

## Solvent hydrogen bonding and structural effects on the reaction of biphenyl and naphthalene sulphonyl chloride with *para*-substituted anilines in dimethylformamide/acetonitrile mixtures

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Manuscript received online 03 March 2012, revised 22 April 2012, accepted 24 April 2012

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**Abstract :** Substitution reactions of some of *para*-substituted anilines with biphenylsulphonyl chloride and naphthalenesulphonyl chloride were carried out conductometrically in dimethylformamide/acetonitrile mixtures. The correlation of second order rate constants with Hammett's substituent constants yields a fairly linear straight line with a negative slope. The correlation of rate data with Kamlet-Taft's solvatochromic parameters is excellent ( $100R^2 = 97\%$ ) in both the substrates. The solvation model proposed is well supported by the solvatochromism exhibited by aniline in the solvent mixture under investigation. The molar extinction coefficient ( $\epsilon_{\max}$ ) of aniline varies appreciably up to  $\sim 25\%$  with the change in composition of the mixture. The multivariate correlation analysis of  $\epsilon_{\max}$  (with  $\alpha$ ,  $\beta$ ,  $\pi^*$ ) suggests that the solvation around  $\text{NH}_2$  moiety of aniline through hydrogen bond donor (HBD) property is found to be dominant in the solvation process and consequently in altering the rate. The observation is that the dominance of HBD property in solvation is further confirmed by the cyclic voltammetric oxidation of aniline in the solvent mixture.

**Keywords :** Aniline, solvent effect, benzenesulphonyl chloride, naphthalenesulphonyl chloride.

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### Introduction

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 in 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<sup>1</sup>.

The study of influence of solvent on the 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<sup>2-7</sup>. It has been shown that the reactivity is influenced by the preferential solvation of the reactants and/or transition state through non-specific and specific solvent-solvent-solute 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<sup>8</sup>, all known as Linear Free Energy Relationships (LFER) have been found useful for correlating reaction rates and equilibrium constants for side chain reactions for *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 revealed that the effects of structure on  $S_N2$  reactions have largely been reported<sup>9-23</sup>. However, only very few attempts have been made to study on the effect of solvent on such reactions in a more systematic manner<sup>24-30</sup>. Hence, in this article, the reaction of few *para*-substituted anilines with biphenylsulphonyl chloride (BiSC) and naphthalenesulphonyl chloride (NSC) in dimethylformamide (DMF)/acetonitrile (AcN) (both po-

lar, aprotic, hydrogen bond acceptor, PAHBA) mixtures of varying compositions has been reported.

Further, the selection of DMF-AcN solvent mixture for the study is based on the fact that the hydrogen bonding abilities of the mixture is well understood and among the PAHBA solvents, AcN exhibits a lower HBA ability and also exhibits a potential ability to donate a hydrogen atom towards the formation of a hydrogen bond<sup>31</sup>. In order to contribute to a more comprehensive analysis of the microscopic properties of binary aprotic solvent mixtures, particularly hydrogen bonding effects, it is of interest to discuss the behavior of solvent mixtures of this type. Further, one of the profound advantages of using mixed solvents is that by varying the mole fraction of the constituent solvents, the properties of the medium can be varied in a smooth and continuous manner.

### Experimental

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

**Kinetic studies** : The reactions of biphenylsulphonyl chloride and naphthalenesulphonyl chloride with substituted anilines in varying mole fractions of acetonitrile in dimethylformamide were followed conductometrically at 30, 40 and 50 ( $\pm 0.1$ ) °C. Pseudo-first order conditions were used in all cases, i.e. [Aniline] > [BiSC or NSC]. The reaction is so slow that it is inconvenient to wait for its completion. Therefore, the Guggenheim method<sup>29</sup> was used to evaluate the rate constants by carrying out the kinetic runs for up to 3 h. The second order rate constants,  $k_A$ , were obtained from the observed rate constants as reported earlier<sup>28</sup>. 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 to within  $\pm 3\%$ . The product analysis was carried out, by employing GC-MS technique.

**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 are recorded on a JASCO double beam spectrophotometer using 1 cm matched quartz cells. The electrochemical ex-

periments 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 a Ag (AgCl) (KCl sat.) reference electrode. The carbon electrodes were polished between experiments with alumina (0.5  $\mu\text{m}$ ) paste. The cyclic voltammetric experiments were carried out with a computer-controlled electrochemical system (CHI643B Electrochemical Analyzer) at 50 mV s<sup>-1</sup>.

