

## ELECTROCHEMICAL REDUCTION OF ACRYLONITRILE ON GLASSY CARBON ELECTRODE IN AQUEOUS SOLUTIONS

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### ABSTRACT

The electrochemical reduction of acrylonitrile has been studied on a glassy carbon electrode in tetraethylammonium bromide electrolyte at pH 8.0 using voltammetry, cyclic voltammetry and controlled potential electrolysis techniques. The Tafel slope analysis has indicated that the reduction mechanism changes with concentration of acrylonitrile. Cyclic voltammetric measurements have revealed that the reduction of acrylonitrile occurs by strong adsorption along with the tetraalkylammonium cations. The reduction mechanism has been discussed.

### INTRODUCTION

Electrohydrodimerization (EHD) of acrylonitrile (AN) [1-3] to adiponitrile (ADN) is an established commercial process, which has undergone further developments [4-6] to economize the cost of production. The study of the mechanistic aspects of the EHD reaction of AN [7-12] is still continued.

It has been established that the proton availability in the electrolytic medium controls the reaction pathways leading either to propionitrile, the saturated monomer or adiponitrile, the hydrodimer. The radical anion  $R^{\cdot-}$ , which is formed by electronation of the activated olefin R, is relatively unstable and may undergo protonation followed by further electronation of the protonated radical  $RH^{\cdot}$  or dimerization reaction. The former reaction pathway which leads to saturated monomer is favoured in the presence of proton donors. In general, a protonated radical is easily reducible than the reactant itself and therefore proton content or protonating agents are to be controlled to achieve EHD reactions. Water itself is considered as an effective proton donor and that is why the amount of water content in the electrolyte, particularly in the vicinity of the electrode, is avoided in the study of many EHD reactions.

It has been possible to control the formation of ADN from AN in preference to propionitrile on a lead cathode in aqueous electrolyte containing large amount of tetraalkylammonium salt as supporting electrolyte. The occurrence of EHD of AN in aqueous solution is explained by the presence of the tetraalkylammonium cations creating a water-poor region within the double layer where EHD can proceed without appreciable competition from the parallel pathway of protonation and further electron transfer leading to the saturated monomer. Later it has been found that even very low concentrations (i.e.  $10^{-4}$  to  $10^{-3}$  M) of strong surfactants [13] like tetraalkylammonium salts are enough to cause EHD to proceed with high current yields in aqueous solutions. There are patents [3,6,14] on the EHD of AN from aqueous solutions differing in minor details. But a very few mechanistic studies [7-12] are reported on the above system and these studies have been made using mercury as cathode. Reports on the mechanistic studies on solid electrodes are found to be very few in spite of the fact that electrodes like lead, cadmium and graphite are used as cathodes in the commercial electrolytic cells.

Preliminary cyclic voltammetric studies on the reduction of acrylonitrile using solid electrodes such as lead, amalgamated lead, cadmium and glassy carbon have revealed that only glassy carbon electrode

gives well-defined peak-shaped cyclic voltammograms among the above mentioned electrodes and the hydrogen evolution potential is also very much shifted to negative potential region. Therefore the present study has been carried out with glassy carbon electrode using voltammetry, cyclic voltammetry and controlled potential electrolysis techniques.

### EXPERIMENTAL

Both steady state measurements and cyclic voltammetric measurements were made in an H-type all-glass cell in which the cathode and anode compartments were separated by a sintered glass frit. A 5 mm diameter glassy carbon rod (Tokai) inserted into a glass tube was used as the cathode and the effective area of the cathode was the exposed bottom disc surface. The anode material was a platinum sheet. Saturated calomel electrode was used as the reference electrode and it was united to the working electrode through a capillary.

Solutions were prepared from double distilled water. The tetraalkyl ammonium salts and other chemicals used as supporting electrolytes were analytical grade chemicals. Experiments were carried out at a constant temperature of  $33^{\circ} \pm 1^{\circ}\text{C}$ . All measurements were made at constant pH 8.0.

