes are formed which would have not been possible in absence of surfactant as shown in Table 3

RESULTS AND DISCUSSION

The dissociation constants of these dyes have been determined by method of Albert and Serjeant [3] (3) in presence of cationic surfactants and compared with the values obtained for these dyes in absence of surfactants. (Table 1). Some of cations form complexes in acidic as well as in alkaline medium while some of them form complexes only in alkaline or in acidic medium. The range of concentration optimum pH and colour change at end point for different metal ion complexes with XO under study are given in Table 4.

Table 1: Dissociation constants of Triphenyl methane dyes in presence of CTAB

System	Pk ₂	Pk ₃	Pk ₄	Pk ₅	Pk ₆
CAS	2.48	2.23	11.46	-	-
CAS+CTAB	0.88	4.91	12.70	-	-
PCV	6.98	8.97	11.78	-	-
PCV+CTAB	4.5	8.20	12.08	-	-
BPGR	3.75	9.10	10.20	-	-
BPGR+CTAB	2.95	7.30	9.15	-	-
XO	2.29	3.90	6.78	10.23	12.86
XO+CTAB	0.98	1.25	4.5	9.8	12.25
MTB	1.87	3.42	7.25	10.72	12.60
MTB+CTAB	1.12	3.44	5.17	8.81	10.48

Table 2: Dissociation constants of Xylenol Orange in presence of Surl

System	Pk ₁	Pk ₂	Pk ₃	Pk ₄	Pk ₅	Pk ₆
XO	-	2.29	3.9	6.78	10.23	12.86
XO+CPC	-	0.92	1.37	4.9	9.7	12.37
XO+CPB	-	0.89	1.49	5.2	9.65	12.34
XO+CTPB	-	0.98	1.25	4.5	9.8	12.25
XO+CDBAC	-	0.96	1.48	5.3	9.57	12.46

Table 3: Colours of different complexes (in presence of surfactants)

System	Acidic range 4-6	Alkaline range without surfactant	Alkaline pH with surfactant
XO	Yellow	Purple Red	Grayish Pink
XO+Zn	Red	Purple Red	Red
XO+Mn	Red	Purple Red	Violet
XO+Ca	Yellow	Purple Red	Blue Violet
XO+Mg	Yellow	Purple Red	Red
XO+CrI	Red	Purple Red	Blue Violet
XO+Th	Red (2-3)	Purple Red	Grayish Pink
XO+La	Red	Purple Red	Grayish Pink
XO+Pb	Red (2-3)	Purple Red	Grayish Pink

Table 4: Range of concentration of metal ions, optimum pH and colour change at end point complexometric titrations

Metal	Acidic			Alkaline		
	Optimum pH range	Colour change	Concentration range	Optimum pH range	Colour change	Concentration range
Zn (II)	6-7	Red to yellow	68.75 mg to 4.70 mg	10-11	Red to colourless	80.20 mg to 1.04 mg
Cd (II)	5.75-6.5	Red to yellow	81.48 mg to 6.80 mg	10-11	Violet to colourless	94.90 mg to 1.36 mg
Mn (II)	5.5-6.5	Red to yellow	77.69 mg to 5.50 mg	10-11	Violet to colourless	87.88 mg to 2.74 mg
Ca (II)		-	-	10-11	-	82.56 mg to 1.26 mg
Mg (II)		-	-	10-11	Red to colourless	97.28 mg to 1.22 mg

Table 5: Analysis of Dolomite samples

Sample No.	SiO ₂ %	CaO %	MgO %	Fe ₂ O ₃ %	Al ₂ O ₃ %	OI %
3042	19.38	26.10	14.95	0.98	0.90	36.90
3043	14.95	27.30	16.23	0.66	0.91	39.35
3044	16.30	27.25	15.86	0.97	0.91	38.22
3045	10.75	28.40	17.55	0.65	0.75	41.23

From Table 4 it is observed that the range of concentration within which cadmium, zinc and manganese can be determined complexometrically is much wider in the alkaline range as compared to the acidic range and thus determination in the alkaline range has additional advantage. Taking advantage at these results, attempts are made for the determination of calcium and magnesium in Dolomite samples.

