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STUDY OF EFFECT OF VARIOUS PARAMETERS OF METHYL THYMOL BLUE-SURFACTANT SYSTEM AND ITS USE IN SIMULTANEOUS DETERMINATION OF THORIUM, URANIUM AND DYSPROSIUM

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Abstract:
Triprlenyl methane dyes are most commonly used in analytical techniques. The addition of surfactants to these also make them useful. Addition of cationic surfactants like Cetyl Pyridinium Chloride (CPC), Cetyl Pyridinium Bromide (CPB) , Cetyl Dimethyl Benzyl Ammonium Chloride (CDBAC), Cetyl Trimethyl Ammonium Bromide (CTAB) in alkaline range results in change in wavelength of maximum absorbance towards acidic range by few units which causes early dissociation of various groups. In this paper the various parameters to study one of Triphenyl methace dye – methyl thymol blue and cationic surfactants and use of these system in simultaneous determination of Thorium, Uranium and Dysprosium is reported.

Introduction :

Triphenyl methane dyes are commonly used in analytical techniques like spectrophotometric and complex metric determination of metal ions in solution. The addition of these surfactants changes their properties and permits their extensive use in alkaline range. This enables the simultaneous determination of more than one metal ion in the mixture.

Experimental :

Standard solution of Methyl Thymol Blue (MTB) BDH, England was prepared by dissolving suitable amount of reagent in 40% ethanol and making up the volume by distilled water. Solutions of Cetyl trimethyl ammonium bromide (CTAB), Cetyl pyridinium bromide (CPB), Cetyl pyridunium chloride (CPC) , (Fluka A.G West Germany), were prepared by dissolving suitable amounts of salts in 20% ethanol solution and final volume was made up with distilled water.

A stock solution of (0.01 M) of disodium salt of EDTA (BDH, AR Grade) was prepared by dissolving calculated amount of salt, in double distilled water and it was standardized with a standard solution of Magnesium sulphate using Eriochrome Black T (EBT) as indicator. The stock solution was diluted as and when required.

Solution of Dysprosium chloride was prepared by dissolving it's corresponding oxide (Johnson Mathey & Co.) in concentrated hydrochloric acid & evaporating off excess of acid. The residue was dissolved in double distilled water & standardized by visual method of titration against standard EDTA solution using BPGR as indicator. Solutions of desired concentrations were obtained by suitable dilution.

Solution of uranium nitrate was prepared by dissolving it in double distilled water and then standardized by visual method of EDTA titration. 0.001 M. solution of Cetyl Trimethyl Ammonium Bromide (CTAB) (Fluka, A. G., West Germany) was prepared by dissolving required quantity of CTAB in 20% ethanol.

Absorption Spectra of MTB With and Without CTAB, CPB, CPC, CDBAC

The λmax of MTB was found to be different at different pH values. The absorption spectra of MTB was, therefore, studied from 380 nm to 650 nm at various pH values, Similar studies were repeated in presence of CTAB, CPB, CPC, CDBAC. The range of pH for the various ionic species of MTB with and without different surfactants are shown in Table-1

An observation of this study shows that the wavelength of maximum absorption of chelating agent changes due to various ionization forms of the dye under different pH conditions. After addition of surfactants CTAB, CPB CPC and CDBAC to deeply coloured solution of MTB, the colour of the dye is altered. This change takes place with the decrease in the colour intensity at the λmax of the dye along with the change in the absorption maximum corresponding to a shift of about 1 to 2 pH units towards acidic range. The effect observed in alkaline medium is much more pronounced than in acidic medium, where the decrease in absorbance values are observed at particular pH. This clearly indicates that there must be an early dissociation of various groups of MTB in presence of micelle forming cationic surfactants.

Composition of MTB and Surfactants :

The effect of varying surfactant concentration on the absorbance spectra of MTB was studies at pH 5.5. The ƛmax of MTB in presence of different surfactants under study, are summarized in 2.

For the determination of MTB-surfactant composition, mole-ratio method was adopted. A series of solution were prepared at pH 5.5 containing the constant amount of MTB (3x10-4 M) and varying amount of surfactants. The absorbance was measured at the ƛmax of respective system and graphs were plotted between absorbance and surfactant concentration. It is observed that with the increasing concentration of surfactants there is decrease in the absorbance till the MTB surfactant ratio reaches to 1:2 and then remains constant even after addition of tenfold excess of surfactant.

