Solvent Hydrogen Bonding and Structural Effects on Nucleophilic Substitution Reactions: Part 5 – Reaction of 2-Bromo-5-nitropyridine with *para*-Substituted Anilines in Acetonitrile/Dimethylformamide Mixtures*

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Substitution reactions of some *para*-substituted anilines with 2-bromo-5-nitropyridine are carried out conductometrically in binary acetonitrile/dimethylformamide mixtures. The second-order rate constants correlate well with Hammett's substituent constants yielding a negative value of ρ. The multiparameter correlation with Kamlet-Taft's solvatochromic parameters is excellent ($100R^2 \sim 98\%$), and the computed percentage contributions of these parameters ($P_\alpha = 58\%$, $P_\beta = 4\%$, $P_{\pi^*} = 38\%$) suggest that both specific and non-specific solute-solvent-solvent interactions influence the reactivity. The solvation model proposed is well supported by the solvatochromism exhibited by the anilines in the solvent mixture under investigation. The molar extinction coefficient ($\varepsilon_{\max}$) of aniline varies appreciably up to ∼ 25% with a change in the mole fraction of the mixture. The multivariate correlation analysis of $\varepsilon_{\max}$ (with α, β, π^*) suggests that the solvation around the NH_2 moiety of aniline through the solvent's hydrogen-bond donor (HBD) property is found to be dominant in the solvation process and consequently in altering the rate. The dominance of the solvent's HBD property in solvation is further confirmed by the cyclic voltammetric oxidation of aniline in the solvent mixture.

Key words: Aniline; Substitution Reaction; Solvent Effect.

1. Introduction

The study of solute-solvent interactions in binary solvent 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 in this microsphere can be different. The solute can interact to a different degree with the components of the solvent 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 [2].

The study of the influence of solvents on reactions of anilines in non-aqueous and aquo-organic solvent mixtures has revealed the important role of non-specific and specific solvent effects on reactivity [3 – 8]. It has been shown that the reactivity is influenced by the preferential solvation of the reactants and/or the activated complex through non-specific and specific solute-solvent-solvent interactions. Further, it has been established that the technique of correlation analysis may well be used to separate and quantify such solvent-solvent-solute interactions on reactivity. Furthermore, one of the important tools in deciding the mechanism of reactions is the study of substituent effects. The Hammett equation and its modified forms [9], all known as linear free energy relationships (LFER), have been found useful for correlating reaction rates and equilibrium constants of side-chain reactions of *meta*- and *para*-substituted derivatives of benzene. The isokinetic relationship is also an important tool for deciding the nature of a mechanism.

Examination of the literature reveals that the influence of structure on S_N2 reactions has often been reported [10 – 24]. However, only very few attempts have been made to study the influence of solvents on such reactions in a more systematic manner [25 – 31]. In the present investigation, the reaction of a few *para*-substituted anilines with 2-bromo-5-

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* Part 4: see [1].

	Rate constant										
	Mole fraction of AN										
Substituent of aniline	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
None	2.53	2.42	2.39	2.36	2.28	2.21	2.12	2.14	2.06	1.93	1.80
	(0.02)	(0.02)	(0.04)	(0.02)	(0.04)	(0.07)	(0.05)	(0.01)	(0.04)	0.04)	(0.03)
p-Et	2.55	2.49	2.48	2.39	2.32	2.26	2.15	2.19	2.11	1.97	1.84
	(0.06)	(0.08)	(0.03)	(0.05)	(0.07)	(0.03)	(0.02)	(0.03)	(0.05)	(0.04)	(0.04)
p-OEt	2.64	2.54	2.52	2.46	2.42	2.32	2.30	2.24	2.15	2.12	2.04
	(0.04)	(0.07)	(0.05)	(0.09)	(0.05)	(0.07)	(0.07)	(0.03)	(0.06)	(0.04)	(0.04)
p-Me	2.59	2.53	2.50	2.44	2.39	2.31	2.28	2.21	2.16	2.04	1.98
	(0.07)	(0.08)	(0.06)	(0.08)	(0.05)	(0.07)	(0.06)	(0.04)	(0.03)	(0.05)	(0.05)
p-OMe	2.66	2.57	2.52	2.50	2.43	2.36	2.33	2.28	2.16	2.15	2.11
	(0.05)	(0.08)	(0.08)	(0.09)	(0.07)	(0.07)	(0.08)	(0.09)	(0.08)	(0.08)	(0.07)
p-COMe	2.26	2.22	2.21	2.12	1.99	1.98	1.85	1.79	1.70	1.64	1.41
	(0.06)	(0.05)	(0.05)	(0.03)	(0.05)	(0.03)	(0.04)	(0.02)	(0.03)	(0.02)	(0.04)
p-NHCOMe	2.49	2.41	2.35	2.30	2.21	2.16	2.07	2.01	2.02	1.89	1.73
	(0.05)	(0.07)	(0.07)	(0.07)	(0.04)	(0.05)	(0.05)	(0.03)	(0.03)	(0.04)	(0.02)
p-F	2.37	2.31	2.29	2.21	2.20	2.10	1.98	1.97	1.93	1.80	1.70
	(0.05)	(0.07)	(0.07)	(0.05)	(0.03)	(0.02)	(0.02)	(0.04)	(0.04)	(0.05)	(0.03)
p-Cl	2.33	2.30	2.29	2.17	2.10	2.06	1.92	1.90	1.86	1.77	1.58
	(0.07)	(0.06)	(0.04)	(0.03)	(0.02)	(0.06)	(0.04)	(0.04)	(0.03)	(0.03)	(0.01)
p-Br	2.31	2.30	2.25	2.17	2.08	1.97	1.88	1.83	1.81	1.72	1.57
	(0.04)	(0.06)	(0.05)	(0.04)	(0.03)	(0.03)	(0.06)	(0.04)	(0.02)	(0.03)	(0.05)

Table 1. Second-order rate constants ($10^3 k_A^{-1}$) with relative errors in parentheses for the reaction of anilines with 2-bromo-5-nitropyridine, determined in AN/DMF mixtures with increasing mole fraction of AN at 303 K.

nitropyridine in acetonitrile (AN)/*N*,*N*-dimethylformamide (DMF) [both dipolar, non-hydrogen-bond donor (HBD)] mixtures of varying compositions is reported. To study the influence of the solvent and reactants structure on the reactivity, 2-bromo-5-nitropyridine was chosen as substrate, as the kinetics of the S_NAr reaction of similar compounds with aniline in neat organic solvents is known [32].

