

Electrochemical oxidation of substituted benzylamines in aquo-acetic acid medium: substituent and solvent effects

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Abstract. Electrochemical oxidation of nine *para*- and *meta*-substituted benzylamines in varying mole fractions of acetic acid in water has been investigated in the presence of 0.1 M sulphuric acid as supporting electrolyte. The oxidation potentials correlate well with Hammett's substituent constants affording negative reaction constants. The correlation of potential values with macroscopic solvent parameters is non-linear suggesting that the operation of both specific and non-specific solvent–solvent–solute interaction mechanisms. Multiple correlation analysis of the experimental data with Kamlet–Taft solvatochromic parameters is employed.

Keywords. Solvent effect; benzylamine; electrochemical oxidation; cyclic voltammetry.

1. Introduction

Aromatic amines and its derivatives are used as intermediates for the manufacturing of various organic compounds such as colorants, agrochemicals, pharmaceutical agents, etc.¹ The compounds have been found to be widely distributed in aqueous environments and cause teratosis in aquatic species.² Aromatic amine is carcinogenic³ and also reacts easily in the blood to convert hemoglobin into methemoglobin, preventing oxygen uptake.⁴ Therefore, a serious effect on human health over a long period of time is possible, even if aromatic amine is in low concentrations.

Currently several treatment methods for wastewater containing aromatic amines have been developed including biodegradation,⁵ catalytic oxidation,⁶ separation using membranes,^{7,8} emulsion liquid membranes,⁹ ultrasonic degradation,¹⁰ decomposition in supercritical water,¹¹ adsorption using activated charcoal,¹² as well as an electrochemical (EC) method¹³. The EC method has some advantages over chemical or biological methods. Chemical methods require a large amount of reactive chemical reagents which can often cause secondary pollution. On the other hand, biological methods are temperature-

dependent and are inhibited by the toxicity of pollutants.¹⁴ EC methods have little or no harmful effects on the environment as they do not involve the use of harmful reagents. EC methods are clean and easy to handle and therefore, there is an increasing interest in the development of practical EC methods for treatment of high toxicity and biorefractory organic pollutants.

Furthermore, the study of solute–solvent interactions in binary mixtures is more complex than in pure solvents. In a pure solvent the composition of the microsphere of solvation of a solute, the so called cybotatic region, is the same as in the bulk solvent but in binary mixtures the composition of this microsphere can be different. The solute can interact to different degrees with the components of the mixture, and this difference is reflected in the composition of the microsphere of solvation. The effect of varying the composition of the mixture from the bulk solvent to the solvation sphere is called preferential solvation.¹⁵

The objective of the present work includes a systematic study of the substituent and solvent effects on electrochemical oxidation of a series of *para*- and *meta*-substituted benzylamines, in varying mole fractions of co-solvent acetic acid in water, and the analysis of the data using linear free energy relationships with an aim to get better insight into the mechanism of benzylamine oxidation.

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2. Experimental

2.1 Materials and methods

All chemicals and solvents used were of analytical grade (Aldrich, Merck or SRL-India). The solid benzylamines were used as such and the liquid benzylamines were used after vacuum distillation. Acetic acid was purified by reported method.¹⁶ Doubly-distilled water was used throughout the work.

Solutions of electrolyte were prepared with doubly distilled water. All electrochemical experiments were performed at room temperature using a standard three-electrode, two compartment configuration with a Glassy Carbon (GC) working electrode, a spiral platinum counter electrode and a Ag|AgCl (KCl sat.) reference electrode. The carbon electrodes were polished between experiments with aluminium oxide (alumina) paste. The cyclic voltammetric experiments were carried out with a computer-controlled electrochemical system (CHI643B Electrochemical Analyzer) at 50 mV s^{-1} . All solutions were de-oxygenated thoroughly by purging with nitrogen gas.

