Solvent effect on the reaction of tosyl chloride with *p*-substituted phenol(s) and triethylamine

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ABSTRACT

Second-order rate constants have been determined conductometrically for the nucleophilic substitution reactions of tosyl chloride with p-substituted phenol(s) and triethylamine in different solvents system. Studies on solvent effects on the reactions by applying correlation techniques(simple and multiple regression) have been done. The rate of the reaction depends on the degree of charge separation on the p-substituted phenol(s)-triethylamine complex, which is influenced by the solvent properties. We have classified the solvents into three sets (A,B and C) to make the study more meaningful. The set A consists of mainly aliphatic polar aprotic solvents, set B consists of aromatic and halogenated solvents and set C consists of protic hydroxylic solvents. Solvent parameters at macroscopic and microscopic level were used. The coefficient of the solvent parameters provide a good information to predict and to analyse the reaction mechanism.

Keywords: Kinetics, nucleophilic substitutions at sulfur / substituent effects/solvent effects, sulfonyl transfer reactions.
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INTRODUCTION

Kinetics is concerned with the study of rate of reaction, the influence of various conditions on these rates and mechanism by which a reaction occurs. The subject of chemical kinetics cover not only reaction rate but also covers a wide range of studies, which includes the effects of concentration, temperature, pH, solvent etc., [1]. The effect of solvent on organic reactions have been extensively studied. The investigation of solvent effect on reaction rates and mechanisms in binary mixtures of H_2O with dipolar aprotic solvents, such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), acetone and acetonitrile (ACN). Significant rate accelerations have often been reported upon additions of aprotic dipolar solvents into H_2O for the reactions involving anionic nucleophiles. However, on the contrary , rate retardations have also been observed for reactions of neutral species developing a charge in the transition state(TS) upon solvent changes from H_2O to aqueous dipolar aprotic solvent mixtures [2].Such solvent effects on reaction rates could be nicely explained by the Hughes-Ingold rules in a qualitative manner[3].Since gradual increase of the mole % of such organic solvent is considered to change H-bonding structure of H_2O and the microenvironment of the reactant and TS.

The nucleophilic substitution at a sulfur atom has been a subject of long-standing interest for organic chemists. In general, the nucleophilic substitution reactions of arenesulfonyl chlorides show a wide range of mechanisms like from dissociative S_N2 to $S_{Ar}N$, for this reaction , the former being preferred than the later [4].The effect of varying solvent compositions were reported in the literature [5-6].Solvent polarity plays a major role in activated state and it is experiment by both Swain and multi-parametric equations [7]. The kinetics of solvent polarity parameters in methanol binary mixtures have been studied by Yeol sakong *et al*. [8]. Ik –Hwan Um and his co-workers have investigated that the kinetics of nucleophilic substitution reactions of aryl acetates in MeCN- H_2O mixtures of

varying compositions[9].The solvent effect on the reactions of dansyl and bansyl chlorides with substituted pyridines have been reported by Dae Dong Sung *et al*. [10].Recently the kinetics of nucleophilic substitution reactions of tosyl chloride with *p*-substituted phenol(s) and triethylamine in methanol, acetone/ACN have been reported by Vembu and his co-worker [11-12]. As an extension of our work on the nucleophilic substitution reaction at sulfur centre[13],we carried out kinetic studies on the reaction of tosyl chloride with *p*-substituted phenol(s)-NEt₃ in various solvents, to find its effect.

MATERIALS AND METHODS

Materials
Tosyl chloride(TsCl), *p*-cyanophenol, *p*-chlorophenol, *p*-methoxyphenol, triethylamine(NEt₃), acetonitrile, acetone, dimethylformamide (DMF), ethyl methyl ketone, cyclohexanone, cyclopentanone, tetrahydrofuran(THF), ethyl acetate, nitromethane, 1,4 dioxan, acetophenone, benzonitrile, nitrobenzene, chlorobenzene, bromobenzene, anisole, chloroform, dichloroethane, methanol, ethanol, 2-ethoxy ethanol, 2-propanol, 2-butanol, 1-butanol and benzyl alcohol were purified before use by either recrystallisation (or) distillation until their physical constants (melting point/ boiling point) agreed with the literature values[14-16].

Kinetic measurements
The rates were followed conductometrically as we reported early[11-12] and the second order rate constant (k_2) were obtained by the Guggenheim's method[17].

RESULTS AND DISCUSSION

The bimolecular reactions of tosyl chloride and the nucleophiles (p-XC_6H_4OH-NEt_3) were carried out in 25 solvents have been determined by conductometric method under equimolar concentrations   at 303K, represented by the following equation.
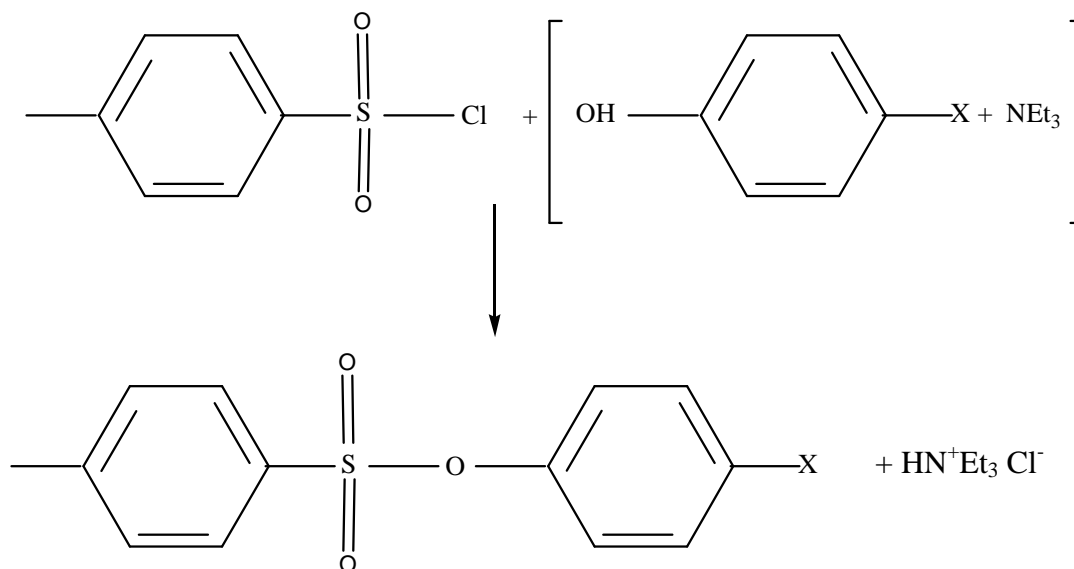
$X = p\text{-}CN, p\text{-}Cl, p\text{-}OCH_3$
$Rate = k_2[p\text{-}CH_3C_6H_4SO_2Cl][p\text{-}XC_6H_4OH \text{ -}NEt_3]$

Arylsulfonyl halides are convenient model compounds for experimental investigations of different nucleophilic processes at sulfonyl sulfur[10,18]. The reactivity of tosyl chloride has been ascribed to a polar effect in which the electron- withdrawing Cl induces an electron deficient centre at the tetra co-ordinated sulfur atom holding the halogen atom, thereby, facilitating the approach of a nucleophile towards the sulfur atom.

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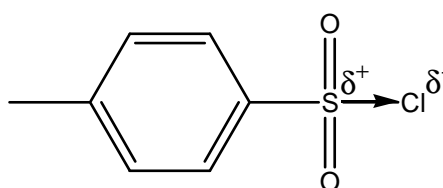
The arenesulfonyl chloride was found to be a good substrate for nucleophilic substitution reactions [19-20]. Banjoko and Okwuiwe have reported the kinetics of nucleophilic substitution reaction of benzenesulfonyl chloride with sodium benzoate(s) in methanol [18]. They concluded that the substitutions at sulfonyl sulfur would take place through the S_N2 mechanism. The kinetics of nucleophilic substitution reaction of tosyl chloride with *p*-substituted benzoic acid(s) and triethylamine in aprotic and protic   solvents were reported in the literature [21-22]. We have also made similar investigation on the reaction of tosyl chloride with *p* –substituted phenol(s) and triethylamine in various solvents with a view to study the solvent effects, substituent effects in the nucleophile, and the solvation behaviour of these solvents. The product was isolated after performing the reaction under kinetic condition and characterized by spectral methods.

Studies on solvent effects on the reactions by applying correlation techniques have been done.To make a systematic study of the effect of solvents, they are grouped in sets A,B and C [23].The set A consists of aliphatic polar solvents,the set B consists of aromatic and halogenated solvents and the set C consists of hydroxylic solvents. Solvent parameters at macroscopic and microscopic level were used. The second order rate constants,k_2 for the reactions of tosyl chloride with *p*-substituted phenol(s) and NEt_3 in various solvents were calculated from conductivity data by least-squares method for equimolar concentration using the following equation [24]which was derived from Guggenheim's principle [17]The results are given in Table 1.

$$X_2 - X_1 = k_2 C_0 [t_1 X_1 - t_2 X_2] - k_2 C_\infty X_\infty [t_1 - t_2]$$

where
X_1 = Conductance at time t_1
X_2 = Conductance at time t_2
X_∞ = Conductance at time t_∞
k_2 = Second order rate constant
C_0 =Initial concentration of the reactants

We have attempted to compare these reactions with the reaction between tosyl chloride and triethylammonium benzoates [21-22].The precise structure, nature of triethylamine - *p*-substituted phenol(s) complex varies depending on the nature of the solvent [25]. In dipolar aprotic solvents, typically in dry acetone the complex exists as a proton transferred hydrogen-bonded Complex [26].

$$X \text{----} \bigcirc \text{----} O^- \dots HN^+Et_3$$
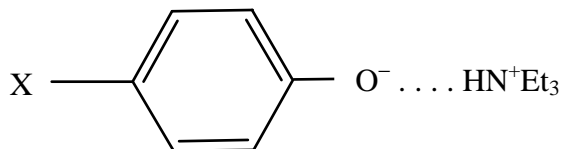
The rate of the reaction will vary depending on the degree of charge separation on the *p*-substituted phenol(s)-NEt_3 complex. The charge separation is influenced by the various properties of the solvents acid strength and base strength.

Effect of solvents – A qualitative approach
The reactions under investigation do not take place in benzene and CCl_4 – This indicates that triethylamine may not cause the ionization of phenol(s) in the solvents [25]. Same time the reaction do occur in $CHCl_3$ and dichloroethane (Table- 2), because the solvents are of intermediate polarity [27].

In general, the rate of the reaction is found to be higher in aprotic solvents than in protic solvents. The nature of the solvent and interaction between *p*-substituted phenol(s) – NEt_3 and solvent may be the reasons for this variation. The *p*-XC_6H_4OH-NEt_3 complex may be less solvated by aprotic solvents which may be the cause for the faster rate [28].

The values of rate constants (k_2) of the reactions in ACN are about 5 (*p*-CN),4 (*p*-Cl) and 15 (*p*-OCH$_3$) times greater than that of the ketonic solvents, whereas 49 (*p*-CN), 23 (*p*-Cl) and 6 (*p*-OCH$_3$) times higher than that in halogenated (aliphatic and aromatic) solvents. The polarity of ACN is higher (ε = 35.95) than other aprotic solvents employed. Phenoxide anion possessing higher charge in the ground state may be solvated less by ACN. Further, the phenoxide anion is also free from the interaction of the counter ion-triethylammonium cation, which may be solvated by ACN. The solvent and the counter ion free nucleophile (*p*-XC_6H_4OH-NEt_3) approaches faster to TsCl and makes it to be more polar. This may be the reason for the formation of more polar transition state (TS), which may be better stabilized by ACN. The dipole moment of the ketonic solvents are oriented towards oxygen atom. Thus, bulky alkyl groups may hinder the stabilization of TS. This may be the cause for the slow rate.

