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Electroorganic Synthesis and Characterization of 4-Ethoxy Acetanilide using Platinum and Graphite as Anodes

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Abstract

Alkoxy group substituted compounds of acetanilide are found to have pharmacological and industrial importance. Synthesis of alkoxy substituted acetanilides via conventional thermal methods involves multi-step processes, formation of side products, and the poor yield of desired products. But, the vast literature studies reveal that electroorganic synthesis of alkoxy substituted acetanilide derivatives would be effectively carried out through electrochemical oxidation methods. The direct substitution of the ethoxy (alkoxy) group onto the aromatic ring, an electrophilic substitution, has not been attempted so far. This concept is taken as a preparatory attempt to find an alternative method to the tedious chemical route and to invent a direct method of introducing the ethoxy groups into the aromatic ring in a single step. A polarization study on acetanilide with ethanol as an electrolyte is carried out on platinum and graphite anodes to find out the oxidation potentials. Electrochemical ethoxylation of acetanilide at the platinum electrode is done by the Potentiostatic method using the oxidation potentials. The products are separated using preparative TLC and purified with suitable solvents. The products are characterized by UV, IR, NMR, and Mass spectra.

Keywords: Anodic ethoxylation; 4-Ethoxy acetanilide; Electroorganic synthesis.

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1. Introduction

The electrochemical methoxylation and ethoxylation of aromatic compounds can be used to synthesize polymers and plasticizers, valuable lubricating oils, emulsifying agents, perfumes, pharmacological drugs, inhibitors of the oxidation of petroleum products, and biologically active preparations [1]. Electrochemical ethoxylation of mono- and di-substituted aromatic compounds on platinum and graphite anodes are found to yield ethoxy substituted aromatic compounds of industrial and pharmaceutical importance [2].

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Literature review reveals that vast anodic oxidative studies on aromatic compounds such as hydroxylation [3], halogenations [4], cyanation [5], and acetoxylation [6] have been done already. But, only a small quantum of work on ethoxylation of acetanilide is found in the literature. Recently the electrochemical analytical studies on methoxylation of various monosubstituted aromatic compounds have been examined and reviewed [7].

In this present work, platinum and graphite are taken as the working electrode. The oxidation potentials of the working electrode are found with respect to Ag/AgCl reference electrode through polarization studies. The anodic ethoxylation of acetanilide was carried out using ethanol as solvent and KOH, KCl, and H_2SO_4 as the supporting electrolytes. The work is carried out to ethoxylate acetanilide and characterize the product using spectral techniques. The supporting electrolytes are used to make the substrate diffuse through the reaction mixture and make the system acidic, neutral, and alkaline, thereby changing the pH of the system.

2. Materials and Methods

2.1. *Apparatus*

Cyclic Voltammograms were recorded with potentiostat CH 10 (Sinsil international) interfaced to 663 VA stand (Metrohm) and SyncMaster B1930 computer. A three-electrode configuration was used with platinum and graphite as the working electrodes, a silver-silver chloride reference electrode, and a platinum electrode wire as the auxiliary electrode. The working electrode was pretreated by polishing it with alumina – water slurry followed by washing in an ultrasonic bath.

2.2. *Reagents and solutions*

Analytical grade reagents and double distilled water were used for the entire experiment. The solutions 0.001 M Acetanilide, 1 M $H_2SO_{4/}$/KOH/KCl, 0.5 M Ethanol were prepared freshly. The pH of the different reaction mixtures was measured with a pen-type pH meter. The solutions were stored in a light-protected, cool location.

2.3. *Methodology*

The three-electrode system with platinum or carbon as the working electrode, platinum wire as the auxiliary electrode, and Ag/AgCl electrode as the reference electrode was constructed in an undivided cell. In order to change the pH of the system, 1 M solutions of $H_2SO_{4/}$/KOH/KCl were taken. As these solutions show high electrical conductivity, they also serve as supporting electrolytes. Cyclic voltammograms were recorded to find out the feasibility of oxidation and its nature of reversibility [8,9].

