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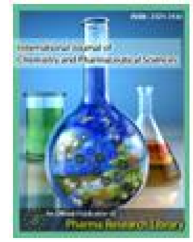

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Electrosynthetic Studies on Ethoxylation at Graphite and Platinum Anodes

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A B S T R A C T

Benzyl alcohol is a naturally occurring organic compound and its alkoxy derivatives find Enormous applications in the industrial sectors as a solvent, preservative and degreasing agents. The electrochemical oxidations such as hydroxylation, acetylation, halogenations have been exhaustively studied for the past five decades. The literature survey revealed that only a limited research work has done on the electrochemical alkoxylation of benzyl alcohol. Hence the present work focused on the electro synthetic studies of benzyl alcohol on both platinum and graphite anodes. The polarization studies were carried out as on pre-analytical tool electro synthesis. The electrochemical ethoxylation of benzyl alcohol yielded 2-ethoxy benzyl alcohol which was duely evidenced by the conventional spectral techniques like IR and UV, based on the earlier work a proable ECEC-mechanism was proposed.

Keywords: Electro synthesis ethoxy benzyl alcohol, ethoxylation, platinum as anode, polarization studies

A R T I C L E I N F O

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1. Introduction

Benzyl alcohol is an aromatic primary alcohol used as a general solvent for inks, paints, lacquers, epoxy resin coatings and as a degreasing agents. Benzyl alcohol readily forms the esters with various acids and thus provides wide finished product applications, including soap, perfume, flavor fragments and food additives. The electrochemical alkoxylation of benzyl alcohol leads to formation of esters, ethers, diketols which in turn find a lot of industrial applications. The literature survey electrochemical alkoxylation showed only a limited work has been done on the electrochemical ethoxylation. The ethoxylated products find applications in the pharmaceutical chemistry such as a bacteriostatic and local anesthetic. Hence the present research work is decided to focus on electrochemical ethoxylation of benzyl alcohol.

2. Experimental

Polarization studies were carried out with three electrode systems in which platinum/ graphite as the working electrode, silver-silver chloride as the reference electrode and platinum wire as the counter electrode. A power supply (besto make) was used for the polarization studies. The substrate benzyl alcohol, electrolyte ethanol and supporting electrolytes such as KCl, KOH, H_2SO_4 were of synthetic analar grades. As a pre-analytical study the current-voltage studies on ethoxylation of benzyl alcohol were carried out on both platinum and graphite as the working electrode. From the polarization studies, the working potentials for the electro oxidation of benzyl alcohol in hydro-alcoholic solutions in acidic, neutral and basic conditions are found out. The electro chemical synthesis were carried out in a divided H- cell by potentiostatic method. The products are separated using preparative TLC and characterized by UV and IR techniques.

3. Results and Discussion

Polarization Studies on benzyl alcohol

Polarization Studies of benzyl alcohol are carried out on Graphite and on Platinum; electrodes in acidic, neutral and basic conditions and the corresponding values of current-voltage are tabulated.

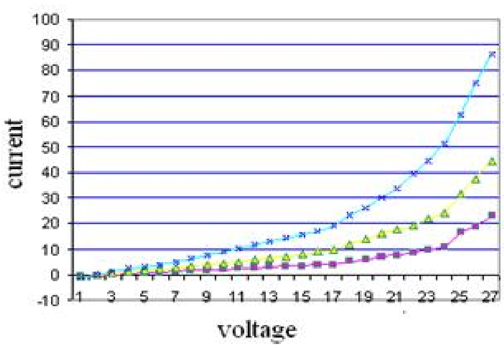


Figure 1: (c) ip Vs Ep (At Graphite Anode)

