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Der Chemica Sinica, 2014, 5(2):62-70



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ISSN: 0976-8505  
CODEN (USA) CSHIA5

### Effect of binary aqueous-organic solvents on the reaction of *p*-toluene sulfonyl chloride with benzoic acid(s) in the presence of triethyl amine

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#### ABSTRACT

Second order rate constants ( $k_2$ ) for the reaction of *p*-toluenesulfonyl chloride with *p*-substituted benzoic acid(s) [ $X$ - $C_6H_4COOH$ , where  $X$ = 4-H, 4- $CH_3$  and 4- $NO_2$ ] in the presence of triethylamine in binary aqueous-Acetonitrile/Acetone mixed solvent have been determined by conductometric method at 25-40 °C. It was found that the rate decreased with increase of water content in Acetonitrile-water binary system. In acetone-water binary system the rate increases with increase in water content to about 10%, reaches a maximum and then decreases. The change in rate with change in concentration of acetone may be explained by solvation behaviour of acetone. Activation parameter ( $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ ,  $\Delta G^\ddagger$ ) are evaluated from the rate data by the usual methods. Influence of solvent properties at microscopic and macroscopic level on the rate is subjected to simple and multiple linear correlations. The  $\log k_2$  values of binary aqueous-acetone system are correlated with Grunwald-Winstein  $Y$  values. The 'm' value is found to be very low which indicates that the bond breaking and bond making would proceed to the same extent. This is the characteristic property of  $S_N2$  reaction.

**Keywords:** Kinetics, binary solvent mixture, solvation, correlation, Grunwald-Winstein, solvatochromatic parameters.

#### INTRODUCTION

Kinetics and reaction mechanism for different reaction using various techniques has been a topic of interest for many researchers. The solvent effects play a key role in many chemical and physical processes in solutions. The study of solute-solvent interactions in binary mixtures is more complex than in pure solvents, because the solute can interact to different extent with the components of the mixture. The influence of solvents on chemical reaction in solution has been observed over a number of years by authors and some of the effects have been noted [1]. Carboxylate anions are found to be potential nucleophiles in substitution reactions. Raghavan and Kalavathy have studied the kinetics of reaction of ethyl bromoacetate with substituted phenoxy acetate ions in 90% aqueous acetone (v/v) [2]. The reaction is found to follow second order kinetics in total and first order with respect to each reactant. Second order rate constants for the reaction between benzyl chloride / phenacyl chloride and N, N-dimethylaniline have been evaluated conductometrically by Nallu *et al.*, [3]. The marked effect of acetone-water solvent mixtures on the rate was found from correlation technique with  $\log k_2$  vs. Grunwald-Winstein ( $Y$ ) and Kosower ( $Z$ ) of solvent polarity parameters. Ranga Reddy *et al.*, have determined the second order rate constants for the reaction of benzyl bromide and diphenylamine in methanol at 25-40 °C [4] and also they studied the effect of protic and dipolar aprotic solvents on the reaction of benzyl bromide and diphenylamine [5]. Effect of solvents on the reaction of Dansyl and Bansyl chlorides with substituted pyridines in methanol-acetonitrile binary mixtures at 0 °C has been studied by Sung *et al.*, [6].

The second order rate constants of the reaction of *p*-toluenesulfonyl chloride with *p*-substituted benzoic acids in the presence of triethylamine in acetonitrile/acetone under equimolar and *pseudo*-first order conditions have been determined by conductometric method using Guggenheim principle at 25, 30, 35, and 40 °C by Ananthalakshmi

and Nallu [7]. They found that the reactions follow second order kinetics with respect to the whole and first order with respect to each of the reactants. Present work is the extension of reported work [7], in which the kinetics has now been studied in binary aqueous- Acetonitrile/Acetone mixed solvents. Effect of solvents on the activation parameters, calculation of solvatochromatic parameters by forming regression equations, and correlation with Grunwald-Winstien Y- values has also been studied.

## MATERIALS AND METHODS

### Materials

All the chemicals such as *p*-toluenesulfonyl chloride, *p*-substitutedbenzoic acid(s), triethylamine, acetonitrile, and acetone were purified before use by recrystallization or distillation until their physical constants (melting/boiling) agreed well with the literature values [9,10].

