

# Substituent and Solvent Effects on the Electrochemical Oxidation of *para*- and *meta*-Substituted Anilines

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Electrochemical oxidation of fifteen *para*- and *meta*-substituted anilines in different mole fractions of acetic acid in water has been investigated in the presence of 0.1 M sulphuric acid as supporting electrolyte. The oxidation potential data of anilines correlates well with Hammett's and Brown-Okamoto's substituent constants affording negative reaction constants. The effect of *para*- and *meta*-substituents on the oxidation potential conforms to Swain's *F* and *R* parameters, affording negative reaction constants. The oxidation potential values correlate well with macroscopic solvent parameters such as relative permittivity,  $\epsilon_r$ , and polarity,  $E_T^N$ . Multiple correlation analysis also shows an excellent correlation with the oxidation potential values.

**Key words:** Solvent Effect, Aniline, Electrochemical Oxidation, Cyclic Voltammetry

## Introduction

Aniline 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]. Aniline is known to be carcinogenic [3] 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 aniline is in low concentrations.

Currently several treatment methods for waste water containing aniline 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) method [13]. 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 harm-

ful reagents. EC methods are clean and easy to handle and therefore, there is increasing interest in the development of practical EC methods for the treatment of high toxicity and biorefractory organic pollutants. Further, chemical and electrochemical oxidation of aniline, which produces a conductive polymer (polyaniline) has received considerable interest in recent years because of its applications in a variety of technological fields, such as electrochromic devices [15], chemical sensors [16], charge storage systems [17] protection against corrosion [18] *etc.*

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 a different degree with the components of the mixture, and this difference in the interactions 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 [19].

The main objective of the present work, therefore, is a systematic study of the substituent and solvent effects on the electrochemical oxidation of a series of *para*- and *meta*-substituted anilines, in varying mole fractions of acetic acid in water, and an analysis of the

data using linear free energy relationships with an aim to get better insight into the mechanism of aniline oxidation.

## Results and Discussion

A cyclic voltammetric study of 1 mM solution of aniline in varying mole fractions of acetic acid in water with 0.1 M sulphuric acid was carried out at the Glassy Carbon (GC) electrode. A typical voltammogram obtained is shown in Fig. 1. During the forward scan, a single well-defined peak appears at 1.059 V *versus* standard Ag/AgCl (KCl sat.) as the reference electrode. On the reverse scan, two reduction peaks were observed. The formation of a single peak during the first forward scan (oxidation) can be easily explained on the basis of an ece mechanism proposed by Adams [20]. According to this mechanism, aniline during oxidation loses one electron to produce a cation radical which through resonance structures undergoes head-to-tail and tail-to-tail couplings resulting in the formation of *p*-aminophenylamine and benzidine, both of which are more readily oxidisable than the parent substance, and undergo further oxidation at the same potential (Scheme 1). The overall process thus consists of a single step two-electron oxidation of aniline. This accounts for the observation of a single oxidation peak during the first forward scan. Parallel observations have been reported in literature for the electrochemical oxidation of anilines [21–24].

