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Reaction kinetics investigation of 1-fluoro-2,4-dinitrobenzene with substituted anilines in ethyl acetate–methanol mixtures using linear and nonlinear free energy relationships

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Aromatic nucleophilic substitution reaction of 1-fluoro-2,4-dinitrobenzene with para-substituted and meta-substituted anilines was kinetically investigated in the mixtures of ethyl acetate and methanol at room temperature. The correlation of second-order rate coefficients with Hammett's substituent constants yields a fairly linear straight line with negative slope in different mole fractions of ethyl acetate–methanol mixtures. The measured rate coefficients of the reaction demonstrated a dramatic variation in ethyl acetate–methanol mixtures with the increasing mole fraction of ethyl acetate. Linear free energy relationship (LFER) investigations confirm that polarity has a major effect on the reaction rate whereas the hydrogen-bonding ability of the media has a slight effect on it. Nonlinear free energy relationship based on preferential solvation hypothesis showed differences between the microsphere solvation of the solute and the bulk composition of the solvents, and non-ideal behavior is observed in the trend of the rate coefficients, which cover the LFER results. Copyright © 2011 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this paper.

Keywords: aromatic nucleophilic substitution reaction; Hammett equation; preferential solvation; solvent effects; solvent–solvent interactions

INTRODUCTION

Solvents play a key role in many chemical and physical processes (reaction rates, selectivity, chemical equilibria, position and intensity of spectral absorption bands).[1,2] In addition to the solvents, others such as the effect of the aromatic ring substituents,[3–6] ring size of the nucleophile,[7] and the electronic nature and position of the substituents[8] affect the rate of the aromatic nucleophilic substitution reactions.

Some of the factors that affect the reaction rates are closely related to the nature and extent of solute–solvent interactions (the solvation effect) locally developed in the immediate vicinity of the solute, solvent–solvent interactions (the general medium effect), and solute–solute interactions (the intersolute effects).[9–13] In mixed solvents, solute–solvent interactions are much more complex than solvent–solvent interactions because of the possibility of preferential solvation by any of the solvent present in the mixture.[9] On the other hand, solvent–solvent interactions can strongly affect solute–solvent interactions. The problem is to identify and assess the relative importance of various factors on the solvent effects for studying on the reaction rates.[14] The solvent effect on a typical property is described by a general correlation model, which gives a simultaneous separate calculation of the contributions of nonspecific solute–solvent interactions (such as polarity and polarizability) and specific solute–solvent interactions (such as electron donor–acceptor and hydrogen-bond donor–acceptor abilities).[1,2,11,15]

Numerous studies have been carried out on the reaction of nitroaryl derivatives with primary and secondary amines in solvent mixtures.[2–8,12–17] Aniline derivatives have been used recently as nucleophiles in the aromatic nucleophilic substitution reactions.[18,19] We therefore choose the reaction of 1-fluoro-2,4-dinitrobenzene with meta-substituted and para-substituted anilines in ethyl acetate–methanol mixture to study the solvent effects and the Hammett parameters on the rate coefficient. In addition, the rate coefficients data were interpreted according to solvent effects and preferential solvation as a linear and nonlinear model, respectively.

RESULTS AND DISCUSSION

Reactions of 1-fluoro-2,4-dinitrobenzene with some substituted anilines (indicated in Table 1) were studied at 25 °C in ethyl acetate and methanol mixtures. Ethyl acetate was taken as the hydrogen-bond acceptor (HBA) and methanol as the hydrogen-bond donor (HBD) and an HBA species. In addition to solute–solvent

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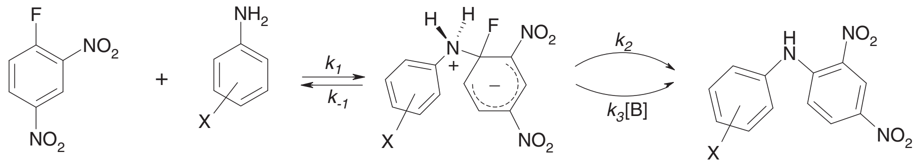
Table 1. Second-order coefficients (k_A, $M^{-1} s^{-1}$) for the reaction of anilines with 1-fluoro-2,4-dinitrobenzene in various mole fraction of ethyl acetate in methanol at 25 °C

