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A Thermodynamic View on Solvent Effects of Selected S_N^2 Reactions

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The present work describes the role of solvents on the kinetics and thermodynamics of closely related S_N^2 reactions of primary, secondary and tertiary iodoalkanes in pure and mixed solvents.

INTRODUCTION

Much work was done on S_N^2 reactions[1–20]. The contributions of Ingold and Hughes[21] represented an important landmark in this field, and more work is quoted[22–51] in literature.

The present work lays emphasis on the role of solvents on the kinetics and thermodynamics of closely related S_N^2 reactions of primary, secondary and tertiary iodoalkanes in pure and mixed solvents. It correlates solvents acceptor numbers with reaction energetics[41–44].

RESULTS AND DISCUSSION

This work includes a study of the reaction:

$$RI + X^- = RX + I^- \qquad (1)$$

where R = CH_3, C_2H_5, C_3H_7 and C_4H_9 and X = Cl^-, Br^- and CN^-

From Bu_4NCl, Bu_4NBr, LiCl, LiBr and KCN: The above reactions were done in different but related solvent systems and their mixtures with water. They were:

1. Aprotic (tetrahydrofuran or THF and acetonitrile).
2. Protic (tertiary pentanol, *n*-propanol and ethanol).
3. Mixture of THF, acetonitrile and tertiary pentanol with 5–15 mole per cent water.

A temperature range of 293 K–358 K at 5 K intervals was chosen to find out k_2, E_a, $\Delta S^{\neq}$ and $\Delta H^{\neq}$ respectively.

Equimolar reactant concentrations were preferred to determine k_2 by Eqn. (2) and rate constants were calculated from (I^-) at 247 nm.

$$\text{Rate constant } k_2 = 1/C - 1/C_0 \qquad (2)$$

where C and C_0 are the reactant concentrations at T = 0 and time of measurement.

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Eqns. (3)–(5) were used to calculate the energies, enthalpies and entropies of activation E_a, $\Delta H^{\neq}$, $\Delta S^{\neq}$.

$$\text{Energy of activation } \log k_2 = \log A - E_a/2.303RT \tag{3}$$

$$\text{Enthalpy of activation} = \Delta H^{\neq} = E_a - RT \tag{4}$$

$$\text{Entropy of activation } \Delta S^{\neq} = \Delta H^{\neq}/T - R \text{ In } k_2 + R \text{ In } h/k \tag{5}$$

where h and k are Planck's and Boltzmann's constants and k_2 in $l\ mol^{-1}\ min^{-1}$, E_a in kJ mol^{-1}, $\Delta H^{\neq}$ in kJ mol^{-1} and $\Delta S^{\neq}$ in J K^{-1} mol^{-1}.

A Schimadzu 240 thermally controlled spectrophotometer was used to determine (I^-) in matched silica cells (kindly donated by Professor A.J. Kresge, University of Toronto, Canada).

Table-A1 includes one example of the experimental data used to find k_2 values; the data refer to the reaction $Bu_4NCl + CH_3I$ in THF and 293 K.

TABLE-A1

KINETIC DATA FOR REACTION $Bu_4NCl + CH_3I$ IN THF AT 293 K, $E = 9400\ l\ mol^{-1}\ cm^{-1}$

Time in (s)	75	90	105	120	135	150	
Abs at 247 nm	0.83	0.93	1.03	1.13	1.22	1.29	
10^4 (I^-) mol	0.88	0.99	1.10	1.20	1.30	1.37	$k_2 = 500\ l\ mol^{-1}\ min^{-1}$

Tables 1 and 2 include all kinetic and energetic data in pure and mixed solvents.

