

VOLTAMMETRIC BEHAVIOUR OF NITROSODIMETHYL AMINE ON LEAD ELECTRODE IN THE ABSENCE AND IN PRESENCE OF UNSYMMETRICAL DIMETHYL HYDRAZINE

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The voltammetric behaviour of nitrosodimethylamine (NDMA) on lead electrode in 1.0M H_2SO_4 indicates that it is reduced in a 4e step to unsymmetrical dimethyl hydrazine (UDMH) as in the case of earlier polarographic works on Hg electrodes. However the electron transfer rate is much slower on Pb electrode and the first electron-transfer step is the rate determining step. This is in contrast to the behaviour on Hg where the charge transfer is totally reversible. At higher NDMA concentrations some inhibiting adsorption effects are also noticed.

Addition of UDMH to 1.0M H_2SO_4 results in substantial positive shift of the hydrogen evolution potential. In presence of UDMH (> 500 mM) the hydrogen evolution process takes place at the potential where nitrosodimethylamine itself is reduced. This parallel competitive hydrogen evolution process explains the sudden drop in current efficiency in the preparative scale for the electroreduction of NDMA.

Key words : Nitrosodimethylamine, unsymmetrical dimethylhydrazine, cyclic voltammetry, lead electrode

INTRODUCTION

Polarographic reduction of aliphatic, alicyclic and aromatic nitroso compounds have been extensively investigated over the past several decades [1-4]. The influence of protonation kinetics [5-6] as well as structure reactivity correlations [6-10] have been reported. Correlations have been found, for example, between $E_{1/2}$ of the nitroso compound and the pK_a of the corresponding amine formed [11]. Hammett σ parameter [12] and also the dipole moment of the nitroso compound [13] have been reported. A comprehensive review covering the voltammetric studies of nitro, nitroso and all related compounds is also available [14].

Compared to the volume of work on nitroso compounds, only a few polarographic works on N-nitrosodimethylamine (NDMA) have been reported [15-18]. It has, however, been clearly established that in acidic conditions NDMA is reduced in a single four electron step to the corresponding amine ($E_{1/2} = -0.560V$ vs SCE). At higher pH values the reduction wave splits into two electron waves, of which the first wave shows pH dependence [15,18]. However, all these works were confined to mercury electrode. No voltammetric work for this compound seems to have been reported on lead electrode which is in fact used in preparative work [19].

Hence in the present work an attempt was made to study the voltammetric behaviour of NDMA on lead electrode and compared the behaviour with that on mercury electrode reported in the literature [15-18]. Since in the electrosynthetic work it was noticed that the current efficiency drops drastically when more than 2.0M level of unsymmetrical dimethyl hydrazine (UDMH) is formed in solution [19], the influence of UDMH on the voltammetric behaviour was also investigated to understand the cause of such loss of efficiency.

EXPERIMENTAL

A high purity lead rod (99.99%) of 6 mm dia, inserted tightly in

a teflon holder was used as the stationary working electrode in the present work. The electrode contact was obtained through a copper rod fixed inside the teflon rod. A Pt foil counter electrode and a saturated calomel (SCE) reference electrode were used.

An H-type cell with a sintered glass frit separating the working and counter electrode compartments was employed. The working electrode compartment had provisions for gas inlets, in and over the solutions, thermometer and KCl salt bridge connecting the reference electrode.

A.R. grade chemicals and triple distilled water were used to prepare all solutions. Nitrogen gas, purified by passing through pyrogallol, concentrated sulphuric acid and distilled water was used for the removal of oxygen from the catholyte and the cell. The cell temperature was maintained at $25.0 \pm 1^\circ C$. All potentials were measured and reported with respect to SCE.