Further, the selection of binary AN/DMF solvent mixtures for our study is based on the fact that the hydrogen-bonding abilities of this mixture is well understood and among the dipolar non-HBD solvents, AN exhibits a lower HBA (hydrogen-bond acceptor) ability and also exhibits a potential ability to donate a hydrogen atom towards the formation of a hydrogen bond [33]. In order to contribute to a more comprehensive analysis of the molecular-microscopic properties of binary aprotic solvent mixtures, particularly hydrogen-bonding effects, it is of interest to discuss the behaviour of solvent mixtures of this type. Further, one of the profound advantages of using binary solvent mixtures is that by varying the mole fraction of the constituent solvents, the physical properties of the medium can be varied in a smooth and continuous manner. The main objective, therefore, of this endeavour is to investigate the effect of solvent hydrogen-bonding and structural effects on the nucleophilic substitution reaction of *para*-substituted anilines with 2-bromo-5-nitropyridine in binary AN/DMF mixtures.

2. Results and Discussion

The nucleophilic substitution reaction of parent aniline and a few *para*- (Et, OEt, Me, OMe, COMe, NHCOMe, F, Cl, and Br) substituted anilines with 2-bromo-5-nitropyridine was studied conductometrically at 303, 313, and 323 K in the presence of varying excess of aniline over the substrate to ensure pseudo-first-order kinetics. A plot (not shown) of k_{obs} versus concentration of aniline had a distinct intercept on the rate ordinate indicating that the reaction is not a base-catalyzed one [25 – 28]. Hence, the second-order rate constants, k_A, were computed and are summarized in Table 1. The reactions were carried out in varying mole fractions of AN, x(AN), in DMF at 303 K. The selection of x(AN) was based on the fact that the solvatochromic parameters for the binary solvent mixtures employed in the present study for correlation analysis, are available in the literature [33].

The product analysis was carried by refluxing a mixture of 2-bromo-5-nitropyridine (3.16 mmol) and aniline (5.38 mmol) for one hour in DMF. The mixture was cooled to room temperature and then poured into ice-cold water with vigorous stirring. The precipitate

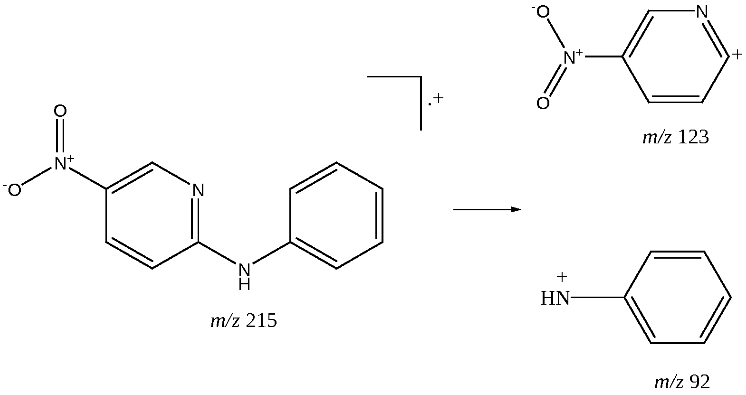

Fig. 1. Mass spectral fragmentation.

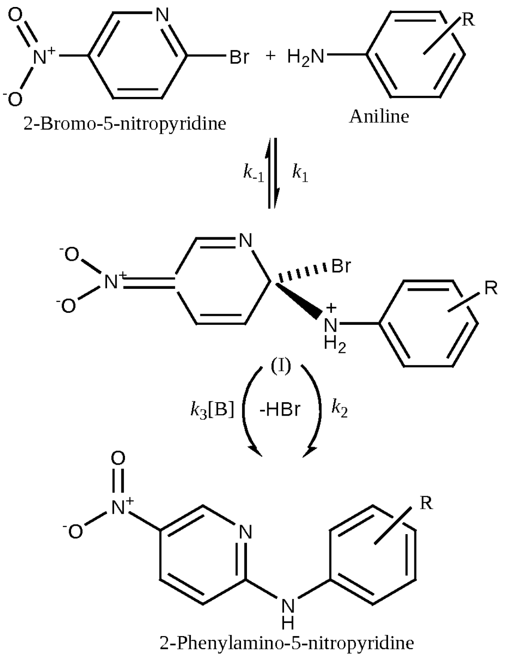

Fig. 2. Reaction scheme.

formed was filtered and recrystallized. The product thus obtained was subjected to GC-MS analysis. The results of the GC-MS analysis revealed that the reaction product was 2-phenylamino-5-nitropyridine (m/z 215 [$M^{+\cdot}$], fragmentation with m/z ratio 123 and 92) (Fig. 1).

Based on the kinetic results, product analysis and the conclusions of previous work [32], the reaction scheme in Fig. 2 has been proposed for the reaction of anilines with 2-bromo-5-nitropyridine, which involves the intermediate (I). The formation of such a type of intermediate was well established in the S_NAr reactions of aromatic amines with various substrates [10 – 14].