TABLE-1

RATE CONSTANTS AND ENERGETICS OF S_N^2 REACTIONS (in $l\ mol^{-1}\ min^{-1}$) AT DIFFERENT TEMPERATURES AND IN DIFFERENT SOLVENTS

			(A) $Bu_4NCl + RI$ in THF (AN = 8.0)			
RI	T = 293	298	303	308 K	E_a kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}
CH_3I	500.00	633.00	760.00	867.10	28.7	–13.7
C_2H_5I	28.90	38.87	48.87	65.00	40.7	–120.7
C_3H_7I	18.00	24.57	35.00	46.42	50.3	–91.4
C_4H_9I	13.13	19.71	28.00	39.33	58.0	–67.7
			(B) $Bu_4NBr + RI$ in THF (AN = 8.0)			
CH_3I	440.0	580.0	707.0	833.0	33.7	–121.0
C_2H_5I	25.0	32.5	43.3	60.6	46.0	–103.0
C_3H_7I	14.4	20.4	30.0	39.0	53.9	–81.0
C_4H_9I	11.2	16.0	24.0	35.0	62.2	–54.8
			(C) Bu_4NCl + RI in acetonitrile (AN = 18.9)			
	T = 318	323	328	333 K	E_a kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}
CH_3I	65.6	90.9	123.4	153.3	47.2	–104.5
C_2H_5I	2.9	4.0	5.8	8.1	58.7	–94.4
C_3H_7I	2.0	3.0	4.5	6.8	67.6	–69.5
C_4H_9I	1.1	1.8	2.9	4.4	70.1	–39.0

(D) Bu_4NBr + RI in acetonitrile (AN = 18.9)

CH_3I	46.7	58.3	68.8	105.6	54.9	–84.4
C_2H_5I	1.9	2.5	4.2	5.9	66.4	–73.5
C_3H_7I	155	2.5	3.5	5.2	72.4	–53.5
C_4H_9I	1.2	1.9	3.2	4.8	83.0	–23.3

(E) LiCl + RI in acetonitrile (AN = 18.9)

CH_3I	8.0	11.8	16.3	24.2	67.6	–73.7
C_2H_5I	0.6	1.0	1.6	2.4	74.0	–60.1
C_3H_7I	0.4	0.6	1.0	1.6	83.0	–35.3
C_4H_9I	0.3	0.5	0.9	1.4	90.6	–12.6

(F) LiBr + RI in acetonitrile (AN = 18.9)

CH_3I	24.5	36.3	46.2	66.1	57.4	–80.2
C_2H_5I	1.4	2.1	2.8	4.4	68.9	–68.6
C_3H_7I	0.9	1.4	2.2	3.2	76.6	–47.6
C_4H_9I	0.7	1.2	1.7	3.0	86.8	–17.9

(G) KCN + RI in acetonitrile (AN = 18.9)

RI	T = 318	323	328	333	E_a kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}
CH_3I	129.0	162.0	202.0	244.0	38.3	–126.1
C_2H_5I	3.4	4.8	5.7	8.1	49.8	–121.1
C_3H_7I	2.1	2.9	4.3	6.1	60.0	–92.9
C_4H_9I	1.3	2.0	2.4	5.0	76.6	–44.8

(H) Bu_4NCl + RI in tertiary pentanol (AN = 24)

RI	T = 343	348	353	358	E_a kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}
CH_3I	5.4	4.2	10.3	14.7	64.4	–86.7
C_2H_5I	0.8	1.2	1.7	2.6	78.3	–63.4
C_3H_7I	0.4	0.7	1.1	1.5	82.0	–42.0
C_4H_9I	0.3	0.5	0.8	1.3	91.9	–21.3

(I) Bu_4NBr + RI in tertiary pentanol (AN = 24)

CH_3I	22.8	27.8	40.8	49.6	57.9	–93.5
C_2H_5I	1.8	2.6	3.8	5.4	71.3	–75.5
C_3H_7I	1.1	1.6	2.4	3.4	79.9	–54.8
C_4H_9I	0.9	1.3	1.9	2.8	87.0	–35.7

(J) Bu_4NCl + RI in propanol (AN = 33.5)

	T = 323	328	333	338	E_a kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}
CH_3I	0.150	0.230	0.360	0.560	81.6	–51.2
C_2H_5I	0.018	0.032	0.054	0.096	98.3	–17.1
C_3H_7I	0.012	0.020	0.035	0.063	103.4	–4.9
C_4H_9I	0.011	0.019	0.031	0.058	111.1	+17.0