### Rate measurement by conductivity method

#### A typical run in aqueous-acetonitrile / aqueous-acetone under equimolar concentration

Rate was measured in pure ACN, 0.9 to 0.4 molar solutions (v/v) of aqueous-ACN binary mixtures and in pure acetone, 0.9 to 0.4 molar solutions (v/v) of aqueous-acetone binary mixtures. The conductivity cell was rinsed with conductivity water and then washed with acetonitrile/acetone. A specially made flat bottomed boiling test tube with B-24 ground joint containing a known volume of solution (10 ml) of TsCl ( $0.002 \text{ mol dm}^{-3}$ ) and a magnetic stirring bar and a flask containing the mixture of benzoic acid-triethylamine ( $0.002 \text{ mol dm}^{-3}$ ) in acetonitrile were kept in a thermostat ( $\pm 0.1 \text{ }^\circ\text{C}$ ) under  $30 \text{ }^\circ\text{C}$  for about an hour. After attaining the thermal equilibrium, the conductance of the solution of TsCl and a mixture of benzoic acid-triethylamine was measured separately. The solution (10ml) of benzoic acid-triethylamine mixture was pipette out into the boiling tube containing TsCl (10ml) solution and simultaneously a stop-watch was started at the time about half addition from the pipette. The conductivity cell was immediately placed in the reaction mixture and the conductance readings were noted as soon as possible, since the reactants started to react very quickly. Specially devised water-powered magnetic stirrer has been used to stir the reaction mixture continuously during the measurement of conductance [7]. The conductance was measured at convenient intervals of time (minutes) until the reaction has been completed i.e., a period when a constant value for the conductance was obtained. The rate constant  $k_2$ , was derived from the special integrated equation reported elsewhere [8].

$$x_2 - x_1 = k_2 C_0 [t_1 x_1 - t_2 x_2] - k_2 C_{\infty} x_{\infty} [t_1 - t_2]$$

Where,

$x_1$	=	conductance at time $t_1$ .
$x_2$	=	conductance at time $t_2$ .
$x_{\infty}$	=	conductance at time $t_{\infty}$ .
$k_2$	=	Second order rate constant
$C_0$	=	Initial concentration of the reactants.
$C_{\infty}$	=	Concentration of the reactants at time $t_{\infty}$ .

According to this equation, the plot of  $(x_2 - x_1)$  against  $-(t_1 x_1 - t_2 x_2)$  should be a straight line. From the slope, the second order rate constant  $k_2$ , can be calculated by the method of Least- Square analysis.

Similar experimental procedure was followed for the same reaction in aqueous-acetonitrile / aqueous-acetone for all the other substituted benzoic acid(s)-triethylamine on *p*-toluenesulfonyl chloride under the same reaction condition. The activation energy ( $E_a$ ), the enthalpy of activation ( $\Delta H^\ddagger$ ), the entropy of activation ( $\Delta S^\ddagger$ ), and free energy of activation ( $\Delta G^\ddagger$ ) are calculated using rate data by usual methods [11-19].

## RESULTS AND DISCUSSION

Second order rate constants ( $k_2$ ), for the reaction of *p*-toluenesulfonyl chloride with substituted benzoic acid(s) [4-H, 4-CH<sub>3</sub>, 4-NO<sub>2</sub>] in the presence of triethylamine in binary aqueous-acetonitrile / acetone mixed solvent have been determined conductometrically at 25-40  $^\circ\text{C}$ . The rate data for acetonitrile-water and acetone-water binary mixtures are given in Table 1 and Table 2 respectively.

The rate of the reaction of *p*-toluenesulfonyl chloride and triethylammonium benzoate was found to increase with increase in the polarity of the aprotic medium. Thus, the rate of the reaction was higher in acetonitrile than in acetone. The rate ratio between acetonitrile and acetone is 10-20 times for 4-H, 4-CH<sub>3</sub>, and 4-NO<sub>2</sub> respectively. Variation in the rate just by the addition of water into organic component is explained in terms of solvation

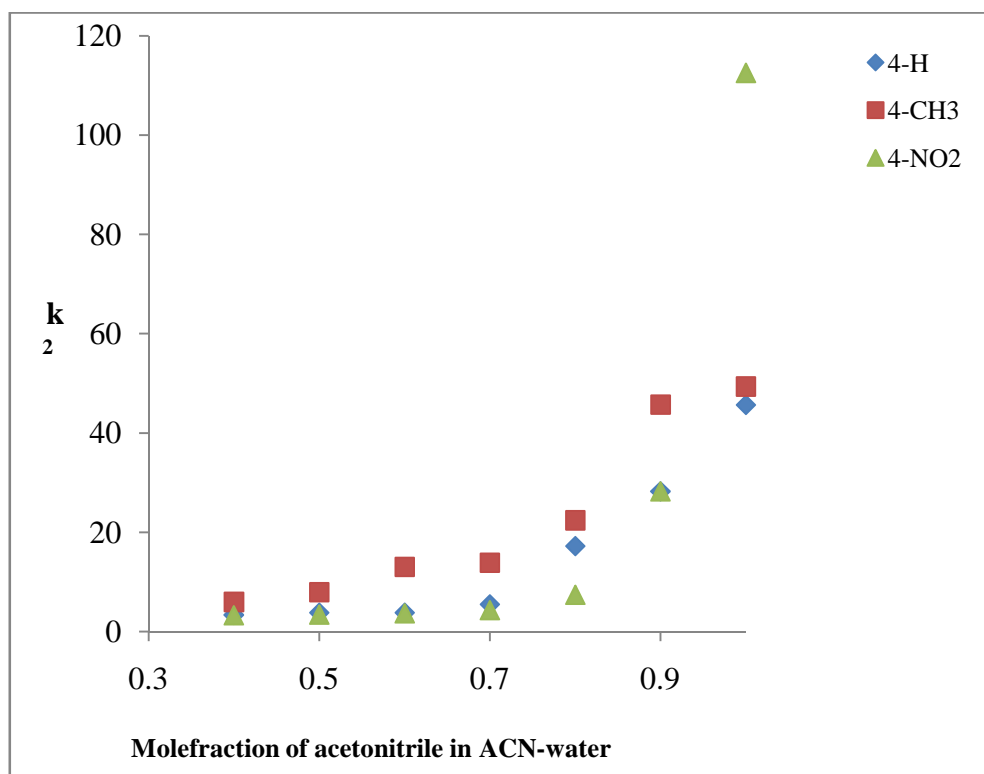
phenomenon. The benzoate anion may be less solvated in more polar aprotic solvents, which is almost free for attacking the substrate.