The working electrode must be properly activated and used to obtain reproducible voltammetric responses. The experimental details regarding cells and experimental reproducibility criteria have been discussed earlier [20]. The lead electrode was mechanically polished to a fine finish, wiped out many times using dry cotton to remove the powdery particles, then washed thoroughly with triple distilled water, again wiped with cotton and finally washed with small quantities of trichloroethylene or methanol. This electrode was immediately transferred to the H-type cell containing already deaerated electrolyte. The electrode is immediately imposed with the starting potential (-0.650V) which is already more cathodic to the rest potential. The voltammetric recordings are also initiated as early as possible. It is felt that this procedure clearly avoids the formation of any trace of $PbSO_4$ on open circuit conditions, thus avoiding any time effect [21]. This assumption finds support from the fact that leaving lead electrode in H_2SO_4 for longer periods of time under open circuit conditions leads to irreproducible voltammetric behaviour and a great deal of time effect.

1.0 M NDMA stock solution in absolute alcohol was added to 99.0 ml working electrolyte solution to obtain different concentrations of NDMA. The maximum volume added was 2 ml (20 mM). The effective change in volume of working electrolyte solution (1% maximum taking 100 ml as a base point) was neglected in calculations.

RESULTS

Voltammetric behaviour of NDMA

Typical cyclic voltammograms of NDMA (1 mM) in 1.0 M H₂SO₄ on lead electrode at various sweep rates are presented in Fig. 1.

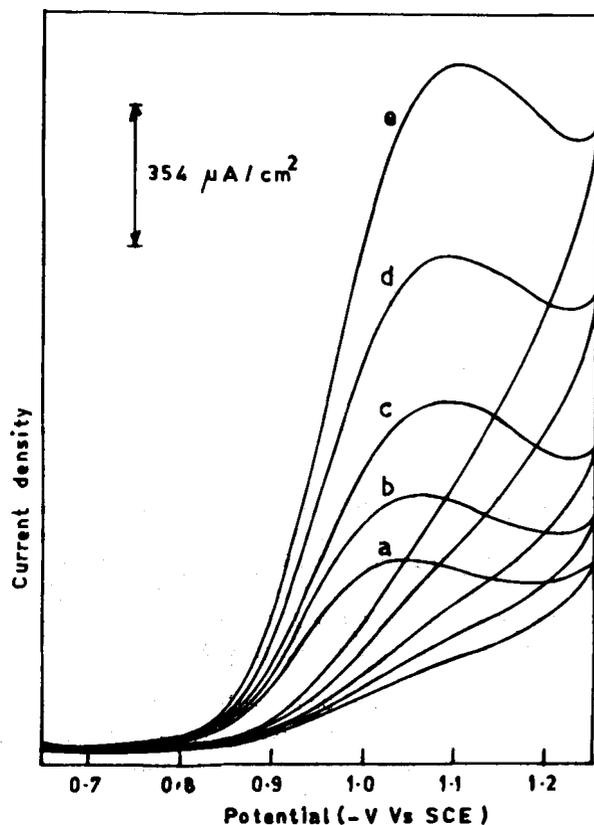


Fig. 1: Cyclic voltammogram of NDMA in 1M H₂SO₄ on lead electrode at different sweep rates (mV S⁻¹) of (a) 10 (b) 20 (c) 40 (d) 80 (e) 160, concentration of NDMA is 1 mM

The voltammogram shows a well defined cathodic voltammetric peak. In the reverse sweep no anodic wave is observed. The cathodic peak current increases with the square root of sweep rate ($i_p / v^{1/2}$ is constant - See Table I). The peak potential also shifts cathodically with increasing sweep rate. The $E_p - E_{p/2}$ value is quite high and this value also increases with increasing sweep rate at identical concentrations (Table I).

Table I: Voltammetric characteristics of NDMA in 1M H₂SO₄ on lead electrode

Area 0.2826 cm²

No	Concentration of NDMA (mM)	Sweep rate V mv/sec	I_p (MA)	E_p (mv)	$E_{p/2}$ (mv)	$E_p - E_{p/2}$ (mv)	$I_p / AC V^{1/2}$
1	1	10	130	1045	925	120	145.5
2	1	20	173	1065	935	130	136.9
3	1	40	240	1090	945	145	134.3
4	1	80	346	1095	950	145	136.9
5	1	160	486	1100	960	140	136.0
6	5	80	1782	1025	910	115	141.0
7	5	160	2498	1030	925	105	139.8
8	5	320	3418	1050	935	115	135.0
9	5	20	955	995	900	95	157.4
10	6.5	20	1290	1000	905	95	157
11	8	20	1560	1005	910	95	144.4
12	10	20	1940	1010	915	95	153.6