(K) LiCl + CH_3I in propanol (AN = 33.5)						
	0.021	0.032	0.050	0.077	90.6	–39.7
(L) KCN + RI in propanol (AN = 33.5)						
CH_3I	0.310	0.420	0.580	0.750	54.7	–128.3
C_2H_5I	0.070	0.103	0.149	0.213	68.9	–94.8
C_3H_7I	0.040	0.062	0.095	0.141	76.6	–77.6
C_4H_9I	0.032	0.053	0.081	0.128	83.6	–57.7
(M) Bu_4NCl + RI in ethanol (AN = 37.1)						
CH_3I	0.0220	0.0390	0.0660	0.1100	93.2	–31.1
C_2H_5I	0.0032	0.0058	0.0006	0.0180	109.6	+3.6
C_3H_7I	0.0024	0.0039	0.0072	0.0130	114.9	+17.6
C_4H_9I	0.0015	0.0029	0.0059	0.0110	121.3	+33.5
(N) LiCl + CH_3I in ethanol (AN = 37.1)						
	0.0043	0.0018	0.0310	0.0522	98.3	–20.9
(O) KCN + RI in ethanol (AN = 37.1)						
RI	T = 323	328	333	338	E_a kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}
CH_3I	0.1192	0.1750	0.2550	0.3550	67.7	–96.1
C_2H_5I	0.0372	0.0605	0.0933	0.1461	79.1	–71.5
C_3H_7I	0.0236	0.0411	0.0583	0.1050	84.3	–58.1
C_4H_9I	0.0197	0.0317	0.0500	0.0847	89.4	–43.8

TABLE-2

RATE CONSTANTS (in l mol^{-1} min^{-1}) OF $Bu_4NCl + C_2H_5I$ AND $Bu_4NBr + C_2H_5I$, IN THF, ACETONITRILE AND TERTIARY PENTANOL WATER MIXTURES

solvent mole % water (AN = k_2)

		T = 318	323	328	333	E_a kJ mol^{-1}	$\Delta S^{\neq}$, J K^{-1}mol^{-1}
$Bu_4NCl + C_2H_5I$ in THF							
5	16	1.74	2.62	4.30	5.30	61.3	–90.43
10	20	0.87	1.42	2.05	3.00	71.5	–64.12
15	23	0.36	0.55	1.08	1.81	94.4	+0.56
$Bu_4NBr + C_2H_5I$ in THF							
5	16	10.33	14.33	20.25	27.75	56.0	–91.7
10	20	4.19	5.86	9.33	13.04	63.8	–73.3
15	23	2.80	3.42	4.62	6.38	70.2	–60.4
$Bu_4NCl + C_2H_5I$ in acetonitrile							
		T = 333	338	343	348	E_a kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1}mol^{-1}
5	27.0	1.21	1.79	2.63	4.00	76.4	–56.0
10	31.0	0.37	0.67	1.16	1.84	97.6	–3.38
15	34.0	0.15	0.27	0.48	0.85	114.9	+41.17

$Bu_4NBr + C_2H_5I$ in acetonitrile							
5	27.0	2.83	4.10	5.53	7.93	69.2	–71.75
10	31.0	1.30	1.70	2.70	3.12	79.5	–47.28
15	34.0	0.65	1.00	1.73	2.46	89.8	22.11
$Bu_4NCl + C_2H_5I$ in pentanol							
		T = 343	348	353	358	E_a kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}
5	26.0	0.53	0.85	1.21	1.89	82.48	–53.25
10	28.0	0.36	0.53	0.87	1.22	88.75	–38.07
15	30.0	0.25	0.41	0.70	1.05	95.00	–22.00
$Bu_4NBr + C_2H_5I$ in pentanol							
5	26.0	1.30	1.84	3.00	3.85	76.81	–62.32
10	28.0	1.12	1.52	2.50	3.50	80.25	–53.53
15	30.0	0.87	1.32	2.05	2.92	84.65	–47.80