Substituents in aniline	Mole fraction of ethyl acetate										
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
None ($10^3 \times k_A$)	15.8	11.8	8.50	5.92	5.06	4.61	3.95	3.25	2.47	1.44	0.203
p-Me ($10^3 \times k_A$)	77.0	61.2	43.6	28.8	22.2	19.2	16.7	14.5	11.3	6.04	0.420
p-OMe ($10^2 \times k_A$)	15.5	11.9	8.64	5.93	4.56	3.67	2.92	2.32	1.82	1.03	0.104
p-OH ($10^2 \times k_A$)	21.2	17.3	13.9	11.2	9.18	7.38	6.15	5.18	3.75	2.16	0.217
p-NHCOMe ($10^3 \times k_A$)	17.3	12.4	8.77	6.61	5.26	4.52	3.99	3.35	2.73	1.54	0.305
p-NH_2 ($10 \times k_A$)	13.4	10.3	7.81	5.81	4.81	4.05	3.41	2.72	2.16	1.16	0.105
p-COOH ($10^5 \times k_A$)	50.5	34.0	23.4	15.7	12.2	9.71	7.92	6.79	5.21	3.05	0.403
p-Cl ($10^4 \times k_A$)	16.1	10.9	7.02	4.65	3.41	2.81	2.46	2.12	1.72	0.814	0.082
p-Br ($10^4 \times k_A$)	15.0	9.72	6.77	4.42	3.18	2.66	2.23	1.81	1.34	0.731	0.078
m-Me ($10^3 \times k_A$)	17.3	12.7	9.35	6.66	5.35	4.62	4.05	3.38	2.81	1.61	0.326
m-OMe ($10^4 \times k_A$)	80.1	57.6	43.5	32.8	25.5	21.1	17.7	15.2	11.9	6.69	0.951
m-OH ($10^4 \times k_A$)	78.6	58.4	44.2	35.0	27.6	23.4	19.1	10.0	12.2	6.40	0.824



Scheme 1.

interactions, the acidic hydrogen atom of methanol can readily form a complex with the oxygen atom of ethyl acetate, which in turn can affect the reaction rate.

The gross mechanism of these reactions in all solvents is given in Scheme 1.[3–6] The breakdown of the zwitterionic intermediate can occur spontaneously or by a base-catalyzed mechanism. The application of the steady-state hypothesis to the gross mechanism shown in Scheme 1 gives Equation (1), where k_A is the observed second-order rate coefficient and B is aniline as a base catalyst.

$$k_A = \frac{k_1(k_2 + k_3[B])}{k_{-1} + k_2 + k_3[B]} \quad (1)$$

Both the formation of the intermediate and its decomposition to products can be a rate-limiting step. If $k_{-1} << (k_2 + k_3[B])$, then $k_A = k_1$, thus the reaction is not base catalyzed, and the formation of the intermediate is the rate-limiting step; otherwise, the reactions proceed through the base catalysis. The second-order rate coefficients of the reactions under pseudo-first-order conditions with excess of parent aniline were determined at different mole fractions of ethyl acetate in methanol, and the results are summarized in Table 1. The selection of mole fractions was based on the fact that the applied solvatochromic parameters were available in the literatures.[16] This solvatochromic parameters represent solute–solvent interactions (so-called empirical scales), such as normalized polarity (E_T^N), dipolarity–polarizability (π^*), and HBD (α) and HBA ability (β).[20] These parameters have been used to explain variations of the reaction rate by modifying the reaction media.

Structure–reactivity correlation

The Hammett correlation classically is applied to predict the effects of substituents on reaction-rate constants between organic compounds.[17,21–24] Both inductive and resonance effects determine the kind of substituents. The substituents can have either an electron-withdrawing or an electron-donating effect. The former decreases the electron density of the aromatic ring whereas the latter has an increase effect. The Hammett constant (σ) reflects the effects of both inductive and resonance effects on substituents. Values of σ were taken from Hansch *et al.*[25] The Hammett correlations were tested for the reaction between 1-fluoro-2,4-dinitrobenzene with substituted anilines in the solvent mixture. A typical plot of Hammett correlations is shown in Figure 1, which demonstrates a good linear behavior with negative slope, and its