The polarization studies were also done using a three-electrode system. By knowing the exact oxidation potential from polarization studies, the synthesis was carried out using platinum/graphite working electrode, platinum auxiliary electrode, and saturated calomel electrode as reference electrodes at constant potential conditions. The preparative electrochemical oxidation was carried out, potentio statically, using 2 –12 V regulated DC power supply [Murphy, India]. All the working potentials of the working electrode were measured with reference to the saturated calomel electrode (SCE) with the help of a digital voltameter, [Philips pp 9000, UK].

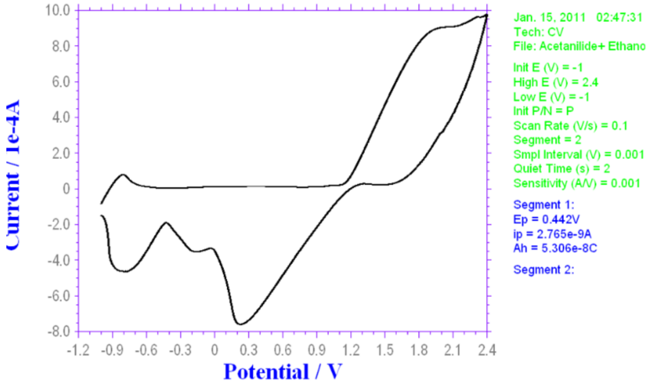
3. Results and Discussion

3.1. *Cyclic voltammetric studies*

In a typical reaction, the substrate acetanilide was dissolved in ethanol, and a 10-20 mM concentration solution was prepared. In order to have pH variation, 1 M solutions of H_2SO_4, KCl and KOH were used to record cyclic voltammogram in acidic, neutral, and alkaline conditions, respectively.

A reaction mixture of substrate (acetanilide) solution and supporting electrolyte solution was made in such a way that the supporting electrolyte concentration was 1000 times greater than the substrate concentration. The mixture was purged with nitrogen gas to remove dissolved oxygen to make the cyclic voltammogram noise-free. The scan rate was fixed at a rate of 100 mV/s for all the substrates in three different media conditions.

The cyclic voltammogram obtained for ethoxylation of acetanilide in the basic medium at platinum electrode presented only one anodic peak at 1.8 V. From the literature [10], it is found that electrooxidation of substituted aromatic compounds is a two-electron process. Hence, two anodic peaks were expected. However, only one peak at 1.8 V was observed. This may be due to the electron-donating nature of the anilide group, which might have made the two electrons leave the system simultaneously at one potential [11]. A cathodic peak in the potential reversal scan was observed at -0.9 V. There are two anodic peaks at 1.7 and 2.1 V in the cyclic voltammogram of acetanilide with ethanol in a neutral medium, with no cathodic peak is observed.



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Low E (V) = -1
Init P/N = P
Scan Rate (V/s) = 0.1
Segment = 2
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 0.001

Segment 1:
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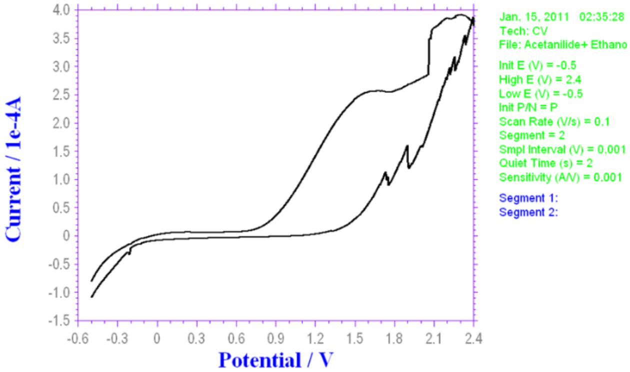
Ah = 5.306e-8C

Segment 2:

Fig. 1. Basic medium (KOH, 1 M).



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Segment = 2
Smpl Interval (V) = 0.001
Quiet Time (s) = 2
Sensitivity (A/V) = 0.001
Segment 1:
Segment 2:

Fig. 2. Neutral medium (KCl, 1M).

