New Voltammetric Applications in the Case of 2-Nitro-9,10-Anthraquinone

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The electrochemical reduction behaviour of 2-Nitro-9,10-anthraquinone has been studied by employing advanced electrochemical techniques such as DC polarography, cyclic voltammetry, AC polarography and differential pulse polarography in media of different pH values. Millicoulometry is employed for the determination of number of electrons involved in the electrode process. Differential pulse polarographic technique has been employed for the analysis of the title compound.

9,10-Anthraquinones are used in production of dyestuffs and pharmaceuticals [1,2]. Spectral properties of these compounds are extensively used in analytical practice, mainly in photometry and fluorimetry and in the study of acid base, redox, complexation and photochemical reactions [3,4]. Anthraquinone derivatives have also been widely used as chelating agents and chromophores [5,6]. The reduction products of quinones are used as dipigmenting agents [7].

The relationship between structure and antineoplastic activity of benzo-, naphtho- and anthra-quinones substituted with amino, and alkylamino side chains have been intensively studied by Cheng [8,9]. Inspite of such importance of this class of compounds, little attention has been paid to their electrochemical behaviour. Recently the electrochemical reduction of 2-ethyl-9,10-anthraquinone and its tetrahydro derivative has been attempted [10].

In continuation of our work on anthraquinones [11,12], electrochemical reduction behaviour of 2-nitro-9,10-anthraquinone has been studied using advanced electrochemical techniques and reported here.

EXPERIMENTAL

The purity of a sample of 2-Nitro-9,10-anthraquinone (Sigma Chemicals, U.S.A.) was tested by melting point determination. All other chemicals used were of analytical grade. Stock solutions of buffer (pH 2-12) were prepared. Stock solution of depolarizer was prepared in methanol-water mixtures.

Test solutions were prepared from the stock solution of depolarizer, buffer and supporting electrolyte and purged with purified nitrogen before the voltammograms were taken. All experiments were carried out at 26 ± 1°C.

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The instruments used are described earlier [13]. Flow rate of dme was 2.73 mg/sec and area 0.0223 cm^2. The area of HMDE used in cyclic voltammetry was 0.0443 cm^2. SCE was the referece electrode in DC polarography. Ag/AgCl(s), Cl^- was the reference electrode in other cases.

RESULTS AND DISCUSSION

The electroactive species get precipitated at pH 12.0 and so experiments are restricted to pH range 2 - 10. Two steps are clearly visible in AC and differencial pulse polarography and cylic voltammetry in the entire pH range. Typical polarograms are shown in figs. 1-4.

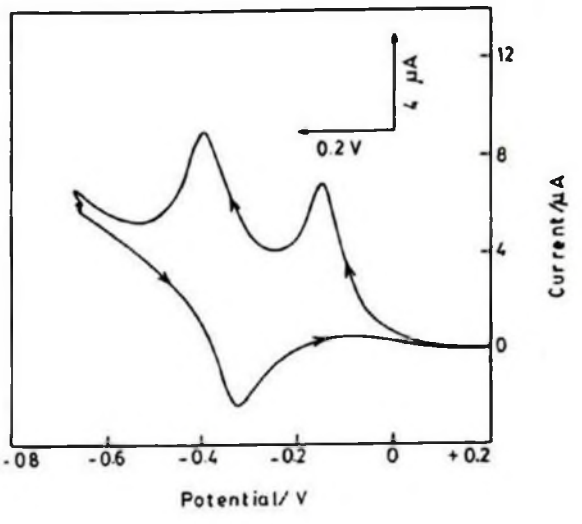


Fig. 2 Typical cyclic voltammogram of 2-nitro-9,10-anthraquinone
pH 4.0; Concentration 0.5 mM; Scan rate 40 mVs^{-1}

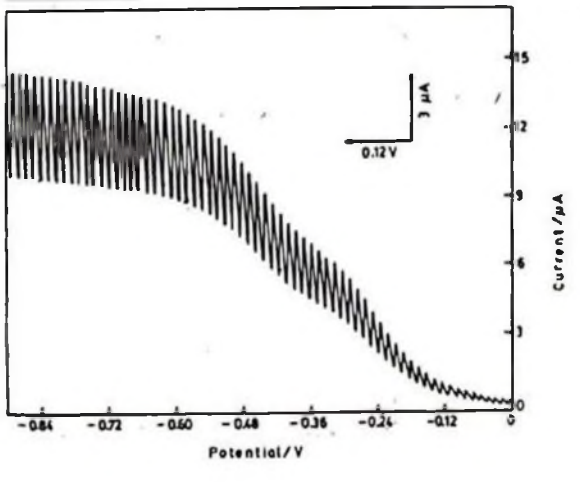


Fig. 1 Typical DC polarogram of 2-nitro-9,10-anthraquinone
pH 6.0; Concentration 0.5 mM; Drop time 3 sec.