Table-3 includes k_2, E_a, $\Delta S^{\neq}$ and $\Delta H^{\neq}$ (over the range 293–308 K) for reactions (A) and (B)

$$\text{(A)} \qquad RI + Bu_4NCl = RCl + Bu_4N^+ + I^- \tag{6}$$

$$\text{(B)} \qquad RI + Bu_4NBr = Bu_4N^+ + I^- + RBr \tag{7}$$

TABLE-3

k_2, E_a, $\Delta S^{\neq}$ AND $\Delta H^{\neq}$ FOR REACTIONS A AND B IN THF

	CH_3I	C_2H_5I	C_3H_7I	C_4H_9I
	(A)			
k_2 l mol^{-1} min^{-1} at 293 K	500	28.9	18.0	12.1
E_a kJ mol^{-1}	28.7	40.7	50.3	58.0
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	–137.0	–120.0	–97.4	–67.6
$\Delta H^{\neq}$ kJ mol^{-1}	26.3	38.3	47.9	55.3
	(B)			
k_2 l mol^{-1} min^{-1} at 293 K	440	25.0	14.4	11.2
E_a kJ mol^{-1}	33.7	46.0	53.9	62.2
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	–121.0	–103.0	–81.0	–54.3
$\Delta H^{\neq}$ kJ mol^{-1}	31.3	43.6	51.5	59.8

The rate constants of Tables 1 and 3 show a repeated pattern and fall in the order

$$CH_3I \ggg C_2H_5I > C_3H_7I > C_4H_9I$$

which projects wide diversity of alkyl group electron releasing abilities with progressive hindrance to ligand substitution due to the bulk of the alkyl chain that obstructs the attacking ligand from effective collision which results in a slower reaction with increase in chain length. A higher k_2 value for Bu_4NCl reaction might be due to higher ionization.

Table-4 includes k_2, E_a, $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values for the reaction (A) LiCl + RI,

(B) LiBr + RI and (C) KCN + RI at 318 K (range 318–333 K) for calculating E_a, $\Delta S^{\neq}$ and $\Delta H^{\neq}$.

TABLE-4

k_2, E_a, $\Delta S^{\neq}$ AND $\Delta H^{\neq}$ FOR REACTIONS (A) LiCl + RI, (B) LiBr + RI AND (C) KCN + RI IN ACETONITRILE

	CH_3I	C_2H_5I	C_3H_7I	C_4H_9I
		(A)		
k_2 l mol^{-1} min^{-1} at 318 K	8.0	0.6	0.4	0.3
E_a kJ mol^{-1}	67.6	74.0	830	90.6
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	–73.7	–60.1	–35.3	–12.6
$\Delta H^{\neq}$ kJ mol^{-1}	64.9	60.1	80.4	90.3
		(B)		
k_2 l mol^{-1} min^{-1} at 318 K	24.5	1.6	0.9	0.7
E_a kJ mol^{-1}	57.4	68.9	76.6	86.6
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	–80.2	–68.6	–47.6	–17.9
$\Delta H^{\neq}$ kJ mol^{-1}	54.8	66.3	73.9	86.3
		(C)		
k_2 l mol^{-1} min^{-1} at 318 K	129.0	3.4	2.1	1.3
E_a kJ mol^{-1}	38.3	49.8	60.6	76.6
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	–126.1	–121.1	–92.9	–44.8
$\Delta H^{\neq}$ kJ mol^{-1}	35.6	47.2	57.4	74.0

The k_2 data in Table-4 show the following order of nucleophilic reactivity:

$$CN^- > Br^- > Cl^-$$

which might be due to ion-pair formation of LiCl, LiBr and KCN according to Eqn. (8):

$$\left.\begin{aligned} LiCl = Li^+ + Cl &\rightleftharpoons Li^+Cl^- \\ LiBr = Li^+ + Br &\rightleftharpoons Li^+Br^- \\ KCN = K^+ + CN^- &\rightleftharpoons K^+CN^- \end{aligned}\right\} \tag{8}$$

with varying equilibrium constants in which $K_{Li^+Cl^-}$ has the largest value and $K_{K^+CN^-}$ has the minimal value on account of the r values for Cl^-, Br^- and CN^-, $r_{Cl} = 0.99$ Å, $r_{Br} = 1.14$ Å, $r_{CN} = 1.33$ Å and their relevant charge densities, which suggests minimal nucleophile reactivity for Cl^- ligand and maximum for CN^- ligand[23–29].