Correlation analyses were carried out using Microcal Origin (version 6) computer software. The goodness of fit was discussed using correlation coefficient (r in the case of simple linear regression and R in the case of multiple linear regression), standard deviation, sd and Exner's statistical parameters, ψ .¹⁷ The percentage contribution (P_x) of a parameter to the total effect on reactivity was computed using the regression co-efficient of each parameter as reported earlier.¹⁸

3. Results and discussion

A cyclic voltammetric study of 1 mM solution of benzylamine in varying mole fractions of co-solvent acetic acid in water with 0.1 M sulphuric acid was carried out at the GC electrode. A typical voltammogram obtained is shown in figure 1. During the forward scan, a single peak appears at 0.897 V versus standard Ag|AgCl (KCl sat.) as the reference electrode. On the reverse scan, one reduction peak is observed. The formation of a single peak during the first forward scan (oxidation) can be easily explained on the basis of the mechanism proposed by Adams.¹⁹ According to this mechanism, benzylamine during oxidation loses one electron to produce a cation radical (scheme 1) and undergoes further oxidation to give the product, at the same potential. Thus the

overall process consists of a single step two-electron oxidation of benzylamine. This accounts for the observation of a single oxidation peak during the first forward scan. Parallel observations have been reported in literature for electrochemical oxidation of benzylamine at a polycrystalline gold electrode in solution of 0.04 M KClO_4 or 0.04 M HClO_4 .²⁰

The results in table 1 indicate that on increasing the mole fraction of acetic acid in the mixture, there is a decrease in polarity and the oxidation becomes more difficult. This suggests that the transition state is more polar than the reactant (scheme 1). Hence, a decrease in polarity of the medium destabilizes such a transition state and consequently makes oxidation difficult, which requires more potential.

3.1 Structure-reactivity correlation

The effect of substituents on oxidation potential was studied with nine *para*- and *meta*-substituted ben-

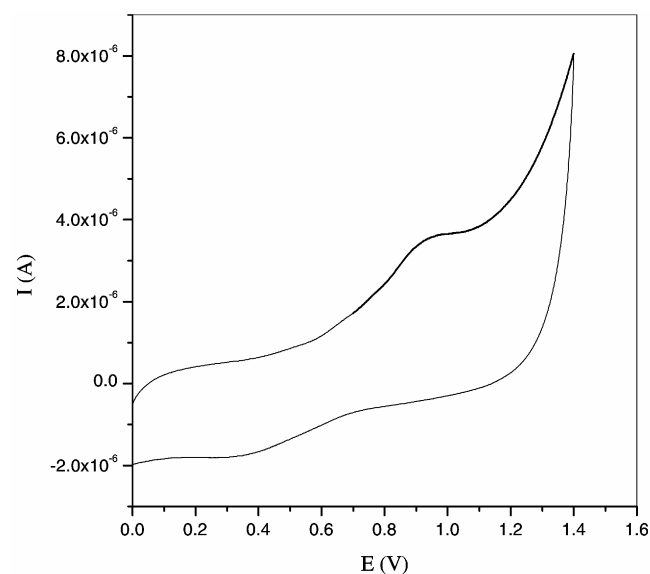
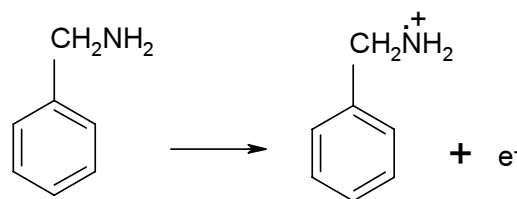


Figure 1. Cyclic voltammogram obtained for 1 mM benzylamine in 0.1 mole fraction of acetic acid in water containing 0.1 M sulphuric acid at a scan rate of 0.05 V s^{-1} .



Scheme 1.

Table 1. Electrochemical data (E_p [V]) from CV for oxidation of benzylamines in varying mole fractions of acetic acid in water.