**Linear free energy relationships** : The effect of substituents on the reactivity was tested using the Hammett<sup>8</sup> :

$$\log k = \log k^0 + \rho\sigma \quad (1)$$

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

**Linear solvation energy relationships** : The rate data were correlated with Reichardt's  $E_T(30)$  polarity parameter<sup>32</sup>. The most celebrated Kamlet-Taft solvatochromic comparison method<sup>33</sup> was also employed [eq. (2)] which incorporates both types of interactions within.

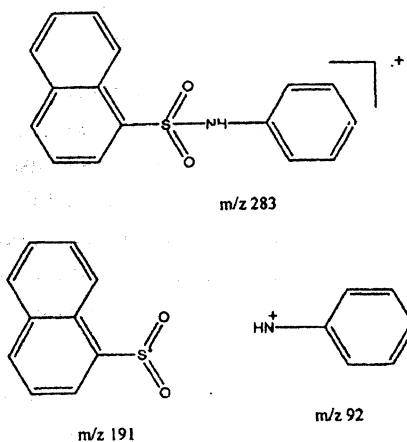
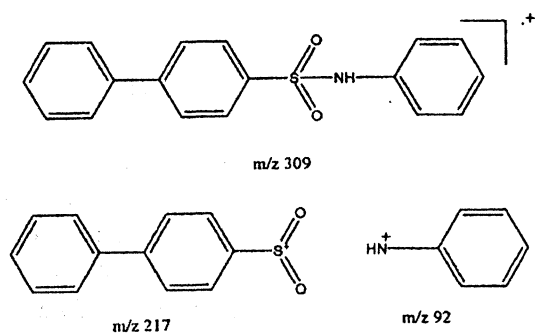
$$\log k = A_0 + s\pi^* + a\alpha + b\beta \quad (2)$$

where  $\pi^*$  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,  $\alpha$  is the solvent hydrogen bond donor (HBD) acidity which describes the ability of the solvent to donate a proton,  $\beta$  is the solvent hydrogen bond acceptor (HBA) basicity which provides a measure of the solvent's ability to accept a proton (donate an electron pair), in a solute to solvent hydrogen bond, and  $A_0$  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<sup>31</sup>.

**Data analysis** : Correlation analyses were carried out using Microcal Origin (version 6) computer software. The goodness of the fit was discussed using correlation coefficient and standard deviation,  $sd^8$ . The percentage contribution ( $P_X$ ) of a parameter to the total effect on reac-

tivity was computed using the regression coefficient of each parameter as reported earlier<sup>34</sup>.

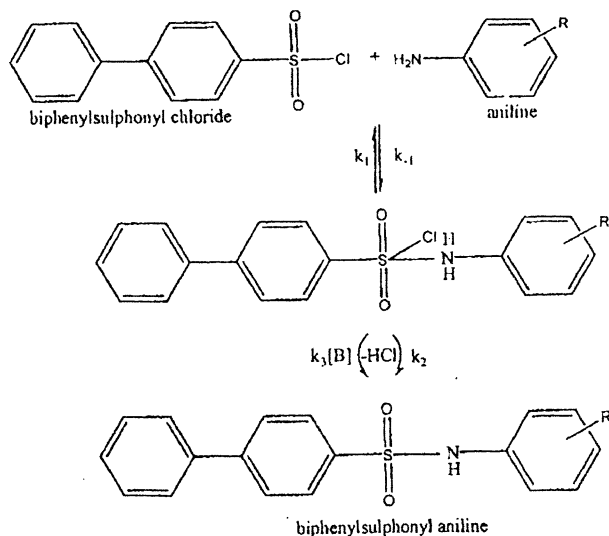
**Product analysis :** The product analysis was carried by refluxing a mixture of BiSC/NSC (3.16 mmol) and aniline (5.38 mmol) for an hour in DMF (5 ml). The mixture was cooled to room temperature and then poured into ice-cold water with vigorous stirring; the precipitate formed was filtered and recrystallized from benzene-ether mixture. The product thus obtained was subjected to GC-MS analysis. The results of the GC-MS analysis reveal that the reaction product was biphenylsulphonyl aniline ( $m/z$  309.08;  $M^+$ ) its fragmentation with  $m/z$  ratio 217.03 and 92 and naphthalenesulphonyl aniline ( $m/z$  283.07;  $M^+$ ) and its fragmentation with  $m/z$  ratio 191.02 and 92 respectively.