The results in Table 1 reveal that a decrease in x(AN) in the solvent mixture increases the rate of the reaction. Figure 3 shows the solution FT-IR spectra of the reaction mixture at different time intervals. The doublet around $\nu = 2930-3000$ cm^{-1} corresponds to asymmetric and symmetric stretching vibrations of the two N-H bonds of the aromatic primary amine [34]. It is evident from the figure that with lapse of time the intensity of the peak decreases, which confirms the participation of the amino group in the reaction.

2.1. Thermodynamic Parameters and the Isokinetic Relationship

The activation parameters for all substituted anilines at 0.6 mole fraction of AN were calculated from k_A at 303, 313, and 323 K, using the van't Hoff plot, by the method of least squares; they are collected in Table 2. The reaction is neither isenthalpic nor isentropic but complies with the compensation law also known as isokinetic relationship. The isokinetic temperature is the temperature at which all compounds of the series react equally fast. Also, at the isokinetic temperature the variation of substituents has no influence on the free energy of activation. In an isentropic reaction the isokinetic temperature lies at infinity and only the enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isenthalpic series, and the reactivity is determined by the entropy of activation [35]. The operation of the isokinetic relationship is tested by plotting the logarithms of rate constants, k_A, at two temperatures ($T_2 > T_1$) against each other, as suggested by Exner [36]:

$$\log k(\text{at } T_2) = a + b \log k \text{ (at } T_1). \qquad (1)$$

In the present study the linear plots obtained im-

Table 2. Influence of temperature on the rate of reaction of anilines with 2-bromo-5-nitropyridine, determined in an AN/DMF mixture with x(AN) = 0.6, and activation parameters for this reaction.

The values in parentheses are relative errors.

Substituent of aniline	Rate constant, 10^3 s^{-1} 303 K	313 K	323 K	Ea, kJ mol^{-1} K^{-1}	$\Delta H^{\#}$, kJ mol^{-1}	$\Delta S^{\#}$, J K^{-1} mol^{-1}	$\Delta G^{\#}$, kJ mol^{-1}
None	2.12 (0.05)	3.93 (0.04)	5.94 (0.10)	42.1	39.5	−166	89.8
p-Et	2.15 (0.02)	3.94 (0.12)	6.01 (0.18)	41.9	39.2	−167	89.6
p-OEt	2.30 (0.07)	4.02 (0.04)	6.10 (0.06)	39.7	37.1	−173	89.5
p-Me	2.28 (0.06)	3.97 (0.09)	6.08 (0.18)	39.9	37.3	−172	89.4
p-OMe	2.33 (0.08)	4.10 (0.12)	6.12 (0.18)	39.4	36.8	−174	89.5
p-COMe	1.85 (0.04)	3.71 (0.11)	5.70 (0.17)	45.9	43.3	−154	89.9
p-NHCOMe	2.07 (0.05)	3.90 (0.12)	5.92 (0.18)	42.8	40.2	−164	90.0
p-F	1.97 (0.02)	3.87 (0.12)	5.86 (0.11)	44.3	41.8	−159	90.0
p-Cl	1.92 (0.04)	3.83 (0.11)	5.79 (0.17)	19.0	16.4	−245	90.0
p-Br	1.88 (0.06)	3.77 (0.11)	5.75 (0.17)	19.2	16.6	−245	89.9

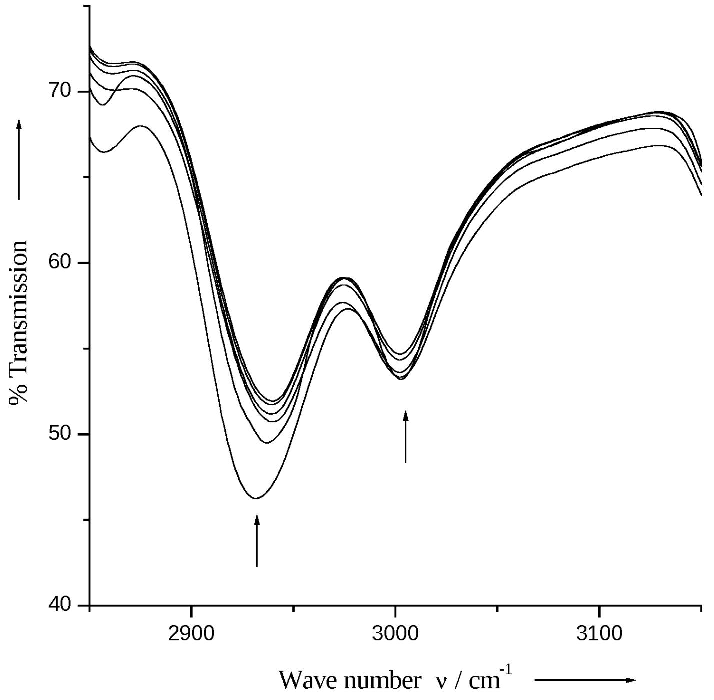

Fig. 3. FT-IR spectra of the reaction mixture in acetonitrile with increase in time.

ply the validity of the isokinetic relationship. A representative plot is shown in Fig. 4 [at x(AN) = 0.6, $r = 0.99$, $sd = 0.001$, isokinetic temperature = (332 ± 11) K]. The operation of an isokinetic relationship reveals that all substituted anilines examined follow a common reaction mechanism. The negative entropy of activation indicates a greater degree of ordering in the activated complex than in the initial state, due to an increase in solvation during the activation process.

