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ELECTROCHEMICAL STUDIES ON *p*-DIMETHYLAMINOBENZYLIDINE RHODANINE AND ITS APPLICATION AS AMPEROMETRIC REAGENT

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ABSTRACT

Electrochemical studies on aromatic compounds have been subject of many investigations during last few years. The compounds, which contain sulphur, were successfully employed as amperometric reagent. Rhodanine and substituted rhodanines are also used in analytical chemistry as highly sensitive reagents for determination of ions. P-dimethylaminobenzylidene rhodanine has been used as a spectrophotometric reagent for determination of cations.

Key words: Electrochemical studies, Amperometry, Rhodanine, ρ-dimethylaminobenzylidene rhodanine.

INTRODUCTION

Rhodanine (4-thiazolidinone-2-thione) and substituted rhodanines are used in analytical chemistry[1-2] as highly sensitive reagents for determination of ions. Rhodanine is a form of thiazole heterocyclic compound, containing sulfur and nitrogen in a five member ring with carbonyl group on fourth carbon and has been considered as a wonder nucleus. The substitution is possible at 2, 3 and 5 position of thiazolidinone. ρ-dimethylaminobenzylidene rhodanine has been used as a spectrophotometric reagent for determination of ions[3-4]. Rhodanine is an inhibitor of mild steel in acidic solution[5], its ability to inhibit the corrosion is its coordination at the metallic surface. Applications of rhodanine and substituted rhodanine as spot test reagent is well known.

Electrochemical studies on aromatic compounds[6-17] have been subject of many investigations during last few years. The importance of electrochemical techniques in solving the theoretical and practical problems of organic chemistry is now well established. Most of the application of electrochemical methods with controlled potential has been in the area of quantitative and qualitative analysis. Electrochemical techniques such as Polarography, Cyclic Voltametry, Linear Sweep Voltametry, Coulometry and Amperometry. The amperometric titrations are sensitive and convenient analytical technique, based on the existence of a simple relationship between the concentration of an electro-active substance and its polarographic current. The principle of amperometric titration was proposed as early as 1897 by Soloman[1] and it was later used by Nerst and Merrian.[18] The first amperometric titration with indicator electrode *dme* was carried out by Heyrovaskey and Berezickey [19]. Theory of such titration was studies more exclusively by Kolthoff *et al*[20-22]. Later on various cations and anions have been estimated by this technique.[23-28]

There are other suitable electrochemical methods for end-point indication, but amperometric titrations possess greater sensitivity than others. The titration can be conducted by utilizing redox system present either before or after the end point. ρ-dimethylaminobenzylidene rhodanine is used as a reagent in the determination of cyanides and argentometric titration in high acidic solution. In present paper we report the synthesis, characterization of ρ-dimethylaminobenzylidene rhodanine and its application as an amperometric reagent for the determination of cations.

EXPERIMENTAL

Materials

All the chemicals and reagents were used as analytical grade reagent and commercially available. ρ-dimethylaminobenzylidene rhodanine has been prepared as reported in literature[29]. Melting points were taken in open capillary and were uncorrected. Infra red spectra were recorded as KBr pellets on Shimadzu PC FTIR, ^{1}H NMR spectra were recorded on a 400MHz FT NMR. Mass spectral analysis was carried out on Jeol SX-102 (FAB) system.

Physical measurements

Structure of the synthesized ρ-dimethylaminobenzylidene rhodanine has been characterized on the basis of their elemental analysis, IR, ^{1}H-NMR and Mass spectral studies. An overview of structure determination via various spectroscopic methods is as following:-

The presence of C=O stretching absorption band in the region 1740-1700 cm^{-1} the presence of double bond in the conjugation with C=O group lowers the frequency to 1680-1660 cm^{-1}, in ρ-dimethylaminobenzylidene rhodanine, it appear at 1678 cm^{-1}. When methylene group adjacent to carbonyl and sulphur groups; it exhibit characteristic peaks in the region 2970- 2960 cm^{-1} and 1465-1435cm^{-1} The double bond character and charge distribution of both C=O and –CN changes during vibration mixed bands of –OCN and –NH moiety appear in the region 1300-1200 cm^{-1} . –CH stretching vibration attached to nitrogen atom for N–N dimethyl substitutent appears at 1434 cm^{-1} in ρ-dimethylaminobenzylidene rhodanine.