The effect of NDMA concentrations on the voltammetric behaviour is presented in Fig.2

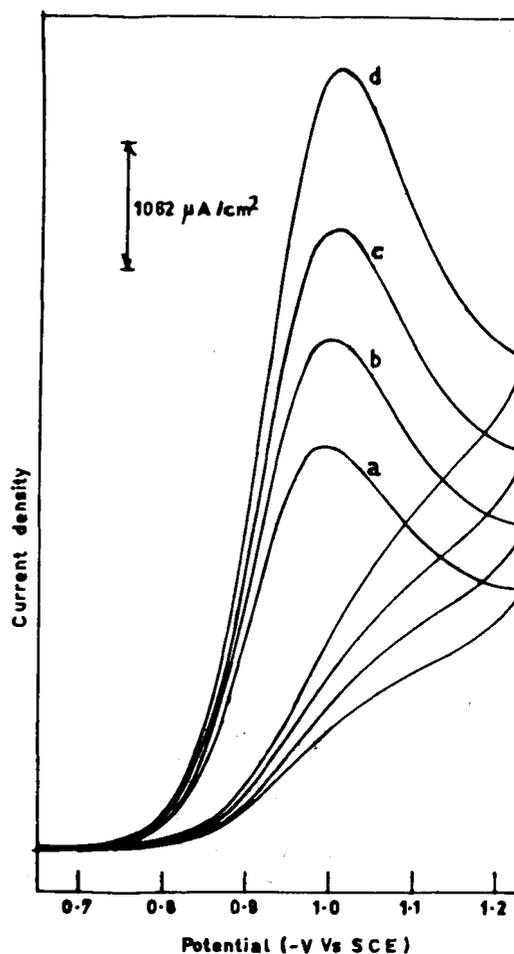


Fig.2: Cyclic voltammogram of NDMA in 1M H₂SO₄ on lead electrode at the sweep rate of 20 mV S⁻¹, Concentration (mM) (a) 5 (b) 6.5 (c) 8 (d) 10

The peak current value again increases linearly with concentration at a constant sweep rate. The peak potential shifts in the anodic direction with increasing concentration when NDMA concentration is lower (< 5 mM) as shown in Table I. At higher concentrations the peak potential again shifts cathodically (Fig.2 and Table I) and the voltammograms show a much sharper shift in peak potential. The $E_p - E_{p/2}$ values also reach a much smaller value (95 mV) at higher concentrations (Table I). In such concentration ranges the $i_p / AC V^{1/2}$ value is slightly higher when compared to the values in low concentration range.

The effect of sweep rate at higher concentration of NDMA (5 mM) is also quite similar (Fig.3) to that at lower concentrations.

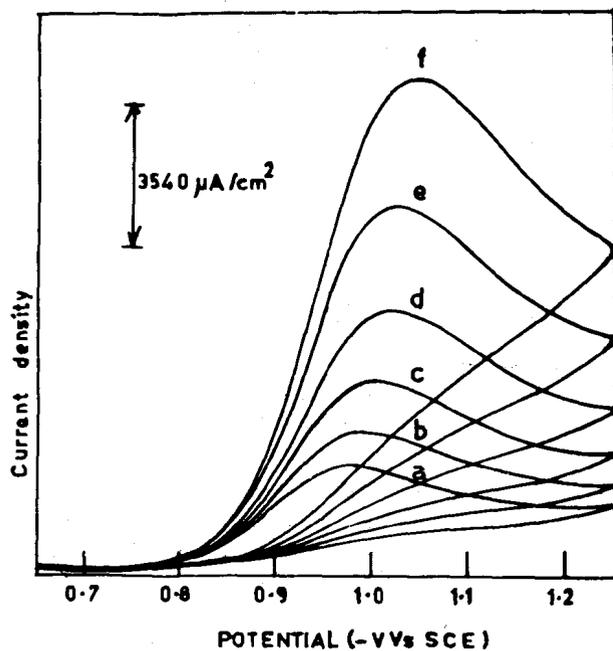


Fig.3: Cyclic voltammogram of NDMA in 1M H_2SO_4 on lead electrode at different sweep rates of $mv s^{-1}$ of (a) 10, (b) 20, (c) 40, (d) 80, (e) 160, (f) 320, concentration of NDMA is 5 mM