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Table 1 Second order rate constants of the reaction of *p*-CH₃C₆H₄SO₂Cl with *p*-X C₆H₄OH-NEt₃ at 303K
[*p*-CH₃C₆H₄SO₂Cl] = [*p*-X C₆H₄OH-NEt₃] = 0.025 mol dm⁻³

S.No.	Solvents	k_2, dm³ mol⁻¹min⁻¹		
		X		
		p-CN	*p*-Cl	*p*-OCH₃
	SET-A Aliphatic polar solvents (aprotic)			
1.	Acetonitrile	203.25	121.65	54.63
2.	Acetone	52.65	22.16	7.89
3.	*N,N*-Dimethylformamide (DMF)	199.75	118.26	52.15
4.	Ethyl Methyl Ketone (EMK)	37.63	27.82	3.5136
5.	Cyclohexanone	39.54	29.85	7.65
6.	Cyclopentanone	36.47	27.66	6.93
7.	Tetrahydrofuran (THF)	2.1096	1.505	1.1096
8.	Ethyl acetate	1.775	1.052	0.895
9.	Nitromethane	38.75	26.30	9.65
10.	1, 4 – dioxan	2.25	1.85	1.60
	SET – B Aromatic and halogenated solvents			
11.	Acetophenone	40.940	23.25	7.1524
12.	Benzonitrile	-	115.33	49.75
13.	Nitrobenzene	53.10	29.325	20.95
14.	Chlorobenzene	15.70	23.65	32.50
15.	Bromobenzene	17.95	25.18	34.10
16.	Anisole	32.15	29.45	27.30
17.	Chloroform (CHCl₃)	13.20	16.460	20.693
18.	Dichloroethane	1.290	1.725	3.0052
	SET-C Hydroxylic solvents (protic)			
19.	Methanol	5.55	11.78	17.96
20.	Ethanol	0.525	0.797	2.1532
21.	2-Ethoxyethanol	0.4824	0.6752	0.9264
22.	2-Propanol	0.1866	0.3216	0.6016
23.	2-Butanol	0.3124	0.4012	0.8048
24.	1-Butanol	0.1560	0.2164	0.4084
25.	Benzyl alcohol	0.0772	0.190	0.2852

Table 2 A comparative study in the second order rate constants of the reaction of *p*-XC₆H₄OH-NEt₃ on tosyl chloride with dielectric constant of the some solvents at 303 K.
**[*p*-CH₃C₆H₄SO₂Cl] = [*p*-XC₆H₄OH-NEt₃] = 0.025 mol dm⁻³**
(Where X = *p*-CN, *p*-Cl and *p*-OCH₃)

S.No	Solvents	Dielectric constants (ε)	k_2 dm³ mol⁻¹ min⁻¹		
			p-CN	*p*-Cl	*p*-OCH₃
1	ACN	35.95	203.25	121.65	54.63
2	DMF	36.71	199.75	118.26	52.15
3	Acetone	20.70	52.65	22.16	7.89
4	1,4-dioxan	2.22	2.25	1.85	1.60
5	Ethyl acetate	6.02	1.775	1.052	0.895
6	Ethyl methyl ketone	18.5	37.63	27.82	3.5136
7	Nitrobenzene	34.80	53.10	29.325	20.95
8	Anisole	4.33	32.15	29.45	27.30
9	Chlorobenzene	5.62	15.70	23.65	32.50
10	Chloroform	4.82	13.20	16.460	20.693
11	Dichloroethane	10.36	1.290	1.725	3.0052
12	Methanol	32.70	5.55	11.78	17.96
13	2-propanol	19.92	0.1866	0.3216	0.6016

In the case of aliphatic chlorinated solvents, the order of reaction rate is chloroform > dichloromethane > 1, 2 dichloroethane although the reverse is the polarity order. This may be explained on the basis of stabilization of *p*-substituted phenol(s) – NEt₃ nucleophiles due to its H-bonding interaction with CHCl₃[29].

Hydrogen bonded *p*-XC₆H₄OH-NEt₃ interacts with TsCl to form more polar and stable TS, which in turn increase rate. The rate of the reaction in aromatic halogenated solvents is faster than that of aliphatic halogenated solvents which may be attributed to more polarizable ability of bromo / chlorobenzene [30].

The high reactivity in DMF (Table -2) is due to anion desolvation [31-32], which increases the nucleophilicity of the phenoxide anions. In DMF the *p*-substituted phenol(s) – amine complex can exist as a tight ion – pair and is in equilibrium with the dissociated ion-pair.

p-XC₆H₄OH + NEt₃ $\longrightarrow$ *p*-XC₆H₄O⁻…HN⁺Et₃   λ   *p*-XC₆H₄O⁻ + HN⁺Et₃
(X = *p*-CN, *p*-Cl, *p*-OCH₃)

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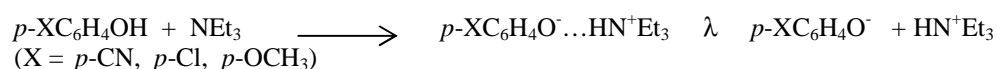
It is evident from the result in Table -1 that the reaction is more than 100 times faster in dipolar aprotic solvents than in protic solvents. This may be due to the anion desolvation [31-32] like in DMF. In dipolar aprotic solvent the negative end is exposed outside whereas the positive charged atom is somewhat inside the molecule. Therefore the negative end is free for co-ordination whereas the positive end is not. Consequently the cations are readily solvated comparatively the negative end of the nucleophile is potential to cause a substitution reaction. In literature this term is coined as "anion desolvation" which makes the nucleophile free and more potent species in comparison with hydroxylic solvent. In hydroxylic protic solvents the anion is very readily solvated and this leads much to retardation in the reaction rate. The nucleophile is made less potent by extensive solvation via., hydrogen bonding by the hydroxylic solvents.

The rate constant of nitrobenzene ($\varepsilon = 34.80$) very high than in methanol ($\varepsilon = 32.70$) although both have nearly same dielectric constant. However, one is hydroxylic solvent and so the comparison meaningless. In ethyl acetate some crystals were thrown out from the reaction mixture during the course of the reaction. However, the rate constants were determined before the solid was thrown out. In DMSO, the colour of the solution is changed to yellow. Moreover, there is a possibility of oxidation of DMSO by tosyl chloride. So DMSO cannot be used as solvent and hence it is not included in our study.

The rate constant of the reaction of tosyl chloride with *p*-cyanophenol and *p*-chlorophenol – NEt$_3$ complex is comparatively higher in dipolar aprotic solvents (Set A and B) than that of *p*-methoxyphenol – NEt$_3$ complex. But in protic hydroxylic solvents the observations are vice versa. This may be due to the reason that the lone pair electrons of oxygen atom in methoxy group of *p*-methoxyphenol is more solvated by protic solvents. Hydroxylic solvents are good H-bond donors and DMF is an excellent H-bond acceptor. The polar non-electrolyte, TsCl is strong hydrogen bond acceptor. So the hydroxylic protic solvents are highly solvated the nucleophile through hydrogen bond and in dipolar aprotic solvents are not like that. So the rate of the reaction is higher in acetone, ACN, DMF, nitrobenzene etc., than in the 2-propanol, benzyl alcohol, 2-butanol etc.,

The reactivity of *p*-substituted phenol(s) – NEt$_3$ (*p* - CN, *p* - Cl, *p*-OCH$_3$) on TsCl in methanol falls almost in the orders, *p* - CN < *p* - Cl < *p* - OCH$_3$. However, higher than that of the other alcoholic solvents employed. The degree of solvation of *p*-XC$_6$H$_4$OH-NEt$_3$ by nucleophilic character of methanol may be less than that of other alcoholic solvents. Hence, the rate of the reaction decreases accordingly.

The "ε" is the another property which control the rate. Only solvents of dielectric constant greater than 5 are considered for our investigations expect chloroform, 1, 4-dioxan and anisole. This arbitrary choice was made because in solvents of lower dielectric constant, ion aggregation is so extensive. Therefore, it becomes difficult to observe the behaviour of solvent on rate by conductometry. The qualitative interpretation in term of our investigation was clear that the reactions are considerably faster in dipolar aprotic solvents than in protic solvents.

Effect of solvents – A quantitative approach
In this chapter, the simple and multiple correlations of log k$_2$ for the reaction of tosyl chloride (TsCl) with *p*-substituted phenol(s) – NEt$_3$ against various solvent parameters were mainly discussed. Attempts have been made to correlate variations in reaction rate with solvent parameters which characterize the properties of the solvent. In order to understand the role of solvents in our studied reactions, the rate data have been subjected to simple regression analyses were attempted first and then multiple regression analyses were resorted subsequently. Solvent parameters were developed by various workers for different solvents taking one solvent as reference for a standard reaction or a physical property of a compound. Numerical value of this parameter , which can be an equilibrium constant, a rate constant, wavelength of an absorption maximum or a polarographic half – wave potential was obtained for the reference process. These can be called the solvent parameters. The values of solvent parameters were correlated with the rate constants studied for the present system and the degree of correlation was established.

The use of solvent parameters is restricted to process of a type those are involved in the reference process. The linear dependence of log k$_2$ on the value of a given solvent parameter indicates the possibility of a mechanism similar to that operating in the reference reaction used in obtaining the solvent parameter.

Table-3 gives the second order rate constants (k$_2$) of the reaction of tosyl chloride with *p*-substituted phenol(s) – NEt$_3$ in various solvents have been determined at 303K along with solvent parameters at macroscopic and microscopic levels. In general, Menschutkin reaction is the most suitable reaction to study the solvent effect since it is very sensitive to medium effect, easy to monitor and the mechanism is fairly well understood. By examining the influence of the dielectric constant of the medium on log k$_2$ for n-Pr$_3$N + MeI at 293K, Lassau and Jungers [33-35] classified the solvents into three groups such as aliphatic polar solvents (Set A) aromatic and poly halogenated solvents (Set B) and hydroxylic solvents (Set C). Abraham [36-37] showed the excellent correlations between rate

constants and solvent parameters for some Menschutkin reactions in the solvents of the same group. In the present investigation, the same classification of solvents was retained and poor correlations were obtained between log k_2 and solvent parameters.

Correlation of reaction rate with dielectric constants (ε) and related properties of the solvents

Dielectric constant is one of the important solvent polarity parameters [30]. Generally, it is expected that the rate constant is increased with increase of dielectric constant if the transition state (TS) is more polar than the reactants. This may be attributed to the growth of positive and negative charges on the TS. In our reactions, the TS is polar one (S_N2 type). But the rate of the reactions did not increase evenly with the dielectric constant of the media. Similar trends have been reported in the literature [33]. Drougard and Decroocq [33] have examined the correlation between the dielectric constant and rate constant of the reaction of ethyl bromoacetate with NEt_3 at 293K and found that there was no strict linearity. Since, the present system under investigation is quite different from that of Drougard and Decroocq system.

The uneven trend in the rate of the reaction with dielectric constant can be explained as follows. The rate constants for the reactions between tosyl chloride and p-X C_6H_4OH-NEt_3 (X = p-CN, p-Cl and p-OCH$_3$) was found to be slow in hydroxylic solvents (Set C) compared with the rates in aliphatic polar solvents (Set A) and aromatic and halogenated solvents (Set B).

It is evident from the result in Table-2 that the rate constant determined in 2-propanol (ε = 19.92) was very less than that in acetone (ε = 20.70) even though both of these solvents have comparable dielectric constants. Though the dielectric constant of 1, 4-dioxan (ε = 2.22) was 10 times less, the rate constant in this solvent was 12 (p-CN), 6 (p-Cl) and 3 (p-OCH$_3$) times greater than that in 2-propanol. Eventhough the dielectric constant of nitrobenzene (ε = 34.80) and methanol (ε = 32.70) are almost same but the rate of the reaction in the former is higher than the latter which is very low to measure the conductance. The dielectric constant in DMF (ε = 36.71) and nitrobenzene (ε = 34.80) are almost same though the rate constant of the latter was 4 (p-CN), 4 (p-Cl) and 2.5 (p-OCH$_3$) times less than the former. The dielectric constant of ethyl acetate (ε = 6.02) and chlorobenzene (ε = 5.62) are almost same but the rate constant in chlorobenzene was greater than ethyl acetate. So in order to understand the role of dielectric constant of solvents on the reaction rate of present reactions, regression analyses were carried out. Since ε or $\dfrac{1}{\varepsilon}$ or $\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$ are interrelated, the choice among them is arbitrary [37]. We have tried to correlate the rate with $\dfrac{1}{\varepsilon}$ and also with Kirkwood function $\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$ with a view to knowing the effect of dielectric constant of the medium on the rate and to test the validity of these two in the present reaction.

