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SOME ACTIVITIES OF TWO MICELLES ON A NEW SPECTROPHOTOMETRIC REAGENT.

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Abstract: This study attempts to synthesize a new reagent for spectrophotometric use with the view of joining the ongoing research efforts in the world on highly sensitive chromogen for the detection of harmful metal ion in solution. This reagent: Dioxallic Dithiophenyl Azomethine Hydrazine (DDAH) was synthesized following the reaction pathway of Carbonyl compounds especially aldehydes in general with primary base, to form condensation products of the type $RCH=NR^1$. The reaction was brought about by heating a mixture of 0.02mole of dioxallic dihydrazide (dissolved in ethanol) to 0.05 mole of 2-thiophene carboxaldehyde and the reacting mixture was refluxed for 7 hours. The solid product, separated on cooling, was filtered and re-crystallized from aqueous alcohol. The optimum reaction conditions of the reagent have been established with three (3) metals namely: chromium (VI), iron (II), iron (III), nickel (II), cobalt (II), zinc (II), mercury (II), cupper (II), vanadium (V), and lead (II). The impact of micelles on the spectrophotometric relevance of the reagent was carried by using both n-Hexadecyl Trimethyl Ammonium Bromide (HTAB) and Sodium Dodecyl Sulphate (SDS). The results emanating from the analytical parameters clearly show the variations in maximum absorbance and absorbance in all the 3-metals used for the study. The study thus concludes that there exists some spectrophotometric relevance in the new reagent.

Keywords: Spectophotometric Reagent, Micelle, Surfactant, Hydrazine, Carbony Compounds.

INTRODUCTION

Surfactants are of widespread importance in the detergents industry, emulsification, lubrication, catalysis, tertiary oil recovery and in drug delivery. Surfactants are water-soluble surface active agents comprising of a hydrophobic portion, usually a long alkyl chain, attached to hydrophilic or water soluble enhancing functional groups. Surfactants molecules aggregate in water forming micelles. Micelles consist of hydrophobic interior regions, where hydrophobic tails interact with one another. The discovery of hydrazine marked the genesis of further studies on hydrazide derivatives. The systematic studies of which formed the chief interests of his Curtis School at Heidelberg, at the turn of the 19^{th} century. Carbonyl compounds especially aldehydes in general react with primary base, to form condensation products of the type $RCH=NR^1$, known as Azomethines Schiff's bases. The reaction may be brought about by heating a mixture of the aldehyde and amine in equimolecular proportion alone or in a diluent such as ethanol or acetic acid. The reaction proceeds almost readily with aromatic aldehyde and aromatic amines, which yield as a rule, stable crystalline substances. Condensation may be effected between aliphatic aldehyde and aromatic amine under proper conditions, but the resulting azomethines are usually unstable. Current studies have confirmed the condensation between aromatic aldehyde and aromatic amine to be having high stable yield. As well as between aromatic aldehyde and aliphatic amine. (See equation below):

$$Ar^1CHO \quad + \quad Ar^2NH2 \longrightarrow \quad \overset{-H2O}{Ar^1CH\ (OH)\ NHAr^2} \quad \underset{-H2O}{\longrightarrow} \quad Ar^1CH=N$$

ArCHO + RNH2 ⟶ ArCH (OH) NHR ⟶ ArCH = NR .

Thus a convincing result to prove the validity of these new chromogens as highly sensitive chromegenic reagents for simultaneous determination of these metals were recorded by Shirakawa et al and Lee et al. However, all surfactants posse the common property of lowering the surface tension when added to water in small amounts. Due to the limited solubility of surfactants in water, micelle may be represented as a globular cylindrical or ellipsoidal cluster of individual surfactants molecules in equilibrium with its monomers .The reverse orientation of the hydrophilic and hydrophobic portion of the surfactant in a hydrocarbon medium leads to reversed micelle. In analytical chemistry, surfactants have been recognized as being very useful for improving analytical methodology, such as chromatography and luminescence spectroscopy.

MATERIALS

Instruments

(a), Melting point apparatus
(b), Jenway UV/VIS spectrophotometer model 6505
(c), Jenway UV/VIS spectrophotometer model 6305
(d), Perking Elmer I.R. spectrophotometer model 1330

Chemicals

All chemicals are analytical grade unless otherwise stated. The water used throughout was distilled and deionized. Hydrochloric Acid (36%), Ammonium Hydroxide (25%), Antibombing Granules, Nickel (II) Sulphate Hexahydrate, Zinc (II) Sulphate Dihydrate, Ammonium Iron (II) Sulphate Hexahydrate, Anhydrous Iron (III) Chloride, Copper (II) Sulphate Pentahydrate, Cobalt (II) Nitrate Hexahydrate, Ammonium Vandate (V), Potassium Dichromate, Lead (II) nitrate, Benzene, Diethyl Oxalate, Hydrazine Hydrate, Chloroform, Carbon Tetrachloride, Ethyl Acetone, Ethanol, Dimethylformamide (DMF), Acetonitrile . All reagents were purchased from Merck (India).