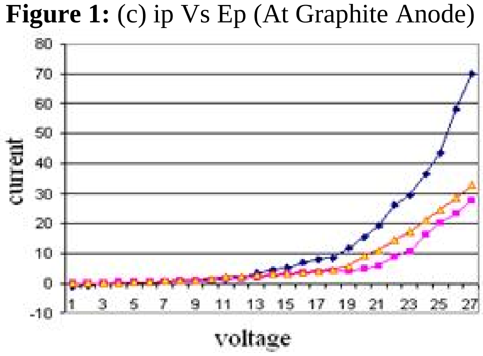


Figure 2: (d) ip Vs Ep (At Platinum Anode)

It is clear from the investigation that all the substrates undergo same kind of electrochemical oxidation processes. It is further confirmed that there are shifts observed towards lesser oxidation potential values for the substrates from the background current potential value, to the extent influenced by different groups of the aromatic system with diversified polar effects.

In general, the working potentials at platinum anode are higher than those at the Graphite anode. The working potentials of various substrates at platinum electrode are found to vary from 1.80 V to 0.90V vs SCE depending on the nature of substituents present in the benzene. The influence of pH, mono & di-substitution show the similar kind of effects on the working potentials as in the case of Graphite electrode. The polarization studies are very much useful to fix the working potentials of the various aromatic substrates under different pH conditions. Further, the current-potential relationships play a vital role in making conclusions on the electrochemical pathways for the chosen electro oxidation processes.

Electrochemical ethoxylation at Graphite and platinum electrodes: In the present study, direct electrochemical ethoxylation in the aromatic ring moiety is attempted. The substrate chosen for this investigation are Benzyl Alcohol. The electrochemical ethoxylation of these substrates (0.1M), are carried out with ethanol (0.5M) and in presence of 1M KCl / KOH at both Platinum and Graphite electrodes. From the cyclic voltammetric studies, the substrates are more susceptible for electrochemical ethxoylation in basic and neutral media. Hence, the electrosynthesis is restricted to these conditions and carried out at a constant potentials i.e, at the specified decomposition potentials from polarization studies (Potentiostatic method) using a divided H-Cell.

Product Analysis

The electrochemical ethoxylated products of Acetanilide, Benzyl alcohol, Salicylic acid and Salicylaldehyde are identified with TLC and separated using preparative HPLC. The individual products are characterized by chemical tests, physical constant determination and spectral data.

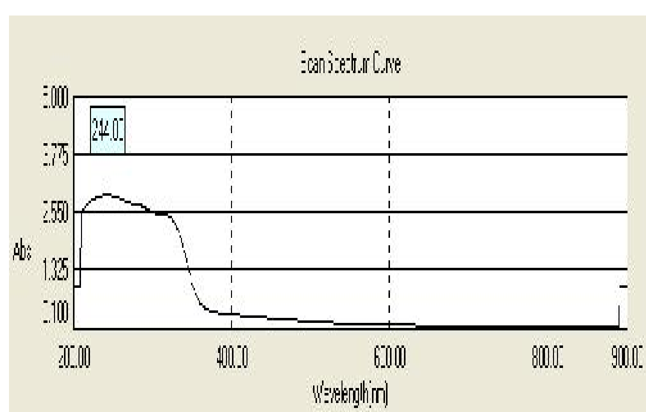


Figure 3: UV spectrum of 2-ethoxy benzyl alcohol (at Platinum)

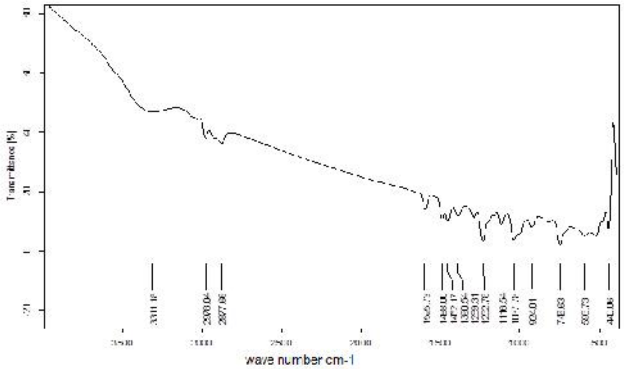


Figure 4: IR spectrum of 2-ethoxy benzyl alcohol (at Platinum)