Kirkwood [38] suggested that the free energy of activation ($\Delta G^{\#}$) was proportional to the term $\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$ where ε is the macroscopic dielectric constant. Laidler and Eyring [39] included this term in a rate equation to account for electrostatic effects on dipolar molecule – dipolar molecule reaction rates. The electrostatic effects of solvents were the cause for the ionization of reactants and led to the formation of highly charged activated complex. This ionizing power of solvents and the charge separation on the activated complex by Kirkwood function alone may not be sufficient to account for the variation of rates in some solvents in the present work.

Although chloroform (ε = 4.82) and anisole (ε = 4.33) have similar dielectric constants, the rate of the reaction was almost 2.0 times higher in anisole than in CHCl$_3$ (Table -2). This may probably be due to further stabilization of charge separation in the transition state complex through π-electrons in aromatic ring [40].

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Table 3 Solvent properties at macroscopic and microscopic level

Sl. No.	Solvents	ε	$1/\varepsilon$	$\varepsilon-1/2\varepsilon+1$	μd	L J log k_2	ET(30)	π^*	ρ	γ	η	3 + log k_2		
												p-CN	*p*-Cl	*p*-OCH₃
	SET - A													
1	Acetonitrile	35.95	0.0279	0.479	3.92	-0.328	46	0.85	0.787	28.7	0.369	5.3	5.08	4.73
2	Acetone	20.7	0.0483	0.465	2.88	-0.827	42.4	0.72	0.78	23.5	0.306	4.72	4.34	3.89
3	Dimethylformamide	36.71	0.0272	0.48	3.86	-0.222	43.8	0.88	0.95	37.1	0.92	5.3	5.07	4.71
4	Ethyl methyl ketone	18.5	0.0541	0.461	2.8	-1.1	41.3	0.67	0.805	23.9	0.405	4.57	4.44	3.54
5	Cyclohexanone	18.3	0.0546	0.455	3.39	-0.796	39.8	0.76	0.9478	34	2.453	4.59	4.47	3.88
6	Cyclopentanone	13.5	0.0741	0.446	3.1	-0.658	40.8	0.75	0.95	33.4	1.29	4.56	4.44	3.84
7	Tetrahydrofuran	7.58	0.1319	0.407	1.75	-1.538	37.4	0.58	0.8892	26.4	0.456	3.32	3.17	3.04
8	Ethyl Acetate	6.02	0.1661	0.385	1.88	-1.658	38.1	0.55	0.897	6.8	0.45	3.24	3.02	2.95
9	Nitromethane	35.87	0.0279	0.479	3.56	-0.041	46.3	0.85	1.14	36.8	0.63	4.58	4.41	3.98
10	1,4-Dioxan	2.22	0.4505	0.224	0.45	-1.432	36	0.55	1.033	0	1.37	3.35	3.26	3.2
	SET - B													
11	Acetophenone	17.48	0.0572	0.458	2.7	-0.377	41.3	0.9	0.788	39.1	1.681	4.61	4.36	3.85
12	Benzonitrile	25.2	0.0397	0.471	3.9	-0.409	42	0.9	1	34.7	0.01267	0	5.06	4.69
13	Nitrobenzene	34.8	0.0287	0.473	3.9	-0.319	42	1.01	1.2	0	0	4.72	4.46	4.32
14	Chlorobenzene	5.62	0.1779	0.377	1.7	-1.155	37.5	0.71	1.107	32.9	0.753	4.19	4.37	4.51
15	Bromobenzene	5.4	0.1852	0.344	1.52	-1.051	37.5	0.79	1.495	35.2	1.074	4.25	4.4	4.53
16	Anisole	4.33	0.2309	0.345	0	-1.051	37.2	0.73	0.995	29.39	1.52	4.5	4.46	4.43
17	Chloroform	4.82	0.2075	0.36	1.3	-0.886	39.1	0.76	1.484	26.7	0.537	4.12	4.22	4.31
18	Dichloroethane	10.36	0.0965	0.431	1.85	-0.42	41.9	0.81	1.257	28.3	0.89	3.11	3.23	3.47
	SET - C													
19	methanol	32.7	0.0306	0.477	2.87	-1.886	55.5	0.6	0.792	22.1	0.544	3.74	4.07	4.25
20	Ethanol	24.55	0.0407	0.47	1.69	-2.022	51.9	0.54	0.789	21.9	1.074	2.72	2.9	3.33
21	2-Ethoxyethanol	13.5	0.0741	0.446	0.375	0	51	0.71	0.931	28.4	0.0214	2.68	2.82	2.96
22	2-Propanol	19.92	0.0502	0.463	1.66	0	48.6	0.46	0.785	20.9	2.038	2.27	2.5	2.77
23	2-Butanol	15.8	0.0633	0.454	2.76	0	0	0	0.808	23	0.03096	2.49	2.6	2.9
24	1-Butanol	17.51	0.0571	0.458	1.65	-2.337	50.2	0.43	0.81	24.9	2.544	2.19	2.33	2.61
25	Benzyl alcohol	13.1	0.0763	0.444	1.7	-1.237	50.8	0.98	1.045	38.8	5.474	1.88	2.27	2.45

Simple regression analyses

The log k_2 values at 303K are correlated with different solvent parameters by simple regression analyses (Table -4) using the equation [15, 41-42].

$$\log k_2 = \log k_0 + m\ X$$

where X is independent variable, m is Co efficient.

Table-4 gives the result of simple regression analyses of log k_2 (aliphatic polar, aromatic and halogenated and protic solvents) with ε, $\dfrac{1}{\varepsilon}$, $\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$, μ_D, ρ, γ, η, $E_T(30)$, π^* and Lassau and Jungers log $k_{2(n\text{-}Pr_3N + MeI)}$ scale [43-44] show a very poor correlation.

Table 4 Summary of the simple regression of 3 + log k_2 versus solvent parameter
Reaction between TsCl and p –XC_6H_4OH–NEt_3 (X= p – CN, p – Cl and p – OCH$_3$)
SET – A
(Aliphatic polar aprotic solvents)

S. No.	Solvent parameters	n	R	S	F	Regression equation log $k_2 =$	Eqn.no
1.	ε	10	0.875	0.3993	26.107	$3.323 + 0.053\varepsilon$	
		(10)	(0.863)	(0.4033)	(23.344)	$3.185 + 0.050\varepsilon$	
		[10]	**[0.900]**	[0.2863]	[34.252]	$2.930 + 0.043\varepsilon$	1
2.	$\dfrac{1}{\varepsilon}$	10	0.725	0.5682	8.844	$4.815 - 4.348\dfrac{1}{\varepsilon}$	
		(10)	(0.702)	(0.5690)	(7.787)	$4.604 - 4.085\dfrac{1}{\varepsilon}$	
		[10]	[0.598]	[0.5271]	[4.465]	$4.081 - 2.866\dfrac{1}{\varepsilon}$	
3.	$\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	10	0.755	0.5405	10.611	$1.148 + 7.486\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(10)	(0.733)	(0.5438)	(9.282)	$1.154 + 7.044\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[10]	[0.632]	[0.5101]	[5.311]	$1.636 + 4.998\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
4.	μ_D	10	**0.903**	0.3550	35.138	$2.591 + 0.639\ \mu_D$	2
		(10)	(0.896)	(0.3549)	(32.569)	$2.474 + 0.615\ \mu_D$	
		[10]	[0.846]	0.3504]	[20.2060]	$2.457 + 0.478\ \mu_D$	
5.	log $k_{2\ (n–Pr_3N+MeI)}$ (Lassau and Jungers)	10	0.876	0.3970	26.498	$5.387 + 1.203\ \log k_2 LJ$	
		(10)	(0.881)	(0.3778)	(27.802)	$5.178 + 1.172\ \log k_2 LJ$	
		[10]	[0.897]	[0.2904]	[33.082]	$4.621 + 0.983 \log k_2 LJ$	
6.	$E_T(30)$	10	0.849	0.4359	20.624	$-3.404 + 0.188\ E_T(30)$	
		(10)	(0.830)	(0.4453)	(17.773)	$-3.187 + 0.179\ E_T(30)$	
		[10]	[0.836]	[0.3616]	[8.496]	$-2.318 + 0.148\ E_T(30)$	
7.	π^*	10	**0.927**	0.3098	48.674	$0.242 + 5.742\pi^*$	3
		(10)	**(0.929)**	(0.2961)	(50.294)	$0.175 + 5.580\pi^*$	4
		[10]	**[0.941]**	[0.2222]	[62.125]	$0.443 + 4.654\pi^*$	5
8.	ρ	10	0.211	0.8060	0.371	$5.678 - 1.444\rho$	
		(10)	(0.163)	(0.7886)	(0.218)	$5.164 - 1.082\rho$	
		[10]	[0.097]	[0.6549]	[0.076]	$4.263 - 0.531\rho$	
9.	γ	10	0.737	0.5571	9.523	$3.207 + 0.046\gamma$	
		(10)	(0.751)	(0.5281)	(10.330)	$3.038 + 0.045\gamma$	
		[10]	[0.675]	[0.4855]	[6.691]	$2.939 + 0.033\gamma$	
10.	η	10	0.014	0.8244	0.002	$4.339 + 0.016\eta$	
		(10)	(0.074)	(0.7971)	(0.044)	$4.099 + 0.083\eta$	
		[10]	[0.032]	[0.6576]	[0.008]	$3.751 + 0.029\eta$	

Value in (   ) is for p–Cl
Value in [   ] is for p–OCH$_3$

SET – B
(Aromatic and halogenated solvents)

S. No.	Solvent parameters	n	R	S	F	Regression equation log k_2 =
1.	ε	8	0.283	1.6268	0.524	$4.216 - 0.039\varepsilon$
		(8)	(0.280)	(0.5235)	(0.511)	$4.163 + 0.012\varepsilon$
		[8]	[0.172]	[0.4485]	[0.184]	$4.290 - 0.006\varepsilon$
2.	$\dfrac{1}{\varepsilon}$	8	0.393	1.5600	1.094	$2.718 + 7.580\dfrac{1}{\varepsilon}$
		(8)	(0.084)	(0.5434)	(0.043)	$4.398 - 0.522\dfrac{1}{\varepsilon}$
		[8]	[0.337]	[0.4287]	[0.766]	$3.981 + 1.744\dfrac{1}{\varepsilon}$
3.	$\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	8	0.410	1.5471	1.213	$8.310 - 11.347\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		(8)	(0.081)	(0.5436)	(0.039)	$4.039 + 0.718\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		[8]	[0.362]	[0.42437]	[0.906]	$5.300 - 2.691\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
4.	μ_D	8	0.454	1.5111	1.561	$4.816 - 0.535\,\mu_D$
		(8)	(0.299)	(0.5205)	(0.587)	$4.093 + 0.113\,\mu_D$
		[8]	[0.008]	[0.4553]	[0.000]	$4.209 - 0.002\,\mu_D$
5.	log $k_{2\ (n\text{-}Pr3N+MeI)}$ Lassau and Jungers	8	0.339	1.5960	0.778	$2.636 - 1.483$ log k_2LJ
		(8)	(0.100)	(0.5426)	(0.061)	$4.231 - 0.141$ log k_2 LJ
		[8]	[0.530]	[0.3860]	[2.350]	$3.762 - 0.624$log k_2LJ
6.	$E_T(30)$	8	0.434	1.5284	1.390	$15.962 - 0.308\ E_T(30)$
		(8)	(0.131)	(0.5407)	(0.104)	$5.520 - 0.030\ E_T(30)$
		[8]	[0.471]	[0.4017]	[1.707]	$7.779 - 0.090\ E_T(30)$
7.	π^*	8	0.169	1.6718	0.177	$5.832 - 2.259\pi^*$
		(8)	(0.189)	(0.5355)	(0.223)	$3.561 + 0.933\pi^*$
		[8]	[0.283]	[0.4367]	[0.522]	$5.166 - 1.165\pi^*$
8.	ρ	8	0.148	1.6776	0.135	$2.582 + 0.948\rho$
		(8)	(0.320)	(0.5168)	(0.683)	$5.097 - 0.657\rho$
		[8]	[0.226]	[0.4435]	[0.324]	$3.751 + 0.388\rho$
9.	γ	8	0.263	1.6317	0.485	$4.688 - 0.035\gamma$
		(8)	(0.141)	(0.5399)	(0.123)	$4.165 + 0.\ 006\gamma$
		[8]	[0.269]	[0.4385]	[0.468]	$3.939 + 0.009\gamma$
10.	η	8	0.503	1.4660	2.033	$2.661 + 1.270\eta$
		(8)	(0.121)	(0.5329)	(0.284)	$4.471 - 0.172\eta$
		[8]	[0.324]	[0.4308]	[0.702]	$4.381 - 0.219\eta$