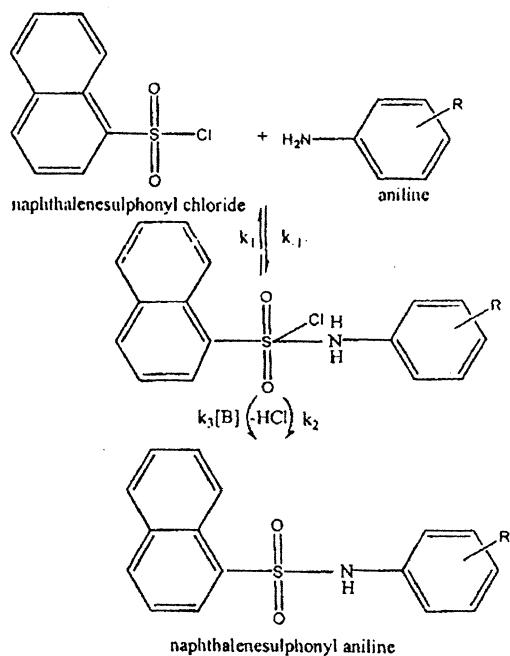
## Results and discussion

The nucleophilic substitution reaction of parent aniline and a few *para*-(Et, Me, OMe, F, Cl and NO<sub>2</sub>) substituted anilines with BiSC and NSC was studied conductometrically at 303, 313 and 323 K in the presence of varying excess [aniline] over the substrate to ensure pseudo-first order kinetics. The selection of the mole

fractions for the reaction was based on the fact that the solvatochromic parameters employed in the present study for correlation analysis are available in the literature<sup>31</sup>. Based on the kinetic results, product analysis and the conclusions of previous work<sup>35</sup> the following reaction (Schemes 1 and 2) have been proposed for the reaction of anilines with the substrate. The formation of such a type of transition state was well established in the S<sub>N</sub><sup>2</sup> reactions of aromatic amines with various substrates<sup>9,13</sup>.



Scheme 1



Scheme 2

Fig. 1 shows the solution FT-IR spectrum of the reaction mixture at different time intervals. The doublet around 2930–3000  $\text{cm}^{-1}$  corresponds to asymmetric and symmetric stretching vibrations of the two N–H bonds of the aromatic primary amine<sup>36</sup>. It is evident from the figure that with lapse of time the intensity of the peak decreases which confirms the participation of the amine group in the reaction.

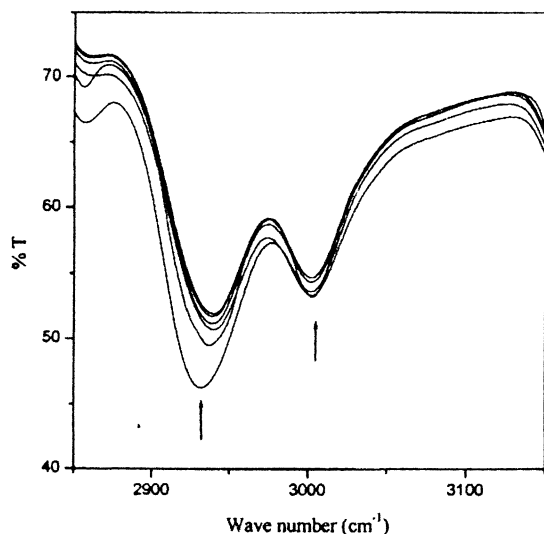


Fig. 1. FT-IR spectra of the reaction mixture in acetonitrile with increase in time.

**Thermodynamic parameters and the isokinetic relationship** : The activation parameters for the reaction of all the substituted anilines with BiSC and with NSC at 0.5 mole fraction of DMF were calculated from  $k_A$  at 303, 313 and 323 K using the van't Hoff plot by the method of least squares and are collected in Tables 1 and 2. The reaction is neither isoenthalpic nor isoentropic but com-

Table 1. Effect of temperature on the rate of reaction of anilines with biphenylsulphonyl chloride in 0.5 mole fraction of DMF and activation parameters for the reaction

Substituents in aniline	Rate constants $10^3 k_A$ ( $\text{s}^{-1}$ )			$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
	303 K	313 K	323 K			
<i>p</i> -Et	5.21	6.8	8.9	19.53	-229	88.9
<i>p</i> -Me	5.80	9.20	9.86	19.50	-228	88.6
<i>p</i> -OMe	2.91	5.93	6.70	32.16	-192	90.3
<i>p</i> -F	5.82	6.93	7.63	8.60	-264	88.8
<i>p</i> -Cl	4.06	4.9	5.01	6.13	-275	89.7
<i>p</i> -NO <sub>2</sub>	4.86	6.98	7.29	14.28	-247	89.1

$\Delta H^\ddagger$  in  $\text{kJ mol}^{-1}$ ;  $\Delta S^\ddagger$  in  $\text{JK}^{-1} \text{mol}^{-1}$ ;  $\Delta G^\ddagger$  in  $\text{kJ mol}^{-1}$ .