METHOD

Synthesis of Dioxallic Dihydrazide

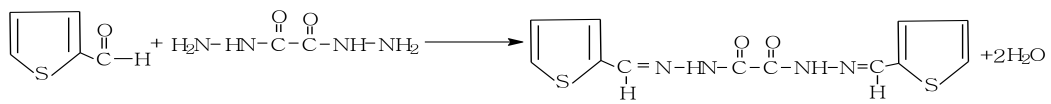
Dioxallic dihydrazide was synthesized by drop wise addition of 10 ml of hydrazine hydrate to 10 ml of diethyl oxalate in a conical flask. The reaction was an exothermic instantaneous one and resulting brightly white color product was washed with water several times, filtered and washed again several times with hot water.

$$2N_2H_4.H_2O + C_2H_5-O-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-O-C_2H_5 \longrightarrow H_2N-HN-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-NH-NH_2 + 2\,C_2H_5-OH$$

Dioxallic dihydrazide

Synthesis of the Reagent (DDAH)

Dioxallic Dithiophenyl Azomethine Hydrazide (DDAH) was synthesized by the addition of 0.02mole of dioxallic dihydrazide (dissolved in ethanol) to 0.05mole of 2-thiophene carboxaldehyde and the reacting mixture was refluxed for 7 hours.



DDAH

Preparation of Reagents for Further Studies

1.0 x10^{-3}M stock solution of each of Dioxallic Dithiophene Azomethine (DDAH), Pyridinyl Thiophenyl Azomethine (PTA), and Thiazoyl Thiophenyl Azomethine (TTA), were prepared by dissolving 0.306g, 0.188g, and 0.194 g respectively in 70% ethanol in 100m1 volumetric flask. The working solutions were prepared by serial dilution of the stock solution with water. 100ppm stock solution of each of Cr(VI), Co(II), Fe(III), Fe(II), Ni(II), Cu(II), Zn(II), V(V), Pb(II), and Hg(II) ions were prepared from the corresponding salts by dissolving the following weights in 250ml volumetric flasks : 0.1414 g of potassium dichromate , 0.1232g of cobalt (II) nitrate hexahydrate, 0.0725g of anhydrous iron (II) chloride , 0.1245g of iron (II) sulphate, 0.11g of nickel (II) sulphate hexahydrate, 0.0786g of copper (II) acetate, 0.0676g of zinc (II)acetate, 0.0574g ammonium monovanadat, 0.202g lead (II) nitrate and 0.068g of mercury (II) chloride, respectively. 1.0 x10^{-1}M stock solutions of (micelle) surfactants were equally prepared by dissolving 3.64g of n-hexadecyl trimethylammonium bromide in 100ml of water, and 2.88g of sodium dodecyl sulphate in 100ml of water, respectively. The working solutions were prepared by serial dilutions of the stock solution with water.

Determination of Nitrogen Content

The determination of nitrogen contents of all the synthesized compounds was carried out by Kjeldal method as follows: 0.2g of each sample was placed in Kjeldal Flask, and digested with 4.0ml concentrated sulphuric acid. 1.4g of potassium sulphate and 0.08g of manganese dioxide were added to the mixture. The mixture was then heated until all the organic matter was destroyed and solution became clear. The content was cooled and transferred quantitatively to a distillation apparatus, few anti-bombing granules were added. Excess sodium hydroxide was then added and the mixture was heated to boiling, the end of the condenser was dipped into a flask containing 100ml 0f 0.1M hydrochloric acid, the distillation was continued until all the ammonia gas evolution ceased as indicated by distillation of water. The excess acid was titrated against standard 0.1M sodium- hydroxide, using phenolphthalein as indicator. The results are shown in the Table 3.

Effect of Micelle (Surfactants)

(a) Hexadocyl Dimethlyl Ammonium Bromide (HTAB)

The effect of 1.0×10^{-3} M of the above named surfactant was studied on the maximum wavelength and absorbance, and the result compared with earlier studies using acid and base. Reagent concentration of 4×10^{-5} M and metal ion concentration of 5ppm were scanned. The results are shown in Table 4 below.

(b) Sodium Dodecyl Sulphate (SDS)

The influence of 1×10^{-3} M of the above named surfactant (SDS) was carried out on the metal ions complexation processes, and the results compared with earlier studies on Hexadocyl Trimethyl Ammonium Bromide (HTMAB), and earlier results without catalysis. The concentration of reagent used for the studies was 4×10^{-5} M and a metal ion concentration of 5ppm. The wavelength at maximum absorbance of each metal ion was scanned and results are shown in Table 4 below.

