Solute–Solvent Interaction Effects on Second-Order Rate Constants of Reaction Between 1-Chloro-2,4-dinitrobenzene and Aniline in Alcohol–Water Mixtures

M. HARATI, M. R. GHOLAMI

Department of Chemistry, Sharif University of Technology, Tehran, Iran

Received 17 December 2003; accepted 18 July 2004

DOI 10.1002/kin.20041

ABSTRACT: The second-order rate coefficients for aromatic nucleophilic substitution reaction between 1-chloro-2,4-dinitrobenzene and aniline have been measured in aqueous solutions of ethanol and methanol at 25°C. The plots of rate constants versus mole fraction of water show a maximum in all-aqueous solutions. The effect of four empirical solvent parameters including hydrogen bond donor acidity (α), dipolarity/polarizability (π^*), normalized polarity (E_T^N), and solvophobicity (*Sp*) has been investigated. This investigation has been carried out by means of simple and multiple regression models. A dual-parameter equation of $\log k_2$ versus *Sp* and α was obtained in all-aqueous solutions ($n = 41, r = 0.962, s = 0.053, p = 0.0000$). This equation shows that solvophobicity and hydrogen bond donor acidity are important factors in the occurrence of the reaction and they have opposite effects on reaction rate. © 2004 Wiley Periodicals, Inc. Int J Chem Kinet 37: 90–97, 2005

INTRODUCTION

The importance of the solvent with respect to the course of organic reactions is well established [1–3]. Furthermore, solvents and mixed aqueous-organic solvent play an important yet extremely complex role in both the reaction rates and the chemical behavior of liquid-phase reactions. The complexity of chemical phenomena in solution has made it necessary to develop a variety of models and computational techniques to represent molecules in the solution. These techniques differ in some factors including the level of detail used to describe the chemical system, the physical role underlying the process of interest, and the mathematical formulas used to describe these rules. The final goal of all these models is the understanding of the behavior of molecules in important environments [2]. On the other hand, the complexity of solvent effects on reaction rates is evident from the fact that there is no perfect single theory to deal with such a complexity and there are

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Correspondence to: M. R. Gholami; e-mail: Gholami@sharif.edu.

several empirical equations that are claimed to explain only certain specific solvent effects, such as polarity [3,4]. However, in addition to polar effects, reaction rate may be affected by the medium in other ways. For example, hydrophobic interactions can affect nonpolar compounds, when they are soluble.

In the last decade, numerous studies [5] have revealed that water is able to induce dramatic rate accelerations in reactions such as Diels–Alder cycloadditions [6], benzoin condensation [7], and Michael reactions [8] and aromatic nucleophilic substitution reactions [9]. The origin of the kinetic effect has been debated. Most of the factors have been identified, but their relative contributions are often not well known. Various factors were suggested and taken into account, such as hydrogen-bond donor (HBD) acidity [10], normalized polarity parameter, and enforced hydrophobic interactions [11]. Most recent views consider that the acceleration is supposed to be caused by two main factors, which are hydrogen bonding effects and enforced hydrophobic interaction between the reactions. There is reaction rate acceleration in aqueous solutions in comparison with traditional organic solvents. This is certainly related to the peculiar interaction of water with the activated complex. Owing to their low solubility in water, organic molecules aggregate in such a way that the water–hydrocarbon interfacial area is reduced. Moreover, water is an environment-friendly solvent, and currently the use of water is receiving much more attention. Unfortunately, there are some features that make water unpopular among chemists. In particular, the limited solubility of most (organic) compounds in water can severely hinder chemical reactions. A second problem is the fact that water is rather a reactive solvent, so that many compounds decompose in water. In spite of these drawbacks there are increasing interests in the use of water as solvent.

In our previous work, we have studied the solvent effect using piperidine as a secondary amine [12]. Here, we are interested in finding out a relationship between the rate of reaction of 1-chloro-2,4-dinitrobenzene and aniline (as primary amine) and solvent–solute interactions.

