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 $\sim 25\%$ 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.