[Aniline] = 0.1 M, [BiSC] = 0.001 M.

Table 2. Effect of temperature on the rate of reaction of anilines with naphthalenesulphonyl chloride in 0.5 mole fraction of DMF and activation parameters for the reaction

Substituents in aniline	Rate constants $10^3 k_A$ ( $\text{s}^{-1}$ )			$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
	303 K	313 K	323 K			
<i>p</i> -Et	5.21	6.3	7.2	10.7	-258	89.1
<i>p</i> -Me	5.91	8.78	9.93	18.9	-230	88.6
<i>p</i> -OMe	3.91	5.63	6.81	20.4	-228	89.7
<i>p</i> -F	6.12	7.23	7.93	8.1	-265	88.6
<i>p</i> -Cl	5.16	6.91	7.01	10.1	-260	89.0
<i>p</i> -NO <sub>2</sub>	5.86	7.00	7.59	8.1	-266	88.7

$\Delta H^\ddagger$  in  $\text{kJ mol}^{-1}$ ;  $\Delta S^\ddagger$  in  $\text{JK}^{-1} \text{mol}^{-1}$ ;  $\Delta G^\ddagger$  in  $\text{kJ mol}^{-1}$ .

[Aniline] = 0.1 M, [NSC] = 0.001 M.

plies with the compensation law also known as isokinetic relationship. The isokinetic temperature is the temperature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature the variation of substituent has no influence on the free energy of activation. In an isoentropic reaction the isokinetic temperature lies at infinite and only enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalpic series and the reactivity is determined by the entropy of activation. The operation of isokinetic relationship is tested by plotting the logarithms of rate constants,  $k_A$ , at two temperatures ( $T_2 > T_1$ ) against each other according to eq. (3) as suggested by Exner<sup>38</sup>.

$$\log k \text{ (at } T_2) = a + b \log k \text{ (at } T_1) \quad (3)$$

In the present study linear plots imply the validity of isokinetic relationship. Representative plot is shown in Fig. 2. The operation of isokinetic relationship reveals that all the substituted anilines examined follow a common mechanism. Negative entropy of activation indicates a greater degree of ordering in the transition state than in the initial state, due to an increase in solvation during the activation process.

Likewise, the activation parameters were also calculated for aniline in different mole fractions of AcN (Tables 3 and 4). The results in Tables 3 and 4 reveal that increase in mole fraction of DMF in the medium increased the rate of the reaction. The existence of a linear relationship indicated that a single mechanism is operating in all the solvent mixtures under scan. Representative plot is shown in Fig. 3.

**Structure-reactivity correlation** : The effect of substituents on the rate was studied with seven *para*-substi-

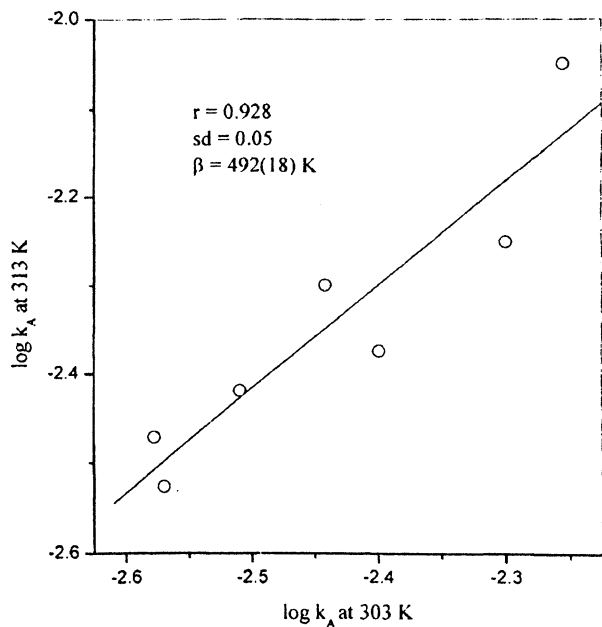


Fig. 2. The isokinetic plot for the substitution reaction of anilines with BiSC.