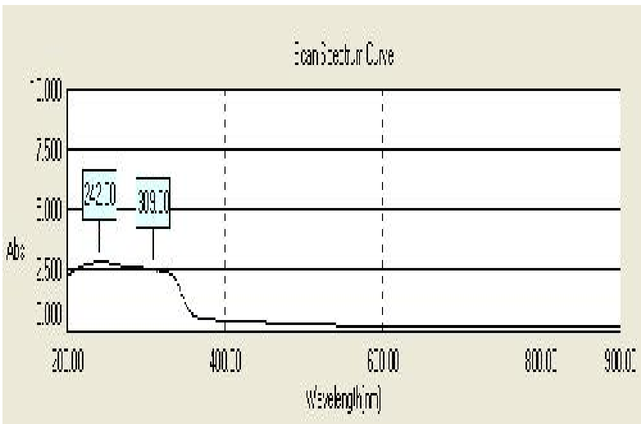


Figure 5: UV spectrum of 2-ethoxy benzyl alcohol (at Graphite)

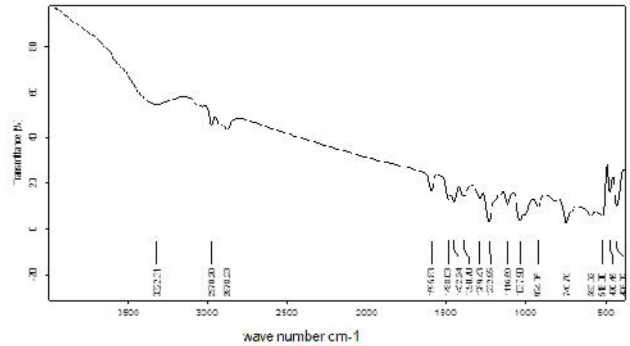
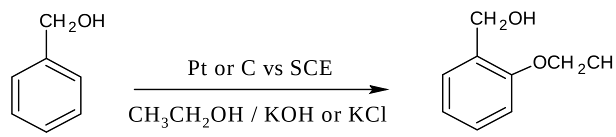


Figure 6: IR spectrum of 2-ethoxy benzyl alcohol (at Graphite)

Spectral interpretation for 2-ethoxy benzyl alcohol: The UV spectrum showed a strong absorption band at 244nm, which indicated presence of benzene ring. In the IR spectrum, the broad band at 3311 cm^{-1} showed the existence of –OH group. The group of three bands in the region 1452 cm^{-1} 1488 cm^{-1} and 1595 cm^{-1} strongly favoured the presence of aromatic moiety. The sharp band at 1116 cm^{-1} revealed the presence of –C-O stretching.

Mechanism proposed for the products



Scheme 1: Electrochemical ethoxylation of Benzyl alcohol

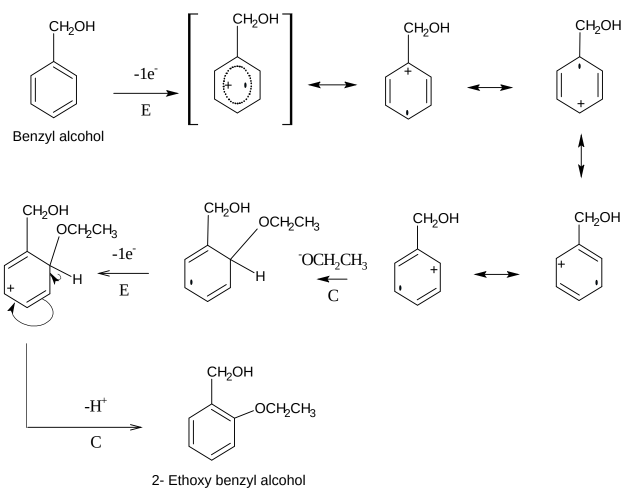
Table 1 (a): Current –Voltage studies for Benzyl alcohol on graphite and Platinum