A potentiostatic three-electrode system was used in the voltammetric measurements. Potentials were applied from a potential scan generator through a potentiostat and the current output was recorded using a fast response X-Y Recorder.

Controlled potential electrolysis experiments were done in a divided cell using the electroprep cell system.

The glassy carbon disc surface was polished stepwise up to 4/0 emery to a mirror finish, degreased with trichloroethylene, washed with double distilled water and then inserted into the cell containing the supporting electrolyte. Both catholyte and anolyte were the same. Purified hydrogen gas was passed through the catholyte for twenty minutes to remove the dissolved oxygen and passed above the solution during the electrochemical measurements. Both the steady state measurement and cyclic voltammetric measurements were made under unstirred condition. The electrode surface was electrochemically pretreated at  $-1.00$  V vs SCE for a few minutes before recording the background current. Each

electrochemical measurement was made after passing hydrogen through the electrolyte and on the electrode surface for 2-3 minutes.

**Controlled potential electrolysis :** Controlled potential electrolysis was performed in a divided cell using a glassy carbon cathode (area 25 cm<sup>2</sup>) at -1.80 to -2.0 V vs SCE. The total passage of coulombs were recorded using the integrator available in the electroprep cell system. The pH of the solution was maintained at 8.0 by adding dilute hydrochloric acid. At the end of electrolysis, the solution was taken out, the products were extracted three or four times with the addition of bulk quantity of AN. This was then distilled over a water bath. The product was mainly ADN which was confirmed by acid hydrolysis leading to the formation of adipic acid.

### RESULTS AND DISCUSSION

**Steady state voltammetry:** Figure 1 shows the steady state current-potential curve for the reduction of AN on glassy carbon electrode in aqueous 0.2 M tetraethylammonium bromide solution at pH 8.0. Concentration of AN was varied from  $1.5 \times 10^{-2}$  M

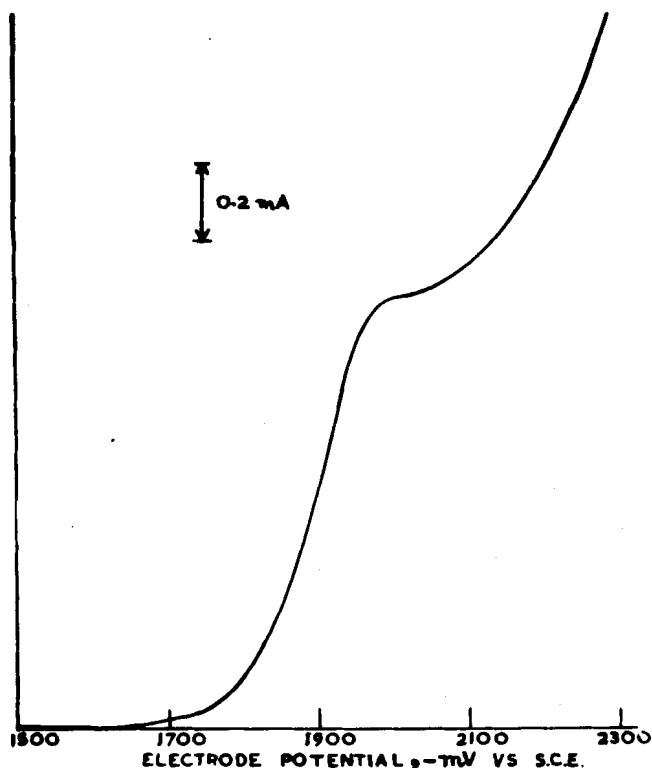


Fig. 1 : Steady state current-potential curve for the reduction of acrylonitrile in 0.2M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr, pH 8.0, temp 32°C, AN conc 0.04527M

to  $1.5 \times 10^{-1}$  M. Well-defined polarographic-type limiting wave was obtained under unstirred condition and the limiting current which was corrected by subtracting the background current was found to increase linearly with AN concentration. The half wave potential was found to shift in the cathodic direction with increase in concentration.

Figure 2 shows the E vs log [(i<sub>L</sub>-i)/i] plots for the reduction of AN.