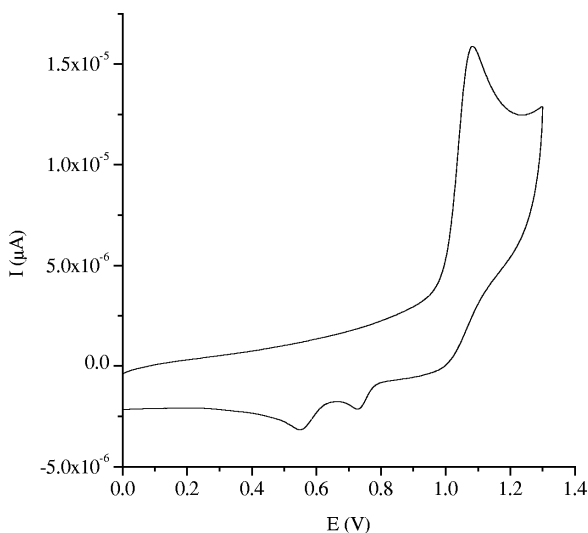
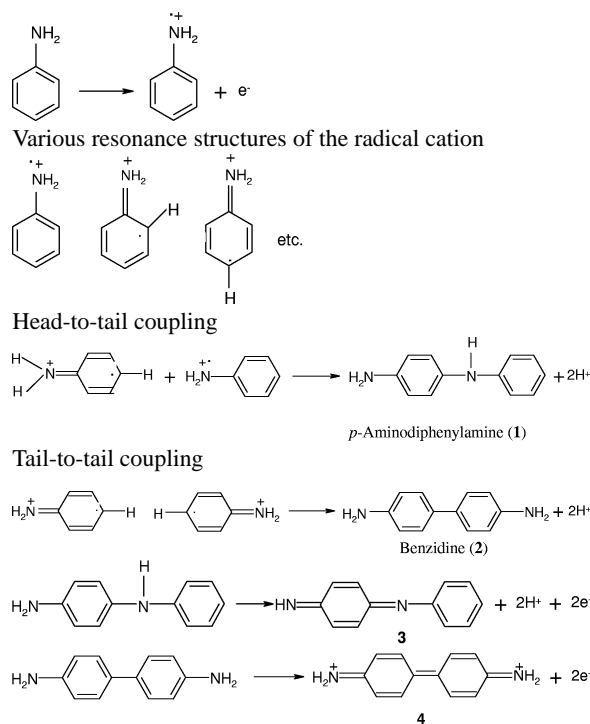


Fig. 1. Cyclic voltammogram obtained for 1 mM aniline in a 0.2 mole fraction of acetic acid in water containing 0.1 M sulphuric acid at a scan rate of 0.05 V s<sup>-1</sup>.



Scheme 1.

According to the above mechanism, only two oxidation products (3 and 4) are produced during the first oxidative scan, and thus two reduction peaks appear in the first reverse scan. The first peak is due to the reduction of 4 to 2 and the second peak is due to the reduction of 3 to 1. Thus this mechanism accounts for a one-step two-electron oxidation of aniline in aquo-acetic acid medium [25].

The oxidation potential values of aniline derivatives depicted in Table 1 indicate that *para*-directing groups require less potential to remove the electron than *meta*-directing groups. But when groups like Cl, Br, F, NO<sub>2</sub> are in the *para*-position, it is difficult to oxidize, because they withdraw electrons and decrease the electron density at the *para*-position [26, 27]. So the oxidation potential for these *para*-substituted anilines is similar to other *meta*-substituted anilines. But the other *para*-substituted anilines require less potential than the *meta*-substituted anilines.

Further, the results in Table 1 indicate that on increasing the mole fraction of acetic acid in the mixture the oxidation becomes more difficult. This suggests that the transition state is more polar than the reactant (Scheme 1). Hence an increase in polarity of the medium stabilizes such a transition state and con-

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

Substituents in aniline moiety	Mole fraction of acetic acid						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
H	1.059	1.084	1.121	1.136	1.193	1.212	1.260
<i>p</i> -Me	0.986	0.998	1.031	1.036	1.068	1.081	1.130
<i>p</i> -OMe	0.819	0.847	0.867	0.892	0.919	0.942	0.963
<i>p</i> -COMe	1.147	1.148	1.167	1.190	1.205	1.217	1.280
<i>p</i> -NHCOMe	0.842	0.859	0.876	0.886	0.896	0.947	0.994
<i>p</i> -NO <sub>2</sub>	1.263	1.272	1.290	1.308	1.330	1.356	1.364
<i>p</i> -Cl	1.034	1.048	1.074	1.101	1.129	1.160	1.204
<i>p</i> -Br	1.056	1.074	1.089	1.108	1.144	1.160	1.197
<i>p</i> -F	1.050	1.062	1.082	1.106	1.136	1.151	1.163
<i>m</i> -Me	1.032	1.051	1.094	1.111	1.148	1.188	1.233
<i>m</i> -COOH	1.172	1.173	1.194	1.216	1.244	1.279	1.292
<i>m</i> -NO <sub>2</sub>	1.241	1.265	1.283	1.309	1.333	1.366	1.416
<i>m</i> -Et	1.041	1.058	1.074	1.116	1.117	1.174	1.219
<i>m</i> -OMe	0.998	1.018	1.039	1.065	1.107	1.154	1.199
<i>m</i> -COMe	1.157	1.169	1.172	1.204	1.242	1.273	1.319

