Polarographic Behaviour of Ammonium Dithiocarbamate (ADC), at the Dropping Mercury Electrode

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THE polarographic behaviour of ammonium dithiocarbamate (ADC) has been studied in 0:05M ammonium tartrate-0.05M KNO_3 medium at the DME. ADC produces two well defined diffusion controlled reversible anodic waves between the pH 3.0 – 10.0, Each anodic wave is preceeded by, an adsorption prewave. The prewaves were also obtained in the presence of surfactants and alcohol. The ratio of the two anodic waves remains constant and is practically 1 : 1. The diffusion current ($i_1 + i_2 = i_d$) is proportional to the ADC concentration upto 6.0 mM, so that its variation can be used for determing ADC concentration.

Dithiocarbamates and the sulphur containing compounds have a wide variety of applications varying from biological-pharmaceutical activity to analytical, and other chemical uses[1-4]. Therefore, the importance of this group of compounds has grown. The electro-chemical behaviour of a number of sulphur containing compounds like potassium ethylxanthate[4,5], ethyl-thioxanthate[6], thioglycollic acid[7], thiomallic acid[8], β-mercap-topropionic acid[9], thiourea[10], monolkyl dithiocarbamates[11], monothiocarbamates[12] and substituted dithiocarbamates[13-23] has been fairly extensively investigated. In alkaline media various amine or alkali metal dithiocarbamate give an unstable absorption cathodic wave and complex anodic waves[17]. For analytical purposes, the anodic absorption waves are most useful.

In view of the important applications of ADC in analytical chemistry[24-29], it was considered worthwhile to investigate the electro-chemical behaviour of ADC at the DME for which no reference could be traced in the literature. In the present investigations, the interest has been focussed mainly on the effect of pH, mercury height and concentration of the nature of the anodic wave.

EXPERIMENTAL

Reagents : All chemicals used were of AnalaR quality. Preparation and standardization of ADC were made by methods reported earlier[24,25].

Apparatus : All the polarograms were recorded with ELICO polarograph with m = 2.0 mg/sec, t = 3.3 sec (in open circuit). Saturated calomel electrode with agar KCl pridge was used as the non-polarizable reference electrode. pH measurements were made with Beckman Zeromatic pH meter. pH adjustments were made with either with ammonia or dil HCl.

Procedure : 3 ml of 0.5 M ammonium tartrate + 0.5 M KNO_3 solution was taken in a beaker and its pH was adjusted to a desired value using the pH meter. This solution was diluted to 30 ml and was transferred into the polarographic cell. Dme and SCE were introduced into the cell through a rubber stopper which just fits at the mouth of the cell. Pure and dry nitrogen was bubbled through the cell for five minutes. Then the polarogram of the solution was recorded (blank). A measured volume of ADC was introduced in the cell. The solution was again deaerated for 4–5 minutes and then the polarogram was recorded. pH of the final solution was measured again.

CHARACTERISTICS OF THE ANODIC WAVE

Effect of pH : At pH lower than 5.5, ADC decomposes In 0.1 M sodium hydroxide solution, a white precipitate was formed, probably a disulphide resulting from autooxidation[11]. Current potential curves at the done obtained with solutions of pH 6 to 10.0 (different buffers like ammonium acetate–ammonia, ammonium nitrate-ammonia, ammonium tartrate-potassium nitrate-ammonia etc) have the same appearence. All the polarograms are split into two anodic waves, the ratio of which practically remains constant at 1 : 1 Each anodic wave is accompanied by an adsorption prewave (i_A and i_B in Fig. 1). These prewaves are observed at a concentration higher than 2 mM.

In acidic solution (ammonium tartrate-KNO_3-HCl) of pH 3.0-5.5, ADC also produces two anodic waves similar in nature to those obtained in alkaline mediums. However the wave heights are slighly less than those found in alkaline media: In acidic solutions, the more positive wave i_2 is indistinct because of its closeness to the current corresponding to the dissolution of mercury in the supporting electrolyte. The half-wave potentials of both the anodic waves shift to more negative values with increase in pH of the solution.

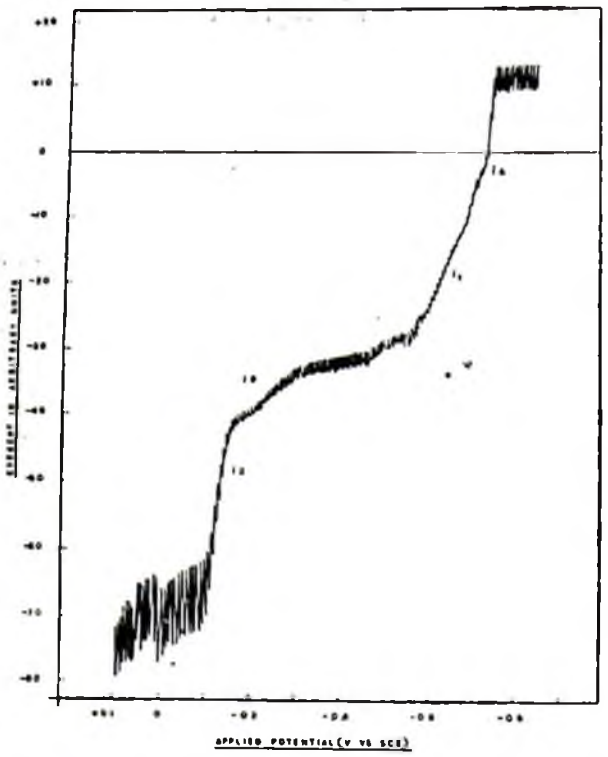


Fig. 1 A typical polarogram of ammonium dithiocarbamate (6.0 mM) in 0.05M ammonium tartrate+0.05M KNO +ammonia (pH 8.0) medium. i^A and i^B are adsorption prewaves.