x(AN)	Rate constant, 10^3 s^{-1}			Ea,	$\Delta H^{\#}$,	$\Delta S^{\#}$,	$\Delta G^{\#}$,
	303 K	313 K	323 K	kJ mol^{-1} K^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}
0	2.52 (0.02)	4.89 (0.09)	6.53 (0.08)	38.8	36.2	−175	89.2
0.1	2.42 (0.02)	4.53 (0.11)	6.32 (0.13)	39.1	37.8	−170	89.3
0.2	2.39 (0.04)	4.33 (0.10)	6.29 (0.15)	39.5	36.9	−173	89.4
0.3	2.36 (0.02)	4.27 (0.10)	6.22 (0.12)	39.5	36.9	−173	89.3
0.4	2.28 (0.04)	4.17 (0.13)	6.20 (0.06)	40.8	38.2	−169	89.4
0.5	2.21 (0.07)	4.01 (0.10)	6.03 (0.18)	40.9	38.3	−169	89.5
0.6	2.12 (0.05)	3.93 (0.08)	5.94 (0.12)	42.1	39.5	−166	89.8
0.7	2.14 (0.01)	3.90 (0.11)	5.89 (0.18)	41.2	38.6	−169	89.8
0.8	2.06 (0.04)	3.86 (0.09)	5.83 (0.07)	42.5	39.9	−165	89.9
0.9	1.93 (0.04)	3.73 (0.07)	5.75 (0.14)	44.6	42.0	−158	89.9
1.0	1.80 (0.03)	3.70 (0.11)	5.67 (0.17)	46.8	44.2	−152	90.2

Table 3. Rate constants ($10^3 k_A$, s^{-1}) and activation parameters for the reaction of aniline with 2-bromo-5-nitropyridine in AN/DMF mixtures with varying mole fraction of AN, x(AN).

The values in parentheses are relative errors.

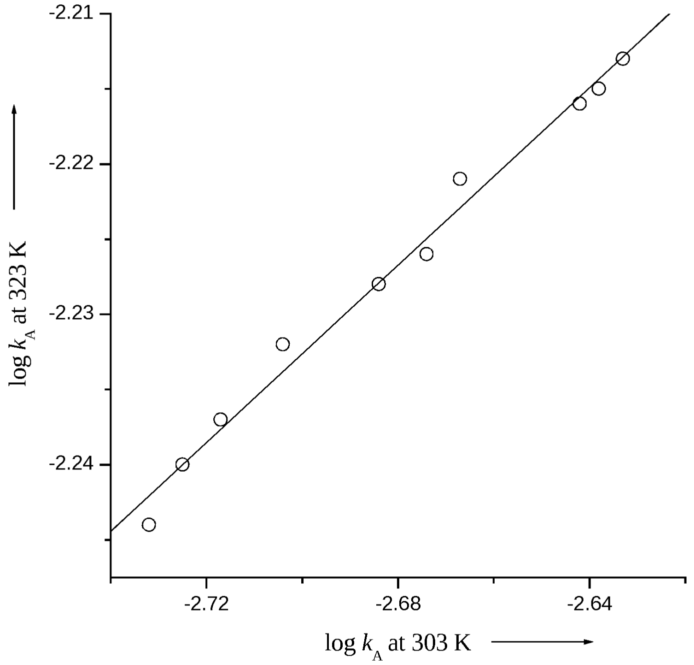

Fig. 4. Isokinetic plot for all anilines in 0.6 mole fraction of acetonitrile in DMF.

Likewise, the activation parameters were also calculated for aniline in solvent mixtures with different mole fractions of AN (Table 3). The existence of a linear relationship [$r = 0.97$, $sd = 0.005$, isokinetic temperature = (340 ± 12) K] between log k_A at 313 K and log k_A at 303 K indicates that a single mechanism is operating in all the solvent mixtures under scan. A representative plot is shown in Figure 5.

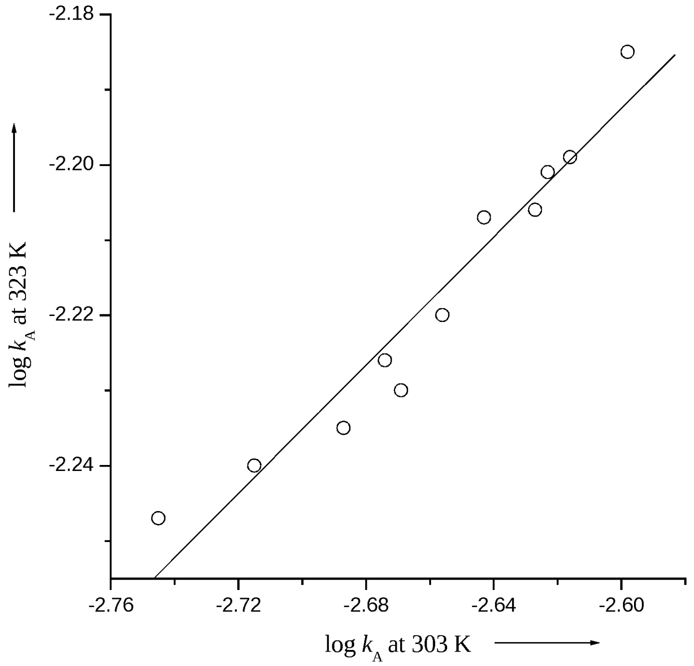

Fig. 5. Isokinetic plot for the parent aniline in all mole fractions investigated.