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

Substituent in aniline moiety	Mole fraction of acetic acid						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
H	0	0	0	0	0	0	0
<i>p</i> -Me	1.231	1.450	1.518	1.686	2.108	2.209	2.192
<i>p</i> -OMe	4.047	3.997	4.283	4.115	4.621	4.199	5.008
<i>p</i> -COMe	-1.484	-1.062	-0.776	-0.911	-0.202	-0.084	-0.337
<i>p</i> -NHCOMe	3.659	3.794	4.131	4.216	5.008	4.469	4.486
<i>p</i> -NO <sub>2</sub>	-3.440	-3.170	-2.850	-2.900	-2.310	-2.428	-1.754
<i>p</i> -Cl	0.421	0.607	0.792	0.590	1.079	0.877	0.944
<i>p</i> -Br	0.051	0.168	0.539	0.472	0.826	0.877	1.062
<i>p</i> -F	0.152	0.371	0.656	0.506	0.961	1.028	1.636
<i>m</i> -Me	0.455	0.556	0.455	0.422	0.759	0.405	0.455
<i>m</i> -COOH	-1.905	-1.501	-1.231	-1.349	-0.860	-1.130	-0.539
<i>m</i> -NO <sub>2</sub>	-3.069	-3.052	-3.057	-2.917	-2.361	-2.597	-2.631
<i>m</i> -Et	0.303	0.438	0.792	0.337	1.298	0.641	0.691
<i>m</i> -OMe	1.028	1.113	1.382	1.197	1.450	0.978	1.029
<i>m</i> -COMe	-1.652	-1.433	-0.860	-1.146	-0.826	-1.028	-0.995

sequently makes the oxidation easier, which requires less potential.

#### Structure-reactivity correlation

The effect of substituents on the oxidation potential was studied with 15 *para*- and *meta*-substituted anilines 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 the oxidation potentials can be calculated using the following eq. (1), as described earlier [27].

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

where  $E_{\text{paH}}$  is the oxidation potential for the unsubstituted aniline and  $E_{\text{paX}}$  is that of X-substituted aniline. The reaction constant  $\rho$  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  $\sigma$  (eq. (2)).

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

The values of  $\Delta \log E_X$  for the first oxidation potentials of all the substituted anilines (Table 2), in all mole fractions of the solvent mixture, showed a linear relationship with respect to resonance-enhanced Brown-Okamoto's substituent constants  $\sigma^+$ , and a typical plot is shown in Fig. 2. The linear Brown-Okamoto plot confirms that the transition state formed should have a considerable positive charge. However, the correlation of the oxidation potential