The compounds exhibit usual; C=C aromatic ring stretching frequency around 1600,1500 and 1400cm^{-1} , in ρ-dimethylaminobenzylidene rhodanine presence of –CH stretching vibrations of aromatic types appear in the region 3100-3000 cm^{-1}, other out of plane bending vibrations in the region 900-675 cm^{-1} . The substitution pattern of ring appears in the region 600-420 cm^{-1}. a few characteristic peak at 1200-1050 cm^{-1} ,1100-1000 cm^{-1} and 700-600 cm^{-1} are due to the C=S/S-C=S/C-N and C-S-C/C-S vibrational mode respectively. When C-S conjugated with double bond a low frequency shift appear in the region 508 cm^{-1} in ρ-dimethylaminobenzylidene rhodanine.

^{1}HNMR spectrum of compound ρ-dimethylaminobenzylidene rhodanine exhibit a singlet at δ 2.5 assignable to two methyl group attached to nitrogen. The appearance of a singlet at δ 6.8 is attributed to vinyl proton. A singlet at δ 7.41 and δ 7.52 may be assigned due to aromatic ring. Signal for proton of –NH is visualized in the far deshielded offset scan at δ 13.55 shows that the C=O group attached with –NH moiety.

Mass spectral data are consistent with respect to molecular compounds where M^{+1} peak are observed due to ionization of the molecule, various signals observed, seems to follow the fragmentation process. The base peak at m/z=154 is due to the most stabilized factor of the molecule which is further justifies the presence of thiazole ring as a part of structure of the compound. Some other daughter ion peaks at m/z= 105, 120,136, 167, 177, 192, 209, 226, 242 and M^{+1} peak is observed at 264. Molecular weight further confirm by C, H, N analysis.

ρ-dimethylaminobenzylidene rhodanine as an amperometric reagent

Electrochemical behaviour of ρ-dimethylaminobenzylidene rhodanine has been investigated in B.R. Buffer – 30% v/v dimethylformamide at various pH; ranging from 4.0 to 11, exhibit reduction wave. The wave is irreversible and value of $E_{1/2}$ shift to more negative potential with increase in concentration of depolarizer.

Experimental sets of titled metal were containing known amount of metal ions i.e 0.2 mg to 2.5 mg approx. in B. R. Buffer at appropriate pH, 0.001% w/v solution of gelatin and 0.1M potassium chloride solution. The plateau potential of metal ion was applied viz. -0.50,-1.10,-1.3V and -1.3V vs SCE for Cu (II), Ni (II) for Fe (II) and Zn(II) respectively at pH 5.00 for Cu (II), 5.70 for Ni (II), 5.30 for Iron (II) and

5.05 for Zn (II). The titration was performed at the plateau potential of the cathodic wave of titled metals using ρ-dimethylaminobenzylidene rhodanine as titrant. Fresh solution of known amount of ρ-dimethylaminobenzylidene rhodanine was prepared in 30% v/v alcoholic dimethylformamide.

Table-1: Amperometric determination of Cu (II), Ni (II), Fe (II) and Zn (II) with ρ-dimethylaminobenzylidene rhodanine

Plateau Potential Cu (II) : 0.5V *vs* SCE, pH at room temp : Cu (II) 5.11 ± 0.1
Ni (II) : 1.1 V *vs* SCE Ni (II) 5.68 ± 0.1