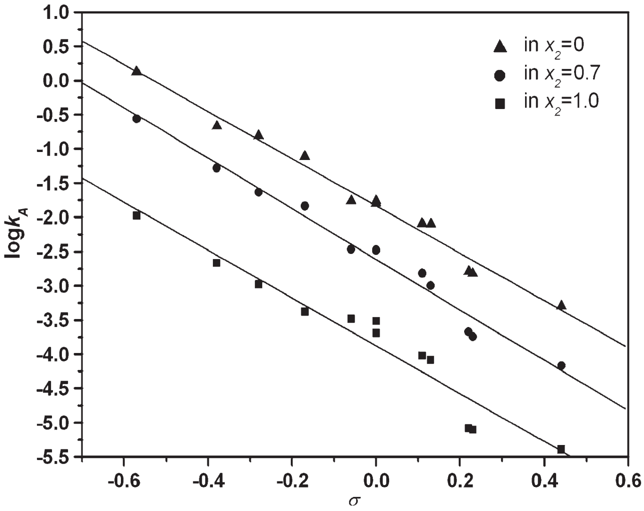


Figure 1. Typical Hammett plot of logk_A versus constant σ for the reaction in the solvent mixtures (x_2 is the mole fraction of ethyl acetate)

Table 2. Hammett's parameters for the reaction of 1-fluoro-2,4-dinitrobenzene with substituted anilines in the mixture of ethyl acetate and methanol at 25 °C

x_2[a]	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
ρ	−3.451	−3.537	−3.591	−3.635	−3.673	−3.678	−3.677	−3.690	−3.655	−3.664	−3.498
R^2	0.982	0.980	0.979	0.976	0.974	0.973	0.973	0.978	0.972	0.969	0.938

[a] x_2 is the mole fraction of ethyl acetate.

Table 3. Statistical (R^2, SD), correlation (*e*, *a*, and *b*), and standardized coefficients ($S_{E_{\mathrm{T}}^{\mathrm{N}}}$, S_α, and S_β) for correlation of logk_A with solvatochromic parameters at 25 °C (11 data were used in these correlations)

Substituents in aniline	R^2	SD[a]	Const.[b]	*e*[c]	*a*[c]	*b*[c]	$S_{E_{\mathrm{T}}^{\mathrm{N}}}$	S_α	S_β
None	0.974	0.09	−4.55 (0.12)	3.41 (0.18)	—	—	—	—	—
	0.998	0.03	−5.54 (0.12)	8.07 (0.52)	−2.43 (0.27)	—	2.34	−1.36	—
	0.988	0.06	−3.50 (0.37)	4.47 (0.39)	—	−2.86 (0.98)	1.30	—	−0.33
p-Me	0.984	0.08	−4.36 (0.11)	4.10 (0.18)	—	—	—	—	—
	0.994	0.06	−5.12 (0.23)	7.71 (1.05)	−1.88 (0.54)	—	1.87	−0.88	—
	0.995	0.05	−3.21 (0.29)	5.57 (0.30)	—	−3.13 (0.76)	1.27	—	−0.30
p-OMe	0.970	0.11	−4.00 (0.15)	3.98 (0.23)	—	—	—	—	—
	0.995	0.05	−5.20 (0.19)	9.63 (0.87)	−2.95 (0.45)	—	2.39	−1.41	—
	0.982	0.08	−2.83 (0.52)	5.16 (0.55)	—	−3.18 (1.38)	1.28	—	−0.31
p-OH	0.993	0.05	−3.56 (0.07)	3.71 (0.10)	—	—	—	—	—
	0.998	0.03	−4.05 (0.12)	6.00 (0.53)	−1.19 (0.28)	—	1.61	−0.62	—
	0.995	0.04	−3.11 (0.25)	4.17 (0.26)	—	−1.23 (0.66)	1.12	—	−0.13
p-NHCOMe	0.954	0.11	−4.35 (0.15)	3.13 (0.23)	—	—	—	—	—
	0.997	0.03	−5.60 (0.13)	9.03 (0.57)	−3.08 (0.29)	—	2.82	−1.85	—
	0.976	0.08	−3.08 (0.48)	4.42 (0.51)	—	−3.45 (1.28)	1.38	—	−0.43
p-NH_2	0.990	0.06	−2.91 (0.08)	3.86 (0.13)	—	—	—	—	—
	0.998	0.03	−3.56 (0.12)	6.93 (0.55)	−1.60 (0.28)	—	1.79	−0.80	—
	0.996	0.04	−2.14 (0.25)	4.64 (0.26)	—	−2.11 (0.66)	1.20	—	−0.22
p-COOH	0.947	0.14	−6.38 (0.19)	3.73 (0.29)	—	—	—	—	—
	0.996	0.04	−7.96 (0.17)	11.18 (0.78)	−3.89 (0.41)	—	2.92	−1.96	—
	0.974	0.10	−4.73 (0.60)	5.41 (0.63)	—	−4.51 (1.58)	1.41	—	−0.48
p-Cl	0.960	0.131	−6.13 (0.18)	4.07 (0.28)	—	—	—	—	—
	0.994	0.05	−7.58 (0.22)	10.89 (0.99)	−3.56 (0.51)	—	2.62	−1.65	—
	0.985	0.06	−4.39 (0.50)	5.83 (0.52)	—	−4.74 (1.31)	1.40	—	−0.45
p-Br	0.955	0.14	−6.18 (0.18)	4.07 (0.29)	—	—	—	—	—
	0.996	0.05	−7.75 (0.19)	11.49 (0.85)	−3.87 (0.44)	—	2.76	−1.80	—
	0.978	0.10	−4.50 (0.59)	5.77 (0.62)	—	−4.57 (1.57)	1.39	—	−0.44
m-Me	0.951	0.11	−4.31 (0.15)	3.09 (0.23)	—	—	—	—	—
	0.996	0.03	−5.57 (0.14)	9.04 (0.63)	−3.01 (0.32)	—	2.85	−1.89	—
	0.974	0.09	−3.05 (0.50)	4.37 (0.52)	—	−3.44 (1.32)	1.38	—	−0.43
m-OMe	0.971	0.09	−4.92 (0.13)	3.48 (0.20)	—	—	—	—	—
	0.997	0.03	−5.99 (0.13)	8.54 (0.58)	−2.64 (0.30)	—	2.42	−1.44	—
	0.985	0.07	−3.81 (0.42)	4.61 (0.44)	—	3.02 (1.10)	1.30	—	−0.34
m-OH	0.959	0.12	−5.02 (0.16)	3.63 (0.25)	—	—	—	—	—
	0.984	0.08	−6.10 (0.33)	8.76 (1.47)	−2.68 (0.76)	—	2.37	−1.40	—
	0.969	0.11	−4.07 (0.63)	4.58 (0.67)	—	−2.56 (1.68)	1.24	—	−0.28