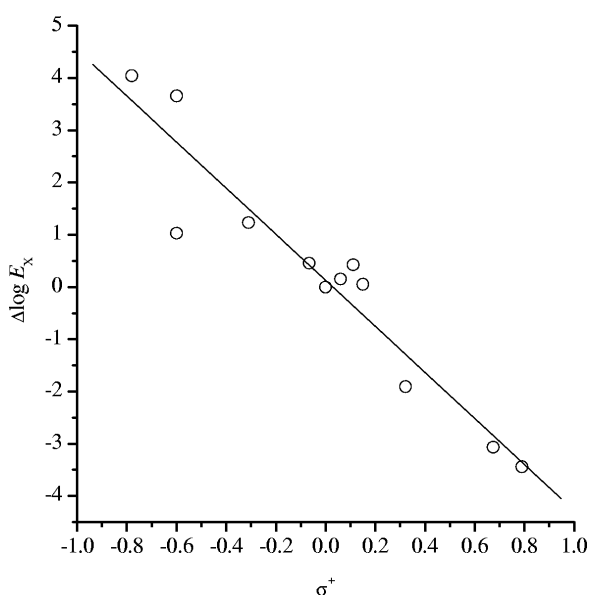


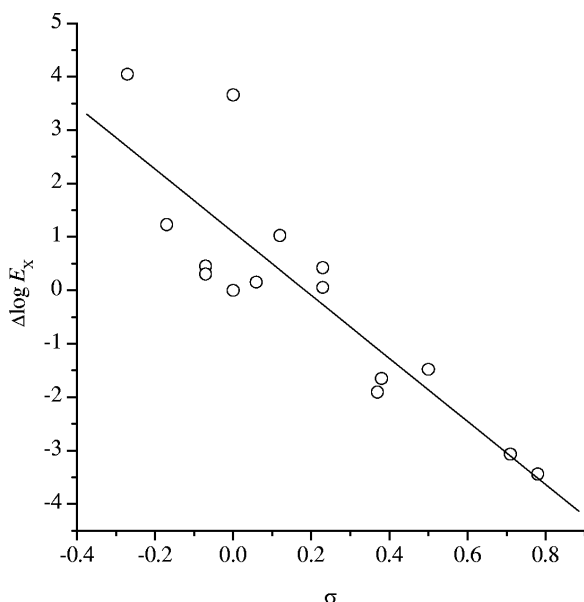
Fig. 2. Correlation of  $\Delta \log k_X$  with  $\sigma^+$  (Brown-Okamoto) for various substituents. Solvent: 0.2 mole fraction of acetic acid in water.

data with Hammett's substituent constants yields a rather poor fit (Fig. 3). The statistical results for these plots are given in Table 3. The values of the reaction constant,  $\rho$ , were found to be negative, which confirms the formation of a positively charged transition state. The reaction constants obtained in the present study are comparable to those of previously reported oxidation of anilines by various oxidants (percarbonate,  $\rho = -2.7$  [28]; perborate,  $\rho = -3.0$  [29]; pyridinium chlorochromate,

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<sup>a</sup>.

Mole fraction of acetic acid in water	$\epsilon_r$	$100R^2$	$sd$	$\psi$	$\rho$
Hammett					
0.2	63.94	87	1.085	0.53	$-5.907 \pm 0.93$
0.3	56.72	86	1.068	0.54	$-5.718 \pm 0.92$
0.4	49.49	85	1.142	0.57	$-5.262 \pm 0.98$
0.5	42.27	84	1.163	0.58	$-5.574 \pm 0.99$
0.6	35.05	82	1.259	0.62	$-5.490 \pm 1.08$
0.7	27.82	81	1.212	0.62	$-5.278 \pm 1.04$
0.8	20.60	80	1.275	0.64	$-5.310 \pm 1.09$
Brown-Okamoto					
0.2	63.94	95	0.747	0.34	$-4.417 \pm 0.46$
0.3	56.72	95	0.737	0.34	$-4.317 \pm 0.45$
0.4	49.49	94	0.784	0.36	$-4.369 \pm 0.48$
0.5	42.27	94	0.797	0.37	$-4.324 \pm 0.49$
0.6	35.05	92	0.944	0.45	$-4.112 \pm 0.58$
0.7	27.82	91	0.944	0.45	$-4.112 \pm 0.58$
0.8	20.60	90	1.041	0.49	$-4.068 \pm 0.64$

<sup>a</sup>  $\epsilon_r$  = relative permittivity of the medium;  $100R^2$  = explained variance;  $sd$  = standard deviation;  $\psi$  = Exner's statistical parameter;  $\rho$  = reaction constant.