RESULTS

The Reagents

The Dioxallic dihydrazide was an exothermic instantaneous one and resulting in brightly white color product (95%), melting point 240 °C.

The Dioxallic dithiophenyl azomethine hydrazide (DDAH) was a solid product, 2.17g (85%), of yellowish crystals. melting point 287 °C.

Identification of samples

The infra – red spectra

The infra-red spectra of the compounds were recorded using IR-spectrophotometer. The spectra were measured at room temperature in KBr disk and the results are shown in Tables (1-4.)

Table 1: IR - Spectra of Dioxallic Dihydrazide

Group	Wave Number (cm^{-1})	
	Found	Literature
N – H	3275	3000- 3500
C = N	1542	1500 – 1600
C=O	1645	1600-1700

Table 2: IR - Spectra of Dioxallic Dithiophene Azomethine Hydrazine

Group	Wave Number (cm^{-1})	
	Found	Literature
C = N	1567	1500 – 1600
N – H	3328	3000 – 3500
C=O	1680	1600-1700

Table 3: Nitrogen Content of all the Reagents Synthesized

Reagents	Nitrogen Content (%)	
	Found	Calculated
Dioxallic Dihydrazide	18.30	16.42
Dioxallic thiophenyl/Azomethine	7.32	6.09

Table 4: Effect of micelle (HTMAB and SDS) on the absorbance of metal-DDAH complexes

	HTMB - CATALYSIS		SDS CATALYSIS		NO CATALYSIS	
Metal	λ_{max}	Absorbance	λ_{max}	Absorbance	λ_{max}	Absorbance
Hg(II)	260	1.717	385	0.017	385	0.039
Co(II)	215	0.921	-	-	390	0.028
Cu(II)	-	-	385	0.018	390	0.088
Zn(II)	210	0.140	365	0.006	385	0.026
Fe(II)	335	0.037	320	0.024	260	0.446
V(V)	210	0.387	-	-	210	1.483
Fe(III)	215	0.648	-	-	390	0.097
Cr(VI)	375	0.676	360	0.412	360	0.541
Pb(II)	210	0.352	380	0.035	395	0.024
Ni(II)	360	0.017	360	0.008	385	0.026

DISCUSSION:

The new reagent has shown a remarkable challenge for use as spectrophotometric reagent for the analytical determination of certain (cations) metals.

Dioxallic Dithiophenyl Azomethine Hydrazide (DDAH), has shown from all the available data in this work to be of extreme relevance for the determination of Vanadium (V), which showed an absorbance of 1.483 , Chromium (VI) , which showed on absorbance of 0.541 without the use of any micelle whatsoever, among others. N - Hexadecyl Trimethyl Ammonium Bromide (HTMAB) has a remarkable influence on DDAH reagent. The only 3-metal that did not show any increase in absorbance include Chromium (VI), Iron (II), and Nickel (II). Others like; Lead (II) showed an increase from 0.024 (λmax = 395) to 0.352 (λmax = 210). Zinc (II) showed an increase from 0.026 (λmax = 385) to 0.140 (λmax = 210). Cobalt (II) showed an increase from 0.028 (λmax = 390) to 0.921 (λmax = 215). Mercury (II) showed an increase from 0.039 (λmax = 385) to 1.717 (λmax = 260). Iron (III) showed an increase from 0.097 (λmax = 390) to 0.648 (λmax = 215). Finally, Vanadium showed an increase from 0.083 (λmax = 310) to 0.387 (λmax = 210). Sodium dodecyl sulphate SDS does not show any significant impact on DDAH reagent reactivity with all the metals under consideration, when compared to HTMAB. All absorbances recorded were very low. Chromium (VI) showed a decrease in absorbance from 0.541 (λmax =360) to 0.412 (λmax =360) . Also affected are the following: Zinc (II) from 0.026 (λmax = 385) to 0.006 (λmax =365), Cupper (II) from 0.088 (λmax =390) to 0.018 (λmax =385). While only Lead (II) showed a slight increase in absorbance from 0.024 (λmax = 395) to 0.035 (λmax = 385)

CONCLUSION

The influences of the micelle surfactant like Sodium Dodecyl Sulphate (SDS) and n - Hexadecyl Trimethyl Ammonium Bromide (HTAB) were studied on the complexation processes between the new reagent and 10 (metals) cations using double beam spectrophotometer. The sensitivity of reagent (DDAH) increased upon the additional HTAB as surfactant, while increasing the absorbance of earlier ones that were detected without surfactants were recorded. No metal complex shows any higher absorbance when SDS was used as surfactant. A detailed mechanism of these reactions will soon be undertaken.

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