[a] Standard deviation.

[b] Intercept of the single or multiparameter correlation.

[c] *e*, *a*, and *b* are the coefficients of $E_{\mathrm{T}}^{\mathrm{N}}$, α, and β, respectively.

values are summarized in Table 2. The negative sign of the Hammett slope implies that positive charge develops on the N-atom as the transition state is formed. This is expectable in nucleophilic substitution reactions. The high magnitude of ρ values suggests preferable influence of nucleophilicity of the substituted anilines on the reaction rate,[19,26] which confirms that the formation of the intermediate is the rate-limiting step in all solvent compositions.

Solvent–reactivity correlations

In order to determine the incidence of each type of solvent properties on the kinetics of the reaction, a linear free energy relationship (LFER) correlation based on Kamlet, Abboud and Taft[27,28] hypothesis was applied. This model is based on the single or multiparameter correlation between the log*k* of the reaction and the solvatochromic parameters of the media. The data derived from these correlation studies are presented in Table 3. Multiparameter regression can be usually used, because combination of some of the solvent properties can affect the rate coefficient. The second-order rate coefficients decrease rapidly with the increasing mole fraction of ethyl acetate (Table 1). Because changes in solvent polarity and hydrogen-bonding interactions are parallel to the variation of the rate coefficients, each solvent parameter can be effective on the reaction rate. Single-parameter correlations of $\log k_A$ versus E_T^N in all composition of the solvents represent a good result, which indicates that the second-order rate coefficient of the reactions increases with the increase of this parameter (Table 3). The intermediate has a zwitterionic characterization, thus the reaction rates are accelerated in polar solvents. A dual-parameter correlation including HBD and E_T^N can produce a better fit compared with the single-parameter regressions, and therefore the former is preferred. Figure 2 shows the ability of the dual-parameter correlation in the reproduction of the reaction-rate coefficients.