3.3. *Polarization studies*

A saturated calomel electrode was coupled with the anode through a salt bridge. One of the limbs was drawn into a lugging capillary to avoid resistance and keep the reference electrode as close as possible to the working electrode. The cell was connected in the circuit, consisting of a digital milliammeter connected in series to note the current. A digital voltammeter was connected in between the anode and the SCE. The applied potential was changed at regular intervals in equal quantum, and the corresponding current variation was recorded. The current–potential curve was drawn for the pure solvent – electrolyte system. The above experimental procedure was repeated with the addition of a 0.1 M substrate. A graph was plotted, taking potential in the X-axis and current in the Y-axis. The current-potential curve provided information about the decomposition potential at which the substrate underwent chemical changes.

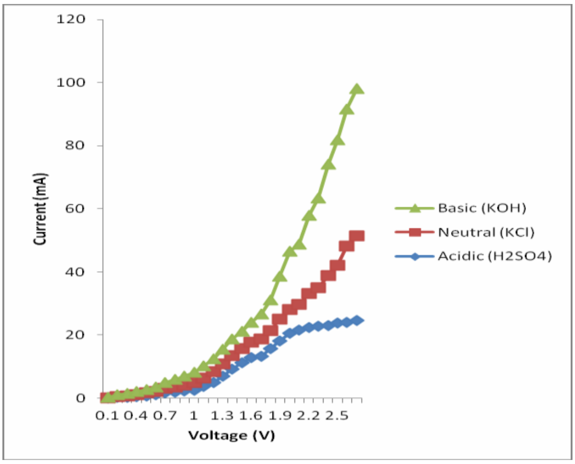


Fig. 3. Graphical representation of polarization studies on acetanilide (Current vs. Potential, at the platinum anode).

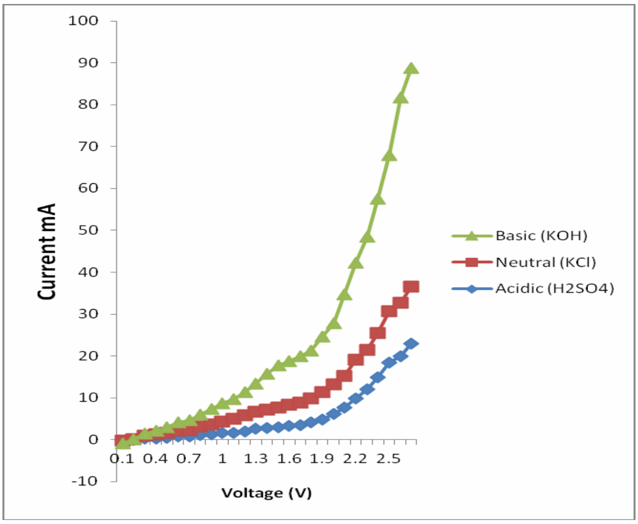


Fig. 4. Graphical representation of polarization studies on acetanilide (Current vs. Potential, at graphite anode).

The working potentials of acetanilide at graphite and platinum electrodes at different pH media are obtained from polarization studies are tabulated below.

Table 1. Working potentials of acetanilide.

Substrates	At Graphite electrode (Volts)			At Platinum Electrode (Volts)		
	Acidic	Neutral	basic	Acidic	Neutral	basic
Acetanilide	1.30	1.20	1.10	1.60	1.50	1.30

The electrosynthesis of acetanilide was carried out at constant potential conditions, i.e., at the specified decomposition potentials obtained from polarization studies (potentiostatic method) using a divided H-Cell and an undivided cell.

3.3. *Product analysis*

An aliquot was drawn periodically from the organic phase and analyzed by HPLC using a SHIMADZU LC-8A column (250 × 4.6 mm) as the stationary phase. The eluent consisted of acetonitrile/water (80:20) at a flow rate of 1 mL/min. Samples were analyzed at a wavelength of 254 nm with a UV detector. UV-1280 UV-Visible spectrometer (make: Shimadzu) was used to record the UV-Visible spectrum of the ethoxylated product.