Table 3. Rate constants ( $10^3 k_A, s^{-1}$ ) and activation parameters for the reaction of aniline with biphenylsulphonyl chloride in various mole fractions of DMF in AcN

Mole fraction of DMF	Rate constants $10^3 k_A (s^{-1})$			$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$ (303 K)
	303 K	313 K	323 K			
0.1	0.23	0.89	1.59	78.0	-62	96.8
0.2	1.07	7.3	7.5	78.9	-44	92.4
0.3	4.38	4.60	13.51	43.5	-153	90.0
0.4	4.41	5.57	6.87	15.7	-220	82.60
0.5	4.44	5.73	6.87	15.5	-244	89.5
0.6	4.7	5.7	7.31	15.6	-243	89.42
0.7	5.63	6.87	10.8	24.2	-213	89.0
0.8	4.91	15.8	15.2	44.7	-145	88.8
0.9	13.5	20.19	22.56	18.1	-223	86.6
1.0	16.6	21.45	23.10	11.1	-247	86.0

$\Delta H^\ddagger$  in  $\text{kJ mol}^{-1}$ ;  $\Delta S^\ddagger$  in  $\text{JK}^{-1} \text{mol}^{-1}$ ;  $\Delta G^\ddagger$  in  $\text{kJ mol}^{-1}$ .

[Aniline] = 0.1 M, [BiSC] = 0.001 M.

Table 4. Rate constants ( $10^3 k_A, s^{-1}$ ) and activation parameters for the reaction of aniline with naphthalenesulphonyl chloride in various mole fractions of DMF in AcN

Mole fraction of DMF	Rate constants $10^3 k_A (s^{-1})$			$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$ (303 K)
	303 K	313 K	323 K			
0.1	3.12	3.47	3.83	5.8	-279	90.4
0.2	3.41	3.79	3.96	3.5	-285	90.1
0.3	3.48	4.38	4.79	10.6	-262	90.1
0.4	4.27	4.43	4.86	2.6	-287	89.6

Table-4 (contd.)

0.5	4.40	4.62	4.92	1.9	-289	89.5
0.6	4.50	4.96	4.98	1.5	-290	89.4
0.7	4.63	5.23	5.34	3.3	-284	89.3
0.8	4.89	5.45	5.57	2.7	-285	89.2
0.9	5.32	5.96	6.16	3.4	-282	89.0
1.0	6.01	6.38	6.58	1.1	-289	88.7

$\Delta H^\ddagger$  in  $\text{kJ mol}^{-1}$ ;  $\Delta S^\ddagger$  in  $\text{JK}^{-1} \text{mol}^{-1}$ ;  $\Delta G^\ddagger$  in  $\text{kJ mol}^{-1}$ .

[Aniline] = 0.1 M, [NSC] = 0.001 M.

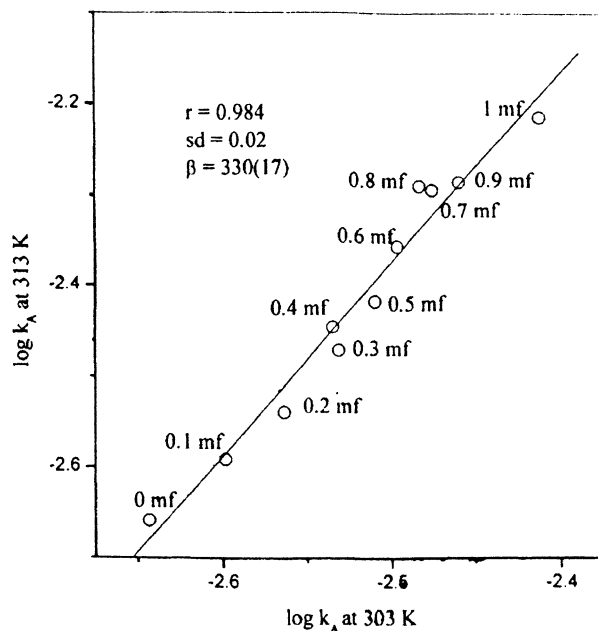


Fig. 3. The isokinetic plot for the aniline with BiSC in all the mole fractions investigated.

tuted anilines. The plot of  $\log k_A$  versus Hammett's substituent constants yields a U-shaped plot with BiSC (Fig. 4). This implies that both electron releasing and electron withdrawing substituent increase the rate compare to the parent aniline. The Hammett plot yields a negative slope with NSC. The negative slope indicated the involvement of a positively charged intermediate during the reaction<sup>8</sup>. This is, in the present study, obviously the nitrogen of the  $\text{NH}_2$  group. This facilitates the bond-breaking process in the intermediate.