Value in (   ) is for p–Cl
Value in [   ] is for p–OCH₃

_____

SET – C
(Hydroxylic solvents - protic)

S. No.	Solvent parameters	n	R	S	F	Regression equation log k$_2$=	Eqn.no
1.	ε	7	0.836	0.3575	11.589	1.178 + 0.071ε	
		(7)	(0.858)	(0.3449)	(13.939)	1.315 + 0.075ε	
		[7]	**[0.906]**	[0.2796]	[22.883]	1.512 + 0.078ε	6
2.	$\dfrac{1}{\varepsilon}$	7	0.720	0.4522	5.368	$3.988 - 25.359\,\dfrac{1}{\varepsilon}$	
		(7)	(0.716)	(0.4686)	(5.264)	$4.242 - 26.019\,\dfrac{1}{\varepsilon}$	
		[7]	[0.795]	[0.4002]	[8.613]	$4.632 - 28.426\,\dfrac{1}{\varepsilon}$	
3.	$\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	7	0.722	0.4505	5.448	$-13.689 + 35.428\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(7)	(0.716)	(0.4686)	(5.263)	$-13.835 + 36.220\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[7]	[0.797]	[0.3992]	[8.683]	$-15.146 + 39.630\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
4.	μ$_D$	7	0.394	0.5985	0.919	2.057 + 0.281 μ$_D$	
		(7)	(0.423)	(0.6084)	(1.089)	2.219 + 0.311 μ$_D$	
		[7]	[0.466]	[0.5842]	[1.388]	2.426 – 0.337 μ$_D$	
5.	log k$_{2\ (n–Pr_3N+MeI)}$ Lassau and Jungers	7	0.210	0.6366	0.232	2.440 – 0.119 log k$_2$LJ	
		(7)	(0.248)	(0.6503)	(0.329)	2.630 – 0.145 log k$_2$ LJ	
		[7]	[0.301]	[0.6297]	[0.497]	2.854 – 0.172 log k$_2$LJ	
6.	E$_T$(30)	7	0.151	0.6438	0.116	2.365 + 0.005 E$_T$(30)	
		(7)	(0.229)	(0.6535)	(0.277)	2.468 + 0.007 E$_T$(30)	
		[7]	[0.197]	[0.6474]	[0.210]	2.771 + 0.006 E$_T$(30)	
7.	π*	7	0.099	0.6480	0.050	2.672 – 0.198π*	
		(7)	(0.027)	(0.6711)	(0.004)	2.755 + 0.054π*	
		[7]	[0.052]	[0.6594]	[0.014]	3.094 – 0.105π*	
8.	ρ	7	0.464	0.5768	1.374	4.932 - 2.778ρ	
		(7)	(0.368)	(0.6241)	(0.786)	4.719 – 0.272ρ	
		[7]	[0.470]	[0.5830]	[1.414]	5.464 - 2.848ρ	
9.	γ	7	0.516	0.5580	1.810	3.820 – 0.049γ	
		(7)	(0.410)	(0.6123)	(1.011)	3.812 - 0.040γ	
		[7]	[0.501]	[0.5716]	[1.672]	4.272 - 0.048γ	
10.	η	7	0.657	0.4912	3.788	2.906 - 0.202η	
		(7)	(0.525)	(0.5713)	(1.905)	3.063 – 0.167η	
		[7]	[0.557]	[0.5483]	[2.251]	3.330 – 0.714η	

Value in (   ) is for p–Cl
Value in [   ] is for p–OCH$_3$

The best-fit equations were given in Table -5. This proves that none of the single properties influence the rates of the reactions.

Table 5. Summary of the best-fit simple regression equation in predicting the effect of solvent parameters on reaction rate

Correlation 3+ log k$_2$versus solvent parameters	Regression equation log k$_2$=	n	R	S	F	Eqn. no.
SET – A Aliphatic polar solvents ε	2.930 + 0.043 ε	[10]	**[0.900]**	[0.2863]	[34.252]	1
μ$_D$	2.591 + 0.639 μ$_D$	10	**0.903**	0.3550	35.138	2
	0.242 + 5.742 π*	10	**0.927**	0.3098	48.674	3
π*	0.175 + 5.580 π*	(10)	(0.929)	(0.2961)	(50.294)	4
	0.443 + 4.654 π*	[10]	**[0.941]**	[0.2222]	[62.125]	5
SET – C Protic solvents ε	1.512 +0.078 ε	[7]	**[0.906]**	[0.2796]	[22.883]	6

It is noted that the effect of the solvents on a reaction is more complex than what we should anticipate. The existence of the reactive species and the activated complex in each solvent may not be same [45]. Perhaps more than one solvent property may influence the reactive species [29]. So, we conclude that it is worthy to do multiple regression analyses of the reaction rate with different solvent parameters. In the following the results of dual and triple parameter regressions were discussed.

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Table 6 Summary of the dual (multiple) regression of 3+log k₂ versus solvent parameters
Reaction between TsCl and *p* –XC₆H₄OH–NEt₃
(X= *p* – CN, *p* – Cl and *p* – OCH₃)

SET – A
(Aliphatic polar aprotic solvents)

</div>

S. No.	Correlation $3+ \log k_2$ Vs parameters	n	R	S	F	Regression equation $\log k_2 =$	Eqn.no
1.	$\mu_D + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	10	**0.926**	0.3325	21.093	$3.919 + 0.995\ \mu_D - 5.398\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	7
		(10)	**(0.930)**	(0.3136)	(22.492)	$4.024 + 1.031\ \mu_D - 6.302\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	8
		[10]	**[0.934]**	[0.2511]	[23.962]	$4.474 + 1.019\ \mu_D - 8.198\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	9
2.	$\mu_D + E_T(30)$	10	**0.911**	0.3631	17.125	$0.680 + 0.480\ \mu_D + 0.057\ E_T(30)$	10
		(10)	**(0.901)**	(0.3698)	(15.187)	$1.006 + 0.493\ \mu_D + 0.044\ E_T(30)$	11
		[10]	[0.869]	[0.3476]	[10.831]	$0.046 + 0.278\ \mu_D + 0.072\ E_T(30)$	
3.	$\mu_D + \pi^*$	10	**0.934**	0.3144	24.006	$0.914 + 0.221\ \mu_D + 3.953\ \pi^*$	12
		(10)	**(0.934)**	(0.3058)	(23.820)	$0.702 + 0.173\ \mu_D + 4.175\ \pi^*$	13
		[10]	**[0.944]**	[0.2330]	[28.396]	$0.144 - 0.099\ \mu_D + 5.453\ \pi^*$	14
4.	$\mu_D + \log k_{2(nPr_3N + MeI)}$ Lassau and Jungers	10	**0.925**	0.3351	20.714	$3.701 + 0.403\ \mu_D + 0.\ 0.535\ \log k_2\ LJ$	15
		(10)	**(0.923)**	(0.3285)	(20.182)	$3.657 + 0.364\ \mu_D + 0.\ 0.570\ \log k_2\ LJ$	16
		[10]	**[0.910]**	[0.2912]	[16.925]	$3.925 + 0.166\ \mu_D + 0.\ 0.707\ \log k_2\ LJ$	17
5.	$\varepsilon + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	10	0.888	0.4050	13.078	$2.548 + 0.042\ \varepsilon + 2.282\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(10)	(0.873)	(0.4165)	(11.235)	$2.532 + 0.042\ \varepsilon + 1.923\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[10]	**[0.902]**	[0.3031]	[15.356]	$3.176 + 0.047\ \varepsilon - 0.726\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	18
6.	$\varepsilon + E_T(30)$	10	0.876	0.4256	11.511	$2.279 + 0.045\varepsilon + 0.029\ E_T(30)$	
		(10)	(0.863)	(0.4316)	(10.222)	$2.834 + 0.048\varepsilon + 0.010\ E_T(30)$	
		[10]	**[0.905]**	[0.2988]	[15.891]	$5.025 + 0.058\varepsilon - 0.058\ E_T(30)$	19
7.	$\varepsilon + \pi^*$	10	**0.927**	0.3311	21.295	$0.251 + 0.000\varepsilon + 5.724\ \pi^*$	20
		(10)	**(0.930)**	(0.3146)	(22.319)	$- 0.186 - 0.007\varepsilon + 6.281\ \pi^*$	21
		[10]	**[0.942]**	[0.2362]	[27.546]	$0.710 + 0.005\varepsilon + 4.137\ \pi^*$	22
8.	$\varepsilon + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	10	0.892	0.3976	13.697	$4.378 + 0.027\varepsilon + 0.638\ \log k_2 LJ$	
		(10)	(0.890)	(0.3895)	(13.347)	$4.450 + 0.019\varepsilon + 0.765\ \log k_2 LJ$	
		[10]	**[0.916]**	[0.2820]	[18.280]	$3.739 + 0.023\varepsilon + 0.489\ \log k_2 LJ$	23
9.	$\rho + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	10	0.755	0.5778	4.643	$1.087 + 0.055\rho + 7.509\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(10)	(0.735)	(0.5797)	(4.104)	$0.767 + 0.354\rho + 7.192\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[10]	[0.638]	[0.5417]	[2.402]	$1.078 + 0.510\rho + 5.211\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
10.	$\rho + E_T(30)$	10	0.871	0.4333	10.982	$-2.146 - 1.333\rho + 0.188\ E_T(30)$	
		(10)	(0.843)	(0.4592)	(8.620)	$-2.265 - 0.977\rho + 0.178\ E_T(30)$	
		[10]	[0.839]	[0.3823]	[8.350]	$-1.899 - 1.444\rho + 0.148\ E_T(30)$	
11.	$\rho + \pi^*$	10	**0.976**	0.1936	69.052	$2.034 - 2.100\ \rho + 5.932\ \pi^*$	24
		(10)	**(0.964)**	(0.2280)	(45.671)	$1.640 - 1.717\ \rho + 5.735\ \pi^*$	25
		[10]	**[0.961]**	[0.1954]	[41.848]	$1.345 - 1.056\rho + 4.750\ \pi^*$	26
12.	$\rho + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	10	0.974	0.1990	65.173	$8.259 - 2.998\ \rho + 1.342\ \log k_2\ LJ$	27
		(10)	**(0.959)**	(0.2432)	(39.691)	$7.648 - 2.579\ \rho + 1.292\ \log k_2\ LJ$	28
		[10]	**[0.951]**	[0.2184]	[32.802]	$6.310 - 1.764\ \rho + 1.065\ \log k_2\ LJ$	29
13.	$\gamma + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	10	0.775	0.5569	5.266	$1.855 + 0.021\ \gamma + 4.603\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(10)	(0.771)	(0.5446)	(5.115)	$2.087 + 0.028\ \gamma + 3.240\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[10]	[0.683]	[0.5139]	[3.056]	$2.472 + 0.025\ \gamma + 1.588\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
14.	$\gamma + E_T(30)$	10	0.874	0.4279	11.347	$-2.031 + 0.018\ \gamma + 0.144\ E_T(30)$	
		(10)	(0.866)	(0.4274)	(10.489)	$-1.625 + 0.020\ \gamma + 0.128\ E_T(30)$	
		[10]	[0.846]	[0.3745]	[8.845]	$-1.606 + 0.009\ \gamma + 0.125\ E_T(30)$	
15.	$\gamma + \pi^*$	10	**0.929**	0.3268	21.967	$0.007 - 0.007\ \gamma + 6.309\ \pi^*$	30
		(10)	**(0.930)**	(0.3147)	(22.302)	$0.026 - 0.004\ \gamma + 5.939\ \pi^*$	31
		[10]	**[0.961]**	[0.1939]	[45.543]	$-0.156 - 0.017\ \gamma + 6.101\ \pi^*$	32
16.	$\gamma + \log k_{2(nPr_3N + MeI)}$ Lassau and Junges	10	0.881	0.4173	12.110	$5.042 + 0.009\ \gamma + 1.053\ \log k_2\ LJ$	