The peak current increases linearly with $v^{1/2}$ and the peak potential shifts cathodically with sweep rate. Constant potential electrolysis was carried out with 10 mM NDMA using $5 cm^2$ area lead working electrode until about 10% of the compound was consumed. The actual amount of unreduced NDMA that remained in solution was again estimated using voltammetry. The n_{ap} obtained by this method was 4.14.

Influence of UDMH on the voltammetric behaviour of NDMA

As a first step towards the study of the effect of UDMH on NDMA reduction, the voltammetric behaviour of UDMH itself was investigated. On addition of 200 mM UDMH to 1.0M H_2SO_4 solution, the background reduction potential corresponding to H_2 evolution was found to shift positively by over 150 mV (compare curve a and b in Fig.4). On further incremental addition of UDMH,

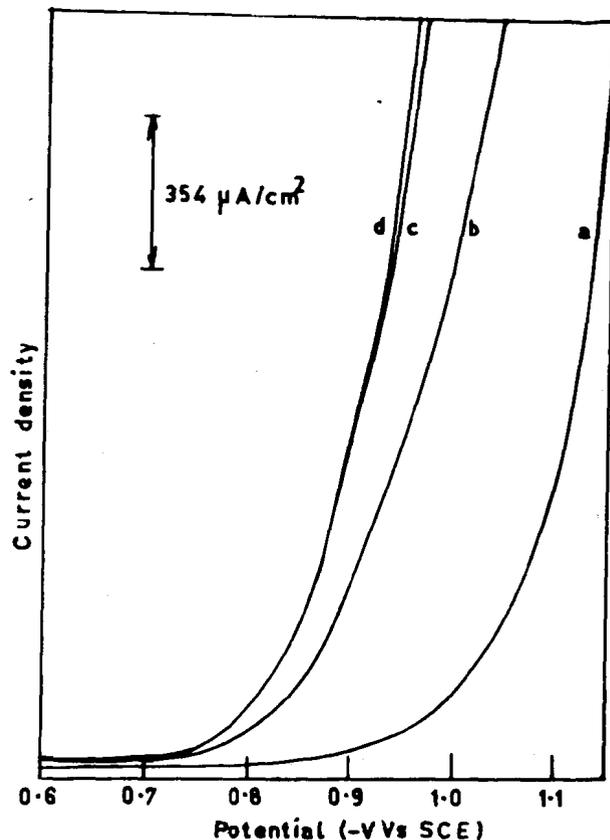


Fig 4: Voltammogram in 1M H_2SO_4 on lead electrode: concentration of UDMH (mM) (a) 0 (b) 200 (c) 400 (d) 600, Sweep rate $20 mv.s^{-1}$

however, the shift in the potential (Fig. 4 curves b, c and d) was quite smaller. It must, however, be noticed that with such a shift in background reduction potential the hydrogen evolution reaction starts right at the potential region where nitroso compound reduction would commence. This factor becomes even more obvious with the addition of NDMA (4mM) to 1.0M H_2SO_4 containing 600mM UDMH (Fig.5) where no reduction peak is noted. The reduction, however, is found to start at slightly more positive potential. The small reduction wave is, however, noticeable when the same voltammogram (Fig. 5-c) was recorded at lower sensitivity (Fig. 6a). Even this type of wave becomes almost indistinct as the UDMH concentration is further increased (Fig. 6b).