Determination of Dissociation Constant of MTB with and without CTAB, CPC, CPB, CDBAC

In a systematic study of dye-surfactant, the first aspect is the study of its absorption spectra of MTB alone and in presence of CTAB, CPC, CPB and CDBAC.

All experiments were carried out at room temperature (30^{0}C). The pH was adjusted by the addition of hydrochloric acid or sodium hydroxide solutions of suitable concentrations. For the absorbance measurements in all the experiments, the surfactant solution was added to dye solution, which was then kept for atleast half an hour for attaining the equilibrium. Total volume of the system was kept 100 ml.

Different mixtures were prepared and their pH values were adjusted from pH 1.0 to 12.0 with a difference of 0.5 pH units. The absorption spectra was then taken over the entire visible region i.e. from 380 nm to 680 nm at a regular interval to 10 nm.

The final concentration of MTB and surfactant used was 3.0 x 10^{-5} M and the ration of the concentration of dye surfactant was kept as 1:1.

pK values are calculated with and without surfactant by Albert Serjeant's mothod . The values are given in table-3

It is seen that the addition of cationic surfactants such as CTAB, CPB, CPC and CDBAC decreases the values of pK_2, pK_4, pK_5, and pK_6.

Complexometric Determination of Thorium, Uranium and Rare-Earths , Methal Thymol Blue and Dysprosium

Pilot Titrations :

In order to determine the approximate volume of EDTA required for complexing of fixed amount of metal ion in the solutions pilot titrations were carried out. An aliquot of metal solution was pipette out into a titration flask, 1-2 ml of CTAB was added, pH was adjusted and a pinch of solid indicator was added and then titrated against EDTA solution till the colour change is observed .. Effect of pH, effect of solvent, effect of temperature on the titrate values ware studied for indicators as tabulated in Table- 4

It is observed from Table-VI.4 that optimum concentration limits of Th (IV), U (VI), and Dy (III) which can be titrated within 0.5% error are as follows :

Thorium-	1.3923 to 43.5112 mg
Uranium-	0.132 to 50.257 mg
Dysprosium-	0.8125 mg to 40.6275 mg.

Metal ion concentrations were maintained within these limits during further investigations.

The results on the effect of concentration on the determination of thorium, uranium and dysprosium using Methyl Thymol Blue as the indicator are described in Table-5. It may be mentioned here that complexometric determination of hexavalent or tetravalent uranium is not possible with Methyl Thymol Blue as indicator, but by use of surface active agents this is possible hence CTAB has been used for the complexometric determination of uranium.

It is observed from Table-VI.5, that optimum concentration limits of Th (IV), U (VI) and Dy (III) which can be titrated within 0.5% error are as follows :

Thorium -	0.8702 mg to 43.5112 mg
Uranium-	0.5294 mg to 79.396 mg
Dysprosium-	0.4875 mg to 48.763 mg

Metal ion concentrations were maintained within those limits during further investigations.

Results

Simultaneous Determination of Thorium, Dysprosium and Thorium-Uranium in a Mixture Using Methyl thymol Blue as the Indicator

The pH range for complexometric determination of thorium, using MTB as the indicaor is 2.0 – 2.5 and that of dysprosium 5.5 to 6.5. Hexavalent uranium does not form a complex with Methyl Thymol Blue between pH 5.5 and 6.5, but on addition of 2 ml of 0.01 M CTAB, forms a greenish blue complex with uranium, Advantage is taken of this property in the simultaneous determination of thorium uranium and thorium-dysprosium mixtures.

In the solutions containing thorium and uranium pH is adjusted between 2.0 to 2.5, a pinch of solid indicator (MTB + KCL misture) is added and the solution is titrated against 0.01 M EDTA till the end point which is indicated by the change in colour from blue to yellow. The volume of EDTA corresponds to the amount of thorium present. The pH of the solution is increased by using sodium acetate buffer and 2 ml of 0.01 M CTAB is added, a greenish blue colour appears. It is titrated against 0.01 M EDTA till the greenish blue colour changes to pink. The volume of EDTA thus required corresponds to the amount of uranium present.

In another set of experiment containing thorium and dysprosium, thorium is determined as described above and pH is adjusted between 5.5 – 6.5 and titrated against EDTA till the colour change from blue to yellow is observed.

The volume of EDTA corresponds to the amount of dysprosium present.