S. No.	Correlation	n				Regression equation	
		(10)	(0.887)	(0.3942)	(12.947)	$4.784 + 0.010\,\gamma + 1.002\,\log k_2\,LJ$	
		[10]	[0.898]	[0.3093]	[14.605]	$4.739 - 0.003\,\gamma + 1.034\,\log k_2\,LJ$	
17.	$\eta + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	10	0.774	0.5582	5.227	$0.828 + 0.199\,\eta + 7.833\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(10)	(0.761)	(0.5482)	(5.004)	$0.740 + 0.257\,\eta + 7.493\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[10]	[0.652]	[0.5332]	[2.591]	$1.392 + 0.152\,\eta + 5.263\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
18.	$\eta + E_T(30)$	10	0.893	0.3962	13.822	$-4.483 + 0.335\,\eta + 0.208\,E_T(30)$	
		(10)	(0.896)	(0.3801)	(14.192)	$-4.449 + 0.391\,\eta + 0.201\,E_T(30)$	
		[10]	[0.885]	[0.3271]	[12.690]	$-3.224 + 0.281\,\eta + 0.164\,E_T(30)$	
19.	$\eta + \pi^*$	10	**0.928**	0.3279	21.795	$0.277 - 0.061\,\eta + 5.766\,\pi^*$	33
		(10)	**(0.929)**	(0.3165)	(22.014)	$0.170 + 0.008\,\eta + 5.576\,\pi^*$	34
		[10]	**[0.942]**	[0.2362]	[27.532]	$0.463 - 0.033\,\eta + 4.667\,\pi^*$	35
20.	$\eta + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	10	0.877	0.4235	11.657	$5.420 - 0.036\,\eta + 1.205\,\log k_2\,LJ$	
		(10)	(0.882)	(0.4032)	(12.221)	$5.149 + 0.032\,\eta + 1.170\,\log k_2\,LJ$	
		[10]	[0.897]	[0.3102]	[14.493]	$4.633 - 0.013\,\eta + 0.984\,\log k_2\,LJ$	

Value in (   ) is for p–Cl
Value in [   ] is for p–OCH₃

SET – B (Aromatic and halogenated solvents)

S. No.	Correlation 3+ log k₂ Vs parameters	n	R	S	F	Regression equation log k₂ =
1.	$\mu_D + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	8	0.454	1.6553	0.650	$4.947 - 0.520\,\mu_D - 0.400\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		(8)	(0.517)	(0.5115)	(0.910)	$6.859 + 0.436\,\mu_D - 8.461\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		[8]	[0.802]	[0.2981]	[4.449]	$8.600 + 0.510\,\mu_D - 13.431\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
2.	$\mu_D + E_T(30)$	8	0.469	1.6414	0.704	$9.915 - 0.352\,\mu_D - 0.138\,E_T(30)$
		(8)	(0.690)	(0.4323)	(2.273)	$12.929 + 0.431\,\mu_D - 0.239\,E_T(30)$
		[8]	[0.780]	[0.3121]	[3.886]	$13.457 + 0.330\,\mu_D - 0.250\,E_T(30)$
3.	$\mu_D + \pi^*$	8	0.651	1.4103	1.840	$-5.233 - 1.519\,\mu_D + 14.671\,\pi^*$
		(8)	(0.333)	(0.5634)	(0.311)	$5.109 + 0.213\,\mu_D - 1.484\,\pi^*$
		[8]	[0.567]	[0.4110]	[1.182]	$7.485 + 0.318\,\mu_D - 4.783\,\pi^*$
4.	$\mu_D + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	8	0.455	1.6547	0.653	$5.007 - 0.570\,\mu_D + 0.166\,\log k_2\,LJ$
		(8)	(0.608)	(0.4743)	(1.466)	$2.727 + 0.362\,\mu_D - 1.\,188\,\log k_2\,LJ$
		[8]	[0.836]	[0.2740]	[5.783]	$2.410 + 0.325\,\mu_D - 1.\,565\,\log k_2\,LJ$
5.	$\varepsilon + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	8	0.446	1.6633	0.620	$11.396 + 0.05\,\varepsilon - 20.660\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		(8)	(0.460)	(0.5306)	(0.669)	$6.606 + 0.044\,\varepsilon - 7.030\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		[8]	[0.486]	[0.4360]	[0.771]	$6.832 + 0.026\,\varepsilon - 7.314\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
6.	$\varepsilon + E_T(30)$	8	0.444	1.6648	0.615	$19.159 + 0.022\,\varepsilon - 0.396\,E_T(30)$
		(8)	(0.638)	(0.4602)	(1.172)	$12.205 + 0.045\,\varepsilon - 0.213\,E_T(30)$
		[8]	[0.571]	[0.4093]	[1.212]	$10.676 + 0.020\,\varepsilon - 0.169\,E_T(30)$
7.	$\varepsilon + \pi^*$	8	0.450	1.6597	0.634	$-8.823 - 0.198\,\varepsilon + 18.370\,\pi^*$
		(8)	(0.390)	(0.5502)	(0.447)	$7.412 + 0.052\,\varepsilon - 4.577\,\pi^*$
		[8]	[0.440]	[0.4479]	[0.600]	$8.346 + 0.043\,\varepsilon - 5.714\,\pi^*$
8.	$\varepsilon + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	8	0.339	1.7488	0.325	$2.739 - 0.003\,\varepsilon - 1.400\,\log k_2LJ$
		(8)	(0.629)	(0.4643)	(1.638)	$2.725 + 0.047\,\varepsilon - 1.363\,\log k_2LJ$
		[8]	[0.692]	[0.3599]	[2.302]	$2.861 + 0.028\,\varepsilon - 1.354\,\log k_2LJ$
9.	$\rho + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	8	0.415	1.6903	0.521	$9.303 - 0.485\,\rho - 12.396\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		(8)	(0.332)	(0.5635)	(0.310)	$5.606 - 0.766\,\rho - 0.938\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		[8]	[0.366]	[0.4642]	[0.387]	$5.088 + 0.103\,\rho - 2.467\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
10.	$\rho + E_T(30)$	8	0.435	1.6735	0.582	$15.519 + 0.184\,\rho - 0.303\,E_T(30)$
		(8)	(0.393)	(0.5492)	(0.458)	$7.434 - 0.795\,\rho - 0.055\,E_T(30)$
		[8]	[0.481]	[0.4373]	[0.752]	$7.356 - 0.176\,\rho - 0.084\,E_T(30)$
11.	$\rho + \pi^*$	8	0.201	1.8203	0.105	$4.631 + 0.718\,\rho - 2.155\,\pi^*$
		(8)	(0.338)	(0.5623)	(0.323)	$4.559 - 0.597\,\rho + 0.566\,\pi^*$
		[8]	[0.325]	[0.4717]	[0.295]	$4.693 + 0.283\,\rho - 0.991\,\pi^*$

S.No.	Correlation	n	R	S	F	Regression equation
12.	$\rho + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	8	0.340	1.7475	0.327	$2.437 + 0.201\,\rho - 1.434\,\log k_2\,LJ$
		(8)	(0.393)	(0.5493)	(0.457)	$5.062 - 0.837\,\rho - 0.345\,\log k_2\,LJ$
		[8]	[0.532]	[0.4223]	[0.987]	$3.689 + 0.073\,\rho - 0.606\,\log k_2\,LJ$
13.	$\gamma + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	8	0.586	1.5057	1.308	$11.432 - 0.057\,\gamma - 15.062\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		(8)	(0.192)	(0.5863)	(0.096)	$3.620 + 0.008\,\gamma + 1.216\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		[8]	[0.399]	[0.4574]	[0.472]	$4.967 + 0.006\,\gamma - 2.294\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
14.	$\gamma + E_T(30)$	8	0.615	1.4660	1.517	$21.811 - 0.059\,\gamma - 0.413\,E_T(30)$
		(8)	(0.618)	(0.5890)	(0.072)	$5.066 + 0.005\,\gamma - 0.022\,E_T(30)$
		[8]	[0.487]	[0.4356]	[0.777]	$7.329 + 0.005\,\gamma - 0.082\,E_T(30)$
15.	$\gamma + \pi^*$	8	0.169	1.6718	0.177	$5.832 - 2.595\,\gamma + 0.03\,\pi^*$
		(8)	(0.347)	(0.5604)	(0.341)	$2.391 + 1.856\,\gamma + 0.014\,\pi^*$
		[8]	[0.315]	[0.4734]	[0.275]	$4.704 - 0.800\,\gamma + 0.006\,\pi^*$
16.	$\gamma + \log k_{2(nPr_3N + MeI)}$ Lassau and Junges	8	0.530	1.5757	0.977	$3.776 - 2.106\,\gamma - 0.056\,\log k_2\,LJ$
		(8)	(0.152)	(0.5904)	(0.059)	$4.128 - 0.084\,\gamma + 0.005\,\log k_2\,LJ$
		[8]	[0.540]	[0.4199]	[1.028]	$3.687 - 0.583\,\gamma + 0.004\,\log k_2\,LJ$
17.	$\eta + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	8	0.548	1.5539	1.075	$5.582 + 1.014\,\eta - 6.661\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		(8)	(0.213)	(0.5837)	(0.118)	$4.513 - 0.176\,\eta - 0.096\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
		[8]	[0.638]	[0.3840]	[1.718]	$6.357 - 0.393\,\eta - 4.506\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$
18.	$\eta + E_T(30)$	8	0.557	1.5437	1.122	$10.390 + 0.979\,\eta - 0.188\,E_T(30)$
		(8)	(0.327)	(0.5647)	(0.299)	$7.057 - 0.270\,\eta - 0.063\,E_T(30)$
		[8]	[0.753]	[0.3284]	[3.268]	$10.297 - 0.442\,\eta - 0.144\,E_T(30)$
19.	$\eta + \pi^*$	8	0.507	1.6021	0.863	$1.746 + 1.345\,\eta + 1.033\,\pi^*$
		(8)	(0.237)	(0.5803)	(0.149)	$3.955 - 0.130\,\eta + 0.582\,\pi^*$
		[8]	[0.576]	[0.4078]	[1.239]	$6.317 - 0.379\,\eta - 2.187\,\pi^*$
20.	$\eta + \log k_{2(nPr_3N + MeI)}$ Lassau and Jungers	8	0.537	1.5680	1.011	$2.178 + 1.110\,\eta - 0.864\,\log k_2\,LJ$
		(8)	(0.277)	(0.5740)	(0.208)	$4.323 - 0.222\,\eta - 0.264\,\log k_2\,LJ$
		[8]	[0.744]	[0.3332]	[3.103]	$3.916 - 0.374\,\eta - 0.832\,\log k_2\,LJ$

Value in ( ) is for p–Cl
Value in [ ] is for p–OCH₃

SET – C
(Hydroxylic solvents - Protic)