**Table 1: Rate constants and activation parameters of reaction between TsCl and 4-X-C<sub>6</sub>H<sub>4</sub>COOH-NEt<sub>3</sub> in binary acetonitrile-water mixed solvents**

(X = 4-H, 4-CH<sub>3</sub>, and 4-NO<sub>2</sub>)  
 [TsCl] = [X-C<sub>6</sub>H<sub>4</sub>COOH-NEt<sub>3</sub>] = 0.002 mol dm<sup>-3</sup> (4-H) = 0.0025 mol dm<sup>-3</sup> (4-CH<sub>3</sub> and 4-NO<sub>2</sub>)

Mole fraction of ACN in ACN-water	k <sub>2</sub> , dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup>			E <sub>a</sub> KJ mol <sup>-1</sup>	ΔH <sup>‡</sup> KJ mol <sup>-1</sup>	ΔS <sup>‡</sup> J mol <sup>-1</sup> deg <sup>-1</sup>	ΔG <sup>‡</sup> KJ mol <sup>-1</sup>
	30 °C	35 °C	40 °C				
1.0	45.67 (49.36) [112.49]	77.45 (80.01) [164.55]	97.48 (105.10) [217.16]	59.78 (59.60) [51.72]	57.26 (57.08) [49.35]	24.92 (24.28) [42.87]	64.81 (64.44) [62.35]
0.9	28.25 (45.72) [28.24]	38.90 (59.56) [35.52]	62.95 (84.02) [56.52]	63.19 (48.05) [54.72]	60.67 (45.53) [52.20]	17.03 (62.99) [44.97]	65.93 (64.61) [65.60]
0.8	17.20 (22.40) [7.418]	32.30 (29.64) [10.56]	36.45 (42.88) [15.64]	59.22 (51.21) [58.17]	56.69 (48.69) [55.65]	34.29 (58.54) [44.62]	67.09 (66.13) [69.17]
0.7	5.48 (13.88) [4.32]	7.20 (19.68) [6.56]	10.65 (27.84) [9.36]	53.55 (56.27) [60.98]	51.04 (53.75) [58.46]	62.55 (45.80) [39.36]	69.99 (67.62) [71.60]
0.6	3.80 (13.04) [3.68]	5.80 (19.92) [5.16]	8.15 (25.36) [7.44]	60.16 (52.46) [55.52]	57.64 (49.94) [52.99]	43.61 (58.88) [59.33]	70.81 (67.78) [70.94]
0.5	3.80 (7.92) [3.44]	5.55 (11.84) [5.24]	7.50 (15.48) [7.04]	53.62 (52.85) [56.47]	51.10 (50.33) [53.96]	65.30 (61.70) [56.66]	70.89 (69.03) [71.13]
0.4	3.35 (5.96) [3.28]	4.70 (8.32) [4.56]	7.35 (12.84) [6.80]	61.96 (60.52) [57.49]	59.44 (58.01) [54.97]	38.83 (38.69) [53.72]	71.02 (69.73) [71.26]

Value in ( ) is for 4-CH<sub>3</sub>  
 Value in [ ] is for 4-NO<sub>2</sub>



**Figure 1: k<sub>2</sub> vs mole fraction of acetonitrile in ACN – water**

The rate is decreased with increase of water content, in acetonitrile. The decrease in the rate is about 38% and 62% when the reaction medium is changed from pure acetonitrile to 0.9 to 0.8 molar solutions of aqueous-acetonitrile binary mixtures respectively. Further, increase in water content (0.7) molar solution of aqueous-acetonitrile system

decreases the value of the rate about 88% and further addition of water content does not alter the rate. The change in rate with change in concentration of acetonitrile is represented in the plot of  $k_2$  vs. solvent composition (Fig 1). These observations indicate the existence of triethylammonium benzoate which may be the further proof for the triethylammonium benzoate exists as an ion-pair.