Effect of supporting electrolyte concentration : Experiments performed with solutions of varying ionic strength (0.025 to 0.5 M ammonium tartrate-KNO_3) at pH 8.0 in the absence and presence of 0.01% gelatin indicate that the ionic strength does not affect the shape and height of the wave. In the presence of 50% ethanol ZmM ADC gives well-defined diffusion controlled wave, proportional to the concentration. The value of $i_1 + i_2 = i_d$ in 50% ethanol is slightly less compared to the in aqueous alkaline medium. The lower value is due to the higher viscosity of the alcohol. The prewaves occur at about the same potentials in aqueous and ethyl alcohol solutions.

Effect of Mercury Column Height : The heights of prewaves are proportional to the length of the mercury column at all concentrations investigated. both in alcohol and aqueous medium. The constancy of $I_d/\sqrt{hH}$ for the total wave indicate that the waves are all diffusion controlled.

DISCUSSIONS

It has been reported that the mono alkyldithiocarbamates produce a single anodic wave above pH 8.0[11]. Below pH 8.0 the main wave (i) is split into two anodic waves. The overall process corresponds to 2 electrons unlike in vast majority of organic sulphur compounds, which gave one electron anodic waves[1-3]. ADC gives two anodic waves in the entire pH range studied (pH 3 to 10.0). Logarithmic analysis of the two anodic waves in Fig. 1 gave a reasonably straight line for the plot of $\log\left(\frac{i_a - c}{i}\right)$ vs potential. The slope of 0.060 mv for the first wave (i_2) indicates one electron process. The slope of the second wave (i_1) is 0.068 mv slightly higher than the theoretical slope for one electron reaction. ADC is oxidised reversibly at the dme with overall two electron process. The two one electron diffusion controlled processes corresponding to wave i_1 and i_2 can be formulated by the following schemes[11].

$$NH_2CSS \rightleftharpoons NH_2CSS + H^+ \qquad (1)$$
$$H^+$$

$$NH_2CSS^- + Hg \rightleftharpoons NH_2CSS + e \qquad (2)$$
$$Hg(i) \quad \text{First oxidation step}$$

$$NH_2CSS \rightleftharpoons H-N=C\begin{matrix}\diagup^{2-}\\ \diagdown_{S^-}\end{matrix} + H^+ \qquad (3)$$
$$Hg\ (i) \quad Hg(i)$$

$$H-N=C\begin{matrix}\diagup^{2-}\\ \diagdown_{S^-}\end{matrix} \rightleftharpoons H-N=C\begin{matrix}\diagup^{2-}\\ \diagdown_{S^-}\end{matrix} + e \qquad (4)$$
$$Hg\ (i) \quad - \quad Hg\ (ii) \quad \text{Second step}$$

The actual form of the mercury compound indicated in reaction (4) is not obtained. Reactions of ADC with $HgCl_2$ solution produces a black precipitate of the formula HgS in alkaline medium. Therefore, a possible decomposition scheme for a complex of metal (M) can be formulated as follows.

$$H-N=C\begin{matrix}\diagup^{2-}\\ \diagdown_{S^-}\end{matrix} \rightarrow H-N=C=S + MS \qquad (5)$$
$$M\ (II)$$

$$H-N=C=S + OH^- \rightarrow H-N=C\begin{matrix}\diagup^{S}\\ \diagdown_{S^-}\end{matrix} + H^+ \qquad (6)$$

$$H-N=C\begin{matrix}\diagup^{2-}\\ \diagdown_{O^-}\end{matrix} + M^{2+} \rightleftharpoons H-N=C\begin{matrix}\diagup^{2-}\\ \diagdown_{O^-}\end{matrix} \qquad (7)$$
$$M\ (II)$$

$$H-N=C\begin{matrix}\diagup^{2-}\\ \diagdown_{O^-}\end{matrix} \quad \text{Several steps} \rightarrow NH_3 + MS\downarrow + CO_3^{2-} \qquad (8)$$
$$M\ (II) \qquad 2OH^-$$

The formation of metal sulphides, isothiocyanates and carbonates as predicated by this scheme was proved.