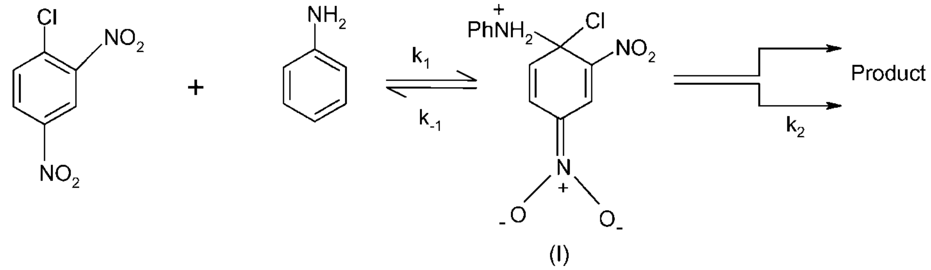
The rates of reaction between 1-chloro-2,4-dinitrobenzene and aniline in water and several aqueous solutions are at least 10 times higher than those of organic solvents, such as dimethyl sulphoxide, nitromethane, and dimethyl formamide [13]. And the reaction rate increases dramatically with the mole fraction increase of water. Hydrophobic interaction has important roles under these conditions, and the reaction rate in aqueous solutions of ethanol is higher than those of methanol. Kinetic studies involving primary and secondary amines as nucleophiles play a central role not only in firmly establishing the two- or multistep nature of the mechanism, but also in answering questions regarding the relative rates of intermediate complex formation and decomposition. The mechanism of aromatic bimolecular nucleophilic substitution reactions with either primary or secondary amines is now well established and is given in Scheme 1 [13a,b,14].

In accordance with the mechanism, intermediate **I** can proceed to products either spontaneously (k_2) or through general base catalysis (k_3). The base B can be tertiary amines, which may be added to the reaction mixture, or it is a nucleophile itself. Thus, by adding or omitting bases in the reaction mixture, the experimenter may sometimes exert considerable control on the relative rates of product formation reversion to reactants of the intermediate, and thus on the overall rate-controlling, steps. This can be expressed by the following rate expression [14]:

$$\frac{\text{rate}}{[\text{Arx}][\text{ArNH}_2]} = k_A = \frac{k_1k_2 + k_1k_3[\text{B}]}{k_{-1} + k_2 + k_3[\text{B}]} \tag{1}$$

The formation of the intermediate **I** or its decomposition to products can be considered as the rate-limiting step. Therefore, two different cases may be established:

1. If $k_{-1} \ll (k_2 + k_3[\text{B}])$, then Eq. (1) will be reduced to $k_A = k_1$, the formation of the intermediate will be the rate-limiting step, and the reaction will not be base catalyzed.



Scheme 1

2. If this condition does not hold, the decomposition to products will be the rate-determining step and the reaction will be base catalyzed.
   In the later case,

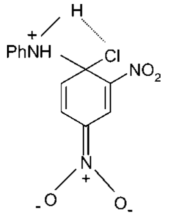
   a. If $k_{-1} \gg (k_2 + k_3[\mathrm{B}])$, Eq. (1) can be converted to Eq. (2) and a linear relation with respect to the base concentration is obtained.

   $$k_\mathrm{A} = k_1k_2/k_{-1} + (k_1k_3/k_{-1})[\mathrm{B}] \qquad (2)$$

   In many aromatic bimolecular substitution reactions a small, linear increase of k_A with increasing nucleophile (or more generally, added base) concentration is observed.

   b. If $k_{-1} \approx (k_2 + k_3[\mathrm{B}])$, Eq. (1) cannot be simplified further and the dependence of k_A on the base concentration is not linear.

Recently, attention has been directed toward the nature of both the catalyzed and the uncatalyzed decompositions of intermediate **I**. The unanalyzed route is usually discussed in terms of either unimolecular decomposition via the internal hydrogen-bond transition state **A** (see below) or by a mechanism similar to that of the catalyzed pathway with a solvent molecule acting as a base, shown in Scheme 2.