S. No.	Amount of Cu (II) mg		Error (%)	Amount of Nickel (II) mg		Error (%)	Amount of Iron (II) mg		Error (%)	Amount of Copper (II) mg		Error (%)
	Taken	Found		Found	Taken		Taken	Found		Taken	Found	
1.	0.4130	0.4110	0.49	0.2641	0.2655	0.53	0.2235	0.2218	-0.76	0.327	0.3288	0.55
2.	0.5210	0.5235	-0.48	0.3521	0.3538	0.48	0.2792	0.2822	1.07	0.425	0.428	0.71
3.	0.6036	0.6011	0.42	0.4755	0.4749	-0.13	0.335	0.3358	0.24	0.4904	0.491	0.12
4.	0.9531	0.9505	0.27	0.6455	0.6448	-0.11	0.4465	0.4452	-0.29	0.7845	0.7834	0.14
5.	1.7156	1.7111	0.26	0.7042	0.7055	0.18	0.5584	0.558	-0.07	0.7846	0.7855	0.11
6.	2.2874	2.2833	0.18	0.8215	0.8228	0.16	0.6700	0.6711	0.16	0.9155	0.9164	0.10
7.	2.9228	2.9188	0.14	0.939	0.9412	0.23	0.782	0.7811	-0.12	1.0462	1.0475	0.12
Standard deviation:			± 0.98			± 0.25			± 0.21			± 0.98
Coefficient of variation :			1.0			1.0			1.0			1.0
S. No.	Amount of Cu (II) mg		Error (%)	Amount of Nickel (II) mg		Error (%)	Amount of Iron (II) mg		Error (%)	Amount of Copper (II) mg		Error (%)
	Taken	Found		Found	Taken		Taken	Found		Taken	Found	
8.	0.4130	0.4110	0.49	0.2641	0.2655	0.53	0.2235	0.2218	-0.76	0.327	0.3288	0.55
9.	0.5210	0.5235	-0.48	0.3521	0.3538	0.48	0.2792	0.2822	1.07	0.425	0.428	0.71
10.	0.6036	0.6011	0.42	0.4755	0.4749	-0.13	0.335	0.3358	0.24	0.4904	0.491	0.12
11.	0.9531	0.9505	0.27	0.6455	0.6448	-0.11	0.4465	0.4452	-0.29	0.7845	0.7834	0.14
12.	1.7156	1.7111	0.26	0.7042	0.7055	0.18	0.5584	0.558	-0.07	0.7846	0.7855	0.11
13.	2.2874	2.2833	0.18	0.8215	0.8228	0.16	0.6700	0.6711	0.16	0.9155	0.9164	0.10
14.	2.9228	2.9188	0.14	0.939	0.9412	0.23	0.782	0.7811	-0.12	1.0462	1.0475	0.12
Standard deviation:			± 0.98			± 0.25			± 0.21			± 0.98
Coefficient of variation :			1.0			1.0			1.0			1.0

Fe (II) : 1.3 V *vs* SCE Fe (II) 5.20 ± 0.1,
Zn (II) : 1.3 V *vs* SCE Zn (II) 5.00 ± 0.1
Maximum suppressor: 0.1M KCL ; Supporting electrolyte : B.R. Buffer

Amperometric titrations were performed in the usual way by adding titrant. Purified nitrogen gas was passed in the experimental set before addition of titrant from micro burette. The current was noted with multiflex galvanometer. On plotting [(V+v/v)] x i against volume of titrant, L- shaped curves were observed. Intersection of two straight lines located the position of the end point. The end point indicated metal to ligand ratio-

Copper	:	5-PDARH	1	:	2
Iron	:	5-PDARH	1	:	2
Nickel	:	5-PDARH	1	:	2
Zinc	:	5-PDARH	1	:	2

The results of amperometric determination shown in Table-1.

RESULTS AND DISCUSSION

It is observed that the micro quantity of Cu (II), Ni (II), Iron (II) and Zn (II) have been determined by the proposed procedure using ρ-dimethylaminobenzylidene rhodanine. The amount of metal ions was detected with less than ± 1% practical error, with minimum detection limit of 0.20 mg approx.