Now, it is well known that monoalkyl dithiocarbamate decomposes below pH 5 and above pH 11[30]. In the pH range below 5, the decomposition is characterised by the existence of two competive reaction pathways; one leading to CS_2 and amine and the other to H_2S, methyl isothiocyanate and elemental sulphur. In alkaline medium, the decomposition is favoured by two mechanisms. The first mechanism is base catalysed and is therefore favoured by a pH > 11. The second is due to an oxidation reaction of the dithiocarbamate by the oxygen contained in the solution. In spite of the above mentioned facts it is quite strange to observe that all the menoalkyldithiocarbamates[11] and substituted dithiocarbamates[31] produce well defined anodic waves in acidic medium. The height of the anodic waves remains practically same between pH 1.0–10.0. Since the anodic waves are generated mainly from the dithiocarbamate moiety (– c –), it is highly
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probable that inspite of their decompositions in acidic medium the – c – moeity remains undisturbed in
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acidic medium and hence well defined anodic waves are obtained.

The polarograms of ADC show that the anodic diffusion current ($i_1 + i_2 = i_d$) is proportional to the concentration upto 6.0 mM in different buffers of varying concentration and pH. The anodic wave of ADC extends over a fairly wide span of potential (+0.4 to −0.6V VS SCE) and this observation finds an immediate application in the amperometric determination of metals precipitated by ADC[24-28]. Because the results obtained for monoalkyldithiocarbamates[11] and ADC are in good agreement with those reported[32,33], for dithiocarbamoyl carboxylic acids, it seems that the observed behaviour is characteristic for a wide range of compounds with the grouping – $NHCSS^-$.

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REFERENCES

1. I. M. Kolthoff and J. J., Lingane "Polarography", Interscience, New York, 2nd Edn. (1952).
2. M. Brezina and P. Zuman, "Polarography in Medicine, Biochemistry and Pharmacy", Revised Eng. Edn. Interscience, New York (1958).
3. J. Heyrovsky, and J. Kuta, "Principles of Polarography", Czech. Academy of Sciences, Prague (1965).
4. K. Saraswathi, *Proc. Indian Acad. Sci.*, 85A, 6 (1975) 514.
5. A L.J. Rao and S. Singh, *J. Electrochem. Soc.* (India) 27 (1978) 169.
6. A L J. Rao and S.B. Bikram, Trans SAEST (India), 13 (1978) 57.
7. D. L. Lenssing and I. M. Kolthoff, *J. Electro. Chem. Soc.*, 100 (1953) 334.
8. R. S. Sexena and K. C. Gupta, *Electrochem. Chem. Acta.*, 13 (1968) 1749.
9. R. S. Sexena and K. C. Gupta, *J. Ind. Chem. Soc.*, 47 (1970) 101.
10. R. J. Edsberg, *Anal. Chem*, 26 (1954) 724.
11. D. J. Halls, A. Townshend and P. Zuman, *Anal. Chem. Acta*, 40 (1968) 459.
12. R. Zahradnik and P. Zuman, *Collec. Chem. Commun.*, 21 (1956) 672.
13. T. Fujinaga and K. Yamashita, *Bull. Chem. Soc.* (Japan) 37 (1964) 989.
14. P. Zuman, R. Zumanova and B. Somcek, *Coll. Cxch. Chem. Commu.*, 18 (1953) 632.
15. P. Nangniot. *Chem. Abst.*, 55 (1961) 23912.
16. P. Nangniot, *Chem. Abst.*, 55 (1961) 5853.
17. J. Pasciak, *Cnam. Anal.*, (Warshaw) 8 (1963) 945.
18. J. Davis, A. J. Eastan and J. Freezer, *Chem.* and *Ind.*, (1955) 241.
19. T. Nagai and K. Yamashita, *Chem. Abs.*, 61 (1964) 1247.
20. T. Zawadzka, *Chem. Abst.*, 65 (1966) 6182.
21. O. Rozaci, *Chem. Abst.*, 54 (1960) 6172.
22. G. Proske, *Agnew. Chem.*, 53 (1940) 550.
23. W. Stricks and S. K. Chakravarti, *Anal. Chem.*, 34 (1962) 508.
24. S.S. Chatterjee, R. Chatterjee and D. Guha, *Ferts. Techno.*, 16 (3 & 4) 1979 (in press).
25. R. Chatterjee, D. Guha and S.S. Chatterjee, *Ind. Acd. Scl.*, (communicated).
26. R. Chatterjee, S.S. Chatterjee and D. Guha, *Fert. Tech.*, 17 (1), 1980 (in press).
27. S. S. Chatterjee, R. Chatterjee and D. Guha, *Analyst.* (London) (Communicated).
28. S. S. Chatterjee, and R. Chatterjee, *Chamische. Technik.*, (Germany) (in press).
29. H. Lund, *Coll. Cxch. Chem. Commun.*, 25 (1960) 2313.
30. S.J. Joris, K. I. Aspila and C.L. Chakrabarti, *Anal. Chem.*, 42 (1940) 647.
31. Yu. I. Ustenko and F. M. Tulyupa, *Chem. Abst.*, 53 (1959) 1991 id.
32. R. Zahradnik L. Jensovsky, *Chem. Listy.*, 48 (1954)11.
33. R. Zahradnik, *Chem. Listy.*, 49 (1955) 1002.