(A)

In Scheme 1, when the substrate contains an ortho–nitro group, hydrogen bonding occurs in intermediate **I** between the ammonium hydrogen atoms and the oxygen of the nitro group. When the nucleophile is a primary amine, a second hydrogen is available for reaction by either mechanism without the prior breaking of the hydrogen bond; hence the mechanism of the uncatalyzed path could be different for primary and secondary amines [13a].

According to Onyido [13b] and our previous work [8b], the reaction between 1-chloro-2,4-dinitrobenzene with aniline should not be base catalyzed in aprotic and protic solvents.

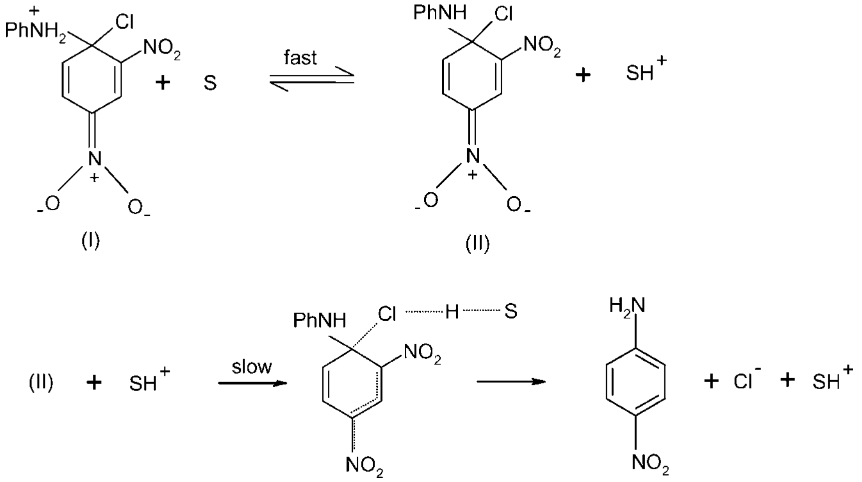
EXPERIMENTAL

Materials

1-chloro-2,4-dinitrobenzene, mp 53°C, was obtained from Aldrich and was purified twice by crystallization in aqueous solution of ethanol. Ethanol was supplied by Merck (≥99.8%) and methanol was supplied by Fluka (≥99.5%), and they were of the highest purity commercially available. Double-distilled water was used in all preparations.

Kinetic Studies

The rate of formation of the product of the reaction was followed spectrophotometrically, using a GBC UV–visible cintra 40 spectrophotometer. Absorbance was recorded at 400-nm wavelength using a thermo cell coupled to the spectrophotometer. The temperature was maintained at 25 ± 0.1°C using thermostated water, which was circulated around the cell of the spectrophotometer. All kinetic runs were carried out at least three times.



Scheme 2

Results

Reaction Order. The concentration of 1-chloro-2,4-dinitrobenzene was 2.9×10^{-4} M and that of aniline was between 0.01 to 0.03 M. Pseudo-first-order (k_{obs}) conditions were used in all cases. Regression coefficients of all the reaction rate constants were around 0.998. Infinity values of absorbance (A_∞) were experimentally determined just for (water mole fraction) $X_{\mathrm{w}} = 0.8$ in ethanol aqueous solution after 13 h. In all of the other cases the kinetic runs were carried out for up to 3 h. The accurate measure of the final absorbance (A_∞) for the former case is determined, and used to extract the reaction rate coefficient from Eq. (3) [15].

$$\ln(A_t - A_\infty) = -kt + \ln(A_\infty - A_0) \qquad (3)$$

In other cases, the reaction is so slow that it is inconvenient to wait for its completion. Therefore, the Guggenheim method was used (Eq. (4)).

