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Electroanalytical studies on ethoxylation of phthalic acid

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ABSTRACT

Phthalic acid is an organic compound of modest commercial importance. The literature revealed that the chemical and physical properties of phthalic acid had been explored much. But a very little work has been done in the electro analysis of phthalic acid and of other aromatic compounds in general. This work is concentrated on the cyclic voltammetric studies of phthalic acid. Cyclic voltammograms have been recorded using different working electrodes, in different pH conditions, in different scan rates and with multiple scans. These studies revealed that ethoxylation of phthalic acid is diffusion controlled and there is no polymer formation on the electrodes.

Key words: Cyclic voltammetry, Phthalic acid, Ethoxylation, Electro analysis, Electrode process

INTRODUCTION

Phthalic acid is a disubstituted aromatic compound of modest commercial importance. It is very much used as an ingredient for the manufacture of polyester and alkyd resins. It is also used in the manufacture of anthraquinone (a dye intermediate), phenolphthalein (a laxative and acid – base indicator) and phthalocyanine pigment. Several chemical and physical studies have been extensively done on phthalic acid. But the literature contains very little reports on electro analysis of phthalic acid. Recently the electro chemical analytical studies on methoxylation[1] of various mono substituted aromatic compounds have been examined and reviewed.

In this present work cyclic voltammograms were recorded using platinum and glassy carbon electrodes as working electrode, Ag/AgCl electrode as reference electrode and platinum electrode as counter electrode. The ethoxylation of phthalic acid was carried out in a solution containing $1 \times 10^{-3} \text{M}$ phthalic acid, 0.5M ethanol and 1M $\text{H}_2\text{SO}_4/\text{KCl}/\text{KOH}$. H_2SO_4 , KCl and KOH were used as supporting electrolytes and also used to change the pH of the medium. In the present work anodic peak potential was found out in different pH conditions and on different working electrodes. The scan rate was varied to find out whether the ethoxylation of phthalic acid is diffusion controlled or adsorption controlled. For assertion of polymer formation on the electrode surfaces, multiple scans study was also done.

MATERIALS AND METHODS

Apparatus

Voltammograms were recorded using Versa STAT 3 (Princeton Applied Research, USA) interfaced with a computer. Three electrodes system containing a working electrode of platinum or glassy carbon, a reference

electrode of Ag/AgCl electrode and a counter electrode of platinum wire was used. The working electrodes and the counter electrode were pretreated by polishing them with alumina-water slurry followed by washing in an ultrasonic bath.

Reagents and solution

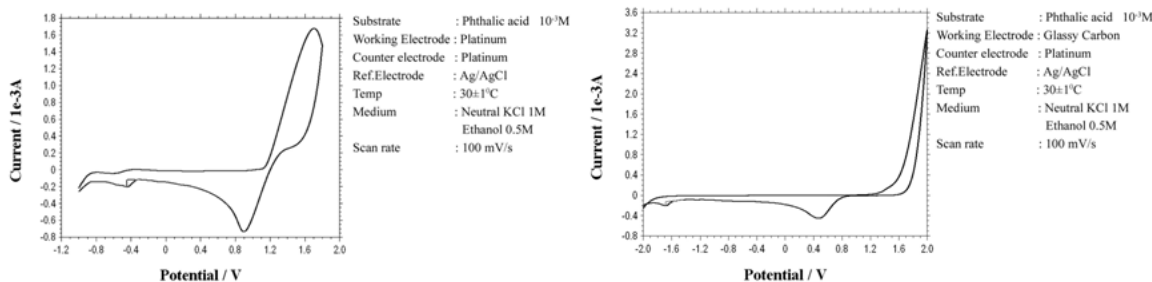
All the chemicals used were of analytical reagent grade. Double distilled water was used to prepare solutions. 0.001M phthalic acid, 0.5M ethanol and 1M H₂SO₄/KCl/KOH were prepared freshly. A pen type pH meter was used to find the pH of the reaction mixture. The solutions were stored in a light tight and cool location.