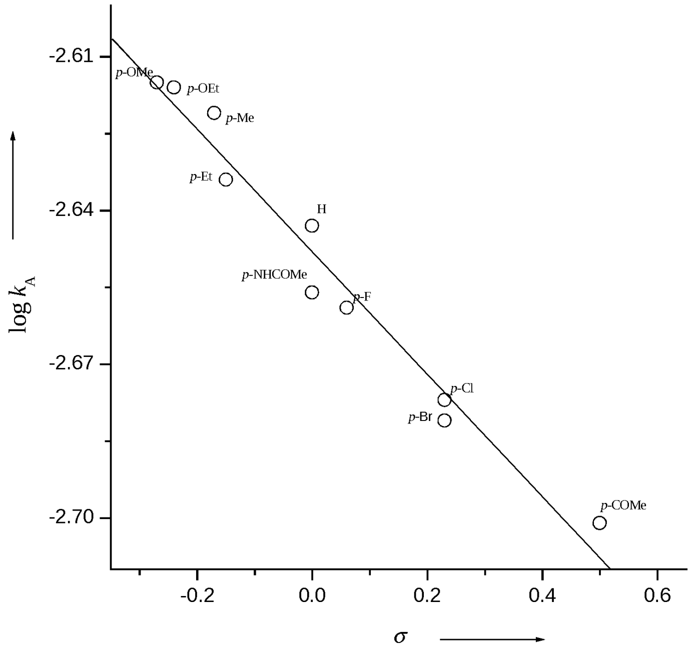

Fig. 6. Hammett plot of $\log k_A$ versus σ in 0.4 mole fraction of acetonitrile in DMF at 303 K.

2.2. Structure-Reactivity Correlation

The influence of substituents on the reaction rate was studied with nine *para*-substituted anilines. The results in Table 1 reveal that in a given solvent mixture, the rate constants vary with the nature of the substituent. A plot of $\log k_A$ versus Hammett's substituent constant, σ is linear with negative slope (Fig. 6). The negative slope indicates that electron-donating groups stabilize, by resonance, an intermediate having a high positive charge on the reaction centre, which in the present study is obviously the nitrogen atom of the

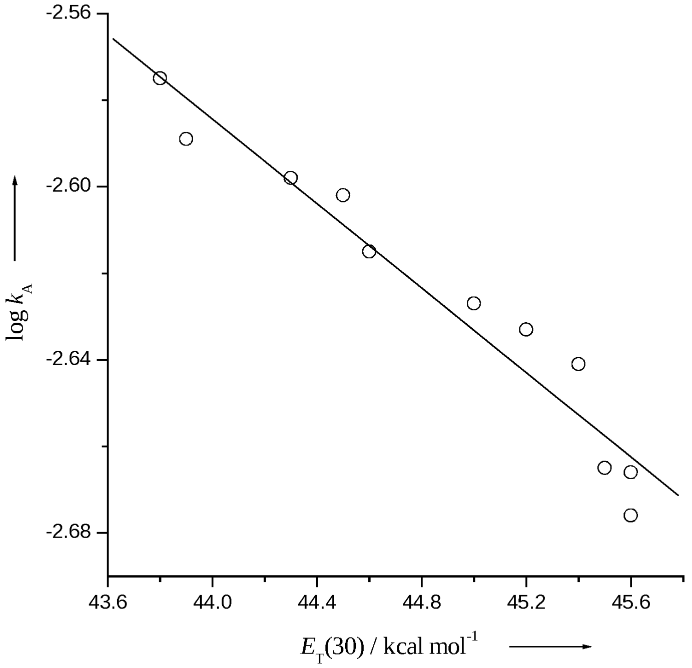

Fig. 7. Plot of $\log k_A$ versus $E_T(30)$ for *p*-methoxyaniline at 303 K.

NH_2 group. This facilitates the bond-breaking process in the intermediate.

2.3. Solvent-Reactivity Correlation

The title reaction has been studied in eleven binary solvent mixtures with different mole fractions of AN in DMF. The second-order rate constants collected in Table 1 decrease with an increase in x(AN) in the mixture. The linear correlation of the rate data (Table 1) with Reichardt's [37] solvent polarity parameter $E_T(30)$ is just satisfactory with an explained variance of less than 90% (Fig. 7). Such a comparatively less good correlation may be due to the fact that bulk solvent properties like $E_T(30)$ will poorly describe the microenvironment around the reacting species, which governs the stability of the intermediate and hence the rate of the reaction. Parallel observations have already been made during the Cr(VI) oxidation [6, 7, 38–40], substitution [1], and electrochemical oxidation [41, 42] of anilines in mixed solvents.

Therefore, in order to obtain a deeper insight into the various solute-solvent interactions, which influence the reactivity, we have tried to adopt the solvatochromic comparison method developed by Kamlet and Taft [43]. The solvatochromic parameters employed in the present study were computed and reported in [33] and are based on various solvent-solvent interactions which can be explained by the following general model using a two-solvent exchange process [2]:

$$\mathrm{I(S1)}_m + m\mathrm{S2} \rightleftharpoons \mathrm{I(S2)}_m + m\mathrm{S1}, \quad (2)$$

$$\mathrm{I(S1)}_m + m/2\,\mathrm{S2} \rightleftharpoons \mathrm{I(S12)}_m + m/2\,\mathrm{S1}. \quad (3)$$

In (2) and (3) S1 and S2 indicate the two pure solvents to be mixed, and S12 represents a solvent-solvent adduct formed by the interaction of solvents 1 and 2. This new solvent can have properties quite different from those of solvents 1 and 2 for so-called synergetic solvent mixtures. m is the number of solvent molecules solvating the solvatochromic indicator I [2].