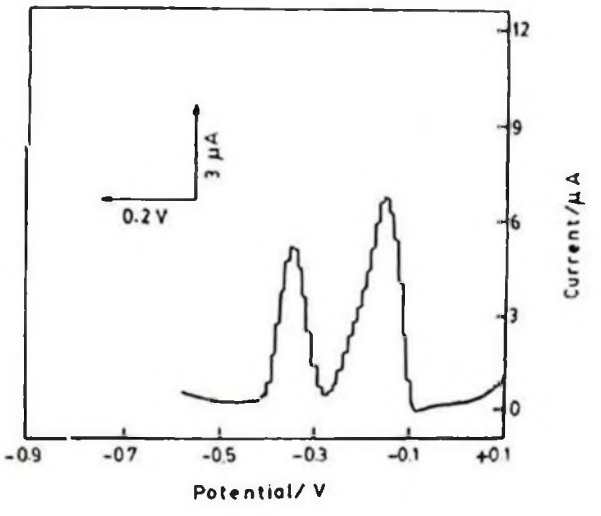


Fig. 3 Typical AC polarogram of 2-nitro-9,10-anthraquinone
pH 4.0; Concentration 0.5 mM; Drop time 3 sec.

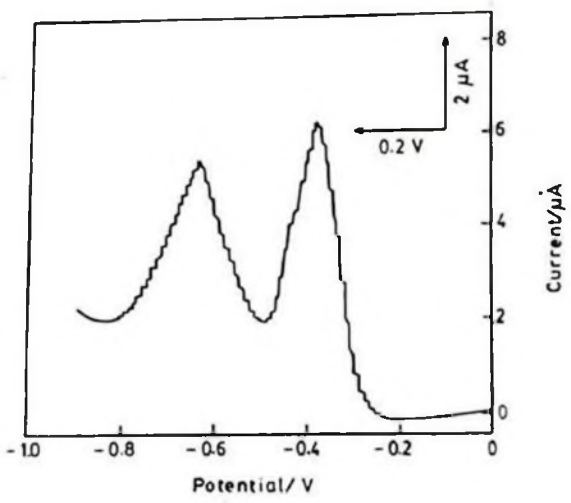


Fig. 4 Typical differential pulse polarogram of 2-nitro-9,10-anthraquinone
pH 10.0; Concentration 0.5 mM; Drop time 2 sec.

The diffusion controlled nature of the electrode processes are seen from the linear plots of i_d *vs.* $h^{1/2}$ (DC), i_p *vs* $v^{1/2}$ (CV) and i_m *vs* $t^{2/3}$ (DPP) passing through origin in all the supporting electrolytes. This also indicates the absence of adsorption complications in all the media studied. In CV, $i_p/Cv^{1/2}$ remains constant with scan rate indicating the absence of any kinetic complications in the above electrode processes.

The reversible nature of the second reduction step is confirmed by the logarithmic analysis of the wave. The E *vs* $\log[(i/(i_d-i)]$ plot has a slope almost equal to 59/n mV and the numerical value of $E_{1/4} - E_{3/4}$ is nearly equal to 56.4/n mV. The reversibility of the electrode process is also indicated from linearity in the plots of i_m *vs* $(1-\sigma)/(1+\sigma)$ and the agreement of summit potentials (E_s) with the half-wave potential ($E_{1/2}$). Moreover, the presence of anodic peak on the reverse scan in cyclic voltammetry confirmed that the reduction process is reversible. $E_{1/2}/E_p$ values of the second wave/peak are also found to be pH dependent and shift cathodically, indicating proton involvement in the electrode process. The irreversible nature of the first step can be proved from the conventional log-plot analysis, shift of $E_{1/2}$ and E_p values towards the more negative potentials with increase of concentration of depolariser, the deviation of AC polarographic half-wave potentials and absence of anodic peak in the reverse scan in cyclic voltammetry.

The number of electrons involved in the electrode processes is estimted by millicoulometric study and found to be four for the first step and two for the second step at pH 2.0 and also 8.0. Reduction product left in solution of pH 4.0 after controlled potential electrolysis at -0.4 V *vs* SCE was identified to be hydroxylamino hydroquinone by usual chemical tests and IR spectral studies. (Nujol, 3100-3000 cm^{-1}, 3320-3220 cm^{-1}).