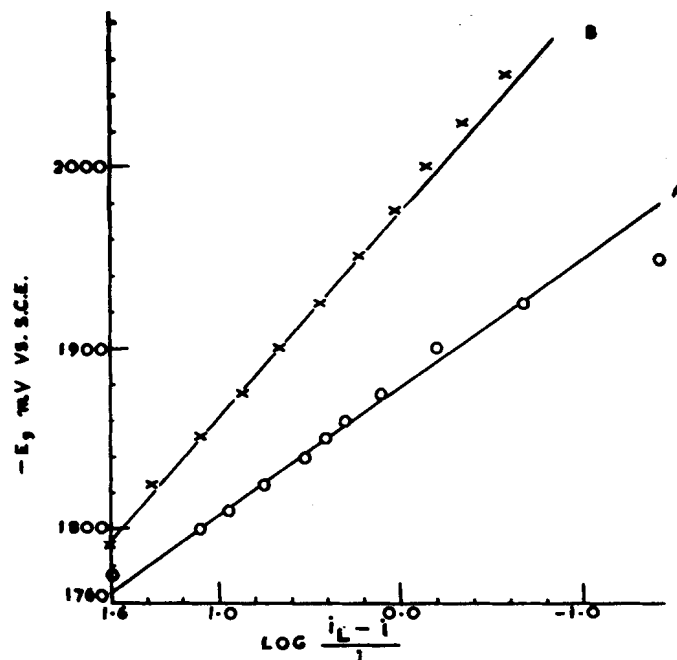


Fig. 2 : E vs log [(i<sub>L</sub>-i)/i] plots for the reduction of acrylonitrile in 0.2M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr, pH 8.0, temp 32°C (A) AN concn 0.03018M, (B) AN concn 0.1509M

The Tafel slope value was found to change with concentration of 45 mM, the Tafel slope was -60 mV and it was -120 mV for a concentration of 150 mM and above under the same experimental conditions. The above observation of change in Tafel slope value with concentration has indicated that the reduction mechanism changes with concentration.

**Cyclic voltammetry :** Figure 3 shows the typical cyclic voltammogram obtained for the reduction of AN on glassy carbon electrode

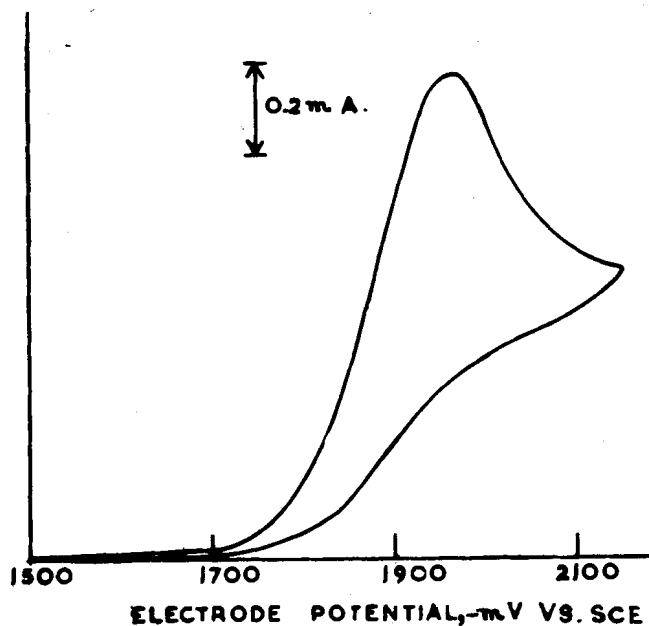


Fig. 3 : Typical cyclic voltammogram for the reduction of 0.01509M solution of acrylonitrile in 0.2M (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr, pH 8.0, temp 32°C

in 0.2M tetraethylammonium bromide at pH 8.0. Single well-defined peak was formed in the cathodic scanning up to the potential of hydrogen evolution and no complementary anodic peak appeared on the reverse scan. The sweep rate was varied from 0.025 V/sec to 2.0 V/sec and the effect of sweep rate on the peak potential and peak current was found out. Figure 4 shows the effect of sweep rate on the cyclic voltammograms recorded for the reduction of  $0.75 \times 10^{-1}$  M AN. The peak potential,  $E_p$ , was