The most celebrated Kamlet-Taft solvatochromic comparison method [43] was employed, which incorporates three types of solute-solvent interactions:

$$\log k = \log k_0 + s\pi^* + a\alpha + b\beta, \quad (4)$$

where π^* is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is the solvent hydrogen-bond donor (HBD) acidity, which describes the ability of the solvent to donate a proton to a hydrogen bond, and β is the solvent hydrogen-bond acceptor (HBA) basicity, which

Table 4. Statistical results and weighted percentage contributions for the correlation of log k_A with Kamlet-Taft's solvatochromic parameters α, β, and π^* at 303 K.

Substituent of aniline	$100R^2$	sd	a	b	s	P_α	P_β	P_{π^*}
None	98	0.006	−0.83	0.07	−0.74	51	4	45
			(0.25)	(0.03)	(0.53)			
p-Et	98	0.008	−0.80	0.06	−0.67	52	4	44
			(0.31)	(0.03)	(0.65)			
p-OEt	98	0.005	−0.73	−0.01	−0.65	52	0	48
			(0.21)	(0.02)	(0.46)			
p-Me	99	0.006	−0.89	0.03	−0.97	47	1	51
			(0.22)	(0.02)	(0.48)			
p-OMe	98	0.006	−0.68	−0.03	−0.59	52	2	46
			(0.25)	(0.03)	(0.53)			
p-COMe	97	0.01	−0.76	0.10	−0.13	77	10	13
			(0.55)	(0.06)	(1.19)			
p-NHCOMe	98	0.008	−0.56	0.03	−0.04	89	5	6
			(0.30)	(0.03)	(0.65)			
p-F	98	0.009	−1.11	0.06	−1.25	46	2	52
			(0.34)	(0.04)	(0.73)			
p-Cl	97	0.01	−0.75	0.06	−0.33	66	5	29
			(0.42)	(0.04)	(0.90)			
p-Br	98	0.009	−1.14	0.02	−1.08	51	1	48
			(0.37)	(0.04)	(0.79)			

Table 5. UV absorption maxima of aniline and 2-bromo-5-nitropyridine, determined in AN/DMF mixtures, with increasing mole fraction of AN, x(AN).

	Aniline		2-Bromo-5-nitropyridine	
x(AN)	λ_{max}, nm	ε_{max}, M^{-1} cm^{-1}	λ_{max}, nm	ε_{max}, M^{-1} cm^{-1}
0	294.7	3700	282.5	11750
0.1	294.2	3445	282.5	8871
0.2	294.3	3365	282.5	8810
0.3	294.1	3355	282.5	8981
0.4	293.7	3320	282.5	8713
0.5	293.2	3105	282.1	8981
0.6	292.6	2955	282.1	8871
0.7	292.6	2930	282.1	8762
0.8	292.2	2880	282.1	8364
0.9	292.0	2770	282.1	8115
1.0	290.9	2740	282.1	11721

provides a measure of the solvent, ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond, and log k_0 is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients s, a, and b measure the relative susceptibilities of the solvent-dependent solute property log k to the indicated solvent parameter. These solvatochromic parameters for the solvent mixtures employed in the present study were obtained from the literature [33].

The kinetic data were correlated with Kamlet-Taft's solvatochromic solvent parameters α, β, and π^* as described earlier [1]. The rates of reaction for all compounds studied showed a good correlation with these three solvent parameters as part of a three-parameter correlation equation with an explained variance of ca. 98%. Such a good correlation indicates the existence of both specific and non-specific solute-solvent interactions in the present study. The contribution of each of these solvatochromic parameters to the reactivity were calculated and are listed in Table 4. The results suggest at first sight that the percentage contribution of the above three solvatochromic parameters depends on the nature of the substituents. However, the percentage contribution data of the solvatochromic parameters failed to correlate either with electrical parameters or size of the substitutents. This may be due the fact that the solvation depends on various factors like the cavity that the dissolved molecule produces in the solvent, the orientation of the solvent molecules, and the unspecific and specific intermolecular forces [37]. Hence, the percentage contribution of a particular solvatochromic parameter, for a given aniline, may be due to the combination of one or more factors mentioned, only the average value was employed for further discussions. Also, the majority of the data is in line with the above-mentioned average.

The observation of this multiple regression analysis led us to the following conclusions. (i) The rate of the reaction is influenced by both specific and nonspecific solute-solvent interactions as indicated by the percentage contributions of the α, β, and π^* parameters. Among specific interactions, the contribution of α is dominant and the negative sign of the coefficient of this term suggests that there exists a specific interaction between the reactants and the solvent through its HBD property. (ii) The positive sign of the coefficients of β for the majority of the reactants suggests that the specific interaction between the intermediate and the solvent, via the HBA property, is stronger than that between the reactants and the solvent. Further, the negative sign of the coefficient of the π^* term suggests that an increase in the solvent's dipolarity/polarizability decreases the rate, hence there is a decrease in the rate and an increase in the mole fraction of acetonitrile in the mixtures [38–42].

The UV-Vis absorption spectra of the reactants in the solvent mixture and the solvatochromism exhibited by them adequately support the conclusions de-

