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Sensitization of Methyl Thymol Blue by Cetyldimethylethylammonium Bromide for The Spectrophotometric Determination of Lead

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Abstract

Cetyldimethylethylammonium bromide(CDMEAB), a cationic surfactant has been used to decolorized Methyl thymol blue(MTB), an anionic triphenyl methane dye. Addition of *Pb* to this decolorized solution resulted into intense colored stable ternary complex. The shift in the λmax with increased in the values of molar absorptivity and sensitivity have been observed in case of ternary complex(Pb-MTB-CDMEAB) i.e. 5600 L $mole^{-1}cm^{-2}$ as compared to binary complex(Pb-MTB) i. e. 3000 L $mole^{-1} cm^{-2}$. The analytical applications like Beer's law range and effective photometric range have been studied at pH 7.0 and at 600nm in absence and at 640nm in presence of CDMEAB.

Keywords: Methyl thymol blue(MTB), Cetyldimethylethylammonium bromide (CDMEAB), Spectrophotometric determintion, binary complexes, ternary complexes.

1. Introduction

Water, soil and food products are contaminated by different sources, like mining steel industry, crop enhancers automobiles etc. These heavy metals show toxic effect on different human organs. The literature on lead toxicity is far too vast to review in this paper. Instead, this section summarizes the international scientific consensus, based on comprehensive evaluations of the literature conducted by international organizations and national governments. Lead paint is a primary source of lead exposure and the major source of lead toxicity in children. The U.S. Department of Housing and Urban Development currently estimates that 38 million homes in the United States contain lead paint. Of those, 24 million are considered to contain significant lead-based paint hazards, including deteriorating paint and/or contaminated dust or soil outside the home. As lead paint deteriorates and airborne lead settles, it contaminates dust and soil. Exposure to soil that contains particulate lead has been shown to be significantly hazardous for children, who are more commonly exposed by ingestion of house dust or soil than by paint chips. Blood lead levels are more closely related to indoor dust exposure than to outdoor soil exposure. Lead exposure can also occur during remodeling of a home built prior to 1978, when lead-based paints were still in commerce. Many workers carried out the determination of lead in many samples.

The analytical and complex ion chemistry of Lead have not kept place with growing interest

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because the heavy metal ions have less tendency to form complexes with normally strong coordinating agents. This may be due to their large size of its cation. With the development of cheletometry in this context very few reagents have been introduced for the determination of Lead.

Spectrophotometric determination of Pb(II), Bi(III) and Fe(III) in complexes with 1,2-diamminocyclohexane-N,N,Ni,Ni-tetraacetic acid has been carried out by Jan Krzek at al[1]. B. Jankiewicz carried out the determination of lead in soil sample[2]. A detail spectrophotometric determination of lead with *o*–hydroxyl-thiobenzmorpholide has been carried out by I. Badea atal[3]. Spectrophotometric determination of lead with 1-(2-pyridylazo)-2-naphthol and non-ionic surfactants has been carried out by Escriche JM at al[4]. A detail Spectrophotometric determination of lead in foods with dibromo-*p*-methyl-bromosulfonazo has been carried out by Escriche. The synthesis and purification of a new chromogenic reagent dibromo-*p*-methyl-bromosulfonazo (DBMBSA) has been synthesized by Guozhen Fang for the spectrophotometric determination of lead in food stuff[5]. A sensitive spectrophotometric method for the determination of lead in aqueous solutions has been developed and applied for a range of concentration of 0–60µg/ml of lead using the complex Lead (II) Using 3-Methyl-1, 2-Cyclopentanodione Dithiosemicarbazone,[6]

Thus it becomes important to sensitize these reagents by some process. The present work primarily been undertaken to explore the utility of cationic surfactant such as cetyldimethylethylammonium bromide(CDMEAB) in the sensitization of Methyl thymol blue for the determination of lead. In this context new and sensitive method is proposed which will helpful to determine percentage toxicity of lead in micrograms. The proposed method will be applicable to control water, air pollution causes because of these toxic metals in future.

2. Experimental part

All the spectral measurements have been taken on chemline model CL 133 microcontroller based spectrophotometer with glass cuvettes of light paths 10mm. distilled water has been used as a reference solution. Chemline model CL 180 pH meter with combine electrode is used for the adjustment of pH. The scale has been standardizing every day before making the pH measurement with buffer solutions of pH 4.0, 7.0 & 9.2. The pH of the each solution has been adjusted with HCl and NaOH solution of suitable concentration.