Fig. 3. Correlation of  $\Delta \log k_X$  with  $\sigma$  (Hammett) for various substituents. Solvent: 0.2 mole fraction of acetic acid in water.

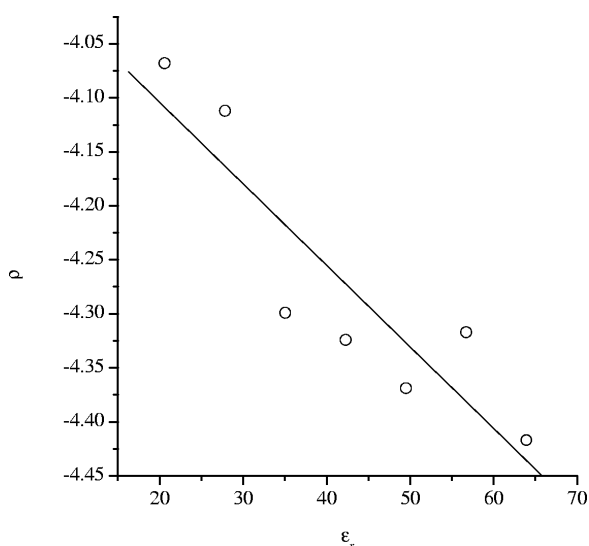
$\rho = -3.75$  [30], and imidazolium fluorochromate,  $\rho = -2.22$  [31]).

It is clear that  $\rho$  values, like  $E_X$  values for given reactants, are influenced by solvent effects. Hammett predicted that, in general, the reaction constant appears to increase with decreasing relative permittivity of the

Table 4. Statistical results of multiple linear correlation analysis for the oxidation of anilines in different mole fractions of acetic acid in water<sup>a</sup>.

Mole fraction	$100R^2$	$sd$	$\psi$	$\rho_F$	$\rho_R$	$P_F$	$P_R$
<i>para</i> substituents							
0.2	95	0.614	0.26	$-0.946 \pm 0.63$	$-2.454 \pm 0.24$	14	86
0.3	93	0.663	0.29	$-0.864 \pm 0.67$	$-2.348 \pm 0.26$	21	79
0.4	93	0.697	0.30	$-0.545 \pm 0.71$	$-2.367 \pm 0.27$	12	88
0.5	92	0.717	0.31	$-0.712 \pm 0.73$	$-2.375 \pm 0.28$	17	83
0.6	89	0.864	0.38	$-0.315 \pm 0.91$	$-2.403 \pm 0.35$	4	96
0.7	88	0.845	0.38	$-0.594 \pm 0.86$	$-2.219 \pm 0.33$	16	84
0.8	93	0.648	0.29	$-0.083 \pm 0.66$	$-2.344 \pm 0.25$	2	98
<i>meta</i> substituents							
0.2	98	0.252	0.16	$-1.718 \pm 0.29$	$-1.180 \pm 0.12$	59	41
0.3	98	0.251	0.16	$-1.755 \pm 0.29$	$-1.131 \pm 0.12$	59	41
0.4	93	0.490	0.31	$-1.692 \pm 0.57$	$-1.119 \pm 0.23$	55	45
0.5	96	0.354	0.24	$-1.517 \pm 0.41$	$-1.085 \pm 0.16$	56	44
0.6	95	0.387	0.27	$-1.519 \pm 0.45$	$-1.052 \pm 0.18$	57	43
0.7	97	0.281	0.18	$-1.553 \pm 0.32$	$-0.930 \pm 0.13$	61	39
0.8	93	0.400	0.30	$-1.593 \pm 0.46$	$-0.877 \pm 0.19$	63	37

<sup>a</sup>  $100R^2$  = explained variance;  $sd$  = standard deviation;  $\psi$  = Exner's statistical parameter;  $\rho_F$  and  $\rho_R$  = field and resonance reaction constants respectively;  $P_F$  and  $P_R$  = percentage contributions of field and resonance factors, respectively.