$$\begin{aligned}\ln(A_{t+\Delta t} - A_t)\\ = -kt + \ln(A_\infty - A_0)(1 - \exp(-k\Delta t))\end{aligned} \qquad (4)$$

However, the more reliable method suggested by Kezdy et al. and Swinbourne [16], Eq. (5), was also used to check the Guggenheim method results.

$$A_t = A_{t+\Delta t}\exp(\Delta t) + A_\infty(1 - \exp(-k\Delta t)) \qquad (5)$$

DISCUSSION

The second-order rate constants of the reaction, k_{A}, in aqueous solutions of methanol and ethanol were obtained at 25°C (Tables I and II). It is expected that the Kezdy–Swinbourne method would be more accurate than the Guggenheim method [15,16a,b]. But the reaction rates in both methods are approximately the same and there is no obvious difference between these two methods.

Figure 1 shows the increase in reaction rate constant in all-aqueous solutions with respect to mole fraction of water. There is a steady rise in the reaction rate constant approximately up to $X_{\mathrm{w}} = 0.85$, and then there is a decrease at $X_{\mathrm{w}} = 0.90$, and the maximum point is observed at $X_{\mathrm{w}} = 0.95$. Finally, a dramatic decrease in reaction rate constant between $X_{\mathrm{w}} = 0.95$ and $X_{\mathrm{w}} = 1.00$ is obtained. However, the maximum rate constant in aqueous solutions of ethanol is approximately twice as in aqueous solution of methanol.

As Tables I and II show, the normalized polarity parameter ($E_{\mathrm{T}}^{\mathrm{N}}$) of media increases with the mole fraction

Table I Second-Order Rate Constants of the Reaction in Aqueous Solutions of Ethanol at 25°C

	k_2 ($\times 10^5$ dm^3 mol^{-1} s^{-1})					
X_{w}	Guggenheim	Kezdy–Swinbourne	π^*	α	*Sp*	$E_{\mathrm{T}}^{\mathrm{N}}$
0.00	4.28	4.28	0.51	0.98	0.144	0.66
0.05	4.03	4.04	0.54	0.97	0.1478	0.66
0.10	4.55	4.56	0.57	0.96	0.1517	0.66
0.15	4.76	4.76	0.60	0.94	0.1557	
0.20	4.94	4.94	0.63	0.93	0.1608	0.67
0.25	4.93	4.67	0.65	0.93	0.1657	0.68
0.30	5.37	5.37	0.68	0.92	0.1764	0.69
0.35	5.63	5.63	0.70	0.91	0.1942	
0.40	5.97	5.97	0.73	0.91	0.2054	0.70
0.45	6.15	6.15	0.75	0.89	0.2210	
0.50	6.62	6.63	0.77	0.90	0.2630	0.71
0.55	6.86	6.85	0.80	0.89		0.72
0.60	7.55	7.55	0.82	0.89		0.73
0.65	7.65	7.64	0.85	0.89		
0.70	8.45	8.36	0.90	0.88	0.3658	0.74
0.75	9.16	9.16	0.94	0.86		0.76
0.80	10.11	10.11	1.00	0.87		0.78
0.85	11.46	11.46	1.06	0.90	0.6265	
0.90	7.81	7.81	1.11	0.97		0.87
0.95	33.08	32.82	1.13	1.11	0.8684	
1.00	13.81	13.79	1.14	1.26	1.0000	1.00

$E_{\mathrm{T}}^{\mathrm{N}}$, π^*, α, and *Sp* are normalized polarity parameter, dipolarity/polarizability, hydrogen-bond donocity, and solvophobicity of solvent, respectively.