DISCUSSION

Electrochemical reduction of NDMA in 1.0M H_2SO_4

In pure H_2SO_4 media, NDMA shows a well defined voltammetric behaviour. The peak current is found to be directly proportional to $V^{1/2}$ and the concentration (c) of NDMA. This type of behaviour should correspond to a simple irreversible charge transfer, or to a reversible charge transfer followed by irreversible chemical reaction [22-24] The peak current constant value (i_p / AC

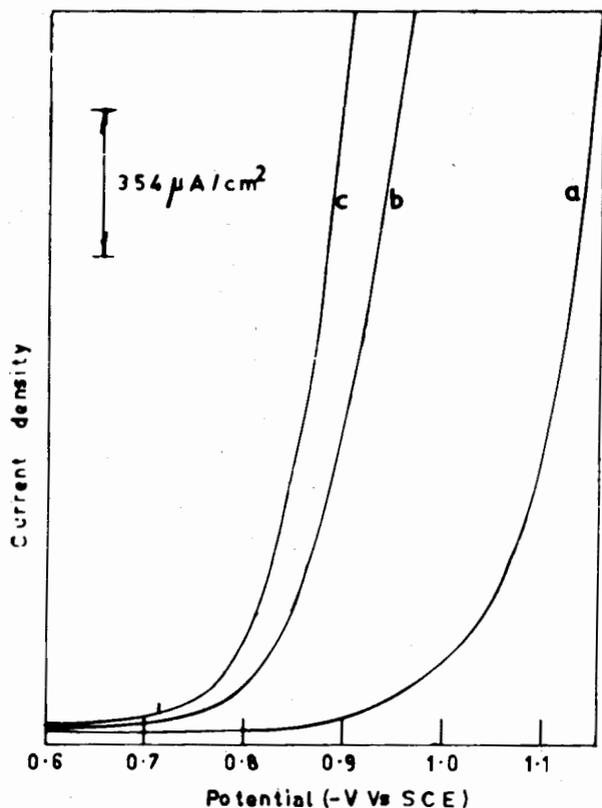


Fig. 5: Voltammogram of NDMA in presence of UDMH in 0.1M H₂SO₄ on Pb electrode at sweep rate 20 mvs⁻¹. Concentration (mM) of (a) UDMH 0 + NDMA 0, (b) UDMH 600 + NDMA 0, (c) UDMH 600 + NDMA 4

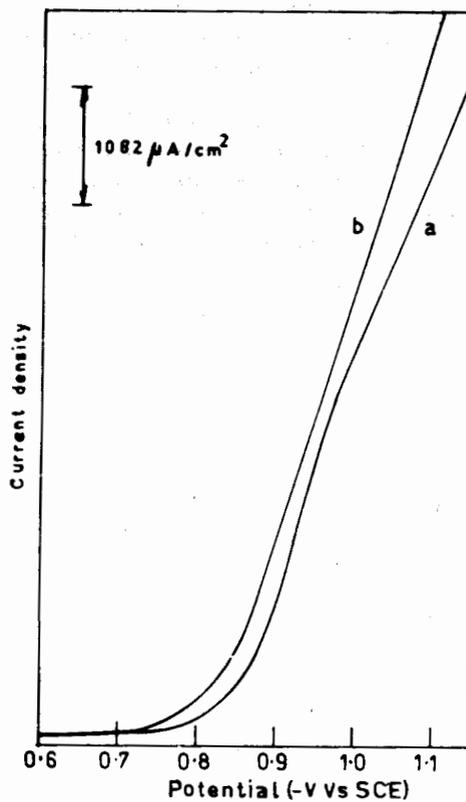


Fig. 6: Voltammogram of NDMA in presence of UDMH in 0.1M H₂SO₄ on Pb electrode at a sweep rate of 20 mVs⁻¹. Concentration (mM) of NDMA + UDMH (a) NDMA - 4 and UDMH - 600 (b) NDMA - 4 and UDMH - 1000

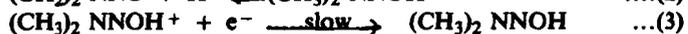
V^{1/2} where A is the electrode area) corresponds to a 4e reduction wave. For example $i_p / AC V^{1/2}$ value of NDMA is close to the value obtained for the nitrobenzene reduction which has already been established to be a 4e wave [25]. Under identical strong acid conditions, NDMA leads to a 4e wave on mercury electrode as well [15-18]. In coulometric work on lead electrode also the value was found to be close to 4. (The slightly higher value is probably associated with the small contribution by simultaneous hydrogen evolution initiated by the UDMH formed during constant potential electrolysis.) All these conclusions point to the fact that NDMA on lead electrode is reduced in 4e step to UDMH. Since this overall reaction is a 4e reduction, the reaction mechanism would correspond to charge transfer coupled with chemical reactions rather than to simple single step irreversible charge transfer.