Methodology

The three electrode system was constructed with platinum/glassy carbon working electrode, platinum counter electrode and Ag/AgCl reference electrode in an undivided cell. To change the pH of the reaction mixture 1M solution of H₂SO₄/KCl/KOH was added. These solutions also worked as sources of supporting electrolytes. Then the cyclic voltammograms were recorded at different working electrodes, with different pH conditions and with different scan rates.

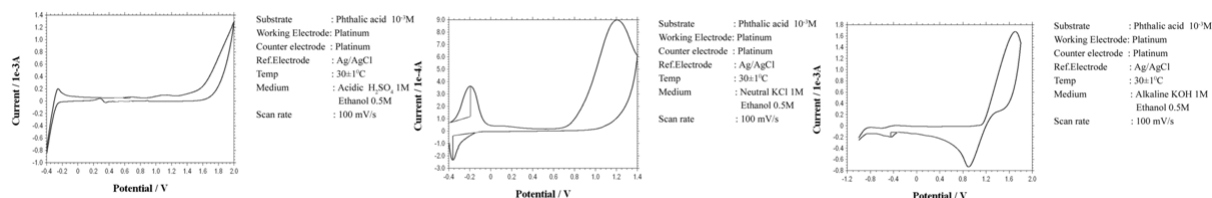
RESULTS AND DISCUSSION

Cyclic voltammograms on platinum and glassy carbon electrodes:



According to the earlier studies done by D.R. Henton[2], the oxidation of substituted aromatic compounds is a two electron process. Hence two distinct peaks were expected but in the cyclic voltammogram only one distinct peak was obtained. This indicates that the electron withdrawing group present in the benzene ring destabilizes the aromatic system and reduces the π electron density, which makes the removal of electron difficult consequently the oxidation potential increases to higher positive value. As a result the potential for the first electron oxidation must have been shifted to the second electron oxidation potential. Therefore even at slow scan rate one single peak was observed with increased current flow. For phthalic acid reduction peak was also observed in the reversal scan. The height of the peak is a qualitative indication of extend of current flow. On the basis of electrokinetic principle, the peak height and the rate of the reaction are in direct correlation [3, 4]. Hence increased height is the indication of difficulty in the formation of intermediate and the low reaction rate [4, 5, 6]. Significant peaks were not observed on glassy carbon electrode. This may be due to the adsorption of the reactant molecules on the electrode surface. Hence the further studies like pH variation study, scan rate variation study and multiple scan study were done with platinum working electrode.

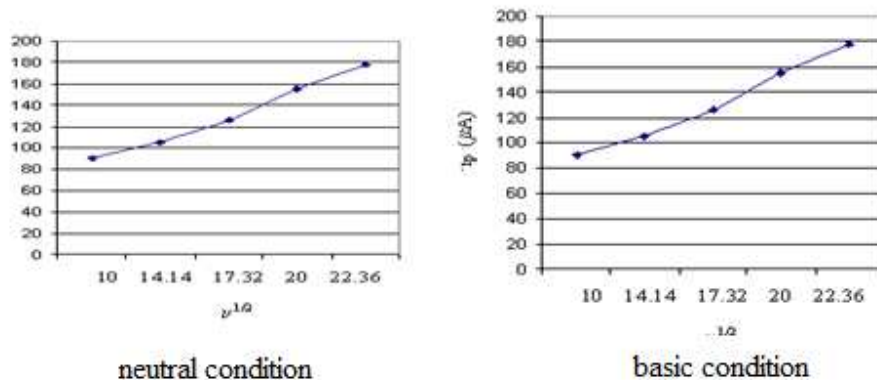
pH variation studies:



In neutral and alkaline condition the peak potentials were almost similar. The oxidation and reduction peaks were not found in the cyclic voltammogram recorded in the acidic condition. This is due to the difficulty in the formation