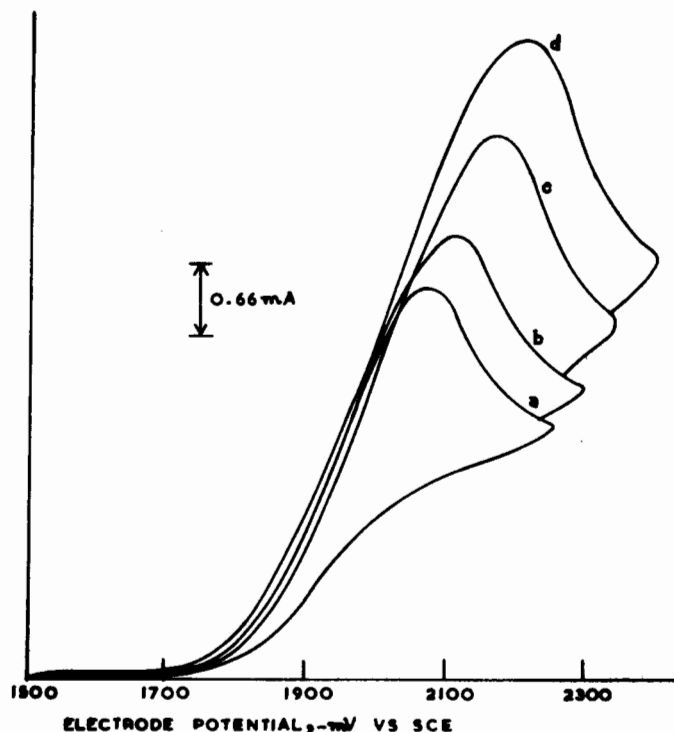


Fig. 4 : Effect of sweep rate on the cyclic voltammograms obtained for the reduction of 0.075M acrylonitrile solution pH 8.0, temp  $32^\circ\text{C}$   
(a) 25 mV/sec, (b) 50 mV/sec, (c) 100 mV/sec and (d) 150

found to shift in the cathodic direction as the sweep rate was increased and this  $E_p$  shift was observed for the whole range of concentration studied. Cathodic shift of peak potential was also observed with respect to concentration of AN as shown in Table I.

**Table I : Effect of concentration of acrylonitrile on peak parameters**

Concn. of AN, M	Scan rate V/sec	$-E_p$ mV	$-E_p/2$ mV	$i_p$ mA
0.01509	0.025	1963	1865	1.08
0.04528	0.025	2025	1895	2.59
0.07547	0.025	2077	1920	3.76
0.1056	0.025	2120	1950	4.00
0.1509	0.025	2200	2015	5.00
0.01509	0.250	2075	1930	2.80
0.04528	0.250	2200	1980	6.14
0.07547	0.250	2300	2025	7.50
0.1056	0.250	2355	2065	10.00
0.1509	0.250	2490	2140	11.70

The observed shift of peak potential in the cathodic direction and the absence of anodic peak on the reverse scan in cyclic voltammetric studies have suggested that the overall process is an irreversible process.

Figure 5 shows the plot of  $E_p$  vs logarithm of sweep rate.

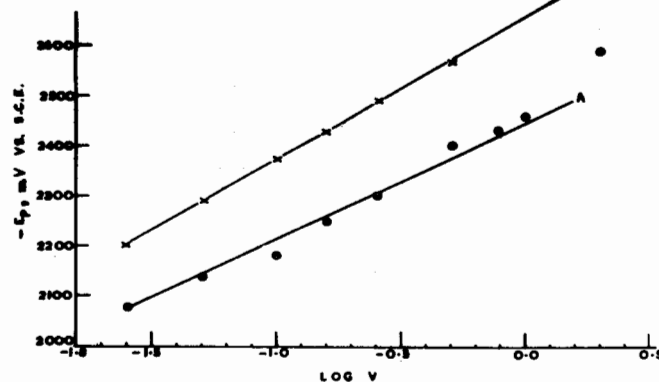


Fig. 5 :  $E_p$  vs  $\log v$  plot for the reduction of acrylonitrile (a) AN concn 0.075M, (b) AN concn 0.1509M.