Table II Second-Order Rate Constants of the Reaction in Aqueous Solutions of Methanol at 25°C

	k_2 ($\times 10^5$ dm^3 mol^{-1} s^{-1})					
X_w	Guggenheim	Kezdy–Swinbourne	π^*	α	*Sp*	E_T^N
0.00	2.96	2.96	0.58	0.98	0.144	0.66
0.05	3.33	3.33	0.61	0.97	0.1478	0.66
0.10	3.24	3.24	0.64	0.96	0.1517	0.66
0.15	3.53	3.53	0.66	0.94	0.1557	
0.20	3.87	3.88	0.70	0.93	0.1608	0.67
0.25	4.12	4.13	0.73	0.93	0.1657	0.68
0.30	4.39	4.40	0.76	0.92	0.1764	0.69
0.35	4.61	4.61	0.78	0.91	0.1942	
0.40	5.02	5.02	0.82	0.91	0.2054	0.70
0.45	5.46	5.46	0.85	0.89	0.2210	
0.50	5.86	5.86	0.88	0.90	0.2630	0.71
0.55	6.36	6.36	0.91	0.89		0.72
0.60	7.35	7.35	0.95	0.89		0.73
0.65	8.04	8.04	0.98	0.89		
0.70	8.06	8.06	1.01	0.88	0.3658	0.74
0.75	8.05	8.04	1.04	0.86		0.76
0.80	10.19	10.19	1.06	0.87		0.78
0.85	11.94	11.99	1.09	0.90	0.6265	
0.90	3.92	3.90	1.11	0.97		0.87
0.95	16.75	16.74	1.12	1.11	0.8684	
1.00	13.81	13.79	1.14	1.26	1.0000	1.00

E_T^N, π^*, α, and *Sp* are normalized polarity parameter, dipolarity/polarizability, hydrogen-bond donocity, and solvophobicity of solvent, respectively.

of water in aqueous solutions of methanol and ethanol. In the same mole fraction of water, E_T^N of aqueous solutions of methanol is higher than aqueous solutions of ethanol. Considering the E_T^N of media as the only effective factor for indicating the solvent effects on the reaction rate, one may expect that the reaction rate in water should be higher than in all-aqueous solutions of alcohols. Single-parameter correlations of $\log k_2$ vs E_T^N do not give a good result (Table III), and therefore this relationship is inappropriate.

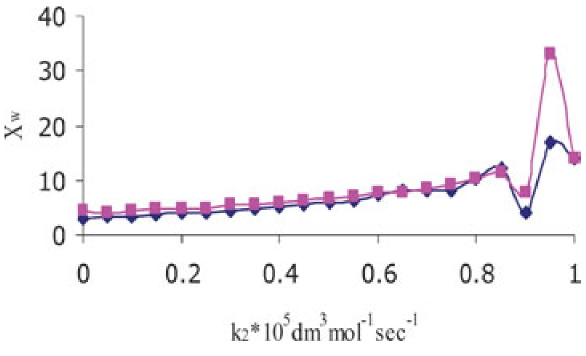


Figure 1 Plot of second-order rate constants of the reaction vs mole fraction of water in aqueous solutions of methanol (♦) and ethanol (■) at 25°C.

The second factor that can be considered for explaining the trends in Fig. 1 is the hydrogen-bond donor (HBD) acidity (α) of solvents [11]. The rate of reaction in some protic solvents decreases with HBD acidity. Owing to the fact that this factor for water is higher than that for methanol and ethanol, we can conclude that stronger HBD acidity means lower reaction rate. The HBD acidity of all-aqueous solutions has a gradual fall with the mole fraction of water. It falls until $X_w = 0.75$ and $X_w = 0.70$ for aqueous solutions of methanol and ethanol, respectively, and then rises steadily with the increasing mole fraction of water in all-aqueous solutions. So, if we consider the HBD acidity of water as the only factor in describing solvent effect on the reaction rate, one would expect that the second-order rate constant of the reaction in water should be less than that in methanol or ethanol [17a,b]. Single-parameter correlations of $\log k_2$ vs α do not give good correlation in the aqueous solutions (Table III). In the latter case, not only the correlation coefficients (r) are very low, but also the p-value is very high. We use the standard analysis of variance (ANOVA) table in order to show and test the overall significance of models. The table also includes R^2, the mean absolute error, and the p-value that serves as a measure of significance. When the p-value is less than 0.01,