S. No.	Correlation 3+ log k₂ Vs parameters	n	R	S	F	Regression equation log k_2 =	Eqn.no
1.	$\mu_D + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	7	0.722	0.5037	2.179	$-13.662 + 0.002\,\mu_D - 35.361\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(7)	(0.717)	(0.5230)	(2.119)	$-13.294 + 0.035\,\mu_D + 34.900\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[7]	[0.798]	[0.4453]	[3.497]	$-14.620 + 0.034\,\mu_D + 38.347\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
2.	$\mu_D + E_T(30)$	7	0.535	0.6151	0.802	$1.285 + 0.408\,\mu_D + 0.012\,E_T(30)$	
		(7)	(0.627)	(0.5846)	(1.297)	$1.202 + 0.479\,\mu_D + 0.016\,E_T(30)$	
		[7]	[0.647]	[0.5630]	[1.439]	$1.457 + 0.497\,\mu_D + 0.015\,E_T(30)$	
3.	$\mu_D + \pi^*$	7	0.407	0.6651	0.396	$1.865 + 0.320\,\mu_D + 0.228\,\pi^*$	
		(7)	(0.496)	(0.6517)	(0.653)	$1.709 + 0.415\,\mu_D + 0.606\,\pi^*$	
		[7]	[0.505]	[0.6373]	[0.684]	$2.052 + 0.414\,\mu_D + 0.445\,\pi^*$	
4.	$\mu_D + \log k_{2(nPr_3N + MeI)}$ Lassau and Jungers	7	0.413	0.6631	0.411	$2.018 + 0.261\,\mu_D - 0.071\,\log k_2\,LJ$	
		(7)	(0.450)	(0.6701)	(0.509)	$2.169 + 0.284\,\mu_D - 0.093\,\log k_2\,LJ$	
		[7]	[0.507]	[0.6364]	[0.691]	$2.363 + 0.303\,\mu_D - 0.\;117\,\log k_2\,LJ$	
5.	$\varepsilon + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	7	0.886	0.3382	7.272	$23.296 + 0.157\,\varepsilon - 51.882\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(7)	**(0.943)**	(0.2502)	(16.003)	$31.772 + 0.194\,\varepsilon - 71.443\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	36
		[7]	**[0.944]**	[0.2427]	[16.507]	$21.962 + 0.158\,\varepsilon - 47.970\,\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	37
6.	$\varepsilon + E_T(30)$	7	0.844	0.3903	4.960	$1.280 + 0.074\,\varepsilon - 0.004\,E_T(30)$	
		(7)	(0.859)	(0.3843)	(5.630)	$1.353 + 0.076\,\varepsilon - 0.001\,E_T(30)$	
		[7]	**[0.911]**	[0.3049]	[9.726]	$1.594 + 0.081\,\varepsilon - 0.003\,E_T(30)$	38

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No.	Parameters		R	s	F	Equation	Ref
7.	$\varepsilon + \pi^*$	7	0.837	0.3985	4.675	$1.228 + 0.071\ \varepsilon - 0.085\ \pi^*$	
		(7)	(0.862)	(0.3803)	(5.790)	$1.212 + 0.076\ \varepsilon + 0.175\ \pi^*$	
		[7]	**[0.906]**	[0.3125]	[9.159]	$1.501 + 0.078\ \varepsilon + 0.020\ \pi^*$	39
8.	$\varepsilon + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	7	0.868	0.3614	6.119	$1.119 + 0.082\ \varepsilon + 0.153\ \log k_2 LJ$	
		(7)	(0.882)	(0.3541)	(6.986)	$1.262 + 0.085\ \varepsilon + 0.137\ \log k_2 LJ$	
		[7]	**[0.922]**	[0.2891]	[11.317]	$1.468 + 0.086\ \varepsilon + 0.113\ \log k_2 LJ$	40
9.	$\rho + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	7	0.742	0.4879	2.454	$-20.093 + 1.676\ \rho + 46.274\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(7)	(0.784)	(0.4655)	(3.201)	$-26.130 + 3.217\ \rho + 57.044\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[7]	[0.838]	[0.4032]	[4.706]	$-24.930 + 2.560\ \rho + 56.202\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
10.	$\rho + E_T(30)$	7	0.521	0.6215	0.745	$4.825 - 3.030\ \rho + 0.007\ E_T(30)$	
		(7)	(0.474)	(0.6608)	(0.580)	$4.580 - 2.601\ \rho + 0.010\ E_T(30)$	
		[7]	[0.594]	[0.6173]	[0.861]	$5.334 - 3.156\ \rho + 0.009\ E_T(30)$	
11.	$\rho + \pi^*$	7	0.575	0.5955	0.990	$6.215 - 4.893\ \rho + 0.976\ \pi^*$	
		(7)	(0.560)	(0.6218)	(0.914)	$6.360 - 4.979\ \rho + 1.248\ \pi^*$	
		[7]	[0.626]	[0.5759]	[1.287]	$7.047 - 5.460\ \rho + 1.204\ \pi^*$	
12.	$\rho + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	7	0.485	0.6366	0.616	$4.735 - 2.647\ \rho - 0.081\ \log k_2 LJ$	
		(7)	(0.417)	(0.6823)	(0.420)	$4.439 - 2.087\ \rho - 0.115\ \log k_2 LJ$	
		[7]	[0.524]	[0.6289]	[0.756]	$5.135 - 2.631\ \rho - 0.134\ \log k_2 LJ$	
13.	$\gamma + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	7	0.723	0.5028	2.193	$-14.855 + 0.006\ \gamma + 37.650\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(7)	(0.742)	(0.5036)	(2.443)	$-19.641 + 0.028\ \gamma + 47.280\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[7]	[0.810]	[0.4329]	[3.818]	$-19.509 + 0.021\ \gamma + 47.942\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
14.	$\gamma + E_T(30)$	7	0.571	0.5979	0.965	$3.593 - 0.053\ \gamma + 0.008\ E_T(30)$	
		(7)	(0.511)	(0.6451)	(0.708)	$3.519 - 0.045\ \gamma + 0.010\ E_T(30)$	
		[7]	[0.578]	[0.6026]	[1.002]	$4.000 - 0.053\ \gamma + 0.009\ E_T(30)$	
15.	$\gamma + \pi^*$	7	0.635	0.5622	1.354	$4.162 - 0.084\ \gamma + 1.040\ \pi^*$	
		(7)	(0.604)	(0.5979)	(1.151)	$4.234 - 0.083\ \gamma + 1.282\ \pi^*$	
		[7]	[0.655]	[0.5576]	[1.506]	$4.668 - 0.800\ \gamma + 1.202\ \pi^*$	
16.	$\gamma + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	7	0.556	0.6053	0.893	$3.692 - 0.049\ \gamma - 0.117\ \log k_2 LJ$	
		(7)	(0.478)	(0.6592)	(0.593)	$3.655 - 0.040\ \gamma - 0.143\ \log k_2 LJ$	
		[7]	[0.582]	[0.6001]	[1.027]	$4.086 - 0.048\ \gamma - 0.171\ \log k_2 LJ$	
17.	$\eta + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	7	0.831	0.4047	4.475	$-9.627 - 0.137\ \eta + 27.075\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		(7)	(0.766)	(0.4824)	(2.843)	$-11.066 - 0.093\ \eta + 30.526\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
		[7]	[0.842]	[0.3979]	[4.884]	$-12.409 - 0.092\ \eta + 34.003\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	
18.	$\eta + E_T(30)$	7	0.766	0.4684	2.833	$2.417 - 0.245\ \eta + 0.013\ E_T(30)$	
		(7)	(0.679)	(0.5511)	(1.710)	$2.514 - 0.215\ \eta + 0.014\ E_T(30)$	
		[7]	[0.690]	[0.5343]	[1.819]	$2.818 - 0.219\ \eta + 0.013\ E_T(30)$	
19.	$\eta + \pi^*$	7	0.754	0.4783	2.635	$2.559 - 0.288\ \eta + 0.924\ \pi^*$	
		(7)	(0.678)	(0.5514)	(1.706)	$2.649 - 0.269\ \eta + 1.103\ \pi^*$	
		[7]	[0.661]	[0.5542]	[1.550]	$2.993 - 0.257\ \eta + 0.897\ \pi^*$	
20.	$\eta + \log k_{2(nPr_3N+MeI)}$ Lassau and Jungers	7	0.773	0.4617	2.973	$2.710 - 0.238\ \eta - 0.240\ \log k_2 LJ$	
		(7)	(0.666)	(0.5596)	(1.598)	$2.860 - 0.204\ \eta - 0.249\ \log k_2 LJ$	
		[7]	[0.731]	[0.5035]	[2.301]	$3.009 - 0.216\ \eta - 0.283\ \log k_2 LJ$	

Value in (   ) is for p–Cl
Value in [   ] is for p–OCH₃

Multiple regression – Dual solvent parameter regression analyses

Solvents will have specific and non-specific interactions with the solute in a concerted fashion. So it is profitable to use more than one solvent parameter in the regression analyses. We have tried two parameter correlation of log k_2 in order to obtain a better correlation. The multiple (dual) regression analyses with the above said solvent parameters were performed with log k_2 at 303K for aprotic, aromatic and halogenated and protic solvents using the equation.

$$\log k_2 = \log k_0 + a_1 X_1 + a_2 X_2$$

where X_1 and X_2 are independent variables.

The results are presented in Table-6. Dual parameter regression gives better correlation than the simple one which reflects in the R values [30,33]. The best-fit equations were given in Table-7.

Table 7 Summary of the best – fit multiple (dual) regression equation in predicting the effect of solvent parameters on reaction rate
SET – A
(Aliphatic polar aprotic solvents)