Normally, the presence of alkanols decreases the reaction rate in this type of reaction because of its HBD character;[5,6] in fact, the low basicity of the aniline derivatives would play a role in the solvent–nucleophile interactions. Contrary to the normalized polarity, the HBD ability of solvent reduces the rate of reaction. Two reasons can be attributed for this reduction. Firstly, in the presence of aniline or its derivations, methanol is known to act as an HBD, and there is evidence of strong hydrogen-bonding interaction between anilines and methanol.[29] Therefore, anilines are stabilized via this interaction, and the reaction rate decreases as the HBD ability of the media increases. Secondly, ethyl acetate is an HBA molecule, and methanol is an HBD species in the solvent mixtures. Strong solvent–solvent interactions in this media can be related to the hydrogen-bonding interaction between methanol and ethyl acetate to give a complex structure that is more or less polar than the two constituents of mixture.[12,14] This behavior is attributed to the preferential solvation of solutes by mixed solvent.[9–14]

Similar correlations were also observed between $\log k_A$ with normalized polarity and the HBA ability of the media (Table 3 and Figure 3). The negative effect of the HBA ability of the solvent on the reaction rate has stark resemblance to that of the HBD ability.

On the other hand, standardized coefficients of the solvent properties in all dual-parameter correlations show that the nonspecific interactions of the solvent is a preferable and effective parameter, compared with specific interactions such as the HBD and HBA abilities of the media.

Preferential solvation model

Interest on preferential solvation as a nonlinear model in mixed solvents has increased noticeably in recent years.[9–14] The interpretation of the main features requires simple models that may describe the behavior of solutes and the structure of binary solvents. These models may provide valuable solute–solvent and solvent–solvent structural information. Preferential solvation was analyzed in this work with the Buhvestov[9,11] models, which are based on a simple exchange of two solvents according to Equations (2) and (3)

$$\mathrm{I(S1)_2 + 2S_2 \leftrightarrow I(S2)_1 + 2S_1} \tag{2}$$

$$\mathrm{I(S1)_2 + S_2 \leftrightarrow I(S12)_2 + S_1} \tag{3}$$

where I stands for the solute, S1 and S2 for the pure solvents, and S12 for the solvent formed by the interaction of solvents 1 and 2. I(S1), I(S2), and I(S12) represent the solute solvated by the S1, S2, and S12 species. Equation (2) reflects the total exchange of solvent 1 by solvent 2 in the solvation sphere of the solute, and Equation 3 corresponds to the exchange by the double-structure solvents. The constants of two processes are defined

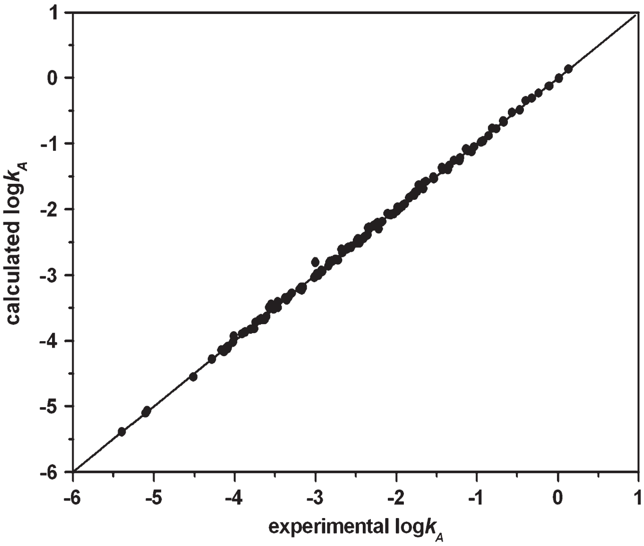


Figure 2. The plot of calculated $\log k_A$ versus the experimental values from dual-parameter correlation with normalized polarity and hydrogen-bond donor ability of the media