A plot of E_a against C_n (C_n equals the number of C atoms in the alkyl chain) shows proportional dependence of E_a on C_n which projects a series of nearly linear plots, Figure 1.

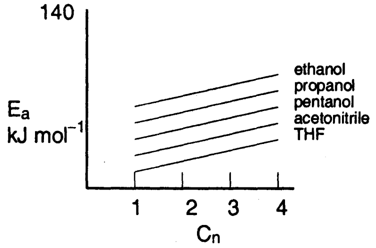

Fig. 1

Figure 1 shows that the reaction $Bu_4NCl + CH_3I$ has a maximum rate constant and minimal E_a in THF and a minimal rate constant and maximal E_a in ethanol. this sequence shows a correlation of k_2 data with solvent acceptor numbers (Table-5).

TABLE-5

CORRELATION OF k_2 DATA WITH SOLVENT ACCEPTOR NUMBERS FOR $Bu_4NCl + CH_3I$

Solvent	THF	Acetonitrile	Tertiary pentanol	2-Propanol	Ethanol
k_2 l mol^{-1} min^{-1}	633	20.7	10.2	0.016	0.001
Acceptor number	8	13	24	33	37

The data in Table-5 suggest the suitability of solvent acceptor numbers (AN) as a reliable parameter for S_N^2 reactions in different solvents[41–44].

Table-6 (A and B) include the entropies of activation $\Delta S^{\neq}$ for the reaction $Bu_4NCl + RI$ ($R = CH_3 \ldots C_4H_9$) in THF (A) and for the reactions $LiCl + CH_3I$, $LiBr + CH_3I$ and $KCN + CH_3I$ in acetonitrile (B).

TABLE-6

(A) $\Delta S^{\neq}$ values for $Bu_4NCl + RI$ ($R = CH_3 \ldots C_4H_9$) in THF (293–308 K)

	CH_3I	C_2H_5I	C_3H_7I	C_4H_9I
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	–137.0	–120.7	–91.4	–67.7

(B) $\Delta S^{\neq}$ values for $LiCl + CH_3I$, $LiBr + CH_3I$ and $KCN + CH_3I$ in acetontrile (318–333 K)

	$LiCl + CH_3I$	$LiBr + CH_3I$	$KCN + CH_3I$
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	–73.7	–80.2	–126.1

Table-6 (A and B) suggest the following order for transition state stabilities.

$(Cl^-C_4H_9I) > (Cl^-C_3H_7I) > (Cl^-C_2H_5I) > (Cl^-CH_3I)$

and $(Cl^-CH_3I) > (Br^-CH_3I) > (CN^-CH_3I)$

The $\Delta S^{\neq}$ values in Table-6 (A and B) confirm two points:

1. The role of molecular geometry on S_N^2 reactions where the volume of the alkyl radicals affects nuclear reactivity.
2. Nucleophile reactivities of halide ligands depend on the nature of the ionisable molecule (Bu_4NX or MX)[30–51]

Values of enthalpies of activation $\Delta H^{\neq}$ were calculated by Eqn (4). Figure-2 shows a plot of $\Delta H^{\neq}$ against $\Delta S^{\neq}$ which shows two parallel modes of behaviour for MeI and BuI and an intermediate mole for EtI and PrI. This difference in behaviour projects differing energetic effects in which BuI like behaviour is dominated by $\Delta H^{\neq}$ factor while with the MeI $\Delta S^{\neq}$ looks to be more significant. $\Delta S^{\neq}$ changes as R radical changes from C_1 to C_4 which could represent a change in the transition structure of the intermediate species. A possible model for the higher iodoalkanes is shown by Figure (3):

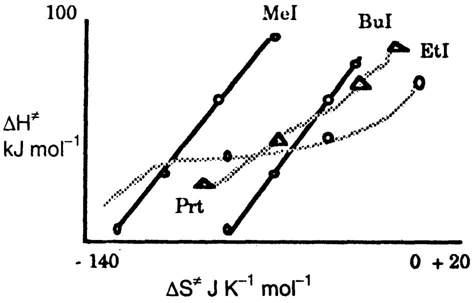

Fig. 2

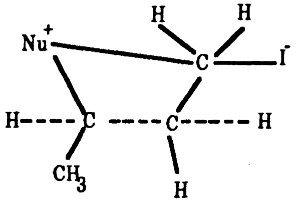

Fig. 3

which tries to balance the minimisation of tortional strain within the alkyl halide when the alkyl radiclal is extended from methyl against the minimisation of steric compression experienced by the incoming nucleofile. More than one conformation of the alkyl chain may be possible leading to higher entropy and higher enthalpy. The minimum energy transition structure may change conformation as the chain increases.