Correlation 3+ log k_2 versus solvent parameters	Regression Equation log k_2	n	R	S	F	Eqn. no.
$\mu_D + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	$3.919 + 0.995\ \mu_D - 5.398\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	[10]	**0.926**	0.3325	21.093	7
	$4.024 + 1.031\ \mu_D - 6.302\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	(10)	**(0.930)**	(0.3136)	(22.492)	8
	$4.474 + 1.019\ \mu_D - 8.198\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	[10]	**[0.934]**	[0.2511]	[23.962]	9
$\mu_D + E_T(30)$	$0.680 + 0.480\ \mu_D + 0.057\ E_T(30)$	10	**0.911**	0.3631	17.125	10
	$1.006 + 0.493\ \mu_D + 0.044\ E_T(30)$	(10)	**(0.901)**	(0.3698)	(15.187)	11
$\mu_D + \pi^*$	$0.914 + 0.221\ \mu_D + 3.953\ \pi^*$	[10]	**[0.934]**	[0.3144]	[24.006]	12
	$0.702 + 0.173\ \mu_D + 4.175\ \pi^*$	(10)	**(0.934)**	(0.3058)	23.820	13
	$0.144 - 0.099\ \mu_D + 5.453\ \pi^*$	[10]	**[0.944]**	[0.2330]	[28.396]	14
$\mu_D + \log k_2\ LJ$	$3.701 + 0.403\ \mu_D + 0.535\ \log k_2\ LJ$	10	**0.925**	0.3351	20.714	15
	$3.657 + 0.364\ \mu_D + 0.570\ \log k_2\ LJ$	(10)	**(0.923)**	(0,3285)	(20.182)	16
	$3.925 + 0.166\ \mu_D + 0.707\ \log k_2\ LJ$	[10]	**[0.910]**	[0.2912]	[16.925]	17
$\varepsilon + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	$3.176 + 0.047\ \varepsilon - 0.726\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	[10]	**[0.902]**	[0.3031]	[15.356]	18
$\varepsilon + E_T(30)$	$5.025 + 0.058\ \varepsilon + 0.058\ E_T(30)$	[10]	**[0.905]**	[0.2988]	[15.891]	19
$\varepsilon + \pi^*$	$0.251 + 0.000\ \varepsilon + 5.724\ \pi^*$	10	**0.927**	0.3311	21.295	20
	$-0.186 - 0.007\ \varepsilon + 6.281\ \pi^*$	(10)	**(0.930)**	(0,31346)	(22.319)	21
	$0.710 + 0.005\ \varepsilon\ 4.137\ \pi^*$	[10]	**[0.942]**	[0.2362]	[27.546]	22
$\varepsilon + \log k_2\ LJ$	$3.739 + 0.023\ \varepsilon + 0.489\ \log k_2\ LJ$	[10]	**[0.916]**	[0.2820]	[18.280]	23
$\rho + \pi^*$	$2.034 - 2.100\ \rho + 5.932\ \pi^*$	10	**0.976**	0.1936	69.052	24
	$1.640 - 1.717\ \rho + 5.735\ \pi^*$	(10)	**(0.964)**	(0.2280)	(45.671)	25
	$1.345 - 1.056\ \rho + 4.750\ \pi^*$	[10]	**[0.961]**	[0.1954]	[41.848]	26
$\rho + \log k_2\ LJ$	$8.259 - 2.998\ \rho + 1.342\ \log k_2\ LJ$	10	**0.974**	0.1990	65.173	27
	$7.648 - 2.579\ \rho + 1.292\ \log k_2\ LJ$	(10)	**(0.959)**	(0.2432)	(39.691)	28
	$6.310 - 1.764\ \rho + 1.065\ \log k_2\ LJ$	[10]	**[0.951]**	[0.2184]	[32.802]	29
$\gamma + \pi^*$	$0.007 - 0.007\ \gamma + 6.309\ \pi^*$	10	**0.929**	0.3268	21.967	30
	$0.026 - 0.004\ \gamma + 5.939\ \pi^*$	(10)	**(0.930)**	(0.3147)	(22.302)	31
	$-0.156 - 0.017\ \gamma + 6.101\ \pi^*$	[10]	**[0.961]**	[0.1939]	[45.543]	32
$\eta + \pi^*$	$0.277 - 0.061\eta + 5.766\ \pi^*$	10	**0.928**	0.3279	21.795	33
	$0.170 + 0.008\ \eta + 5.576\ \pi^*$	(10)	**(0.929)**	(0.3165)	(22.014)	34
	$0.463 - 0.033\ \eta + 4.667\ \pi^*$	[10]	**[0.942]**	[0.2362]	[27.532]	35
SET – C Protic Solvents						
$\varepsilon + \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	$31.772 + 0.194\ \varepsilon - 71.442\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	(7)	**(0.943)**	(0.2502)	(16.003)	36
	$21.962 + 0.158\ \varepsilon - 47.970\ \dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$	[7]	**[0.944]**	[0.2427]	[16.507]	37
$\varepsilon + E_T(30)$	$1.594 + 0.08\ \varepsilon - 0.003\ E_T(30)$	[7]	**[0.911]**	[0.3049]	[9.726]	38
$\varepsilon + \pi^*$	$1.501 + 0.078\ \varepsilon + 0.020\ \pi^*$	[7]	**[0.906]**	[0.3125]	[9.159]	39
$\varepsilon + \log k_2\ LJ$	$1.468 + 0.086\ \varepsilon + 0.113\ \log k_2\ LJ$	[7]	**[0.922]**	[0.2891]	[11.317]	40

Value in (   ) is for p–Cl
Value in [   ] is for p–OCH₃

In the case of dual parameter regression treatment there is a satisfactory correlation only in the combination of μ_D along with Kirkwood function $\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$, $E_T(30)$, π^*, Lassau and Jungers log $k_{2(nPr_3N+MeI)}$ and ε along with $\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$, $E_T(30)$, π^*, Lassau and Jungers log $k_{2(n\ Pr_3\ N\ +\ MeI)}$ and ρ along with π^*, Lassau and Jungers log $k_{2\ (nPr_3\ N\ +\ MeI)}$ and γ with π^* and η with π^*. This reflects in equations 7 to 35 for aliphatic polar solvents (Set A). For protic solvents, there is a satisfactory correlation only in the combination of ε along with Kirkwood function $\dfrac{(\varepsilon-1)}{(2\varepsilon+1)}$, $E_T(30)$, π^* and Lassau and Jungers log $k_{2\ (n\ Pr_3\ N\ +\ MeI)}$ scale. This reflects in equations 36 to 40. From these observations, it is concluded that the influence of density (ρ) along with polarizability (π^*),

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Lassau and Jungers log $k_{2(n \, Pr_3N + MeI)}$ for aliphatic polar solvents and dielectric constants (ϵ) with Kirkwood functions $\dfrac{\epsilon-1}{2\epsilon+1}$ for protic solvents on the rate is found to be more than other parameters. This reflects in equations 24, 27, 36 and 37. μ_D+ π^* (eqn 14), ϵ + π^*(eqn 22), ρ+ π^* (eqn 25 and 26), ρ+ log k_2 LJ (eqn 28 and 29). γ + π^* (eqn 32) and η + π^* (eqn 35) improves the correlation coefficient to a large extent. This is observed in the aliphatic polar solvents (Set A) but not in the aromatic and halogenated (Set B) and protic solvents (Set C). There is a satisfactory correlation in solvent set A and poor correlation in solvent sets B and C.

Generally dual parameter regression gives better correlation than the simple one as reflected in the R values of most of the regression equations (Table-6). Among the dual parameter treatments the regression analyses of solvent set A gives the best linearity. From the observations it may be concluded that more than one solvent parameter interaction has to be considered to understand the effect of solvents on the rate of the reaction.

Multiple regression – Triple solvent parameter regression analyses
Apart from the dual parameter regression analyses, we have attempted triple solvent parameter regression to understand the influence of solvents on the rate of the reaction.The triple regression analyses with solvent parameters were performed against log k_2 at 303K for aliphatic polar, aromatic and halogenated and protic solvents using the equation. The regression analyses results were presented in Table -8.

$$\log k_2 \;=\; \log k_0 + a_1 X_1 + a_2 X_2 + a_3 X_3$$

where X_1 , X_2 and X_3 are independent variables.

Table 8 Summary of the multiple regression (Triple) of 3+log k_2 versus solvent parameters
Reaction between TsCl and p –XC_6H_4OH–NEt_3 (X= p – CN, p – Cl and p – OCH$_3$)
Triple regression analysis

SET – A
(Aliphatic polar aprotic solvents)

S. No.	Correlation 3+ log k_2 versus parameters	n	R	S	F	Regression equation log k_2 =	Eqn.no.
1.	$\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + μ_D + log k_2 LJ	10	**0.931**	0.3483	12.941	4.092 - 3.459 $\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + 0.729 μ_D + 0.313 log k_2 LJ	41
		(10)	**(0.934)**	(0.3298)	(13.660)	4.176 - 4.598 $\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + 0.797 μ_D + 0.275 log k_2 LJ	42
		[10]	**[0.941]**	[0.2578]	[15.368]	4.640 - 6.332 $\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + 0.763 μ_D + 0.301 log k_2 LJ	43
2.	$\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + μ_D + E_T(30)	10	**0.931**	0.3483	12.940	2.399 - 4.991 $\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + 0.850 μ_D + 0.042 E_T(30)	44
		(10)	**(0.932)**	(0.3344)	(13.237)	3.090 - 6.051 $\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + 0.942 μ_D + 0.026 E_T(30)	45
		[10]	**[0.944]**	[0.2514]	[16.268]	2.706 - 7.724 $\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + 0.851 μ_D + 0.049 E_T(30)	46
3.	$\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + μ_D + π^*	10	**0.935**	0.3366	14.000	1.701 - 1.789 $\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + 0.425 μ_D + 3.134 π^*	47
		(10)	**(0.938)**	(0.3206)	(14.573)	2.093 - 3.158 $\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + 0.535 μ_D + 2.730 π^*	48
		[10]	**[0.953]**	[0.2299]	[19.825]	1.929 - 4.056 $\dfrac{(\epsilon-1)}{(2\epsilon+1)}$ + 0.365 μ_D + 3.597 π^*	49
4.	log k_2 LJ + μ_D + E_T(30)	10	**0.925**	0.3619	11.842	3.885 + 0.551 log k_2 LJ + 0.408 μ_D - 0.004 E_T(30)	50
		(10)	**(0.925)**	(0.3507)	(11.855)	5.060 + 0.698 log k_2 LJ +0.402 μ_D - 0.034 E_T(30)	51
		[10]	**[0.911]**	[0.3139]	[9.713]	4.412 + 0.751 log k_2 LJ +0.180 μ_D - 0.012 E_T(30)	52
5.	log k_2 LJ + μ_D + π^*	10	**0.939**	0.3267	14.986	- 3.134 - 0.882 log k_2 LJ + 0.057 μ_D + 9.179 π^*	53
		(10)	(0.820)	(0.5947)	(4.116)	0.917 - 0.151 log k_2 LJ + 0.357 μ_D + 3.182 π^*	
		[10]	**[0.968]**	[0.1894]	[30.184]	-7.088 - 1.575 log k_2 LJ - 0.391 μ_D + 14.789 π^*	54

SET – B
(Aromatic and halogenated solvents)

| S. No.	Correlation 3+ log k_2 versus parameters	n	R	S	F	Regression equation log k_2 =
1.	$\frac{(\varepsilon-1)}{(2\varepsilon+1)} + \mu_D + \log k_2\,LJ$	8	0.458	1.8470	0.354	$7.701 - 6.168\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} - 0.458\,\mu_D + 0.755\,\log k_2\,LJ$
		(8)	(0.611)	(0.5289)	(0.793)	$1.738 + 2.266\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.320\,\mu_D - 1.404\,\log k_2\,LJ$
		[8]	[0.853]	[0.2914]	[3.549]	$4.793 - 5.458\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.424\,\mu_D - 1.044\,\log k_2\,LJ$
2.	$\frac{(\varepsilon-1)}{(2\varepsilon+1)} + \mu_D + E_T(30)$	8	0.493	1.8081	0.427	$13.947 + 16.261\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} - 0.635\,\mu_D - 0.391\,E_T(30)$
		(8)	(0.706)	(0.4733)	(1. 322)	$14.197 + 5.084\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.342\,\mu_D - 0.318\,E_T(30)$
		[8]	[0.831]	[0.3101]	[2.977]	$11.390 - 8.281\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.474\,\mu_D - 0.121\,E_T(30)$
3.	$\frac{(\varepsilon-1)}{(2\varepsilon+1)} + \mu_D + \pi^*$	8	0.679	1.5257	1.139	$-2.663 - 12.853\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} - 1.188\,\mu_D + 17.055\,\pi^*$
		(8)	(0.517)	(0.5718)	(0.486)	$6.815 - 8.532\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.432\,\mu_D + 0.098\,\pi^*$
		[8]	[0.853]	[0.2908]	[3.570]	$9.783 – 11.495\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.614\,\mu_D - 2.652\,\pi^*$
4.	$\log k_2\,LJ + \mu_D + E_T(30)$	8	0.653	1.5742	0.989	$87.099 + 10.722\,\log k_2\,LJ - 0.263\,\mu_D - 1.890\,E_T(30)$
		(8)	(0.724)	(0.4606)	(1.470)	$24.927 + 1.667\,\log k_2\,LJ + 0.445\,\mu_D - 0.511\,E_T(30)$
		[8]	[0.838]	[0.3044]	[3.141]	$-0.493 - 1.938\,\log k_2\,LJ + 0.314\,\mu_D + 0.067\,E_T(30)$
5.	$\log k_2\,LJ + \mu_D + \pi^*$	8	0.729	1.4230	1.509	$-13.934 - 2.872\,\log k_2\,LJ - 1.445\,\mu_D + 22.540\,\pi^*$
		(8)	(0.647)	(0.5095)	(0.958)	$0.370 - 1.566\,\log k_2\,LJ + 0.253\,\mu_D + 2.807\,\pi^*$
		[8]	[0.839]	[0.3036]	[3.166]	$3.071 - 1.459\,\log k_2\,LJ + 0.356\,\mu_D - 0.787\,\pi^*$

SET – C
(Hydroxylic solvents - protic)