Reagent solutions:-

The Methyl thymol blue and cetyldimethylethylammonium bromide were used in this work was of analytical grade and supplied by Sigma chemical company, USA. The solution of the reagent has been prepared by using distilled water and ethanol. The stock solution of reagents has been prepared in the concetration1.0×10^{-3}M. lead nitrate has been used in this work was supplied by E. Merck. The HCl and NaOH used was supplied by SD fine chemical laboratories.

3. Result and discussion

It has been considered necessary to have prior information on the nature of interaction between MTB and CDMEAB before evaluating the MTB as sensitive reagent for the estimation of Lead in the presence of CDMEAB. Therefore, absorption spectra of MTB in absence and presence of CDMEAB, composition of dye-surfactant complex, absorption spectra of lead in absence and presence of CDMEAB, effect of pH, composition of the chelates in absence and presence of CDMEAB, have been studied.

Absorption spectra of MTB in the absence and presence of CDMEAB[7].

The color of MTB has been found to be different at different pH values. The addition of CDMEAB brings about a slight change in color of MTB at the same pH value. The absorption spectra of MTB, has been therefore, studied at different pH values (3.0 to 10.0) in the absence and presence of

CDMEAB. The wavelength of maximum absorbance of MTB in the absence and presence of CDMEAB are summarized in table 1.Absorption spectra of alkaline MTB solution at pH 7.0 show a characteristics maximum at 580nm in presence of CDMEAB with the increase in the absorbance value. This may be due to the formation of dye-detergent complex.

Table 1 : Wavelengths of maximum absorbance of MTB in the presence and absence of CDMEAB.

MTB		MTB +CDEAB	
pH	λ_{max} (nm)	pH	λ_{max} (nm)
3.0	440	3.0	440
4.0	440	4.0	440
5.0	440	5.0	440
6.0	440	6.0	440
7.0	580	7.0	440
8.0	580	8.0	440
9.0	580	9.0	480
10.0	580	10.0	480

Composition of MTB-CDMEAB Complex.

The effect of varying CDMEAB concentration on the absorbance of MTB has been studied in basic medium at pH 8.0, at λ_{max}, 440nm where the maximum discoloration takes place. The absorbance of different concentrations of MTB is plotted against the variable concentration CDMEAB. It has been observed that the two times higher concentration of CDMEAB required for complete decolorization of MTB. Thus, the ratio of MTB: CDMEAB will be 1:2 The modified reagent species thus formed, may therefore, be written as [MTB (CDMEAB) $_2$].

Absorption Spectra of Lead Chelates in Presence and Absence of CDMEAB[8].

A series of solutions were prepared keeping the ratio of Pb^{2+}: MTB: CDMEAB as 1:1:5 and 4:1:5. A number of sets were prepared for each ratio and pH was adjusted to 3.0 to 10.0 The absorption Spectra were recorded in the entire visible region from 400nm to 700nm. Absorbance maxima of MTB and its complexes with Lead in the absence and presence of CDMEAB have been summarized at different pH values in table 2.

Table 2: Absorbance Maxima (nm) of MTB and its Chelates in the Absence and presence of CDMEAB at different pH.

SYSTEM	4.0	5.0	6.0	7.0	8.0	9.0	10.0
MTB	440	440	440	580	580	580	580
MTB +CDMEAB	440	440	440	440	440	480	480
MTB +Pb^{2+}	480	480	600	600	600	--	--
MTB +CDMEAB+Pb^{2+}	520	640	640	640	640	640	--

The absorption spectra of MTB shows peak at 520nm in the presence of CDMEAB in the pH range 3.0 to 4.0 but shows peak at 600nm in absence and at 640nm in presence in the pH range 6.0 to 8.0. In the pH range 3.0 to 4.0, in absence and presence of CDMEAB, the wavelength maxima of MTB shows small change in λ_{max} and absorbance values;

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indicating poor complexation. But, change in λ_{max} and increase in the absorbance value in pH range 6.0 to 8.0 show complex formation in absence and presence of CDMEAB. By comparing the absorption spectra and the absorbance values of the reagent and complex in presence of CDMEAB, it has been observed that the maximum complexation takes place at pH 7.0. Thus bath chromic shift of 20 nm in absence and 200nm in the presence of CDMEAB have been observed for Lead.