Substituents in benzylamine moiety	Mole fraction of acetic acid								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
H	0.897	0.898	0.900	0.903	0.909	0.936	0.959	0.982	1.009
<i>m</i> -OMe	0.991	1.006	1.015	1.047	1.050	1.059	1.076	1.088	1.097
<i>m</i> -Me	0.921	0.941	0.956	0.962	0.982	0.994	1.003	1.015	1.027
<i>m</i> -Cl	0.980	1.018	1.024	1.044	1.085	1.094	1.103	1.109	1.123
<i>p</i> -OMe	0.912	0.918	0.924	0.936	0.947	0.956	0.971	0.985	1.000
<i>p</i> -Me	0.947	0.956	0.962	0.974	0.980	0.985	0.991	1.006	1.021
<i>p</i> -F	0.959	0.971	0.991	1.006	1.021	1.035	1.041	1.065	1.083
<i>p</i> -Cl	0.988	0.997	1.015	1.030	1.050	1.074	1.094	1.100	1.103
<i>p</i> -COOH	1.030	1.041	1.053	1.059	1.076	1.082	1.096	1.106	1.112

Table 2. The oxidation potential data ($\Delta \log E_X$ [V]) for the substituents.

Substituents in benzylamine moiety	Mole fraction of acetic acid								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
<i>m</i> -OMe	-1.551	-1.821	-2.546	-2.428	-2.378	-2.074	-1.973	-1.787	-1.484
<i>m</i> -Me	-0.405	-0.725	-0.944	-0.995	-1.231	-0.978	-0.742	-0.556	-0.303
<i>m</i> -Cl	-1.366	-2.024	-2.091	-2.378	-2.968	-2.664	-2.428	-2.142	-1.922
<i>p</i> -OMe	-0.253	-0.337	-0.405	-0.556	-0.641	-0.337	-0.202	-0.051	-0.152
<i>p</i> -Me	-0.843	-0.978	-1.045	-1.197	-1.197	-0.826	-0.539	-0.405	-0.202
<i>p</i> -F	-1.045	-1.231	-1.531	-1.731	-1.889	-1.669	-1.383	-1.399	-1.248
<i>p</i> -Cl	-1.534	-1.669	-1.939	-2.142	-2.378	-2.327	-2.276	-1.990	-1.585
<i>p</i> -COOH	-2.243	-2.411	-2.580	-2.630	-2.816	-2.462	-2.310	-2.091	-1.737

zylamines in varying mole fraction of acetic acid in water. The oxidation potential was measured for each substituent by cyclic voltammetry using the same scan rate, working electrode, electrolyte concentration, and compound concentration. The difference in oxidation potentials can be calculated using the following (1), as described earlier.²¹

$$\Delta E_X = E_{paH} - E_{paX} \quad (1)$$

where E_{paH} is the oxidation potential for unsubstituted benzylamine and E_{paX} is that of X-substituted benzylamine. The reaction constant ρ for the electrode process can then be determined by plotting $\Delta \log k_X$ ($\Delta \log E_X$ in the present case) against substituent constants σ (2).²¹

$$\Delta \log E_X = \rho \sigma \quad (2)$$

The values of $\Delta \log E_X$ for the first oxidation potentials of all the substituted benzylamines (table 2), in all mole fractions of the solvent mixture, showed a

linear relationship with respect to Hammett's substituent constants¹⁷ and a typical plot is shown in figure 2. The statistical results for these plots are given in table 3. The values of the reaction constant, ρ , were found to be negative, which confirms the formation of a positively charged transition state. The magnitude of reaction constants obtained in the present study is lesser when compared to that for the electrochemical oxidation of anilines in acetic acid-water media ($\rho > -5.26$).²² This may be due to the fact that structural changes in the side chain may be expected to affect the reaction constants.²³ Introduction of methylene group between the reaction site and the benzene ring might have reduced the transmission of the electrical effect of substituents through the side chain and hence the observed low reaction constants.