**Solvent-reactivity correlation :** The title reaction has been studied in eleven different mole fractions of DMF in AcN. The second order rate constants increased with an increase in mole fraction of DMF in the mixture. The correlation of rate data with Reichard's<sup>32</sup> polarity para-

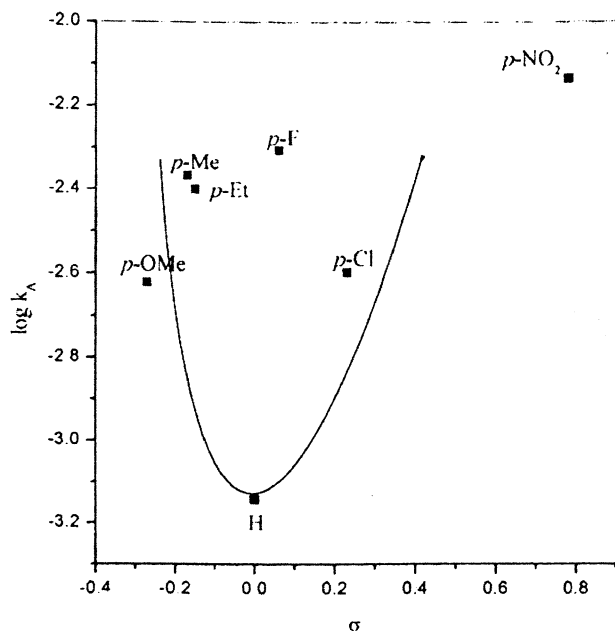
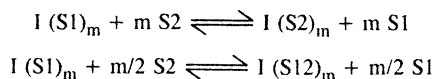


Fig. 4. The Hammett plot in DMF/AcN mixture.

eters  $E_T$  (30) is just satisfactory with an explained variance of less than 93%. Such a 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 transition state and hence the rate of the reaction. Therefore, in order to obtain a deeper insight into the various solute-solvent interactions, which influence reactivity, we have tried to adopt the solvatochromic comparison method developed by Kamlet and Taft<sup>33</sup>. The solvatochromic parameters employed in the present study were computed and reported<sup>32</sup> based on various solvent-solvent interactions which can be explained by the following general model and is based on a two solvent exchange processes (Scheme 3)<sup>1</sup>.



Scheme 3

where S1 and S2 indicate the two pure solvents to be mixed, and S12 represents a solvent 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 synergetic mixtures. The term  $m$  is the number of solvent molecules solvating the solvatochromic indicator I<sup>1</sup>.

The kinetic data were correlated with the Kamlet-Taft's solvatochromic parameters  $\alpha$ ,  $\beta$  and  $\pi^*$  [eq. (4)]. The rates of the reaction of aniline with both BiSC and NSC studied showed an excellent correlation with the solvent with an explained variance of 97%. The statistical results and weighted percentage contributions of the solvatochromic parameters are shown in the following equations. Such an excellent correlation indicates the existence of specific solute-solvent interactions in the reactions.

With BiSC :

$$\begin{aligned} \log k_A &= 17.5 (\pm 5.03) - 28.1 (\pm 7.16)\pi^* + \\ &\quad 1.5 (\pm 1.22)\alpha + 4.8 (\pm 1.75)\beta \\ (N = 11, R^2 = 0.97, sd = 0.016, P_\alpha = 4\%, \\ &\quad P_\beta = 14\%, P_{\pi^*} = 82\%) \end{aligned} \quad (4)$$

With NSC :

$$\begin{aligned} \log k_A &= -0.6 (\pm 0.05) - 2.3 (\pm 0.75)\pi^* + \\ &\quad 0.25 (\pm 0.13)\alpha + 0.1 (\pm 0.02)\beta \\ (N = 11, R^2 = 0.97, sd = 0.06, P_\alpha = 9\%, \\ &\quad P_\beta = 4\%, P_{\pi^*} = 87\%) \end{aligned} \quad (5)$$

The percentage contribution of the 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 substituents. This may be due to 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<sup>32</sup>. Hence, the percentage contribution of a particular solvatochromic parameter, for given aniline, may be due to the combination of one or more factors mentioned the average value was employed for further discussions. Also majority of the data is in line with the above mentioned average.