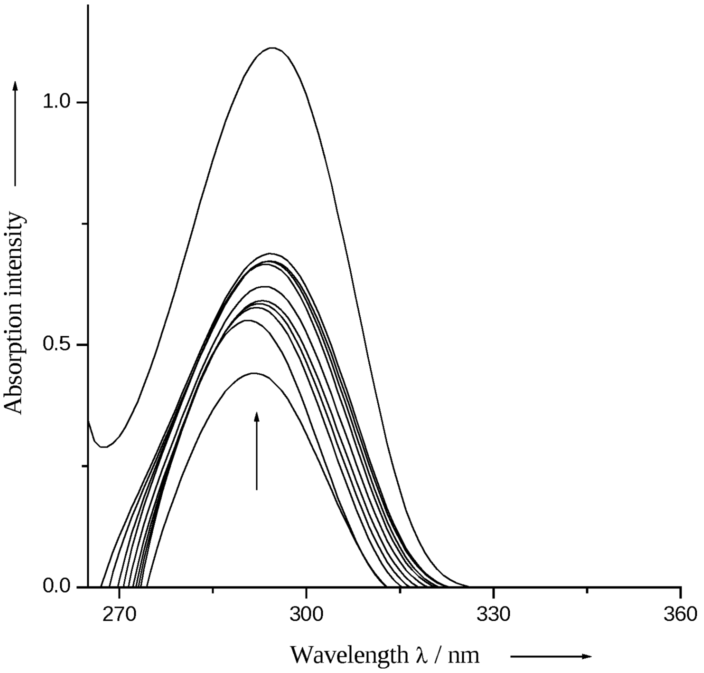

Fig. 8. UV-Vis spectra of aniline in different mole fractions of acetonitrile. (The upward arrow indicates the increase in intensity with the decreasing mole fraction of acetonitrile.)

rived before. Figure 8 shows the UV-Vis absorption spectra of aniline ($2 \cdot 10^{-4}$ M) in binary AN/DMF mixtures with different mole fractions of AN. The wavelengths (λ_{max}) and molar extinction coefficients (ε_{max}) of maximum absorption of aniline and 2-bromo-5-nitropyridine in these solvent mixtures are summarized in Table 5. It is evident from the results that, for aniline, the peak position of the UV absorption (λ_{max}) shows little dependence on the solvent ($< 1\%$). In contrast, the absorption intensity (ε_{max}) exhibits a significant increase ($> 25\%$) from 2740 M^{-1} cm^{-1} in AN to 3700 M^{-1} cm^{-1} in DMF. Thus, ε_{max} is likely to be affected by solute-solvent hydrogen-bonding [44].

This observation can be qualitatively explained as follows: Since DMF is a non-HBD solvent while AN exhibits a potential ability to donate a hydrogen atom towards the formation of a H-bond, the latter can interact with aniline through its HBD property but not the former one. This point of observation has also been explained quantitatively through correlation analysis. The intermolecular solute-solvent interactions through H-bonding were examined by correlating ε_{max} of aniline with the Kamlet-Taft's solvatochromic parameters α, β, and π^* as this equation comprises both the solvent's HBD and HBA terms. The result of the correlation is as follows:

$$\begin{aligned}\log \varepsilon_{\text{max}} &= 4.59(\pm 0.78) - 1.03(\pm 0.85)\pi^* \\ &\quad - 1.02(\pm 0.40)\alpha - 0.10(\pm 0.04)\beta, \\ N &= 11, R^2 = 0.96, sd = 0.009, \\ P_\alpha &= 47\%, P_\beta = 5\%, P_{\pi^*} = 48\%.\end{aligned} \tag{5}$$

From (5) it can be seen that the absorption intensity is influenced by both specific and non-specific solute-solvent interactions, as indicated by the percentage contributions of the α, β, and π^* parameters. Among specific interactions, the contribution of the α term is found to be dominant, and the negative sign of its coefficient suggests that the absorption intensity would decrease with an increase in the solvent's HBD property. The contribution of the solvent's HBA property (P_β) towards the solvation of aniline by the solvent mixture is less significant. Thus, an increase in the mole fraction of AN in the mixture increases the solvation around the NH_2 moiety of the aniline molecule through the HBD property, and consequently decreases the absorption intensity. Hence, the observed decrease in the rate of the reaction between anilines and 2-bromo-5-nitropyridine with an increase in the mole fraction of AN might be due to the solvation of the NH_2 moiety by the HBD solvent AN to a relatively greater extent. Such an extensive solvation around the reaction centre

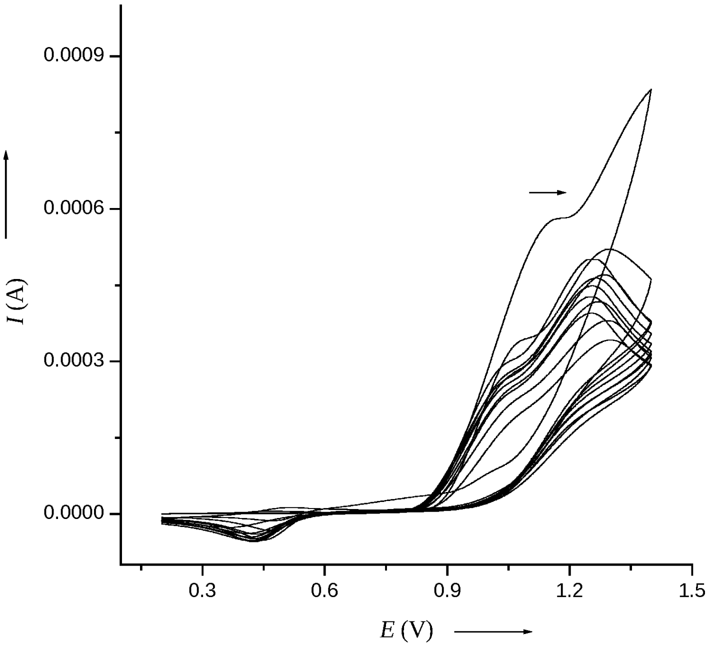

Fig. 9. Cyclic voltammogram for the oxidation of aniline ($1 \cdot 10^{-3}$ M) in different mole fractions of acetonitrile at a scan rate of 50 mV s^{-1}. (The direction of the arrow indicates the shift in oxidation potential with increasing mole fraction of acetonitrile.)