Ligand solvations also vary according to the conformer, again with entropy effects due to the ordering involved[46, 49–51]

Mixed solvents

Table-7 (A, B and C) includes k_2 and E_a data for the reactions $Bu_4NCl + C_2H_5I$ and $Bu_4NBr + C_2H_5I$ in THF, acetonitrile and tertiary pentanol in 5–15 mole per cent water.

TABLE-7

(A)			
Mole percent water	5	10	15
$Bu_4NCl + C_2H_5I$ in THF (318–333 K)			
k_2 l mol^{-1} min^{-1} at 318 K	1.74	0.87	0.36
E_a kJ mol^{-1}	61.3	71.5	94.4
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	-90.4	-64.1	+0.56
Acceptor number	16.0	20.0	23.0
$Bu_4NBr + C_2H_5I$ in THF (318–333 K)			
k_2 l mol^{-1} min^{-1} at 318 K	10.3	4.2	2.8
E_a kJ mol^{-1}	56.0	63.8	70.2
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	-91.7	-73.3	-60.4
(B)			
$Bu_4NCl + C_2H_5I$ in acetonitrile (318–333 K)			
k_2 l mol^{-1} min^{-1} at 318 K	1.21	0.37	0.15
E_a kJ mol^{-1}	76.4	97.6	114.9
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	-56.0	-3.4	+41.2
Acceptor number	27.9	31.0	34.0
$Bu_4NBr + C_2H_5I$ in acetointrile (318–333 K)			
k_2 L mol^{-1} min^{-1} at 318 K	2.83	1.30	0.65
E_a kJ mol^{-1}	69.2	79.5	89.8
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	-71.8	-47.3	-22.1
(C)			
$Bu_4NCl + C_2H_5I$ in tertiary pentanol (348–358 K)			
k_2 l mol^{-1} min^{-1} at 348 K	0.53	0.33	0.25
E_a kJ mol^{-1}	82.5	88.8	95.0
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	-53.3	-28.1	-22.0
Acceptor number	26.0	28.0	36.0
$Bu_4NBr + C_2H_5I$ in tertiary pentanol (348–358 K)			
k_2 l mol^{-1} min^{-1} at 348 K	1.84	1.52	1.32
E_a kJ mol^{-1}	76.8	80.3	84.0
$\Delta S^{\neq}$ J K^{-1} mol^{-1}	-62.3	-53.5	-47.8

Mixing of water with polar solvents (aprotic or protic) causes changes in the physical properties of solvents which result in solvent-solvent and solvent solute interactions causing slower reaction in the mixed solvent[33–51].

Table-8 includes a comparison of the ratios of acceptor numbers and energies of activation for the data in Table-7.

TABLE-8
RATIOS OF ACCEPTOR NUMBERS AND E_a IN PURE AND MIXED SOLVENTS

	THF	Acetonitrile	Tertiary pentanol
	(A) $Bu_4NCl + C_2H_5I$		
AN/AN in 15%	0.35	0.54	0.80
E_a/E_a in 15%	0.43	0.51	0.82
	(B) $Bu_4NBr + C_2H_5I$		
E_a/E_a in 15%	0.65	0.74	0.84

The data show that addition of 15 mole per cent water to the organic solvent has a greater solvating effect on the Cl^- than on the Br^- ligand with a consequently slower reaction and higher energy of activation for the Cl^- ligand reaction. It is also clear that acceptor numbers for pure and mixed solvents represent a reliable parameter which explains the diversity in k_2, E_a and $\Delta S^{\neq}$ for the systems surveyed in this work.

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