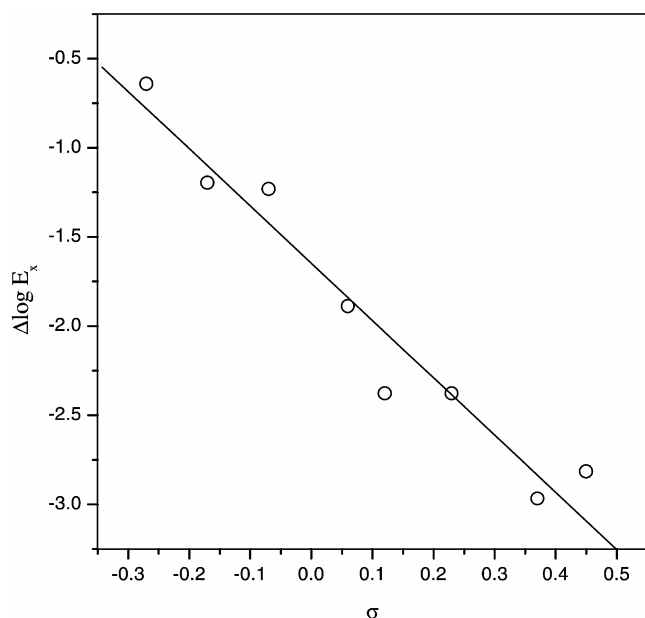
3.2 Solvent-reactivity correlation

The electro-oxidation of benzylamine has been studied in nine mole fractions of acetic acid in water ranging

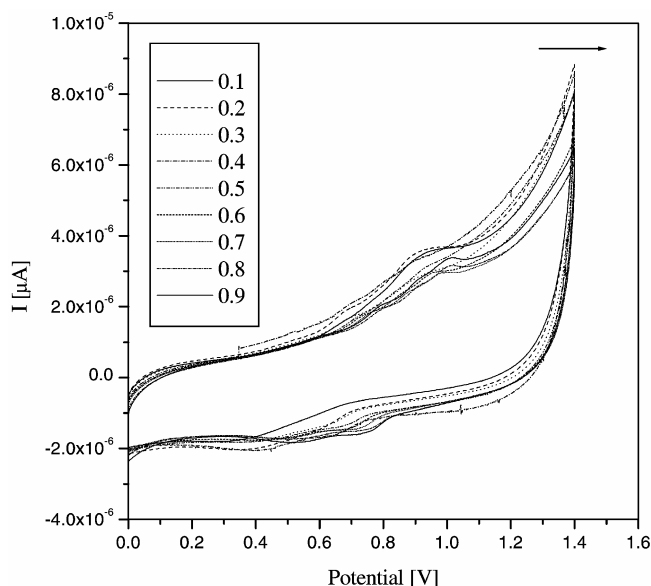
Table 3. Results of simple linear correlation of the oxidation potential data, $\Delta \log E_x$, with substituent constants as a function of relative permittivity of the medium.

Mole fraction of acetic acid in water	ϵ_r	$100r^2$	sd	ψ	ρ
0.1	71.17	89	0.316	0.51	-2.31 ± 0.47
0.2	63.94	96	0.223	0.34	-2.64 ± 0.33
0.3	56.72	89	0.394	0.53	-2.76 ± 0.58
0.4	49.49	93	0.305	0.43	-2.79 ± 0.45
0.5	42.27	97	0.216	0.27	-3.21 ± 0.32
0.6	35.05	97	0.241	0.30	-3.63 ± 0.36
0.7	27.82	96	0.275	0.33	-3.35 ± 0.41
0.8	20.60	95	0.274	0.35	-3.16 ± 0.41
0.9	13.37	94	0.271	0.39	-2.74 ± 0.40

ϵ_r , Relative permittivity of the medium; $100r^2$, Explained variance; sd , Standard deviation; ψ , Exner's statistical parameter; ρ , Reaction constant

**Figure 2.** Correlation of $\Delta \log k_x$ with σ (Hammett) for various substituents solvent: 0.5 mole fraction of acetic acid in water.