The situation in acetone-water binary mixed systems is different. The rate increases with increase in water content to about 10% ( $k_2 = 3.611$  to  $3.845 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ ) up to 0.7:0.3 (Acetone:Water) molar concentrations. Afterwards, the rate decreases ( $k_2 = 3.845$ - $2.600$  (4-H),  $2.840$ - $1.135$  (4- $\text{NO}_2$ ),  $5.745$ - $1.160$  (4- $\text{CH}_3$ )  $\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ ) by the addition of water (0.6 to 0.4 molar conc.) (Table 2). The change in the rate with change in concentration of acetone is represented in (Fig 2), which indicates the solvent dependence of the rate constant of the system studied.

The unexpected increase of rate in binary mixture of acetone water may be explained in terms of solvation nature, which depends on the intermolecular forces as well as hydrogen bonding. The added water (0.1) makes acetone more polar specifically by forming hydrogen bond with carbonyl group. Acetone-water mixture may selectively solvate the benzoate anion and trimethylammonium cation. Hence, the benzoate anion is made free to react with *p*-toluenesulfonyl chloride, thus accelerating the reaction [13].

**Table 2: Rate constants and activation parameters of reaction between TsCl and 4-X-C<sub>6</sub>H<sub>4</sub>COOH-NEt<sub>3</sub> in binary acetone-water mixed solvents**

(X = 4-H, 4-CH<sub>3</sub>, and 4-NO<sub>2</sub>)  
[TsCl] = [X-C<sub>6</sub>H<sub>4</sub>COOH-NEt<sub>3</sub>] = 0.02 mol dm<sup>-3</sup>

Mole fraction of acetone in acetone-water	$k_2, \text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$			E <sub>a</sub> KJ mol <sup>-1</sup>	$\Delta H^\ddagger$ KJ mol <sup>-1</sup>	$\Delta S^\ddagger$ J mol <sup>-1</sup> deg <sup>-1</sup>	$\Delta G^\ddagger$ KJ mol <sup>-1</sup>
	30 °C	35 °C	40 °C				
1.0	3.611	4.597	7.351	50.95	48.43	74.46	70.99
	(3.135)	(5.042)	(6.450)	(56.97)	(54.45)	(55.91)	(71.39)
	[5.381]	[8.371]	[10.628]	[53.67]	[51.15]	[6216]	[69.99]
0.9	3.625	4.170	6.765	49.19	46.68	80.25	71.09
	(4.750)	(6.115)	(9.665)	(56.02)	(53.50)	(55.55)	(70.34)
	[5.925]	[9.785]	[11.025]	[48.97]	[46.46]	[76.91]	[69.76]
0.8	3.730	5.585	7.645	56.59	54.08	55.65	70.94
	(5.610)	(7.710)	(10.880)	(52.24)	(49.72)	(64.39)	(69.23)
	[3.475]	[5.160]	[6.600]	[50.59]	[48.07]	[76.03]	[71.10]
0.7	3.845	5.970	7.875	56.54	54.02	55.56	70.85
	(5.745)	(8.220)	(11.400)	(54.04)	(51.52)	(60.45)	(69.84)
	[2.840]	[4.395]	[5.665]	[54.46]	[51.94]	[64.19]	[71.60]
0.6	3.890	5.875	7.735	54.21	51.68	63.18	70.83
	(4.570)	(6.375)	(9.030)	(53.71)	(51.19)	(63.45)	(70.41)
	[2.750]	[4.085]	[5.395]	[53.15]	[50.63]	[69.57]	[70.70]
0.5	2.750	4.275	5.560	55.51	52.99	61.71	71.70
	(3.719)	(5.260)	(7.055)	(50.68)	(48.16)	(75.15)	(70.93)
	[2.715]	[4.060]	[5.415]	[54.44]	[51.92]	[65.35]	[71.73]
0.4	2.600	4.080	5.445	58.29	55.77	50.25	71.00
	(1.160)	(1.740)	(2.310)	(54.32)	(51.80)	(72.84)	(73.87)
	[1.135]	[1.725]	[2.265]	[51.04]	[48.52]	[72.44]	[73.92]

Value in ( ) is for 4-CH<sub>3</sub>

Value in [ ] is for 4-NO<sub>2</sub>

In general, the rate of the reaction is very much affected when the concentration of water is increased in acetonitrile/acetone solvent. The rate constant  $k_2$ , attains a steady value at a higher concentration of water i.e., after the addition of 0.4 molar concentration of water. The decrease in rate with increasing degree of polarity on the binary aqueous-acetonitrile/acetone solvent mixtures was accounted on the basis of Hughes-Ingold theory for S<sub>N</sub>2 reactions [14].