S. No.	Correlation 3+ log k_2 versus parameters	n	R	S	F	Regression equation log k_2 =
1.	$\frac{(\varepsilon-1)}{(2\varepsilon+1)} + \mu_D + \log k_2\,LJ$	7	0.738	0.5675	1.194	$-15.473 + 39.555\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} - 0.003\,\mu_D + 0.097\,\log k_2\,LJ$
		(7)	(0.725)	(0.5973)	(1.106)	$-14.570 + 37.853\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.032\,\mu_D + 0.068\,\log k_2\,LJ$
		[7]	[0.802]	[0.5088]	[1.807]	$-15.680 + 40.802\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.032\,\mu_D + 0.057\,\log k_2\,LJ$
2.	$\frac{(\varepsilon-1)}{(2\varepsilon+1)} + \mu_D + E_T(30)$	7	0.723	0.5812	1.092	$-14.115 + 36.532\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} - 0.019\,\mu_D - 0.001\,E_T(30)$
		(7)	(0.728)	(0.5939)	(1.130)	$-10.904 + 28.717\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.143\,\mu_D + 0.006\,E_T(30)$
		[7]	[0.799]	[0.5122]	[1.770]	$-13.641 + 35.816\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.079\,\mu_D + 0.002\,E_T(30)$
3.	$\frac{(\varepsilon-1)}{(2\varepsilon+1)} + \mu_D + \pi^*$	7	0.727	0.5770	1.123	$-13.774 + 35.242\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.036\,\mu_D + 0.196\,\pi^*$
		(7)	(0.758)	(0.5650)	(1.353)	$-13.622 + 34.551\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.136\,\mu_D + 0.574\,\pi^*$
		[7]	[0.817]	[0.4912]	[2.012]	$-14.854 + 38.097\,\frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.106\,\mu_D + 0.410\,\pi^*$
4.	$\log k_2\,LJ + \mu_D + E_T(30)$	7	0.561	0.6962	0.458	$1.027 + 0.132\,\log k_2\,LJ + 0.501\,\mu_D + 0.018\,E_T(30)$
		(7)	(0.664)	(0.6483)	(0.787)	$0.856 + 0.177\,\log k_2\,LJ + 0.603\,\mu_D + 0.023\,E_T(30)$
		[7]	[0.633]	[0.6384]	[0.783]	$1.231 + 0.116\,\log k_2\,LJ + 0.578\,\mu_D + 0.020\,E_T(30)$
5.	$\log k_2\,LJ + \mu_D + \pi^*$	7	0.416	0.7644	0.210	$1.912 - 0.057\,\log k_2\,LJ + 0.288\,\mu_D + 9.136\,\pi^*$
		(7)	(0.499)	(0.7511)	(0.331)	$1.738 - 0.034\,\log k_2\,LJ + 0.395\,\mu_D + 0.550\,\pi^*$
		[7]	[0.521]	[0.7275]	[0.373]	$2.121 - 0.084\,\log k_2\,LJ + 0.366\,\mu_D + 0.308\,\pi^*$

In the case of triple parameter regression treatment there is a satisfactory correlation in solvent set A and a poor correlation in solvent sets B and C. This it could be concluded that among the triple parameters regression analyses, the solvent set A i.e., aliphatic polar solvents (aprotic) show best correlations. This reflects in equations 41 to 54 (Table-9).

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Table 9 Summary of the best – fit triple regression equation in predicting the effect of solvent parameters on reaction rate
(Aliphatic polar aprotic solvents)

S. No.	Correlation 3+ log k_2 versus solvent parameters	Regression equation log k_2 =	n	R	S	F	Eqn.no.
1.	$\frac{(\varepsilon-1)}{(2\varepsilon+1)} + \mu_D + \log k_2 \, LJ$	$4.092 - 3.459 \frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.729\,\mu_D + 0.313 \log k_2 \, LJ$	10	**0.931**	0.3483	12.941	41
		$4.176 - 4.598 \frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.797\,\mu_D + 0.275 \log k_2 \, LJ$	(10)	**(0.934)**	(0.3298)	(13.660)	42
		$4.640 - 6.332 \frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.763\,\mu_D + 0.301 \log k_2 \, LJ$	[10]	**[0.941]**	[0.2578]	[15.368]	43
2.	$\frac{(\varepsilon-1)}{(2\varepsilon+1)} + \mu_D + E_T(30)$	$2.399 - 4.991 \frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.850\,\mu_D + 0.042\, E_T(30)$	10	**0.931**	0.3483	12.940	44
		$3.090 - 6.051 \frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.942\,\mu_D + 0.026\, E_T(30)$	(10)	**(0.932)**	(0.3344)	(13.237)	45
		$2.706 - 7.724 \frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.851\,\mu_D + 0.049\, E_T(30)$	[10]	**[0.944]**	[0.2514]	[16.268]	46
3.	$\frac{(\varepsilon-1)}{(2\varepsilon+1)} + \mu_D + \pi^*$	$1.701 - 1.789 \frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.425\,\mu_D + 3.134\,\pi^*$	10	**0.935**	0.3366	14.000	47
		$2.093 - 3.158 \frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.535\,\mu_D + 2.730\,\pi^*$	(10)	**(0.938)**	(0.3206)	(14.573)	48
		$1.929 - 4.056 \frac{(\varepsilon-1)}{(2\varepsilon+1)} + 0.365\,\mu_D + 3.597\,\pi^*$	[10]	**[0.953]**	[0.2299]	[19.825]	49
4.	$\log k_2 \, LJ + \mu_D + E_T(30)$	$3.885 + 0.551 \log k_2 \, LJ + 0.408\,\mu_D - 0.004\, E_T(30)$	10	**0.925**	0.3619	11.842	50
		$5.060 + 0.698 \log k_2 \, LJ + 0.402\,\mu_D - 0.034\, E_T(30)$	(10)	**(0.925)**	(0.3507)	(11.855)	51
		$4.412 + 0.751 \log k_2 \, LJ + 0.180\,\mu_D - 0.012\, E_T(30)$	[10]	**[0.911]**	[0.3139]	[9.713]	52
5.	$\log k_2 \, LJ + \mu_D + \pi^*$	$- 3.134 - 0.882 \log k_2 LJ + 0.057\,\mu_D + 9.179\pi^*$	10	**0.939**	0.3267	14.986	53
		$-7.088 - 1.575 \log k_2 LJ - 0.391\,\mu_D + 14.789\pi^*$	[10]	**[0.968]**	[0.1894]	[30.184]	54

The reaction of TsCl with p - XC_6H_4OH-NEt_3 (X = p-CN, p-Cl, p-OCH$_3$) does not take place in benzene and CCl$_4$. This indicates that triethylamine has not caused the ionization of phenols in the above two solvents. The complex has the structure shown below.
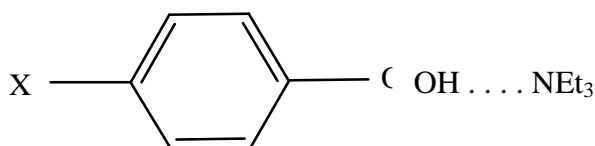
But the reaction does occur in CHCl$_3$ and dichloroethane, because the solvents are of intermediate polarity.
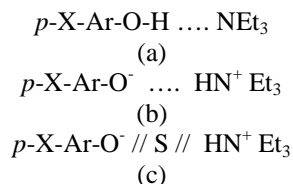
There is no appreciable reaction when the p-substituted phenol(s) was treated with TsCl (a potential substrate for nucleophilic substitution reaction) in the absence of triethylamine [27]. Free unionized phenols (in acetone) was found to be not potent nucleophile in this reaction.

It is interesting to note that the rate of the reaction in chloroform (moderately polar solvent) is higher than the rate of the reaction in methanol (a highly polar solvent). The nucleophile (p-X C_6H_4 OH - NEt$_3$) is made less potent in methanol due to extensive solvation through hydrogen bonding.Whereas in CHCl$_3$, the phenol(s) –amine complex may have a pseudo-asymmetric structure. The reactivity order doesn't conform with the basicity order of the nucleophile. Perhaps the nature of the active species may differ depending on the nature of the phenol(s).

Hydroxylic solvents are good H-bond donors and DMF is excellent H-bond acceptor. The polar non-electrolyte, TsCl is found to be hydrogen bond acceptor. Hence hydroxylic solvents are excepted to solvate the nucleophile

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extensively through hydrogen bonding while the solvation will be expected to be less in dipolar aprotic solvents. The rate of the reactions were higher in acetone, acetonitrile (ACN), DMF, ethyl methyl ketone, nitromethane, acetophenone, nitrobenzene etc., than in the 2-propanol, benzyl alcohol, 2-ethoxyethanol etc., which is in agreement with the prediction made on the basis of their H-bonding properties. The distinction between protic and dipolar aprotic solvents, is so far as they influence rates of reaction, is a sharp one. The above observations suggest that hydrogen bonding will be an important interaction in determining the effect of solvent on rates.

An analysis of the results presented in the tables-5, 7 and 9 indicates that the correlation is good in solvent set A but poor in solvent sets B and C. It may be inferred that a similar reactive species may exist in solvents of set A. *p*-Substituted phenol(s)-NEt$_3$ can exists as (a) H – bonding with triethylammonium ions (b) a tight- ion pair with complete proton transfer (c) solvent separated ion pair

$$p\text{-X-Ar-O-H} \ldots \text{NEt}_3$$
(a)
$$p\text{-X-Ar-O}^- \ldots \text{HN}^+\text{Et}_3$$
(b)
$$p\text{-X-Ar-O}^- \text{ // S // } \text{HN}^+\text{Et}_3$$
(c)

Only solvents of dielectric constant greater than 5 are considered for our investigation except chloroform, 1, 4-dioxan and anisole. This arbitrary choice was made since there is an extensive ion aggregation in solvents of lower dielectric constant which makes the rate of the reaction very slow in these solvents.

The poor correlation observed in solvent sets B and C may be due to the dual nature of hydroxylic solvents (electrophilic and nucleophilic) along with their H-bonding ability resulting in random interaction with the active species.

In the solvents such as ACN, acetone, DMF, cyclopentanone, cyclohexanone, nitromethane, nitrobenzene etc., the rate is high compared with other solvents. This may be due to the repulsion between the phenoxide anion and the more electronegative atom (oxygen or nitrogen) of the solvents which may allow the phenoxide ion is free from the solvent molecules resulting in a higher reactivity than in the other solvents.

CONCLUSION

The rate constants for the reactions of tosyl chloride with *p*-substituted phenol(s) and triethylamine are determined in different aprotic, aromatic and halogenated and protic solvents. Attempts are made to correlate variations in reaction rate with solvent parameters at macroscopic and microscopic levels, such as dielectric constant(ε),Kirkwood function $\dfrac{\varepsilon-1}{2\varepsilon+1}$,dipole moment(μ_D),refractive index(n),viscosity(η),surface tension(γ), Grunwald and Winstein solvent polarity scale(Y), Lassau and Jungers log $k_{2\ (n\,Pr_3\,N\,+\,MeI)}$ scale, Kosower factor (Z), E_T(30)-value and Kamlet *et al*. scale (π^*). First simple regression and then multiple regressions are carried out on the kinetic data against the various solvent parameters. Correlation results indicate that more than one solvent parameter may influence the rate of the reaction.

The failure to get good correlations either by simple regression (or) multiple regression in all cases is due to following situation we presume. The reactant should exist as a similar species in any solvent chosen that is the gross structure should not change solvent to solvent. Then only the influence of the solvent on the rate of the reaction can be analyzed. In the present system it has been concluded by various physico-chemical methods that the triethylamine - *p*-substituted phenol(s) complex exists as different species in different solvents. However this fact has not been investigated by kinetic method. Our main aim is to verify whether kinetic observation conforms with the physico-chemical conclusions. We have proved by qualitative and quantitative analyses of kinetic data that the phenol(s) – amine complex does exist as different species which differ in its finer structure details in different solvents. This lead to the less success of regression analyses.

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