The first step is attributed to the reduction of nitro group to the corresponding hydroxylamine in a four electron process. The second wave/peak is due to the reduction of quinone to the corresponding hydroquinone with two electron addition. Anodic peak observed in the reverse scan of cyclic voltam-

mogram corresponds to the second cathodic wave.

The values of the diffusion coefficient and heterogeneous forward rate constant have been evaluated and reported in Table I. The diffusion coefficient values and hetrogeneous rate constant evaluated from all the techniques are in good agrement. Rate constant from AC polarography are different because they refer to a different potential. The diffusion coefficient values are seen to decrease gradually with pH which account for the decrease in diffusion current with increase in pH. This may be due to non-avilability of protons. The reduction mechanism of both nitro and quinone groups appear to be the same as reported in literature.

The reduction schemes proposed earlier for reduction of nitro and quinone groups appear to hold good here also.

Analysis

Differential pulse polarography is

Table 1

Typical Voltammetric data of 2-nitro-9,10-anthraquinone

Conc 0.5 mM; Solvent 40 % methanol

pH	2.0		4.0		6.0		8.0		10.0	
Wave	I	II	I	II	I	II	I	II	I	II
DC Polarography:			**Drop time 3 secs**							
$E_{1/2}$	0.05	0.26	0.13	0.34	0.22	0.42	0.38	0.51	0.46	0.59
$Dx10^6$	3.82	4.47	3.65	3.81	3.5	3.43	3.31	3.57	3.18	3.84
k^*_m	$1.15x10^{-3}$	-	$4.06x10^{-4}$	-	$2.18x10^{-6}$	-	$6.13x10^{-7}$	-	$4.21x10^{-8}$	-
Cyclic Voltammetry:			**Scan rate 40 mVsec^{-1}**							
E_p	0.06	0.15	0.16	0.35	0.24	0.46	0.39	0.53	0.47	0.61
$Dx10^6$	3.84	4.49	3.65	3.79	3.50	3.41	3.33	3.64	3.19	3.86
k^*_m	$1.06x10^{-3}$	-	$6.19x10^{-3}$	-	$2.04x10^{-6}$	-	$5.82x10^{-7}$	-	$4.65x10^{-8}$	-
AC Polarography:			**Drop time 3 secs**							
E_a	0.06	0.16	0.15	0.35	0.23	0.44	0.41	0.52	0.48	0.61
$Dx10^6$	3.82	4.46	3.67	3.80	3.53	3.47	3.31	3.56	3.20	3.84
k_a	$2.09x10^{-1}$	-	$3.12x10^{-2}$	-	$5.43x10^{-4}$	-	$1.17x10^{-5}$	-	$9.28x10^{-6}$	-
Differential Pulse Polarography:			**Drop time 2 secs**							
E_m	0.06	0.16	0.14	0.35	0.23	0.45	0.40	0.51	0.39	0.67
$Dx10^6$	3.85	4.47	3.66	3.83	3.54	3.47	3.31	3.67	3.18	3.84
k^*_m	$4.23x10^{-3}$	-	$1.86x10^{-4}$	-	$6.11x10^{-5}$	-	$2.29x10^{-7}$	-	$7.01x10^{-8}$	-

Potentials in Volts; D in cm^2sec^{-1}; Rate constants in cms^{-1}

employed for standardising an analytical procedure for the estimation of the title compound using both calibration and standard addition methods. The peaks attributed to the reduction of nitro and quinone groups are found to be highly reproducible. It is observed that well resolved peaks are obtained at pH 4.0 and is suitable for analysis. The peak current is found to vary linearly with the concentration over the range 1.0 x 10^{-5} M to 2.5 x 10^{-6} M and the lower detection limit is found to be 2.3 x 10^{-6} M.

Analytical procedure recommended is as followes: A standard solution of 2-Nitro-9,10-anthraquinone (1x10^{-4}M) is prepared in methanol. 1 ml of the standard solution is transferred to a polarographic cell and made up with 3 ml of solvent and 6 ml of supporting electrolyte (pH 4.0) and the solution is purged with oxygen - free nitrogen for 10 minutes. After taking the polarogram, small increments (0.2 ml of standard solution) are added and polarograms are recorded after each addition under similar conditions. The best precision is found to be obtained with drop time of 2 sec and a pulse amplitude of 60 mV. The relative standard deviation for 10 replications is found to be 1.56% and correlation coefficient is seen to be 0.992.

ACKNOWLEDGEMENT

The authors wish to thank Department of Non-conventional Energy Sources (DNES), New Delhi for providing finanical assistance.

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