CONCLUSION

The precision of the procedure was checked up by carrying replicate determinations and the standard deviation was found to be less than 1% and coefficient of variation is in between 0.9% to 1.0% for titled metals with respect to ρ-dimethylaminobenzylidene rhodanine. Thus, it could be concluded from the data that synthesized compounds are sensitive, useful and selective amperometric reagent for titled metal determination.

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REFERENCES

1. V. Anger and S. Ofri, *Microchim Acta,* **918** (1964).
2. J. H. Yoe and L.G. Overholser, *J. Amer. Chem Soc.* **63,** 3224 (1941).
3. R. Solmaz G. Kardas B. Yazici and M. Erbil, *J of Transition metal chemistry.* **2,**1, 207(1977)
4. F. J. Welcher “Organic Analytical Reagents. D. Von., *Nostrand. Co. In.* **417,** (1955).
5. France E. Piercy and D.E. Ryan *Can. J. Chem/ Rev Can Chim.,* **41(3)**, 667 (1963).
6. K.Y. Chiu, T.H. Su, C.W. Huang, G. S. Liou, and S.H. Cheng, *J. Electroanalysis,* **578,** 283 (2005).
7. M.C. Corredor, and J.M.R. Mellado, *Electrochimica Acta,* **49,** 1843 (2004).
8. G. Dryhurst, Electrochemistry of Biological Molecules, Academic Press, N.Y. (1997)
9. F.C De Abreu, A.C.O. Lopes, A. A. Do Monte, N. A. Soares, and M.O.F. Goulart, *J. Electroanal.Chem.,***560,** 79 (2003).
10. L. D. Hicks, A. J. Fry, and V. C. Kurzweil, *Electrochimica Acta*., **50,** 1039, (2004).
11. Y.I. Moharram, and M.M. Ghoneim, *J. Electroanal. Chem.,* **570,**135 (2004).
12. G. Diao, and W. Zhou, *J. Electroanal.Chem.,* **567,** 325 (2004)

13. N. V. Rees, J. D. Wadhawan, O. V. Klymenko, B. A. Coles, and R.G. Compton, *J. Electroanal.Chem.,* **563,** 191 (2004).
14. N. Laventis, G. Zhang, A.M. Rawashdeh, and C. S. Lenventis, *Electro-Chimica Acta,* **48,** 2799 (2003).
15. M.J. Higuera, M.R. Montoya, M.R. Galvin, and J.M.R. Mellado, *J. Electro- anal. Chem.,* **474,** 174 (2004).
16. J. A. Squella, J. C. Sturm, B. Weiss-Lopez, M. Bonta, and L. J. N. Vergara, *J. Electroanal. Chem.,* **466**, 90 (1999).
17. S. Bollo, L.J. Nunez-Vergara, and J. A. Squella, *Bull. Soc. Chill. Quim.,* **44,** 67 (1999).
18. W. Nerst and E. S. Merriam, Z. Physik. Chem. **53,** 235 (1905).
19. S. Berezickey and J. Heyrovaskey, *Collection Czech. Chem. Commun.* **1,** 19 (1929).
20. L.J. Smith, I.M. Kolthoff and L.J. Spillane., *J. Am Chem. Soc.,* **64,** 646 (1942).
21. I.M. Kolthoff and Y.D. Pan, *J. Ame. Chem. Soc*., **61,** 3402 (1939).
22. I.M. Kolthoff el al., *Analyst*, **74,** 635 (1949).
23. D. Price and F.R. Coe, *Analyst,* **89,** 55 (1959).
24. A. Stier, *Z. Anal. Chem.,* **193,** 195 (1963).
25. G.A. Aylward, J. L. Garnett, J. W. Hayes and S. W. Law, *J. Inorg. Nucl. Chem.,* **16,** 350 (1961).
26. B. Sharma, *Bull. Chem. Soc. Japan,* **33,** 277 (1960).
27. D.R. Gere and C.E. Meloan, *Anal. Chem.,* **35,** 597 (1963).
28. C.L. Sharma and A.K. Singh, *J. Indian Chem. Soc.,* **55,** 31 (1978).
29. Mackie, Misra *J. Chem Soc.,* **3919** (1954).

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