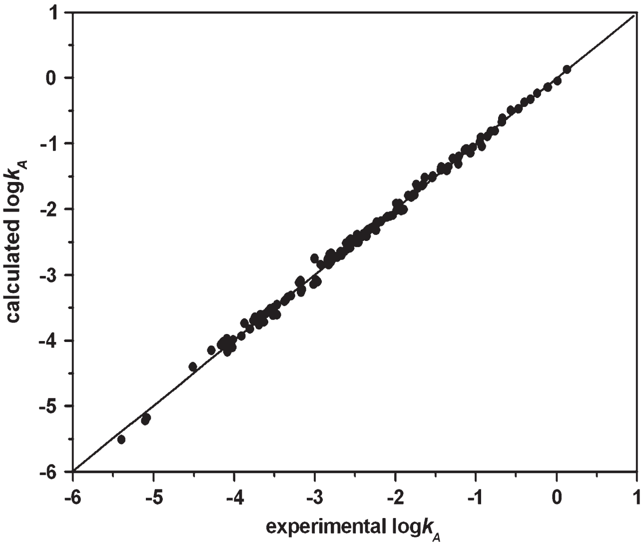


Figure 3. The plot of calculated $\log k_A$ versus the experimental values from dual-parameter correlation with normalized polarity and hydrogen-bond acceptor ability of the media

Table 4. Parameters from Equation (8) for the mixture of ethyl acetate with methanol for second-order rate coefficient of the reaction at 25 °C[a]

Substituents in aniline	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	SD	R^2
None	−1.79	−3.69	−2.44	0.178	3.24	0.0008	0.998
p-Me	−1.08	−3.38	−1.87	0.0889	2.55	0.0017	0.997
p-OMe	−0.791	−2.98	−1.72	0.0661	1.82	0.0005	0.999
p-OH	−0.667	−2.66	−1.32	0.0745	1.65	0.0001	0.999
p-NHCOMe	−1.75	−3.52	−2.44	0.191	3.21	0.0006	0.998
p-NH_2	0.138	−1.98	−0.534	0.111	2.39	0.0003	0.999
p-COOH	−3.28	−5.40	−4.23	0.103	2.51	0.0005	0.999
p-Cl	−2.77	−5.09	−3.68	0.140	3.15	0.0021	0.997
p-Br	−2.81	−5.11	−3.77	0.121	2.66	0.0008	0.999
m-Me	−1.75	−3.49	−2.46	0.159	2.88	0.0007	0.998
m-OMe	−2.09	−4.02	−2.82	0.125	2.51	0.0003	0.999
m-OH	−2.11	−4.08	−3.04	0.0375	1.32	0.0044	0.991

[a] Y_1, Y_2, and Y_{12} are logk_A in methanol, ethyl acetate and mixed solvent, respectively.

by the preferential solvation parameters $f_{2/1}$ and $f_{12/1}$ according to Equations (4) and (5)

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2^0/x_1^0)^2} \tag{4}$$

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{x_2^0/x_1^0} \tag{5}$$

where x_i^s is the mole fraction of the solvent *i* in the microsphere solvation of the solute, and x_i^0 represents the mole fraction of the solvents in the bulk mixed solvent. The parameters $f_{2/1}$ and $f_{12/1}$ measure the tendency of the solute to be solvated by solvents S2 and S12 with reference to solvent S1.

Considering that the addition of all different mole fractions must be equal to unity Equation (6)

$$x_1^s + x_2^s + x_{12}^s = 1 \tag{6}$$

the mole fractions in the sphere of solvation of solute can be easily calculated from the preferential solvation parameters and solvent composition.[30]

The physical property (*Y*) in the solvent mixtures is calculated as an average of the properties in pure solvents S1, S2, and S12 (Y_1, Y_2, and Y_{12}, respectively) according to the mole fractions of these solvents in the solute's microsphere of solvation:

$$Y = x_1^s Y_1 + x_2^s Y_2 + x_{12}^s Y_{12} \tag{7}$$

and by substituting x_1^s, x_2^s, and x_{12}^s into Equation (7), the physical property *Y* can be evaluated from those of pure solvents, Y_1 and Y_2, according to Equation (8).

$$Y = \frac{Y_1(1-x_2^0)^2 + Y_2 f_{2/1}(x_2^0)^2 + Y_{12} f_{12/1}(1-x_2^0)x_2^0}{(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0} \tag{8}$$