Effect of pH

Effect of pH on λ_{max} and on the absorbance, of the Lead complexes of PCV in the absence and presence of tenfold excess of CDMEAB have been studied. It is found that the $\lambda_{max\ of}$ the complexes remain constant in the pH range 6.0 to8.0 in absence and 5.0 to 9.0 in presence indicating pH range of stability of complex formation.

Composition of Chelates

The composition of the chelates has been studied by the Mole ratio method. solutions of Lead and MTB have been taken in two equimolar concentrations of $2.0x10^{-5}$ M and, $4.0x10^{-5}$ M; Five times excess of CDMEAB has been then added for studying the composition in the presence of surfactant.

The stoichiometric composition between the Pb^{2+} and MTB in the presence and absence of CDMEAB has been found to be 1:2. It has been observed that MTB reagent at pH 8.0 exists as [MTB $(CDMEAB)_2$] and therefore, the composition of complexes in the presence of CDMEAB may be written as $Pb^{2+}[MTB(CDMEAB)_2]_2$ for lead.

Pb^{2+} + 2 [MTB $(C\ D\ E\ A\ B)_2$] $Pb^{2+}[MTB(CDMEAB)_2]_2$

Analytical applications of lead chelates with PCV in absence and in presence of CDMEAB Order of Addition of Reactants

The sequence of addition of reactants must be followed strictly. In all the experiments, CDMEAB was first added to MTB solution. This solution was kept for at least 30 minutes for equilibration. To this solution of modified MTB, Pb^{2+} solution was then added which again kept for 30 minutes for complete formation of the ternary complex.

Rate of Color Formation and Stability of Color at Room Temperature.

The color formation does not depend on reaction time and is almost instantaneous. However, the mixtures were kept for 30 minutes for equilibration. The temperature was found to have no effect on color intensity of ternary complexes from 20^0 C to 60^0 C.

Beer's Law and Effective Photometric Ranges

The linearity between the absorbance of the chelates and concentration of metal ion has been tested by taking the different volumes of metal ion solution (1.0×10^{-3} M in absence in presence of CDMEAB). The final concentration of MTB taken was 2.0×10^{-5} M, of CDMEAB was 1.0×10^{-4} M. Total volume was kept constant at 25ml at pH 8.0. The absorbance values were measured in the absence of CDMEAB at 580 nm. However, in the presence of CDMEAB, all the spectral measurement was made at 600 nm. The range of Beer's law is given in table 4 in absence and presence of CDMEAB. The effective range for photometric determination was also calculated from this data by Ringbom[9-10] plot of log of metal ion concentration versus percentage transmittance. Thus, the range as derived by the slope of the curve is selected to be range for the effective photometric determination as given in table 4.

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Table 4: Photometric Determination of rare earths with MTB in the Absence and Presence of CDMEAB.

MTB Chelates	pH of study	Wavelength of study, (nm)	Beer's law Range (ppm)	Effective Photometric range (ppm)	Molar Absorptivity	Sensitivity ($\mu g/cm^2$)
MTB+Pb^{2+}	7.0	600	0.064-0.096	0.252 – 0.448	3000	1.7
MTB+CDMEAB+ Pb^{2+}	7.0	640	0.064-0.096	0.252 – 0.512	5600	0.718

4. Conclusion

The spectrophotometeric determination of lead with Methyl thymol blue in the presence and absence of Cetyldimethylethylammonium bromide has been studied. Following are the merits of modified method.

The sensitization of MTB by the addition of CDMEAB is clear from the fact that the formation of stable ternary complexes with Rare earths occurs at pH 7.0 with bath chromic shift in the λ_{max} of Pb-PCV complexes in the presence of cationic surfactant. This change λ_{max} and high absorbance value is attributed due to the formation of ternary complex system in the presence of CDMEAB compared to the binary system in the absence of CDMEAB. Due to the shifted λ_{max} towards higher wavelength (From 440 nm to 640 nm) a large difference in the absorbance between the reagents blank (MTB-CDMEAB) and its ternary complex results in enhancement of the sensitivities and molar absorptivities again indicate the great sensitivity of color reaction.

Further, the modified method requires smaller molar concentration of MTB over the metal ion concentration for full color development and is instantaneous in the presence of CDMEAB, again indicates the stability of the color reaction.

The modified reagent i.e. [MTB $(CDMEAB)_2$] has also been found to be extremely useful in the complexometric titration of the Lead. This modified reagent act as sensitive metallochrome indicator giving a very sharp color change at the end of complexometric titration. The increase in the sensitivity and absorptivity facilitate the determination of lead in the given photometric range.

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