

NOTE

Anodic Investigation and Determination of N-methyl Pyrrole

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In the present research, the anodic oxidation of N-methyl pyrrole (NMP) by CV method in aqueous solution and different pH on platinum and glassy carbon electrodes have been studied. The rate of anodic oxidation of NMP in phosphate buffer (pH = 6.8) at Pt electrode is higher than in acidic or alkaline media and the increase of scan rate in this pH increases the peak current. The CV method results show that, when anionic species such as ferricyanide are present in acid solution, the polymerization rate of NMP increases considerably. The results by controlled potential coulometry ($E_a = 1.1$ V) show that the oxidation of NMP in acidic and neutral media gives up one electron per one molecule of monomer. The optimum condition for the determination of NMP by DPV is also determined.

Key Words: Anodic oxidation, Electropolymerization, N-methyl pyrrole, Coulometry.

Preparation of polymers by electropolymerization has been investigated at different situations for production of insoluble, compact and smooth films. Electropolymerization of some monomers¹⁻⁴ and specially pyrrole⁵⁻⁹, recently has been widely applied to conductive polymers¹⁰⁻¹⁴. The electropolymerization of N-methyl pyrrole by CV, coulometry methods and its determination by DPV have been studied.

All chemicals were of analytical grade (Merck). Sodium trifluoroacetate buffer (0.2 M) (pH = 2) and phosphate buffer (pH = 2) for acidic media, phosphate buffer (pH = 6.8) for neutral media and phosphate buffer (pH = 9) for alkaline media have been used.

Experiments were conducted at constant temperature ($25^\circ\text{C} \pm 0.1$). Measurements were carried out with a polarograph 746 VA trace analyzer and 747 VA stand (Metrohm, Swiss), using Ag/AgCl/KCl 3 M as reference electrode. Experimental conditions were chosen for CV and DPV as follows:

CV: t. step = 20.0 m s, U. step = 2 mV/s, sweep rate = 100 mV/s, I. range = 450 μA .

DPV: U. step = 6 mV, t. pulse = 40.0 m s, t. means. = 20.0 m s, t. step = 0.30 s, U. ampl. = 50 mV, sweep rate = 20 mV/s.

In coulometry, Behpajoo (BHP, Iran) 2050 coulometer and carbon working electrode have been used.

RESULTS AND DISCUSSION

The electropolymerization of N-methyl pyrrole has been studied by CV coulometry methods and its determination by DPV as discussed in the following parts:

(a) CV studies: Cyclic voltammetry experiments showed that NMP belongs to one irreversible system at Pt and glassy carbon electrodes.

Anodic oxidation of NMP 0.028 M in phosphate buffer at different pH (2, 6.8 and 9) has been investigated and the results showed the best oxidation occurs in pH = 6.8 (Fig. 1).

The increase of scan rate in pH = 6.8, showed a positive potential shift and the variation of the peak current vs. the square root of scan rate ($v^{1/2}$) from 100 to 300 mV/s is linear ($R^2 = 0.9823$).

The presence of 2 mM of potassium ferricyanide $K_3Fe(CN)_6$ ¹⁵ in 0.2 M sodium trifluoroacetate buffer (pH = 2) at Pt electrode caused an increase rate of electropolymerization of NMP about 100% (Fig. 2).

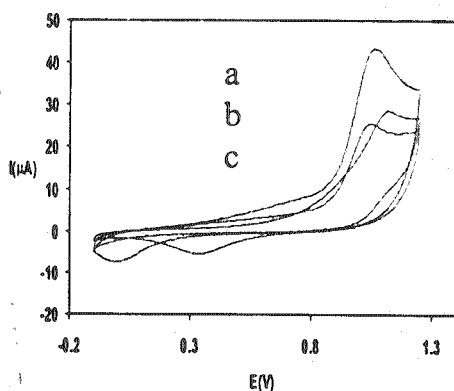


Fig. 1. CV voltammograms of N-methyl pyrrole 0.028 M in the different pH phosphate buffer: (a) 6.8, (b) 2 and (c) 9 (scan rate = 100 mV/s)

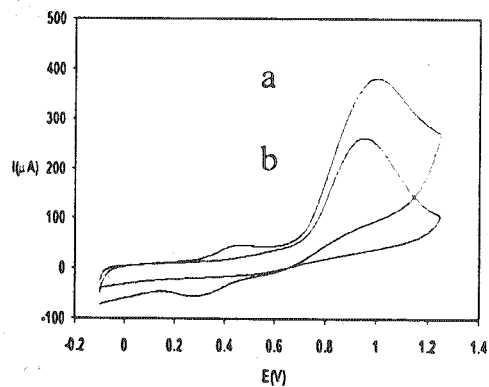


Fig. 2. CV voltammograms of 0.028 M N-methyl pyrrole in the 0.2 sodium trifluoroacetate buffer (pH = 2) at Pt electrode: (a) after and (b) before addition of 2 mM potassium ferricyanide

(b) Coulometric studies: The results of coulometric studies by controlled potential coulometry ($E_a = 1.1$ V) at carbon electrode in sodium trifluoroacetate buffer (pH = 2) and phosphate buffer (pH = 6.8) showed the oxidation of NMP in acid and neutral media, gives up one electron per one molecule of monomer.

(c) Determination by DPV: In DPV, the normal voltammograms were obtained with a peak potential nearly same as seen in CV studies. The present results show a linear dependence between I_p and concentration, in the range of 4.7×10^{-3} to 1.8×10^{-2} M ($R^2 = 0.9944$) (Fig. 3) in the phosphate buffer (pH = 6.8), with 380 ppm detection limit.

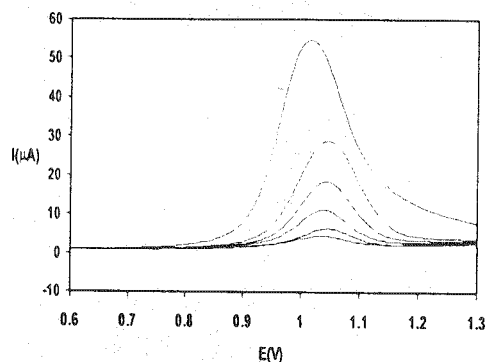


Fig. 3. DPV voltammograms of N-methyl pyrrole in the range of 4.7×10^{-3} to 1.8×10^{-2} M (scan rate = 20 mV/s)

Conclusion

The present experiments by CV showed that NMP did not have a reversible behaviour, but variation of I_p vs. $v^{1/2}$ is linear and anodic oxidation of NMP in neutral media is faster than acid and alkaline media. The presence of ferricyanide ions increases the rate of electropolymerization, only in acid media. Finally, the electroanalytical determination of NMP is possible by DPV method.

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(Received: 11 October 2005; Accepted: 6 March 2006)

AJC-4736