The statistical results of the correlation of the rate of the reactions of aniline with sulphonylchlorides in DMF/AcN mixtures and the resultant percentage contributions of the solvatochromic parameters [eqs. (4) and (5)] indicated that the reactivity is influenced by both non-specific and specific solute-solvent interactions. Since AcN possesses HBD property, it can solvate the  $NH_2$  moiety of aniline through specific solute-solvent interactions. In-

crease in the mole fraction of DMF in the mixture may have progressively removed the solvation around the NH<sub>2</sub> moiety, allowing the reaction partner to approach the aniline relatively easier and consequently increased the rate of the reaction as observed. An attempt was also made to employ UV-Visible and cyclic voltammetric techniques to support the presumption.

The UV-Visible absorption spectra of the reactants in the solvent mixture and the solvatochromism exhibited by them adequately support the conclusions derived above. Fig. 5 shows the UV-Visible absorption spectra of aniline in different mole fractions of DMF. The wavelengths ( $\lambda_{\max}$ ) and molar extinction coefficients ( $\epsilon_{\max}$ ) of maximum absorption of aniline in these solvent mixtures are summarized in Table 5. It is evident from the results that, the peak position of UV absorption ( $\lambda_{\max}$ ) shows little dependence on the solvent (<1%). In contrast, the absorption intensity ( $\epsilon_{\max}$ ) exhibits a significant increase (>25%) from 2740 M<sup>-1</sup> cm<sup>-1</sup> in AcN to 3705 M<sup>-1</sup> cm<sup>-1</sup> in DMF. Thus,  $\epsilon_{\max}$  is likely to be affected by hydrogen

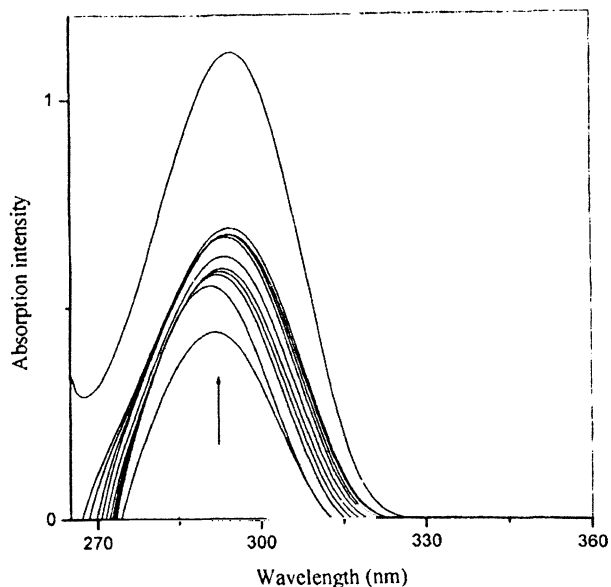


Fig. 5. UV-Visible spectra for the aniline in different mole fraction of DMF (The upward arrow indicates the increase in intensity with the increase in mole fraction of DMF).

bonding<sup>39</sup>.

This observation can qualitatively be explained as : since DMF is a non-hydrogen-bonding solvent while AcN exhibits a potential ability to donate a hydrogen atom towards the formation of an H-bond, the latter can inte-

Mole fraction of DMF	Aniline $\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (M <sup>-1</sup> cm <sup>-1</sup> )
0	290.9	2740
0.1	292.3	2775
0.2	292.4	2885
0.3	292.8	2935
0.4	292.9	2960
0.5	293.5	3115
0.6	293.8	3325
0.7	294.5	3365
0.8	294.7	3375
0.9	294.5	3455
1.0	294.9	3705

ract with aniline through 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  $\epsilon_{\max}$  of aniline against the Kamlet-Taft's solvatochromic parameters  $\alpha$ ,  $\beta$  and  $\pi^*$  [(eq. (6))], as this equation comprises both the HBD and HBA terms in it. The result of the correlation is represented as :

$$\log \epsilon_{\max} = 3.15 (\pm 0.17) + 0.44 (\pm 0.21)\pi^* - 0.14 (\pm 0.04)\alpha - 0.05 (\pm 0.01)\beta$$

$$(N = 11, R^2 = 0.96, sd = 0.01, P_{\alpha} = 22\%, P_{\beta} = 8\%, P_{\pi^*} = 70\%) \quad (6)$$