Fig. 4. Plot of reaction constant,  $\rho^+$ , vs. relative permittivity of the medium,  $\epsilon_r$ .

medium. In the present study, however, there is a very marked deviation from the relationship between  $\rho$  and  $\epsilon_r$  (Fig. 4). This suggests that  $\rho$  values, like  $E_X$  values, are influenced both by non-specific and by specific solvent effects [32].

As suggested by Glatzhofer *et al.* [27], dual-parameter correlation and higher-level calculations of the electronic and structural differences may lead to

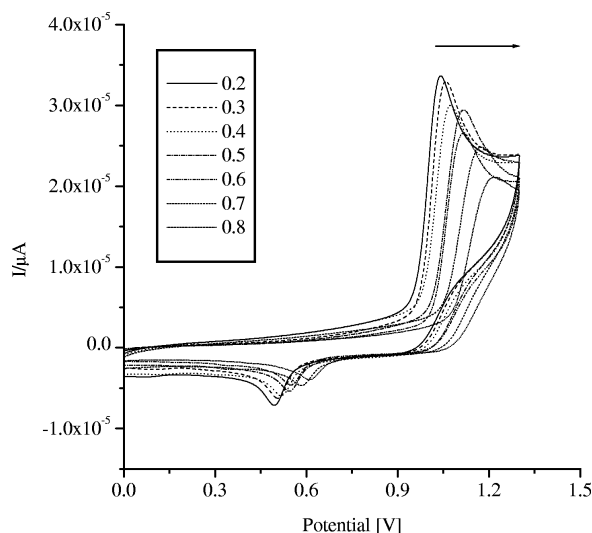


Fig. 5. Cyclic voltammograms obtained for *m*-Et aniline in varying mole fraction of acetic acid in water.

a better understanding of the inductive and resonance contributions of substituents toward the oxidation potentials. Therefore, we have done multiple correlation analysis for the  $\Delta \log E_X$  of *para*- and *meta*-substituted anilines using biparametric equations including the Swain *et al.* equation which reveals that the substituent constants  $F$  and  $R$  explain better than others the variation of  $\Delta \log E_X$  with substituents (Table 4). A better description of the composition of the electrical effects is given in terms of the percent field factor ( $P_F$ ) where  $P_F = |F| \cdot 100/(|F| + |R|)$  and the percent resonance factor ( $P_R$ ), where  $P_R = |R| \cdot 100/(|F| + |R|)$  [33]. In all the solvent mixtures studied, the *para*-substituted anilines show  $P_R$  values of *ca.* 88%, and the  $P_F$  values are *ca.* 12%. In *para*-substituted compounds, the resonance effect predominates and the inductive effect is secondary. In case of the *meta*-substituted compounds the observed results (*i.e.* inductive and resonance effects operating almost equally) are as expected. Electron release favours radical-cation formation and the negative reaction constants are in consonance with the observation. The values of  $\Delta \log E_X$  for the first oxidation potentials of all the *para*-substituted anilines also correlates satisfactorily with  $\sigma_I$  and  $\sigma_R$  ( $0.788 < r < 0.837$ ,  $1.087 < sd < 1.392$ ,  $-3.063 \pm 1.81 < \rho_I < -4.478 \pm 1.68$ ,  $-7.929 \pm 2.05 < \rho_R < -8.923 \pm 1.82$ ). Similarly, the *meta*-substituted anilines also correlate satisfactorily with  $\sigma_I$  and  $\sigma_R$  ( $0.948 < r < 0.985$ ,  $0.213 < sd < 0.416$ ,  $-2.904 \pm 0.60 < \rho_I < -3.325 \pm 0.38$ ,  $-3.456 \pm 0.71 < \rho_R < -4.564 \pm 0.56$ ).