from 0.1 to 0.9 (table 1). A typical cyclic voltammogram for the oxidation of the benzylamine in varying mole fractions of acetic acid in water is shown in figure 3. Curvilinear plots are obtained for the correlation of oxidation potential data with the inverse of relative permittivity of the medium through the Laidler–Eyring²⁴ equation. A representative plot is shown in figure 4. Likewise, the correlation of oxidation potential data with the Grunwald–Winstein²⁵ solvent ionizing power, Y , is also non-linear. The solvent parameter values used in the present study viz. relative permittivity²⁶ and ionising power²⁵ of the mixtures employed was calculated as

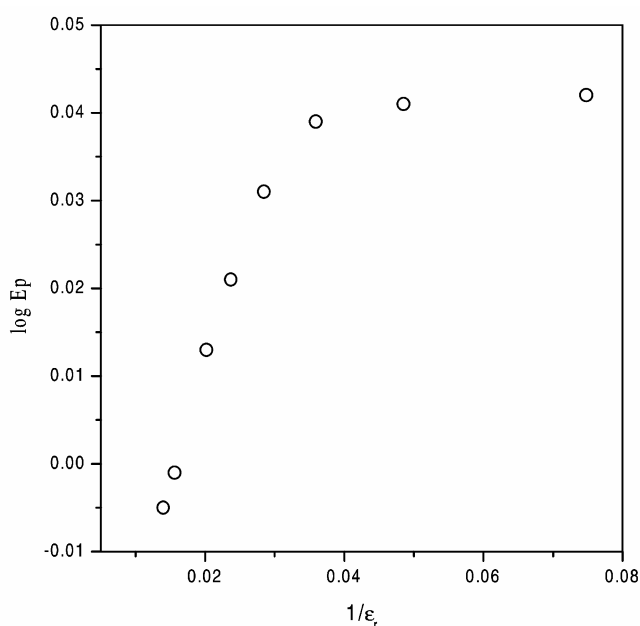
**Figure 3.** Cyclic voltammograms obtained for benzylamine in varying mole fractions of acetic acid in water.

described in literature. A representative plot is shown in figure 5.

Such poor correlations observed in the present study indicate that no single macroscopic solvent parameter such as relative permittivity or ionizing power can possibly account for the multitude of solute–solvent interactions on the molecular microscopic level. Thus these bulk properties will poorly describe the micro-environment around the reacting species, which governs the stability of the transition state. Hence, the operation of selective or preferential solvation, which includes both non-specific solute–solvent association caused by dielectric enrichment

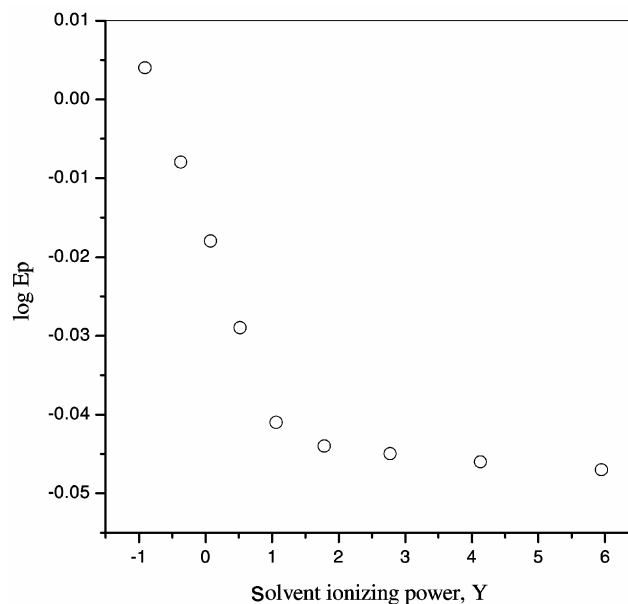
Table 4. Statistical results and weighted percentage contributions for the correlation of log Ep for the electrochemical oxidation of substituted benzylamines with Kamlet–Taft's solvatochromic parameters α , β and π^* .