### EFFECT OF TEMPERATURE

Activation parameters are evaluated from the rate data by the usual methods [11-18] and are presented in Tables 1 and 2. It is observed that the values of E<sub>a</sub> in all the binary aqueous-acetonitrile/acetone composition are almost in the same range in both of the systems. This is the indication of the formation of stabilized transition state in these sets of reactions [6, 19].

The entropies of activation are found to be negative ( $-\Delta S^\ddagger$ ) as expected for bimolecular reactions. Relatively large value of entropy of activation shows that the more ordered activated complexes are formed in the transition state. The near constancy values of  $\Delta G^\ddagger$  indicate the formation of solvated transition state in these reactions. A linear relationship is found between  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$ . The moderate value of  $\Delta H^\ddagger$  and fairly high constant values of  $\Delta G^\ddagger$  support the proposed mechanism (S<sub>N</sub>2) which exists throughout the reaction series.

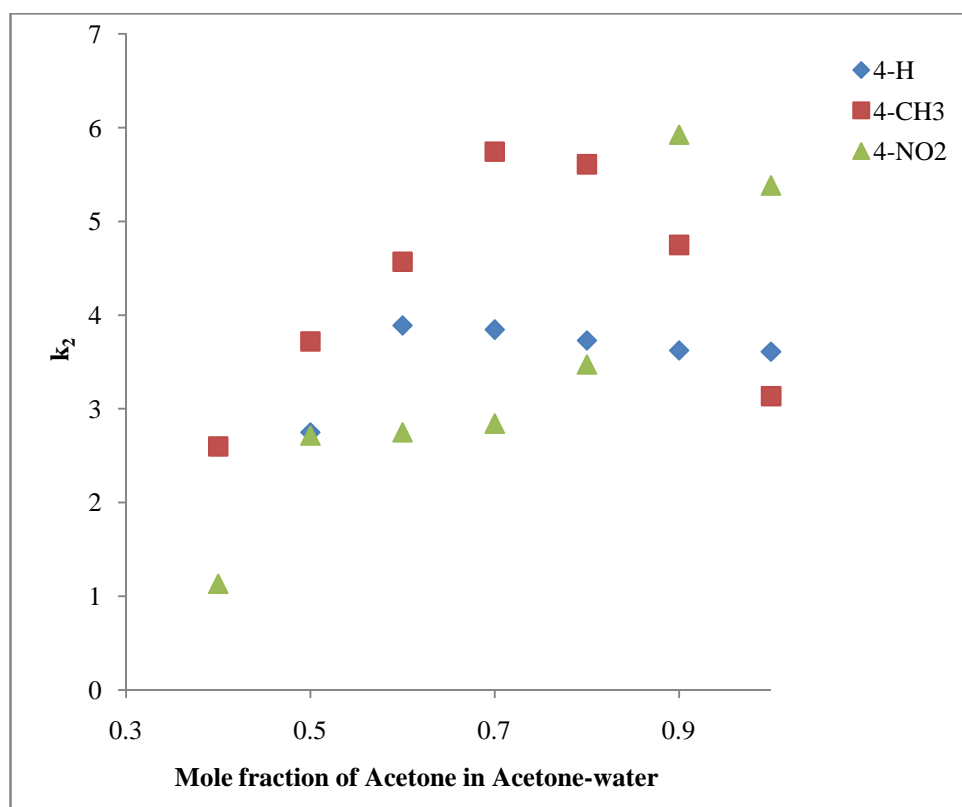


Figure 2:  $k_2$  vs mole fraction of acetone in acetone – water

#### EFFECT OF SOLVENTS ON THE REACTION IN TERMS OF SOLVENT PARAMETERS

With the view to know the influence of solvent properties at macroscopic and microscopic level on the rate, the  $\log k_2$  values are subjected to simple and multiple linear correlations with solvent properties such as Dimroth-Reichardt  $E_T(30)$  value, the Kosower  $Z$  value, the Kamlet-Taft dipolarity/polarizability  $\pi^*$  scale, hydrogen bond accepting ability  $\beta$ , hydrogen bond donating ability  $\alpha$  and Grunwald-Winstein  $Y$  values of the aqueous mixtures [20,23]. The properties of acetonitrile-water and acetone-water mixed solvents are given in Tables 3 and 4. The results of correlation of both systems are presented in Tables 5 and 6.