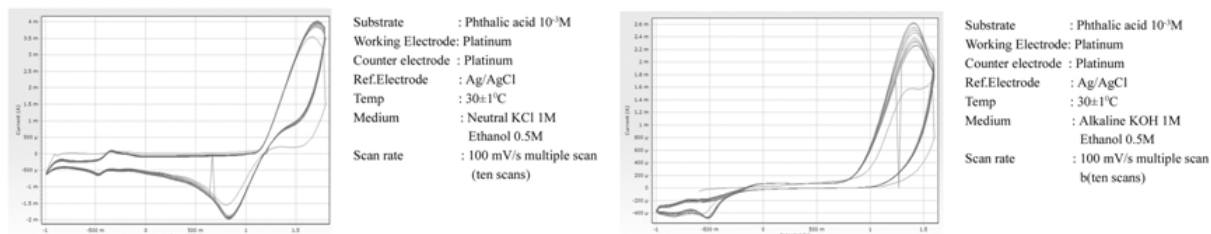
of ethoxide ion and also due to the protonation of the medium to a greater extent. In the ethoxylation process, production ethoxide ion from ethanol was expected to happen. Production of ethoxide ion is evident by the work done by Reeve, Erikson and Alutto[7]. According to them ethoxide ion formation is favored in neutral and alkaline conditions but such ion formation is not found in acidic condition.

Scan rate variation studies



As significant peaks were missing in the cyclic voltammograms recorded in acidic condition, scan rate variation studies were done in neutral and alkaline media. In both cases a linear relationship is observed between $\log(i_{pa})$ and $\log v$ (where i_{pa} is anodic peak current and v is scan rate). Furthermore the plot between the peak current and the square root of scan rate produces a straight line which does not pass through origin which suggests the irreversible character of the electron transfer [8] and the direct proportional relation between anodic peak current and the square root of scan rate indicates that the electron transfer process is diffusion controlled [9].

Multiple scan studies



In the multiple scan studies, the potential sweep at a scan rate of 100mV/s was repeated for ten times, through the same reaction mixture without disturbing the assembly of the experimental setup. This was done to ascertain the probability of formation of polymers on the electrode surface. If polymerization was possible, anodic peak current would be present in the first scan, at this potential polymerization would take place and a film would be formed on the electrode, and the peak would be missing in the subsequent scans. In the present study anodic peak was observed in all scans, but there was a small lowering of the anodic peak current, with the number of successive scans, this was due to the adsorption tendency of the ethoxylated product but not due to polymer formation [10].

CONCLUSION

In the present work the cyclic voltammograms of phthalic acid were recorded by changing the conditions like pH, working electrodes, scan rate and multiple scan. The following are the conclusions arrived at from the observations

- Phthalic acid is susceptible for oxidation
- Ethoxylation is not taking place on glassy carbon electrode
- Ethoxylation is effective in neutral and alkaline conditions.

- The process is diffusion controlled on platinum electrode.
- Ethoxylation process is irreversible.

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REFERENCES

- [1] Norman L, Weinberg, *J. Org. Chem.*, **1968**, 33 (12), 4326 – 4329.
- [2] Henton D. R, Chenard B. L and Swenton J.S, *J.Chem. soc, Chem. Commun*, **1979**, 326.
- [3] Ahlberg E and Parker V.D, *Acta Chem. Scand. B* **1980**, 34,71.
- [4] Scharbert B and Speiser B, *J. Chemomet*, **1988**, 3, 61-80,.
- [5] Evans C. H, *Chem. Rev.* **1990**, 90, 739-751,
- [6] Amatore C and Saveant J. M, *J. Electro anal. Chem.* **1997**, 85, 27-46,
- [7] Reeve, Erikson and Aluotto, *Can. J. Chem.*, **1979**, 57, 2747.
- [8] Feldberg S.W and Jetic L, *J. Phys.Chem* **1972**, 76, 2439.
- [9] Shui Ya Kishika and Akifuni Yawada, *Electrochimca Acta*, **2005**, 51, 464.
- [10] Yuan D.S, Tan S.Z, Zeng J.H, Hu F.P, Wang X and Shen P.K, *Carbon* **2008**, 46, 531.