Experiments were carried out by varying concentrations of thorium, uranium and thorium-dysprosium. Results are shown in tables – 6 and 7

Table 1 Variation of λmax with pH

	pH	λmax (nm)
MTB	0.41-1.85 2.25-8.55 8.85-10.35 Above 10.35	440 420 600
MTB + CTAB	0.45-1.57 2.20-10.30 Above 10.30	420 430, 440 640
MTB + CPB	0.87-9.60 Above 9.60	430, 440 640
MTB + CPC	0.78-9.38 Above 9.60	430, 440 640
MTB + CDBAC	0.41-1.85 2.225-10.85 Above 10.85	40 430, 440 640

Table – 2 Wavelengths of maximum absorbance of MTB surfactant

System	pH	λmax (nm)
MTB-CTAB	5.5	420
MTB-CPB	5.5	430
MTB-CPC	5.5	430
MTB-CDBAC	5.5	440

Table 3 Dissociation constants of MTB with and without surfactants

System	pK_2	pK_3	pK_4	pK_5	pK_6
MTB	1.87	3.42	7.25	10.72	12.6
MTB + CTAB	1.12	3.44	5.17	8.81	10.48
MTB + CPC	1.08	3.49	5.20	8.79	10.54
MTB + CPB	1.19	3.47	5.20	8.84	10.57
MTB + CDBAC	1.17	3.5	5.25	8.77	10.44

Table – 4 Determination of Dysprosium, Thorium and Uranium using MTB as indicator

	Thorium	Uranium	Dysprosium
Colour change at end point	Blue to Yellow	Greenish blue to pink	Blue to Yellow
Optimum pH range	2.0 to 2.5	5.5 to 6.5	5.5 to 6.5
Effect of solvent	Nil	Nil	Nil
Effect of temperature	20-90^0 C	20-90^0 C	20-90^0 C
pH of study	2.0 adjusted by HCL	6.0 (sodium acetate buffer)	6.0 (sodium acetate buffer)

Table – 5 Range of concentrations for the complexometric determination using MTB as indicator

Amount of Thorium (VI) taken (mg)	Amount of Thorium (IV) found (mg)	% Relative error	Amount of U (VI) taken (mg)	Amount of U (VI) found (mg)	% Relative error	Amount of Dy (III) taken (mg)	Amount of Dy (III) found (mg)	% Relative error
87.023	79.262	8.080	79.404	79.396	0.010	48.753	48.763	0.020
43.511	43.445	0.260	66.170	66.980	0.288	40.628	40.627	0.002
17.405	17.340	0.392	50.257	50.167	0.199	16.251	16.251	0.000
8.702	8.700	0.013	26.468	26.468	0.000	6.500	6.501	0.0123
6.961	6.950	0.088	13.234	13.234	0.000	4.875	4.874	0.021
5.221	5.210	0.040	7.940	7.922	0.228	3.250	3.233	0.502
3.409	3.406	0.023	1.323	1.320	0.043	1.625	1.620	0.345
1.741	1.730	0.035	0.529	0.529	0.000	0.813	0.812	0.037
1.392	1.382	0.008	0.132	0.112	17.914	0.488	0.487	0.021
0.870	0.920	0.425	0.212	0.216	19.90	0.163	0.159	0.030

Table – 6 Simultaneous determination of Thorium-Uranium using MTB as indicator

Amount of Th (IV) taken (mg)	Amount of Th (IV) found (mg)	% Relative error	Amount of uranium UO_2^{2+} taken (mg)	Amount of UO_2^{2+} found (mg)	% Relative error
43.511	43.395	0.478	26.468	26.470	0.008
17.405	17.474	0.398	13.234	13.233	0.076
8.702	8.672	0.352	10.587	10.578	0.086
5.221	5.221	0.000	5.294	5.302	0.234
3.409	3.408	0.035	1.323	1.323	0.030

Table – 7 Simultaneous determination of Thorium-Dysprosium using MTB as indicator

Amount of Th (IV) taken (mg)	Amount of Th (IV) found (mg)	% Relative error	Amount of Dy (III) taken (mg)	Amount of Dy (III) taken (mg)	% Relative error
43.571	43.394	0.476	40.628	40.519	0.267
17.405	17.474	0.398	16.251	16.225	0.157
8.702	8.672	0.352	8.125	8.125	0.000
5.221	5.221	0.000	4.873	4.873	0.000
3.409	3.408	0.035	3.250	3.245	0.170

Conclusion

Thus it is possible to determine Dysprosium , Thorium &Uranium in a mixture the present work is of importance for the determination of metal ions in a mixture without adopting tedious separation techniques with are necessary in the determination of metals when present in solution. Determination of metal ions when present in such a mixture such as ores & minerals. where tried and results were compared with the results of method used in laboratory on Indian Bureau of Mines

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