#### CALCULATION OF SOLVATOCHROMATIC PARAMETERS BY FORMING REGRESSION EQUATIONS

Marcus reported solvatochromatic parameters for aqueous mixtures of several organic solvents [20]. When the entire range of mole fraction of water in the binary mixture ( $X_w = 0-1.0$ ) was considered, solvatochromatic parameter did not vary linearly with the mole fraction. Regression equations were formed between  $X_w$  and the reported values of the parameters of aqueous mixtures of solvents under considerations [20]. The correlation coefficient ( $r$ ) determined by simple, multiple regression analysis (Table 5 and 6) are found to be satisfactory in all cases except the  $E_T(30)$  and  $Z$  values of aqueous-acetonitrile and  $\pi^*$ ,  $\alpha$  values of aqueous-acetone systems [20]. The good correlation between  $\log k_2$  (4-NO<sub>2</sub>) and  $E_T(30)$  with less standard estimation of error ( $s = 0.063$ ) and value of goodness of fit ( $F = 519.11$ ), (eqn.1) shows that the contribution of  $E_T(30)$  over the reacting species is significantly felt. Equations (4-11, 14-16) indicate that the inclusion of the parameters  $\alpha$  and  $\beta$  improved the correlation. The solvents acetonitrile and acetone are dipolar, strong hydrogen bond acceptor and poor hydrogen bond donors. Their hydrogen bond donating ability increases by increasing the amount of co-solvent water. The improvement in correlation on using  $\alpha$  and  $\beta$  brings out the preferential solvation of benzoate ion by water through H-bonding. From the tabulated results it is observed that the  $E_T(30)$ ,  $Z$ ,  $\pi^*$  and  $\alpha$  of the solvents enhance the charge separation in the nucleophilic substitution reactions.

Table 3: Value of  $Z$ ,  $E_T(30)$ ,  $\pi^*$ ,  $\beta$ , and  $\alpha$  for binary ACN-Water mixed system

Mole fraction of ACN in ACN-water	ACN-water binary mixed solvent parameter				
	$Z$	$E_T(30)$	$\pi^*$	$\beta$	$\alpha$
1.0	71.7	46.0	0.75	0.47	0.25
0.9	76.3	50.8	0.81	0.53	0.55
0.8	79.7	53.6	0.82	0.57	0.70
0.7	82.2	54.9	0.82	0.59	0.78
0.6	84.1	55.4	0.82	0.59	0.83
0.5	85.5	55.6	0.83	0.59	0.86
0.4	86.7	55.8	0.87	0.60	0.89

Table 4: Value of  $Z$ ,  $E_T(30)$ ,  $\pi^*$ ,  $\beta$ , and  $\alpha$  for binary acetone-Water mixed system

Mole fraction of acetone in acetone-water	Acetone-water binary mixed solvent parameter				
	$Z$	$E_T(30)$	$\pi^*$	$\beta$	$\alpha$
1.0	65.7	42.2	0.69	0.56	0.08
0.9	70.5	45.6	0.72	0.61	0.33
0.8	74.1	48.3	0.74	0.62	0.48
0.7	76.8	50.3	0.76	0.63	0.60
0.6	79.0	51.6	0.79	0.64	0.68
0.5	81.6	52.4	0.83	0.65	0.73
0.4	82.9	52.7	0.88	0.67	0.76

Table 5: Results of regression analyses for  $\log k_2$  against solvent parameters in binary ACN-water mixed system

Parameters	n	R	s	F	Eqn. No
$E_T(30)$	7 (7) [7]	0.919 <b>(0.995)</b> [0.864]	0.226 <b>(0.063)</b> [0.203]	10.93 <b>(519.11)</b> [14.76]	1
$Z$	7 (7) [7]	0.972 <b>(0.968)</b> [0.959]	0.335 <b>(0.161)</b> [0.114]	6.835 <b>(74.45)</b> [57.99]	2 3
$\pi^*$	7 (7) [7]	0.760 (0.838) [0.811]	0.335 (0.351) [0.236]	6.84 (11.80) [9.61]	
$E_T(30) + \beta$	7 (7) [7]	0.919 (0.969) [0.866]	0.226 (0.174) [0.225]	10.93 (31.15) [6.019]	
$E_T(30) + \alpha$	7 (7) [7]	0.940 <b>(0.979)</b> [0.939]	0.196 <b>(0.146)</b> [0.155]	15.21 <b>(45.16)</b> [14.89]	4
$Z + \beta$	7 (7) [7]	<b>0.974</b> <b>(0.987)</b> [0.974]	<b>0.129</b> <b>(0.116)</b> [0.103]	<b>37.54</b> <b>(72.79)</b> [36.31]	5 6 7
$Z + \alpha$	7 (7) [7]	<b>0.978</b> <b>(0.986)</b> [0.984]	<b>0.119</b> <b>(0.118)</b> [0.079]	<b>44.78</b> <b>(69.89)</b> [62.78]	8 9 10
$\pi^* + \beta$	7 (7) [7]	0.918 (0.964) [0.880]	0.228 (0.189) [0.214]	10.73 (26.23) [6.89]	
$\pi^* + \alpha$	7 (7) [7]	0.943 <b>(0.981)</b> [0.895]	0.191 <b>(0.139)</b> [0.200]	16.18 <b>(50.04)</b> [8.072]	11

Value in ( ) is for 4-CH<sub>3</sub>Value in [ ] is for 4-NO<sub>2</sub>

According to the results the contribution of  $E_T(30)$  and  $Z$  in aqueous-acetonitrile systems and polarity, polarizability ( $\pi^*$  and  $\alpha$ ) in aqueous-acetone systems reflect the degree of bond formation between the S-atom and O-atom and the degree of bond cleavage between S-atom and Cl-atom at the transition state of the reaction of p-toluenesulfonyl chloride with p-substituted benzoic acids. The best fit single and dual parameter regression equations are shown in boldface and are presented in table 7.