Voltage (V)	At Graphite(Current (mA))			At Platinum (Current (mA))		
	Acidic (H_2SO_4)	Neutral (KCl)	Basic KOH)	Acidic H_2SO_4)	Neutral (KCl)	Basic (KOH)
0.1	-0.6	0.1	-0.3	-0.6	0	-0.1
0.2	-0.4	0.4	0.1	-0.1	0.1	0
0.3	0	0.5	0.7	0.2	0.2	0.1
0.4	0.4	0.7	1.3	0.3	0.3	0.2
0.5	0.6	0.9	1.4	0.4	0.4	0.3
0.6	0.9	1.1	1.8	0.6	0.5	0.7
0.7	1.3	1.4	2.4	0.7	0.6	0.9
0.8	1.6	1.7	3	0.9	0.7	1.1
0.9	1.8	2	3.6	1	0.8	1.5
1.0	2.2	2.3	4.3	1.3	1.4	2
1.1	2.4	2.7	5	1.7	1.6	2.3
1.2	2.8	3.1	5.8	3.4	1.8	2.6
1.3	3.2	3.5	6.5	4.4	2.4	2.8
1.4	3.3	3.9	7.1	5.2	3	3.3
1.5	3.5	4.7	7.6	6.8	3.3	3.6
1.6	3.9	4.9	8.2	7.9	3.8	3.9
1.7	4.2	5.5	9.7	8.5	4	4.5
1.8	5.4	6.7	11.2	11.8	4.2	5.9
1.9	6	7.9	12.1	15.4	4.8	9.2
2.0	7.2	8.8	14	19.1	6	11.2
2.1	7.6	9.7	16.5	26.2	8.8	14.3
2.2	8.6	10.8	20	29.4	10.8	17.3
2.3	9.7	12.1	22.9	36.3	16.1	20.8

2.4	10.8	13.6	27	43.5	20.2	24.5
2.5	16.5	14.8	31.2	58.4	23.1	28.5
2.6	18.8	19	37.5	70.2	27.5	32.9
2.7	22.7	21.8	42.1	74.2	29.3	34.2

Table 2: The working potentials of aromatic substrates at different pH media are obtained from polarization studies

S. No	Substrates	At Graphite electrode (Volts)			At Platinum Electrode (Volts)		
		Acidic	Neutral	basic	Acidic	Neutral	Basic
1	Benzyl Alcohol	1.10	1.00	0.90	1.40	1.20	1.00



Scheme 2: Mechanistic pathway for the electrochemical ethxoylation of Benzyl alcohol

4. Conclusion

From the electro synthetic studies, the following conclusions are drawn. The electrochemical oxidation processes are 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 for the same kind of electrochemical oxidation processes. The working potentials for the electro synthetic process are arrived at, by conducting the polarization studies.

a. The electrosynthesis was carried out by keeping the oxidation potential constant throughout the course of the reaction. (Potentiostatic method). After the electrolysis, the organic components of the anolyte are extracted with solvent ether. Using thin layer chromatogram, analytical and preparative TLC techniques, the products are identified and separated.
b. The electrochemical ethxoylation of benzyl alcohol yielded ortho ethoxylated products namely 2-Ethxoy benzyl alcohol on Graphite and Platinum electrodes. The probable reason for the formation of ortho products in these two cases must be due to the formation of hydrogen bond between the ethoxy group and the carbonyl hydrogen.
c. The products are characterized by chemical tests and UV, IR analysis.
d. A mechanism comprising of cation radical intermediate and aromatic nucleophilic substitution is proposed to justify the formation of ethoxylated products. An ECEC mechanism is suggested for the electrochemical conversions.

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