The above relationship was found to be linear but the shift of peak potential with a slope of  $-240$  mV and  $-290$  mV per decade change of sweep rate for slightly lower and higher concentrations of AN respectively did not fit into the normal values (30-40 mV per decade) expected for an irreversible charge-transfer process or reversible charge-transfer process followed by a fast irreversible chemical reaction [9].

Peak current ( $i_p$ ) values obtained at different sweep rates were corrected to the background current recorded at the corresponding sweep rates and the current function values  $i_p/V^{1/2}$  were not found to be constant as shown in Table II. This indicates that the

**Table II : Current function values ( $i_p/V^{1/2}$ ) at different sweep rates and concentration conditions.**

Concn. of AN M	Sweep rate V/sec	$V^{1/2}$ S $^{-1/2}$	$i_p$ mA	$i_p/V^{1/2}$ *
0.0453	0.025	0.1581	2.590	0.0164
	0.050	0.2236	3.200	0.0143
	0.100	0.3162	4.100	0.0130
	0.150	0.3872	4.800	0.0124
	0.250	0.5000	6.138	0.0123
0.075	0.500	0.7071	8.200	0.0116
	0.025	0.1581	3.762	0.0238
	0.050	0.2236	4.224	0.0189
	0.100	0.3162	5.148	0.0163
	0.150	0.3872	6.138	0.0159
0.151	0.250	0.5000	7.500	0.0150
	0.500	0.7071	10.400	0.0147
	0.025	0.1581	5.000	0.0316
	0.050	0.2236	6.100	0.0273
	0.100	0.3162	7.900	0.0250
	0.150	0.3872	9.500	0.0245
	0.250	0.5000	11.700	0.0234
	0.500	0.7071	15.600	0.0221

\*  $i_p/V^{1/2}$ ,  $i_p$  in amperes, V in Volt. sec.  $^{-1}$ .

coupled chemical reaction and/or adsorption are controlling the overall electrode process.

**Adsorption:** Table III shows the  $E_p^{1/2}$  and  $E_p$  values obtained in cyclic voltammetric measurements for the reduction of AN on carbon electrode using different electrolytes.

**Table III: Cyclic peak parameters with different electrolytes: 0.04528 M AN; Sweep rate, 0.025 V sec<sup>-1</sup>; pH 8.0; temp. 33°C**

Supporting electrolyte	$-E_p$ mV	$-E_p^{1/2}$ mV	$i_p$ mA
0.2M KCl	2090	1970	2.64
0.2M NaClO <sub>4</sub>	2125	1990	2.40
0.2m (C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr	2025	1895	2.59
0.2M (CH <sub>3</sub> ) <sub>4</sub> NCl	2095	1970	2.17
1.0M (CH <sub>3</sub> ) <sub>4</sub> NCl	1995	1905	2.44

The lower values of  $E_p^{1/2}$  and  $E_p$  obtained with tetraalkylammonium salt as supporting electrolyte indicate that the reduction of AN is accelerated by the presence of tetraalkylammonium cations.

Adsorption of AN on mercury cathode has already been established [15,16]. The co-adsorption of AN with tetraalkylammonium cations has been confirmed by differential capacity measurements. The adsorption of AN on glassy carbon electrode is also confirmed by the present cyclic voltammetric studies. Enormous cathodic shift of peak potential is also observed unusually in the cathodic direction with increasing concentration of AN. These observations are characteristic for strong adsorption and are comparable with some of the reactant adsorption-involved systems [17,18] and therefore give an indirect evidence that the reactant is strongly adsorbed on glassy carbon electrode.