Table 6: Results of regression analyses for log k<sub>2</sub> against solvent parameters in binary acetone-water mixed system

Parameters	n	R	s	F	Eqn. No
E <sub>T</sub> (30)	7 (7) [7]	0.467 (0.829) [0.973]	0.071 (0.146) [0.225]	1.39 (10.96) [215.55]	12
Z	7 (7) [7]	0.569 (0.879) [0.315]	0.068 (0.124) [0.256]	6.23 (17.05) [0.551]	
π*	7 (7) [7]	0.770 (0.929) [0.591]	0.051 (0.096) [0.217]	7.29 (31.65) [2.17]	13
E <sub>T</sub> (30) + β	7 (7) [7]	0.632 (0.849) [0.503]	0.067 (0.154) [0.288]	1.33 (1.33) [0.678]	
E <sub>T</sub> (30) + α	7 (7) [7]	0.494 (0.836) [0.979]	0.077 (0.160) [0.156]	0.647 (4.656) [137.39]	14
Z + β	7 (7) [7]	0.591 (0.884) [0.896]	0.070 (0.136) [0.337]	1.07 (7.166) [24.56]	
Z + α	7 (7) [7]	0.897 (0.944) [0.965]	0.038 (0.095) [0.077]	8.256 (16.53) [27.36]	15
π* + β	7 (7) [7]	0.876 (0.930) [0.880]	0.042 (0.107) [0.142]	6.58 (12.87) [6.82]	
π* + α	7 (7) [7]	0.920 (0.930) [0.975]	0.034 (0.515) [0.066]	10.99 (12.76) [37.99]	16

Value in ( ) is for 4-CH<sub>3</sub>Value in [ ] is for 4-NO<sub>2</sub>

Table 7: The Best-fit regression equation in predicting the effect on preferential solvation

Parameters	Log k <sub>2</sub> =	n	r	s	F	Eqn. No
ACN-water E <sub>T</sub> (30)	(11.570-0.162 E <sub>T</sub> (30))	7	0.995	0.062	519.11	1
Z	(11.493-0.106 Z)	7	0.968	0.162	74.456	2
	[8.520-0.066 Z]	7	0.959	0.114	57.99	3
E <sub>T</sub> (30)	(10.242+0.112 E <sub>T</sub> (30)-4.264α)	7	0.979	0.231	45.16	4
Z + β	10.181-0.105 Z+2.236β	7	0.974	0.129	37.57	5
	(8.042-0.039 Z-3.430 β)	7	0.988	0.116	72.79	6
	[9.183-0.109 Z+5.11β]	7	0.974	0.103	36.31	7
Z + α	12.993-0.134 Z+1.151 α	7	0.978	0.119	44.78	8
	(5.882-0.0231 Z-0.774α)	7	0.986	0.118	69.89	9
	[13.773-0.147 Z+1.944α]	7	0.984	0.079	62.78	10
π* + α	4.32-0.013 π*-1.944 α	7	0.981	0.139	50.04	11
acetone-water E <sub>T</sub> (30)	[0.69+0.037 E <sub>T</sub> (30)]	7	0.973	0.225	215.56	12
π*	(5.19-3.50π*)	7	0.972	0.096	31.65	13
E <sub>T</sub> (30)+α	[3.8-0.027 E <sub>T</sub> (30)+0.22α]	7	0.975	0.067	37.99	14
Z + α	[19.99-0.027 Z+6.49]	7	0.965	0.077	27.36	15
π* + α	[7.828-0.079 π*+1.676α]	7	0.975	0.066	37.99	16

Value in ( ) is for 4-CH<sub>3</sub>Value in [ ] is for 4-NO<sub>2</sub>

### CORRELATION WITH Y

The log k<sub>2</sub> values of binary aqueous-acetone system are correlated with Grunwald-winstein Y-values [22]. The values are taken from the literature [21]. This parameter can be used to find whether the reaction follows S<sub>N</sub>1 or S<sub>N</sub>2 type in aqueous-organic binary solvent mixtures. To apply Grunwald-Winstein equation,

$$\text{Log } k_2 = \text{log}k_0 + mY$$

The six data points have been fitted to the above equation by least squares analysis to yield the regression equations (Table 8) for 4-H, 4-NO<sub>2</sub>, and 4-CH<sub>3</sub> respectively.