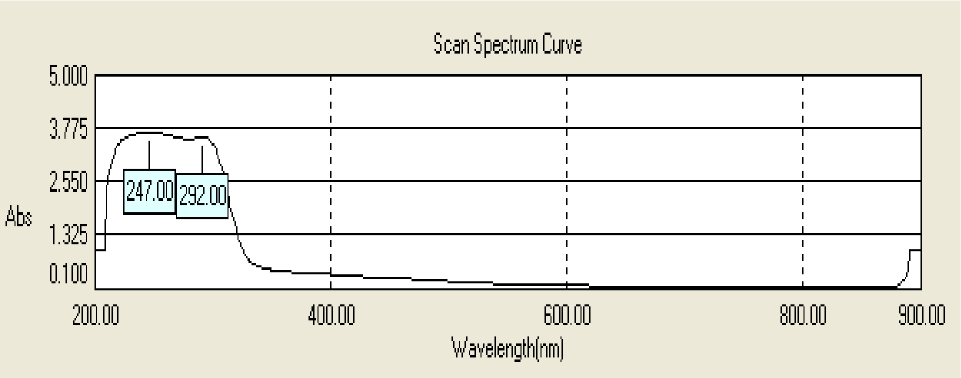


Fig. 5. UV spectrum of ethoxylated acetanilide.

There are two bands observed at 247 and 292 nm in the UV-Visible spectrum of ethoxylated acetanilide. These two absorptions are due to π - π* transitions which confirmed the existence of the benzene ring in the product.

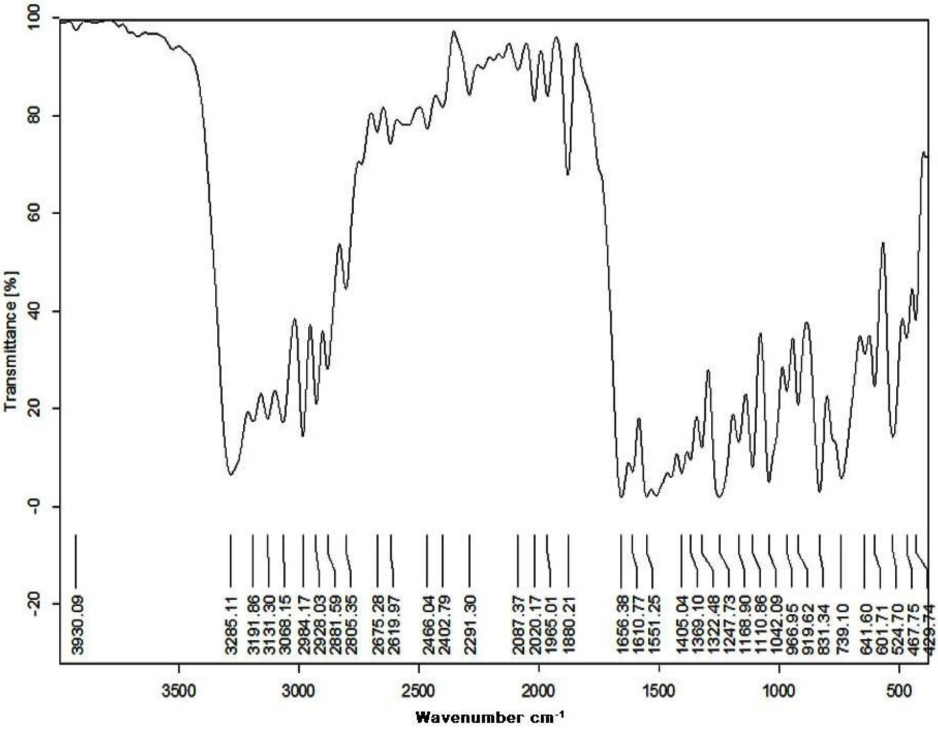
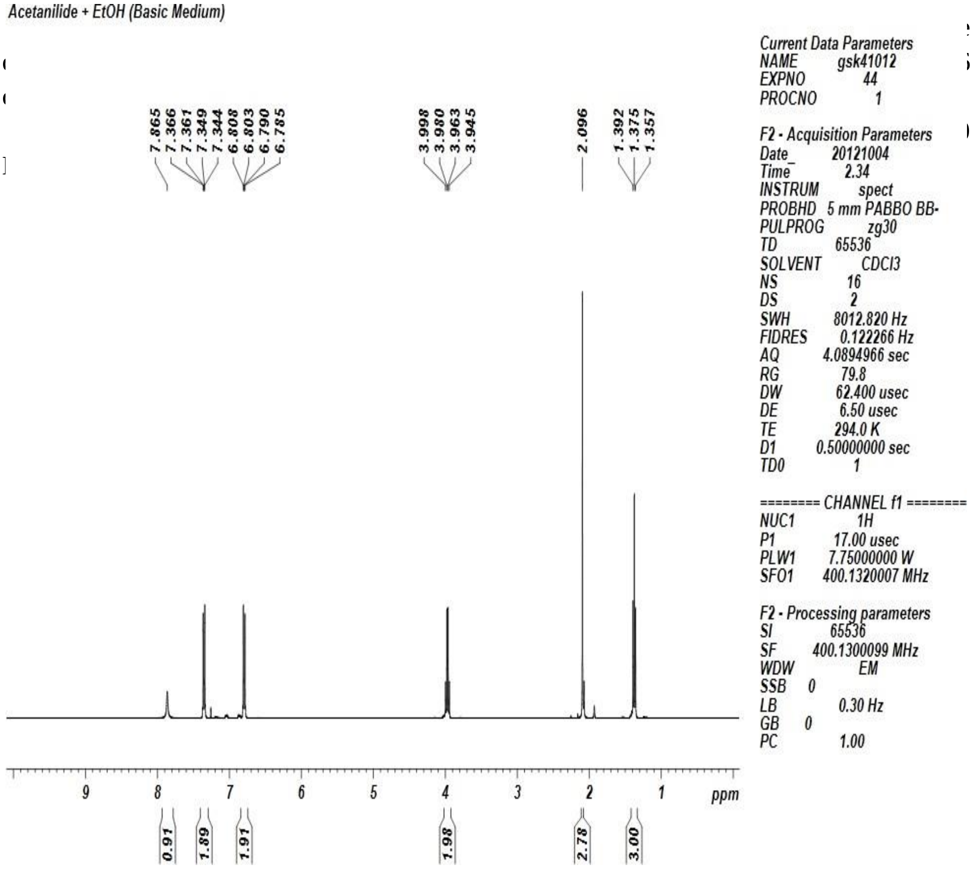