Four pre-analyzed Dolomite samples have been obtained from Indian Bureau of Mines Laboratory, Nagpur and their analysis is shown in Table 5.

Determination of calcium and magnesium in dolomite samples using XO as indicator

1 gm each Dolomite sample was dissolved in concentrated HCl and dry dehydrated. After baking for half an hour the mass was extracted in dilute HCl boiled and filtered for silica. After ignition of the residue and hydrofluorisation the remaining mass was fused with potassium pyrosulphate and extracted in the mother liquor. This solution was treated with NH₄Cl/NH₄OH for separation of R203 group. Thus the filtrate and washings were collected in 250ml volumetric flask and the volume was made up to the mark with distilled water [4-6].

Table 6: Analysis of Calcium and Magnesium in Dolomite Samples using XO as indicator

Sample No.	CaO % Known value	Calculated value	MgO% Known value	Calculated value
3042	26.10	26.50	14.95	15.25
3043	27.30	26.82	16.23	15.9
3044	27.25	26.2	15.86	15.66
3045	28.40	28.2	17.55	17.30

pH = 3, 5				pH = 3.5		pH = 5.5		
Mount of Thorium taken (rag)	Amount of Thorium found (mg)	%Relative error	Amount of UO ₂ taken (mg)	Amount of CO ₂ found (mg)	%Relative error	Amount of dysprosium taken (mg)	Amount of dysprosium found (mg)	%Relative error
17.405	17.474	0.398	13.234	13.234	0,001	16.251	16.225	0.157
17.405	17.474	0.398	13.234	13.234	0.001	40.628	40.519	0.267
8.702	8.672	0.352	26.468	26.603	0,506	40,628	40.519	0.257
8,702	8.672	0,352	26.468	26.603	0.506	16.251	16.261	0.062
43.511	43.395	0.478	13.234	13.215	0,144	8.125	8.125	0.000
5.221	5.221	0.000	7.940	7.922	0.228	4,873	4.873	0.000
3.409	3.408	0.035	5.294	0,306	0.236	3.250	3,245	0.170
3.409	3.408	0.035	5.294	5.306	0.236	40.628	40.610	0.170

From these solutions, requisite aliquot was taken in a conical flask, pH was adjusted to 10.5 by the addition of $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ buffer. 2ml of CTAB 20% solution was added and the volume was made up to 50ml by addition of distilled water. After adding a pinch of XO indicator the solutions were titrated against 0.01 M EDTA till the end point which was observed by the colour change from blue violet to colourless. The volume of EDTA used gives the value of calcium and magnesium both (VI).

Some aliquot was taken in another conical flask and 15ml of 20% KOH was added to bring the pH 12.0 and a few drops of Patton's and Reeder indicator was added. The volume was made up to 50ml. The solution was then titrated against 0.01 M EDTA till the colour change from wine red to blue was observed at the end point. The volume of EDTA used is for calcium alone (V2).

$V_1 - V_2 =$ Volume of EDTA required for magnesium present. Calcium and magnesium are determined using the following relation:

1 ml of 0.01 M EDTA = 0.4008mg. Ca (II)

1 ml of 0.01 M EDTA = 0.2432mg. of Mg (II)

From the amount of calcium and magnesium obtained the percentages calcium as calcium oxide and percentage of magnesium oxide is determined. The results are given in Table 6.

Thus it is seen that this method can be usefully adopted using XO as indicator in presence of surfactants, for the determination of calcium and magnesium. This method has additional advantage that the end point which is from blue violet to colourless is sharper than the end point which is observed while using Eriochrome Black T i.e. wine red to blue[7-9]. Similar studies are being carried out in these laboratories for the determination of other metals in different ores and minerals.

Conflicts of interest: The authors stated that no conflicts of interest.

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