It can be seen from the results that the absorption intensity is influenced by both specific and non-specific solute-solvent interactions as indicated by the percentage contributions of  $\alpha$ ,  $\beta$  and  $\pi^*$  parameters. Among specific interactions, the contribution of  $\alpha$  term is found to be dominant and the negative sign of coefficient of this term suggests that the absorption intensity would decrease with increase in HBD property of the medium. The contribution of HBA property ( $P_{\beta}$ ) towards the solvation of aniline by the solvent mixture is less significant. Thus increase in the mole fraction of DMF in the mixture progressively decreases the solvation around the NH<sub>2</sub> moiety of aniline molecule and consequently increases the absorption intensity. Hence the observed increase in rate of the reaction between aniline and 2-halo-5-nitropyridines with increase in the mole fraction of DMF might be due to the desolvation of the NH<sub>2</sub> moiety to a relatively greater extent. Such a solvation of aniline by can through HBD

property around the reaction centre would make the approach of the reaction partner comparatively difficult and consequently retard the rate of the overall reaction.

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 DMF is depicted in Fig. 6. The anodic peak at  $\sim 1.3$  V corresponds to the electro-oxidation of aniline. This oxidation potential shifts towards the

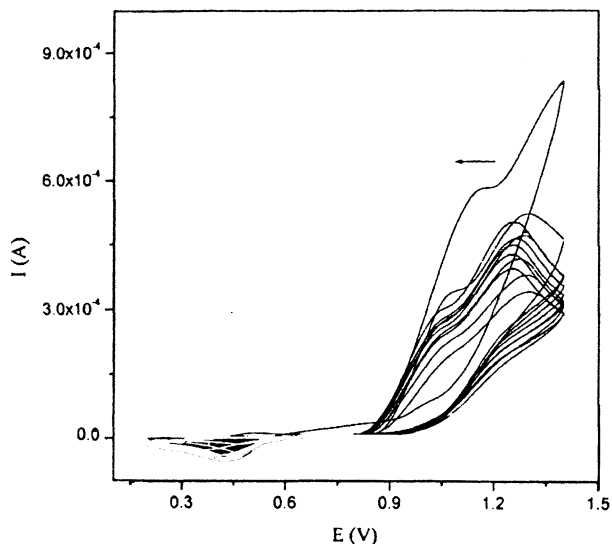


Fig. 6. Cyclic voltammogram for the oxidation of aniline ( $1 \times 10^{-3}$  M) in different mole fractions of DMF at a scan rate of  $50 \text{ mV s}^{-1}$  (The direction of the arrow indicates the shift in oxidation potential with increase in mole fraction of DMF).

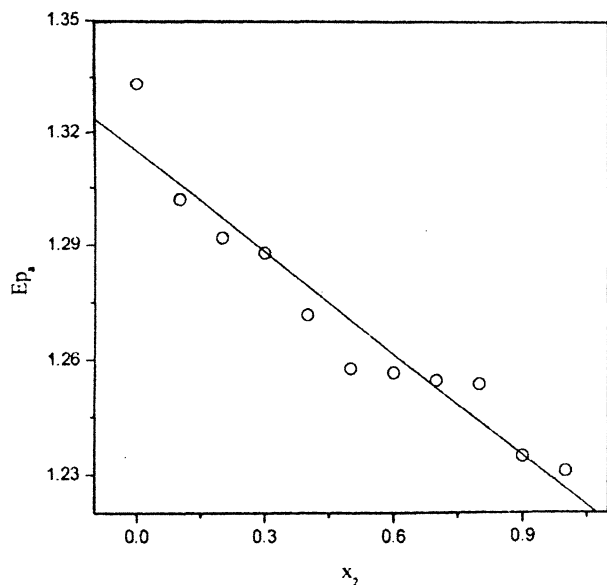


Fig. 7. Plot of oxidation potential of aniline ( $E_{p_a}$ ) versus mole fraction of DMF ( $x_2$ ).

less positive side with an increase in the mole fraction of DMF in the mixture suggesting that the removal of electron from  $\text{NH}_2$  moiety (oxidation) becomes increasingly easier. A plot of oxidation potentials,  $E_{p_a}$ , versus mole fraction of DMF is linear ( $r = 0.96$ ,  $sd = 0.009$ ) with negative slope (Fig. 7). As the pair of electrons on the  $\text{NH}_2$  moiety is well surrounded by the HBD solvent molecules, its participation in the formation of the transition state ( $I$ ) will be difficult and consequently the rate of the reaction will be decelerated.

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