Substituent	100R ²	sd	ψ	a	b	s	P_α	P_β	P_{π^*}
H	89	0.008	0.39	-0.38 ± 0.37	-0.96 ± 0.82	-0.05 ± 0.06	27	70	03
<i>m</i> -OMe	98	0.003	0.16	-0.11 ± 0.12	-0.33 ± 0.26	-0.06 ± 0.02	22	65	13
<i>m</i> -Me	99	0.001	0.13	-0.11 ± 0.07	-0.38 ± 0.16	-0.14 ± 0.01	17	61	22
<i>m</i> -Cl	97	0.004	0.09	0.42 ± 0.20	1.06 ± 0.46	-0.20 ± 0.03	25	63	12
<i>p</i> -OMe	99	0.002	0.11	-0.14 ± 0.09	-0.32 ± 0.21	-0.07 ± 0.01	26	61	13
<i>p</i> -Me	99	0.001	0.05	-0.20 ± 0.02	-0.38 ± 0.05	-0.05 ± 0.01	32	60	08
<i>p</i> -F	99	0.001	0.19	-0.10 ± 0.05	-0.13 ± 0.11	-0.12 ± 0.01	30	37	33
<i>p</i> -Cl	99	0.002	0.13	0.28 ± 0.12	0.56 ± 0.27	-0.15 ± 0.02	28	57	15
<i>p</i> -COOH	99	0.002	0.13	0.02 ± 0.08	0.07 ± 0.18	-0.08 ± 0.01	11	40	49

**Figure 4.** Laidler–Eyring plot for the electrochemical oxidation of *p*-chlorobenzylamine in acetic acid–water media.

in the solvation shell of solute ions or dipolar solute molecules and specific solute–solvent association such as hydrogen bonding or electron pair donor/electron pair acceptor interactions, is likely in the present case.¹⁶

The influence of specific and non-specific solute–solvent–solvent interactions on the reactivity was studied by employing the Kamlet–Taft solvatochromic method.²⁷ The correlation of oxidation potential data with solvatochromic parameters α , β and π^* is excellent. The correlation suggests the operation of both specific and non-specific solute–solvent interactions which govern the reactivity. Further, results of the multiple correlation and the weighted percentage contributions of the solvatochromic parame-

**Figure 5.** Grunwald–Winstein plot for the electrochemical oxidation of benzylamine in acetic acid–water media.

ters (table 4) indicate that the specific solvent–solvent–solute interactions, as indicated by P_α and P_β , play a major role in governing the oxidation process. These two parameters alone accounts for about 80% of the observed solvent effect. Further, the contribution of hydrogen bond acceptor basicity (represented by β term) to the total solvent effect was found to be predominant. The signs of the coefficients of these two terms are randomly observed and this may be due to complexing interactions between solute and the solvent.

However, the sign of the coefficients of the polarity/polarizability term, π^* , is negative. The negative sign of the coefficients of this term also suggests that with decrease in polarizability/dipolarity of the

medium makes the oxidation process difficult. Increase in mole fraction of acetic acid in the mixture decreases the polarity/polarizability of the medium and consequently increases the oxidation potential and hence the oxidation becomes more difficult. This suggests that the transition state is more polar than the reactant. Hence an increase in polarity of the medium stabilizes such a transition state and consequently makes the oxidation easier, which requires less potential.

It may be concluded that since amines are very harmful to human health and the environment, the removal of amines from the environment is the ultimate goal of research today. For this a deep understanding of the mechanism of the oxidation process of amines are needed. In this work we have studied the detailed mechanism of electrochemical oxidation of some *para*- and *meta*-substituted benzylamines. The results of solvent effects indicate that an increase in polarity of the medium makes the oxidation process easier. Further, the reactivity is influenced both by non-specific and specific solute-solvent interactions. The correlation of oxidation potential data with substituent constants reveals that a positively charged transition state is formed during the oxidation process.

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