Fig. 6. IR spectrum of ethoxyated acetanilide.

Table 2. IR spectral value for the product, 4-ethoxy acetanilide.

Sl. No	Wave number (cm^{-1})	Absorbance
1	3930.39	O-H stretch
2	3285.11	O-H stretch, alcohols
3	3191.86	N-H stretch, amines
4	3131.30	N-H stretch, hydrogen-bonded
5	1405.04	C-O stretch (esters, ethers, and alcohols)
6	1247.73	C-O stretch, ethers
7	1168.09	$-OCH_3$ group ethers
8	1110.86	$-OCH_2CH_3$ group ethers
9	831.34	p- Di-substituted aromatic derivatives



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PROCNO             1

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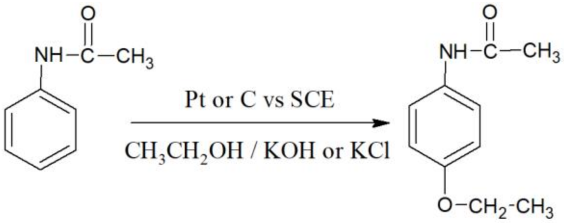
PULPROG         zg30
TD             65536
SOLVENT        CDCl3
NS                16
DS                 2
SWH      8012.820 Hz
FIDRES   0.122266 Hz
AQ      4.0894966 sec
RG              79.8
DW       62.400 usec
DE         6.50 usec
TE           294.0 K
D1     0.50000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              1H
P1        17.00 usec
PLW1    7.75000000 W
SFO1  400.1320007 MHz