**Mechanism of reduction:** Recent study of the electrochemical reduction of AN on mercury electrode in lithium citrate containing very low concentration of dodecylethyldimethylammonium bromide revealed that the reduction mechanism and the reduction product changes with concentration of AN. Similarly in the present study, an increase of AN concentration by only one order of magnitude (from 10<sup>-2</sup> to 10<sup>-1</sup> M) has caused a change in the Tafel slope value and therefore a change in the mechanism of reduction on glassy carbon electrode. Tafel slope value of -60 mV per decade obtained at lower concentration (Fig. 2) indicates that the charge transfer reaction is reversible though the exact product is not identified. At higher concentration of AN the observed Tafel slope value of -120 mV per decade and the slope value of -130 mV for  $\delta E_{1/2} / \delta \log C_{AN}$  indicate that as the concentration of

acrylonitrile increases, the charge transfer reaction is retarded on glassy carbon electrode and the transfer of the first electron is the rate-determining step in the overall electrode process. This is in accordance with the observation [10] in experiments with higher concentration of AN in higher concentration of tetraalkylammonium salt as supporting electrolyte. The above type of reduction of AN may be due to the change in the adsorption behaviour with concentration.

Controlled potential electrolysis experiment has shown that the hydrodimer, ADN, is the reduction product formed under higher concentration of AN. Since adsorption effects are involved, the present experimental results could not be utilised to distinguish between the possible pathways for the formation of hydrodimer such as radical anion-radical anion coupling and radical anion-substrate coupling.

## REFERENCES

1. M M Baizer, *J Electrochem Soc* **111** (1964) 215.
2. M M Baizer and D E Danly, *Chemistry and Industry*, 7 July (1979) 433.
3. Asahi Chemical Industry Co. Ltd., Fr Pat 1503244, Nov 24 (1967) c.f. C.A. **69** (1968) 76685.
4. M V Childs and H C Walters, *Hydrocarbon Process*, **57** (1978) 139.
5. D E Danly, *Hydrocarbon Process*, **60** (1981) 161
6. Monsanto Co., US Pat 3193480 (1961)  
H M Fox and F N Ruchlin, US Pat 3689382, Sep 5 (1972)  
D L Sadler and W A Heckle, US Pat 3897318, Jul 29 (1975)  
J H Lester and J S Stewart, US Pat 3898140, Aug 5 (1976)
7. M M Baizer and J P Petrovich in A Streitwieser and P W Taft (Eds), *Progress in Physical Organic Chemistry*, Vol. 7 Wiley Interscience, New York, (1970) 189-227.
8. F Beck, *Angew Chem Int Ed Eng*, **11** (1972) 760.
9. E Lamy, L Nadjio and M Saveant, *J Electroanal Chem* **42** (1973) 189.
10. F Beck, *Ber Bunsenges Phy Chem* **72** (1968) 379.
11. G Piccardi and R Guidelli, *J Electroanal Chem* **90**(1978) 173.
12. A P Tomilov, E V Kryukova, V A Klimov and I N Brago, *Elektrokhimiya*, **3** (1967) 1501.
13. M Krumpelt, E Y Weissman and R C Alkire (Eds), *Electroorganic Synthesis Technology*, AIChE symposium Series No. 185, V. 75, (1979) 19.
14. A Verheyden, A Hendrickx, C Van Eygen and J Walravens, Brit Pat 1117677, Jun 19 (1968); c.f. C.A. **69** (1968) 43483.  
J Bizot, G Bourat and D Michelet, Fr Pat 1491516, Aug 11 (1967); c.f. C.A. **69** (1968) 7875.  
J Bizot, G Bourat and D Michelet, Fr Pat 1548304 Dec 6 (1968) c.f. C.A. **71** (1969) 80743.
15. A P Tomilov, L A Fedorova, V A Klimov and G A Tedoradze *Elektrokhimiya* **4** (1968) 1264; **7** (1971) 976.
16. G Piccardi, I Nucci, F Pergola and R Guidelli, *J Electroanal Chem* **164** (1984) 145.
17. R Celdran and Gonzalez-Velasco, *Electrochim Acta* **26**(1981) 763.
18. Ch Slifstein and M Ariel, *J Electroanal Chem* **75** (1977) 551.