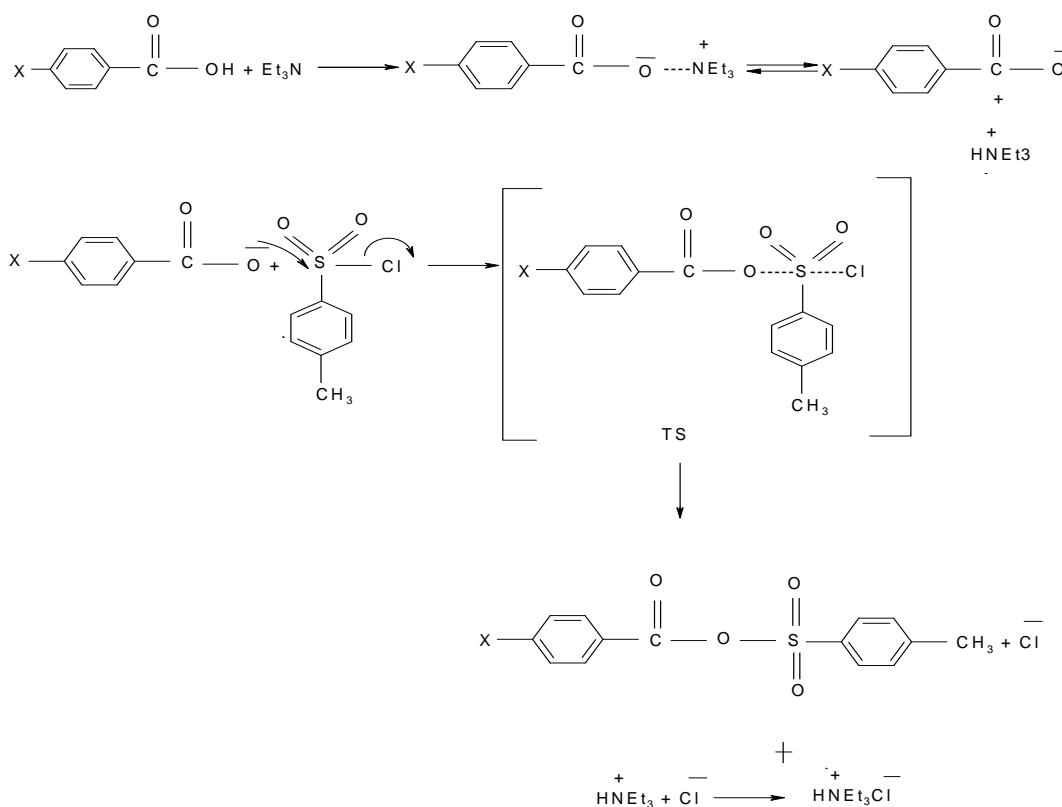


Table 8: Grunwald-Winstein correlation of log k<sub>2</sub> with Y in binary acetone-water mixed system

Log k <sub>2</sub>	n	R	s	F	Eqn. No
2.428-0.060 Y	6	0.722	0.062	4.349	(17)
(2.099-0.207 Y)	6	(0.875)	(0.126)	(13.024)	(18)
[2.261-0.188]	6	[0.708]	[0.206]	[4.014]	(19)

Value in ( ) is for 4-NO<sub>2</sub>Value in [ ] is for 4-CH<sub>3</sub>

The correlation co-efficient are poor. The magnitude of the decrease in rate constants is significant during the addition of water. The very low value of m (-0.060 to -0.207) indicates that the bond breaking and bond making would proceed to the same extent, which is the characteristic of S<sub>N</sub>2 reaction. Based on the kinetic data and thermodynamic parameters we proposed the direct bimolecular nucleophilic substitution mechanism (S<sub>N</sub>2) for this reaction (Scheme 1).



## CONCLUSION

The effect of binary aqueous-acetonitrile/acetone mixed solvents on the rate of the reaction between *p*-toluenesulfonyl chloride and *p*-substituted benzoic acid(s) in the presence of triethylamine was studied at 30, 35 and 40 °C. Changes in the rate just by the addition of water into organic component are rationalized on the basis of preferential solvation phenomenon. Correlation technique was employed to find out the influence of the parameters of binary aqueous-acetonitrile/acetone mixed solvents on these reactions. The log *k*<sub>2</sub> values of binary aqueous-acetone system are correlated with Grunwald-Winstein Y-values. The very low value of 'm' indicates that the reaction takes place through S<sub>N</sub>2 mechanism. Based on kinetic data and thermodynamic parameters, we proposed the direct bimolecular nucleophilic substitution mechanism (S<sub>N</sub>2) for this reaction.

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