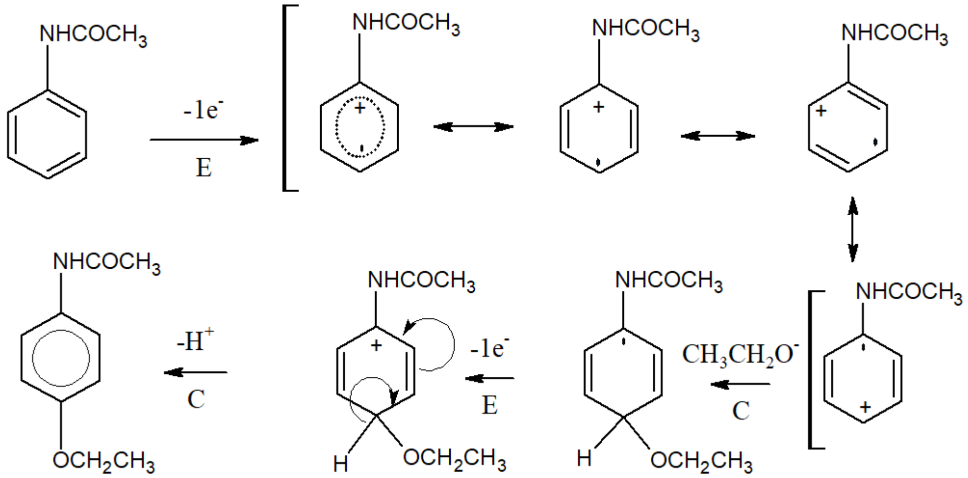
F2 - Processing parameters
SI             65536
SF    400.1300099 MHz
WDW               EM
SSB    0
LB           0.30 Hz
GB     0
PC              1.00
```

Fig. 7. NMR spectrum of ethoxylated acetanilide.

The proton integration in the NMR spectrum noticed the presence of 13 hydrogens. The broad peak at δ 7.8 ppm accounted for the existence of –NH proton. The triplet peak at δ 1.3 ppm favored the presence of the $–CH_3$ group attached to $–CH_2$. Another sharp peak at δ 2.0 ppm showed the presence of $–CH_3$ attached to a carbonyl group. The two doublet peaks at δ 6.7 ppm and at δ 7.3 ppm showed the presence of four aromatic protons. The multiplet at δ 3.9 ppm strongly favored the deshielding nature of -CH_2 group. Finally, the structure was confirmed by the mass spectrum. The fragmentation pattern is shown by the mass spectrometry also confirmed the substitution of the ethoxy group in the fourth position in the benzene ring. From the mass spectrum, the molecular formula of the compound was found to be $C_{10}H_{13}O_2N$ (M^+: 180.3) which confirms the product 4-ethoxy acetanilide. From the spectral characterization, a suitable mechanistic pathway is proposed for ethoxylated acetanilides at both graphite and platinum anodes in neutral and basic conditions [12]. The most probable reaction mechanism is given below.



Electrochemical ethoxylation of acetanilide



Scheme 1. Mechanistic pathway for the electrochemical ethoxylation of acetanilide.

4. Conclusion

The electrosynthetic studies on ethoxylation of acetanilide reveal the following facts. The electrochemical oxidation processes were studied on platinum and graphite electrodes. It is clear from the polarization studies that the working potentials are higher at the platinum anode than at graphite at the same reaction conditions.

Ethoxylation is preferred in acetanilide forming 4-ethoxy acetanilide on graphite and platinum electrodes. The variation of percentage yield of the products is studied with graphite and platinum electrodes. The percentage of product yield is higher with graphite electrodes than with the platinum electrode. This may be due to the porous nature of the graphite electrode, which favors the adsorption of the reactant molecules on the surface, making the electrode process highly efficient, which is not realized in the case of the platinum electrode due to its smooth surface. Similarly, more yields are observed when H-cell is used. This shows that the substituted product tends to move towards the cathode in the undivided cell to undergo decomposition. The increase in ethanol concentration leads to a higher product yield (4-ethoxy acetanilide). This observation leads to the conclusion that ethanol acts as both solvent and electrolyte.

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