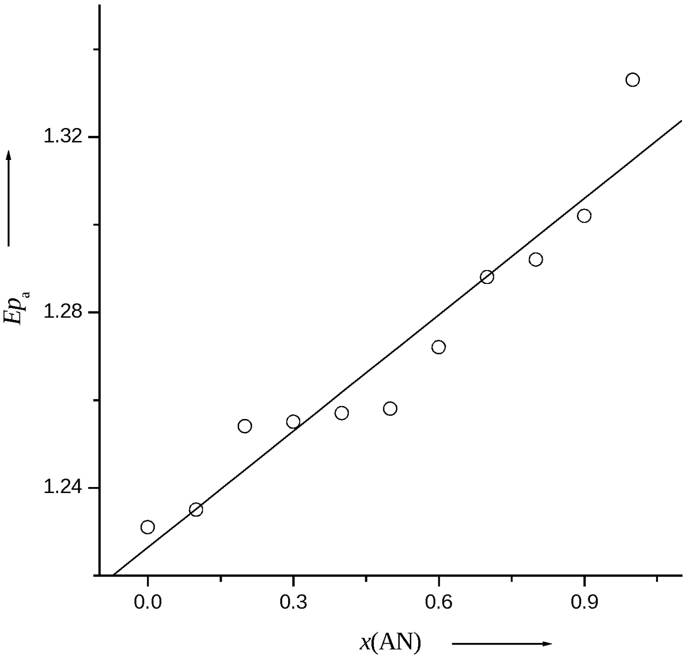

Fig. 10. Plot of oxidation potential of aniline, Ep_a, versus mole fraction of acetonitrile, x(AN).

makes the approach of the reaction partner comparatively difficult and consequently retards the rate of the overall reaction. The absorption spectra of 2-bromo-5-nitropyridine, however, do not vary in a smooth manner with the solvent, further the correlation of log ε_{max} of this compound with α, β, and π^* is very poor ($R^2 = 0.300$), and hence the solvatochromism exhibited by it is deferred here.

The above-mentioned fact was further supported by cyclic voltammetric studies of aniline in the given solvent mixtures. The cyclic voltammogram of aniline with varying mole fraction of AN is depicted in Figure 9. The anodic peak at ~ 1.3 V corresponds to the electro-oxidation of aniline. This oxidation potential shifts towards the positive side with increase in the mole fraction of AN in the binary mixture, suggesting that the removal of an electron from the NH_2 moiety (oxidation) becomes increasingly difficult. A plot of oxidation potentials, Ep_a, versus mole fraction of AN is linear ($r = 0.96$, $sd = 0.009$) with positive slope (Fig. 10). The increase in the oxidation potential of aniline with increase in the HBD property of the medium was observed earlier by us in the study of the electro-oxidation of anilines in water/2-methylpropan-2-ol [41] and water/acetic acid [42] mixtures. As the pair of electrons on the NH_2 moiety is well surrounded by HBD solvent molecules, its participation in the formation of intermediate (I) will be difficult and consequently the rate of reaction will be decelerated.

3. Experimental

3.1. Materials

All chemicals used were of analytical grade (Aldrich or Merck, India). The solvents acetonitrile and *N*,*N*-dimethylformamide were of chromatographic grade and used as received. The solid anilines were used as such and the liquid anilines were used after vacuum distillation.

3.2. Kinetic Studies

The reactions of 2-bromo-5-nitropyridine with substituted anilines in binary mixtures with varying mole fractions of acetonitrile in *N*,*N*-dimethylformamide were followed conductometrically at 30, 40, and 50 (±0.1) °C. Pseudo-first-order conditions were used in all cases. The concentration of 2-bromo-5-nitropyridine was $5 \cdot 10^{-4}$ M and that of aniline was from 0.01 to 0.02 M. The reaction is that slow that it is inconvenient to wait for its completion. Therefore, the Guggenheim method [30] was used to evaluate the rate constants (k_A) by carrying out the kinetic runs for up to 3 h. Regression coefficients of all the reaction rate constants were around 0.99. All rate determinations were carried out at least in duplicate, and the rate constants are accurate within ±3%. The product analysis was carried out, under kinetic conditions, by employing GC-MS.

3.3. Spectral Measurements

The solution FT-IR experiment was done with a horizontal attenuated total reflectance ZnSe flat prism plate in a JASCO FT-IR 460 Plus spectrometer. The electronic absorption spectra were recorded on a Shimadzu (UV 240, Graphicord) double beam spectrophotometer using 1 cm matched quartz cells. The electrochemical experiments were performed at 25 °C using a standard three-electrode, two-compartment configuration with a glassy carbon (GC–3 mm) working electrode, a spiral platinum counter electrode, and an Ag|AgCl (KCl sat.) reference electrode. The carbon electrodes were polished between the experiments with alumina (0.5 μm) paste. The cyclic voltammetric experiments were carried out with a computer-controlled electrochemical system (CHI643B Electrochemical Analyzer) at 50 mV s^{-1}.

3.4. Linear Free Energy Relationships

The effect of substituents on the reactivity was tested using the Hammett equation [9]

$$\log k = \log k^0 + \rho\sigma, \tag{6}$$

where k is the rate constant, k^0 denotes the statistical quantity corresponding approximately to k for the unsubstituted compound, σ is characteristic of the substituent (in a given position, *meta* or *para*) and independent of the reaction, whereas ρ is determined by the reaction and its conditions (reagent, solvent, catalyst, temperature) and is independent of the substituent.

3.5. Data Analysis

Correlation analyses were carried out using Microcal Origin (version 6) computer software. The goodness of the fit was discussed using a correlation coefficient and standard deviation, *sd* [9]. The percentage contribution (P_X) of a parameter to the total effect on the reactivity was computed using the regression coefficient of each parameter as reported earlier [45].

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