Table III Regression Coefficients and Slopes of Solvent Parameters in Aqueous Solutions of Methanol and Ethanol and in All-Aqueous Solutions at 25°C

Aqueous Solutions	π^*	α	Sp	E_T^N	Intercept	p	R
Methanol	0.971				−5.084	0.0000	0.870
		0.338			−2.923	0.0000	0.800
			0.825		−4.638	0.0000	0.983
				2.398	−6.226	0.0018	0.735
	0.734		0.304		−5.012	0.0036	0.995
		0.852	−0.505		−4.107	0.0002	0.993
			1.191	−1.373	−3.681	0.0207	0.991
	1.189		0.348	−0.038	−5.611	0.9188	0.994
		−0.668	0.671	0.778	−4.483	0.6259	0.993
Ethanol	0.932				−4.896	0.0000	0.879
		−1.798			−2.801	0.0000	0.874
			0.610		−4.379	0.0000	0.940
				1.422	−5.229	0.0000	0.859
	0.716		1.044		−4.768	0.0056	0.998
		−0.690	0.782		−3.783	0.0000	0.993
			1.301	−1.905	−3.214	0.2967	0.945
	0.573		−0.157	0.244	−4.555	0.1362	0.998
		−0.899	0.309	1.460	−4.499	0.1279	0.997
All-aqueous solutions	0.899				−4.920	0.0000	0.798
		−1.359			−3.223	0.0000	0.658
			0.606		−4.467	0.0000	0.858
				1.121	−5.083	0.0001	0.571
	0.788		0.050		−4.882	0.7532	0.905
		−1.004	0.825		−3.532	0.0000	0.962
			1.425	−2.374	−2.949	0.0000	0.959
	−0.387	−1.262	1.154		−3.087	0.0781	0.966
		−0.501	1.154		−3.081	0.0414	0.969

there is a statistically significant relationship between variables at the 99% confidence level. But, according to Table III, the p-value for aqueous solutions of methanol, ethanol, and all-aqueous solutions are 0.9282, 0.0462, and 0.7218, respectively. The p-values and the correlation coefficient show that this statistical model is not valid for describing the changes in the reaction rate constant.

The normalized polarity parameter (π^*) is a blend of dipolarity/polarizability and hydrogen bond donor acidity of media. This π^* is so named because it is derived from solvent effects on the $\pi \rightarrow \pi^*$ electronic transitions of a selection of seven positively solvatochromic nitroaromatics of the type D—C_6H_4—A, where D and A stand for electron donor (e.g. NMe_2) and electron acceptor (e.g. NO_2) groups [11]. There is a steady increase of π^* with mole fraction of water. Simple regression models of $\log k_2$ vs π^* do not give good results in all-aqueous solutions. Although one can be satisfied by the p-value, the correlation coefficient is less than the value needed to apply the model (Table III).

As aniline is not completely soluble in water, we conclude that we can consider the solvophobicity parameter as the fourth factor [18]. Poor linear correlations of $\log k_2$ vs Sp were found (Table III), because we do not have a steady increase in k_2 with mole fraction of water. A sharp decrease in the reaction rate X_w is observed, i.e. between 0.95 and 1.

Therefore, we decided to consider multiple regression analysis. Table III shows that all of the statistical models with multiple regression analyses are not suitable, except one. The only model that has good values for both the p-value and the correlation coefficient is the result of fitting a multiple linear regression to describe the relationship between rate constants with both Sp and α as independent variables.