The solute–solvent interactions have been widely investigated by using the physical property *Y* as a solvatochromic parameter.[9–14,30] In addition, this model can be explained by applying the free activation energy. Hence, logk_A was taken as *Y* parameter in Equation (8), and its correlation with solvatochromic parameters of the solvent was tested. Interesting results were observed, which have been summarized in Table 4. The ability of Equation (8) in reproducing the reaction rate coefficients has been shown in Figure 4. In addition to the good agreement of the data with preferential solvation model, low $f_{2/1}$ values show that solutes are preferentially solvated by methanol. Likewise, the $f_{12/1}$ parameter reveals that solutes are preferentially solvated by the mixed solvent in ethyl acetate–methanol mixtures. Preferential solvation arises whenever the bulk mole fraction solvent composition differs from the solvation microsphere.[14] Thus, we expect that free molecules of ethyl acetate are rarely found in the microsphere solvation of the solutes. The non-ideal behavior that was observed for logk_A values in these mixtures can be related to the solvent–solvent interaction. As mentioned before, complex molecules formed from hydrogen-bonding interactions between two solvents, which are preferentially present in the microsphere solvation of the solutes, solvated strongly the reactants and the transition state. Therefore, a positive deviation from the ideality is observed for logk_A.

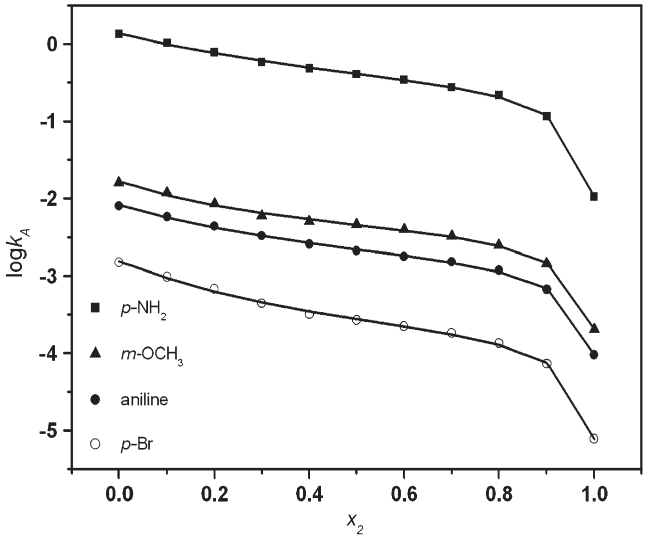


Figure 4. The typical plot of logk_A versus x_2. The solid curves have been calculated from coefficients of Equation (8) given in Table 4, and the points are experimentally determined

EXPERIMENTAL METHODS

Materials

Aniline and its derivatives were purchased from Merck (Whitehouse Station, NJ, USA). The former was purified by vacuum distillation, and the latter were in analytical grade. Solid compounds were recrystallized from water/ethanol and water/acetone. 1-fluoro-2,4-dinitrobenzene (m.p. 26–28 °C) was obtained from Fluka (St. Louis, MO, USA). The solvents methanol and ethyl acetate were of chromatographic grade and used without further purification.

Kinetic procedures

The kinetics of 1-fluoro-2,4-dinitrobenzene with substituted anilines were measured spectrophotometrically using UV–Vis Cintra 40 spectrophotometer (Braeside, VIC, Australia) coupled with a thermocell (1.00 cm quartz cell) at 25 °C. The kinetic runs were carried out by measuring the product absorbance from 350 to 360 nm at constant concentration of substituted anilines (0.01 mol L^{-1}). Other components, such as solvents, reactants, and intermediates, did not show absorbance in this wavelength. The reaction kinetics of 1-fluoro-2,4-dinitrobenzene were studied under pseudo-first-order condition with concentration of 8×10^{-6} mol L^{-1}. The pseudo-first-order ($k_{\underline{obs}}$) and the second-order (k_A) rate coefficients were obtained from the slope of the $\ln(A_\infty - A_t)$ versus time. In all cases, the infinity value of absorbance, A_∞, was experimentally determined for each run. All the kinetic runs were carried out at least in duplicate, and the error was $\leq 5\%$ for all the experimentally determined k_A.

CONCLUSIONS

The kinetic investigation of the reaction of 1-fluoro-2,4-dinitrobenzene with the substituted anilines in methanol–ethyl acetate mixtures showed that the main effective factor on the rate coefficient is the normalized polarity of the solvent, and the HBD and HBA abilities of the media have a slight effect on it. The lowest value for polarity and HBD ability were obtained in pure ethyl acetate; therefore, the reaction rate was very slow in ethyl acetate. Preferential solvation in mixtures of ethyl acetate and methanol confirms intense solvent–solvent interactions in mixtures. Calculated results from the propose model are in good agreement with the LFER observations. In addition, the correlation of rate data with Hammett equation suggests an uncatalyzed mechanism for the reaction.

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