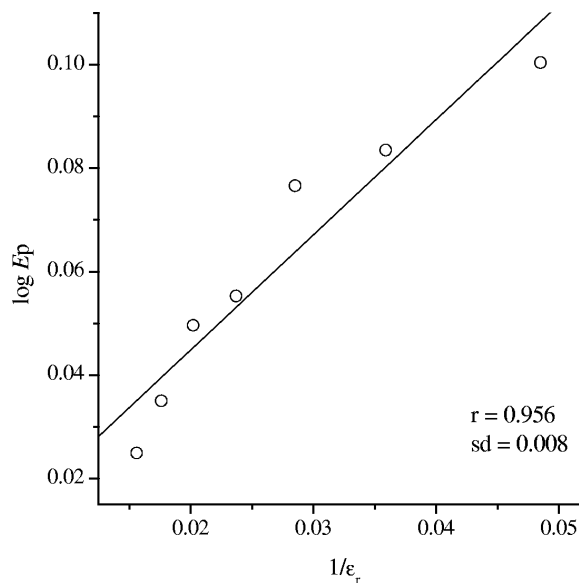


Fig. 6. Laidler-Eyring plot for the electrochemical oxidation of aniline.

#### Solvent-reactivity correlation

The electro-oxidation of anilines has been studied in seven mole fractions of acetic acid in water ranging from 0.2 to 0.8 (Table 1). A typical cyclic voltammogram for the oxidation of the *m*-Et compound in varying mole fractions of acetic acid in water is shown in Fig. 5. The oxidation potential data correlate satisfactorily with the inverse of relative permittivity of the medium through the Laidler-Eyring [34] equation with an explained variance of  $85 < 100r^2 < 98$ . A representative plot is shown in Fig. 6. The slopes of these plots are positive indicating that the transition state is more polar than the reactant. Likewise, the correlation of oxidation potential data with the Grunwald-Winstein [35] solvent ionizing power,  $Y$ , is also satisfactory (explained variance  $78 < 100r^2 < 94$ ) affording negative slopes.

The explained variances 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 microenvironment 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

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 [36]. The influence of specific and non-specific solute-solvent-solvent interactions on the reactivity has been studied by employing the Kamlet-Taft solvatochromic method [37]. The correlation of oxidation potential data with the solvatochromic parameters  $\alpha, \beta, \pi^*$  is excellent (explained variance:  $92 < 100R^2 < 99$ ). Such an excellent correlation suggests the operation of both specific and non-specific solute-solvent interactions which govern the reactivity. Further, results of the multiple correlation (not shown) indicate that specific solute-solvent interactions play a dominant role in governing the reactivity. This is in line with the results of the relation between Brown-Okamoto's reaction constant and relative permittivity of the medium (Fig. 4) showing that the reactivity is influenced both by non-specific and by specific solvent effects.

## Conclusion

Since anilines are very harmful to human health and the environment, removal of aniline from the environment is the ultimate goal of research today. For this a deep understanding of the mechanism of the oxidation process of aniline is needed, so in this work we have studied the detailed mechanism of electrochemical oxidation of some *para*- and *meta*-substituted anilines. The results 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 the oxidation potential data with substituent

constants reveals that a positively charged transition state is formed during the oxidation process.

## Experimental Section

All the chemicals and solvents used were of analytical grade (Aldrich, Merck or SRL-India). The solid anilines were used as such and the liquid anilines were used after vacuum distillation. Acetic acid was purified by a reported method [36]. 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 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  $50 \text{ mV s}^{-1}$ . All solutions were deoxygenated thoroughly by purging with nitrogen gas. The oxidation product was identified as azobenzene by employing FT-IR and UV/vis techniques.

Correlation analyses were carried out using Microcal Origin (version 6) computer software. The goodness of fit was discussed using correlation co-efficient ( $r$  in the case of simple linear regression and  $R$  in the case of multiple linear regression), standard deviation,  $sd$  and Exner's statistical parameters,  $\psi$  [32]. 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 [38].

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