The main difference between the electroreduction behaviour of NDMA on mercury and lead seems to be the reduction potential. NDMA is reduced around -0.560V itself on mercury [15] but the reduction process does not start at all until about -1.0 V is reached on lead electrode (Figs. 1 and 3 and Table I). This implies that the electroreduction is much more difficult on lead when compared to mercury. Because of the slowness in electron transfer step it is

likely that the charge transfer becomes the slowest step in the overall process [24]. This viewpoint is further supported by the fact that $E_p - E_{p/2}$ values are much larger. For a reversible charge transfer this value should correspond to 56/n or about 14 mV for a 4e process. For an irreversible charge transfer with first electron transfer as a slow step, $E_p - E_{p/2}$ would be given by eq.1

$$E_p - E_{p/2} = \frac{48}{\alpha n A} \text{ mV} \dots (1)$$

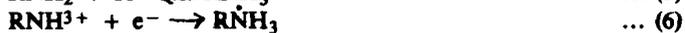
The experimental values (120 mV) correspond to the transfer coefficient value of less than 0.5 at lower NDMA concentrations. This is probably associated with work done in displacing the solvent molecule by NDMA before charge transfer. As the concentration increases the $E_p - E_{p/2}$ value attains a value of 95 mV (Table I) which corresponds exactly to α_{na} value of 0.5 that would be expected for an electrochemical process where the first electron transfer is the rate determining step. Taking into consideration all the above experimental facts and also noting the pH - dependence reported in polarography [15, 18] the following reaction mechanism may be proposed for the reduction of nitroso dimethylamine on lead electrode.



This reaction mechanism, however, cannot explain the slight decrease in $i_p / AC V^{1/2}$ at high sweep rates and the slight cathodic shift in E_p with concentration at higher concentration ranges. These processes, however, are associated with some adsorption effects [26, 27] which are commonly observed on solid electrodes at higher concentration ranges [25].

Catalytic effect of UDMH on hydrogen evolution and its influence on the electroreduction of NDMA

Polarographic studies have clearly established that organic bases such as amines and substituted amines can function as proton carriers and catalyse the hydrogen evolution process on mercury electrodes [28].



Such polarographic waves are termed as catalytic hydrogen waves and have been studied quite extensively [28]. Similar catalytic hydrogen evolution was recently noticed on glassy carbon electrodes as well [29].

The 150 mV positive shift for hydrogen evolution reaction noticed on lead electrode on addition of UDMH is also associated with such a catalytic hydrogen evolution process. On further addition of UDMH the reduction shift is less pronounced because the electrochemical process now is the same (reactions (5) - (7) where R refers to $(\text{CH}_3)_2\text{N}-$) and the potential shift is related to the protonation process (5) alone.

In presence of UDMH, the electroreduction of nitrosodimethylamine is thus faced with a parallel competing process, that is, the catalytic hydrogen evolution (Fig.5). The competition becomes pronounced as the UDMH concentration increases (Fig. 6). This reaction scheme also correctly explains the sudden drop in the current efficiency of the electrochemical process at a particular NDMA/UDMH concentration ratio, noted in preparative electrolysis.

CONCLUSION

The present voltammetric studies clearly indicate that N-nitrosodimethylamine is reduced in a well-defined 4e single wave on lead electrode in H_2SO_4 medium. Compared to mercury electrode, the electron-transfer rate on lead electrode is much slower. The first electron transfer is probably the rate determining step in the overall process on lead electrode. UDMH functions as a proton carrier in a catalytic hydrogen evolution process on lead electrode. This parallel process competes with the reduction of N-nitrosodimethylamine at higher UDMH concentrations and hence brings down the efficiency of the process. This voltammetric investigation also serves as a clearcut example of how voltammetric investigations can be used to identify the causes for the type of

problems one encounters in preparative scale experiments in electroorganic chemistry.

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