Using dual-parameter correlation of $\log k_2$ vs Sp and α in aqueous solutions of methanol and ethanol gives Eqs. (6) and (7) for methanol and ethanol, respectively.

$$\begin{gathered}\log k_2 = -4.107(\pm 0.109) - 0.505(\pm 0.103)\alpha \\ + 0.852(\pm 0.026)Sp \qquad (6) \\ (n = 21, r = 0.993, p = 0.0002, \\ S = 0.027, F\text{-ratio} = 555.93)\end{gathered}$$

$$\log k_2 = -3.783(\pm 0.067) - 0.690(\pm 0.076)\alpha + 0.783(\pm 0.029)Sp \quad (7)$$

$$(n = 21, r = 0.993,\ p = 0.0000,\ S = 0.020,\ F\text{-ratio} = 396.30)$$

Since the p-value in statistical models for aqueous solutions of methanol as well as ethanol is less than 0.01, a statistically significant relationship between the variables at the 99% confidence level is presented. The correlation coefficient indicates that the model as fitted explains 99.3% of the variability in $\log k_2$.

It can be seen that the solvophobicity and HBD acidity of the media have opposite effects on the reaction rate. In the presence of aniline, alcohols are known to act as HBD, and there is plentiful evidence of strong hydrogen-bonding interactions between aniline and alcohols [19]. Therefore, aniline will be stabilized via hydrogen-bonding interactions with hydrogen-bond donors. Hence, the reaction rate decreases with the increasing HBD acidity of the media. According to dual-parameter regression, both *Sp* and α coefficients are significant, but *Sp* plays a more important role in determining the reaction rates. This dual-parameter model represents a significant improvement with regard to the previous single-parameter models. Because of the opposite effects of HBD acidity and solvophobicity of the media, a peak appears in the plots of second-order rate constants of the reaction vs mole fraction of water.

Furthermore, a dual-parameter correlation of $\log k_2$ vs *Sp* and α was obtained in the all-aqueous solutions of the alcohols (Eq. (8)).

$$\log k_2 = -3.532(\pm 0.108) - 1.004(\pm 0.115)\alpha + 0.825(\pm 0.043)Sp \quad (8)$$

$$(n = 41, r = 0.962,\ p = 0.0000,\ S = 0.053,\ F\text{-ratio} = 186.87)$$

In this equation, the difference effects of *Sp* and α on the reaction rate constant are high, and, because *Sp* and α have the opposite effect, a maximum appears in the plot of rate constant vs X_w.

In order to show the efficiency of the suggested dual-parameter correlations, experimental values of $\log k_2$ vs their predicted values from Eq. (8) were plotted for different aqueous solutions of alcohols. As Fig. 2 shows, there is good agreement between the experimental and the calculated values of $\log k_2$ in all-aqueous solutions ($r = 0.958$).

In our previous work [12], we studied the solvent effect on reaction rate constant between 1-choro-2,4-dinitrobenzene and piperidine. We figured out that the best dual-parameter correlation is for $\log k_2$ vs α and π^*, because piperidine is completely soluble in water. But when the primary amine (aniline) instead of the secondary one (piperidine) is used, the best-fitted statistical model is the relation of $\log k_2$ vs α and *Sp*, because aniline is more hydrophobic than piperidine.

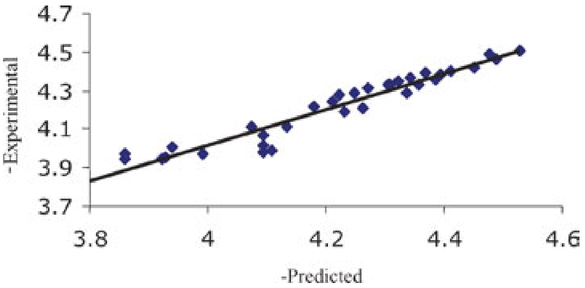


Figure 2 Plot of experimental values of $\log k_2$ vs the predicted values from Eq. (8) in the all-aqueous solutions at 25°C.

The authors thank Professor Ikenna Onyido (University of Ibadan, Ibadan, Nigeria) for helpful advice on base-catalyzed reactions and Mr. M. Izadyar (Sharif University of Technology) for helpful comments.

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