African Journal of Pure and Applied Chemistry Vol. 5(4), pp. 69-91, April 2011
Available online at http://www.academicjournals.org/AJPAC
ISSN 1996-0840 ©2011 Academic Journals

Full Length Research Paper

Multiple regression analyses of kinetics of aquation reactions of some chromium (III) – alkyl amine complexes in mixed solvent media - A study of solvation mechanics

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Accepted 23 February, 2011

Molecular dynamics of the aquation reactions of the complexes $[Cr(en)_2Cl_2]Cl$,$[Cr(tn)_2Cl_2]Cl$,$[Cr(tetren)Cl]Cl_2$, $[Cr(pn)_2Cl_2]Cl$, $[Cr(trien)Cl_2]Cl$ and $[Cr(dien)Cl_3]$ have been extensively studied in mixed solvent media. Kinetics and thermodynamic parameters have been evaluated and the results are interpreted carefully in the light of statistical and regression models.

Key words: Cr (III) complexes, molecular dynamics, aquation reaction, kinetic parameters, thermodynamic parameter, statistical model, regression model.

INTRODUCTION

A large amount of kinetic data has accumulated in the literature on simple substitution reactions of Chromium (III) complexes (Rajendran, 2010). The three types of substitution reactions which have been studied are:

(1) Aquation, or replacement by water in neutral or acid solution.
(2) Hydrolysis or replacement by hydroxide in basic media.
(3) Agnation or substitution of X by another anion.

Although many studies have been carried out to study the kinetics of Chromium (III) complexes, they have not made a precise study on the solvent dependence of the reaction, nor determine the activation energy. Generally solvent variations may affect the kinetics and energetic of substitution reactions particularly in mixed solvent media are often quite different from those of the pure solvents or their ideal mixtures (Anbalagan and Rajendran, 2006). Investigations in mixed solvents, which are common in studies of reaction dynamics, have been hampered due to non-availability of solvatochromic parameters for the binary aqueous solvent mixtures (Rajendran, 2010). This reactivity of Chromium (III) complexes is strongly affected by solvation of the reactants/transition state species (Shorter, 1982; Reichardt, 1988). Hence, for a better understanding of ion-solvent interaction, it was interesting to investigate the aquation of Chromium(III) complexes in aqueous mixtures of methanol and 1,4-dioxane. These two extreme solvents have been selected as they are having varied relative permittivity and dipole moments forming typically aqueous mixtures with water (Anbalagan and Rajendran, 2006). Methanol is a better hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) solvent; 1, 4-dioxane is a better HBA solvent. In such systems, the relative permittivity of the mixture of solvents can reflect long range ion- solvent interactions directly.

Several solvent polarity scales have been established in order to quantify the influence of solvent on chemical properties, which could be an equlibrium constant, reaction rate constant and spectral shift using absorption spectroscopy, etc., A single solvent polarity scales like the Grunwald-Weinstein parameter, YGW, is a measure of solvent ionizing power and a linear combination of other empirical parameters were also used (Amis and

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Hinton, 1973). Although the separation of solvent effects into various solvent-solvent-solute interactions is purely formal, a multiparameter approach has been shown to work well (Karthikeyan et al., 2000). Solvatochromic parameters like Kamlet-Taft and Swains vectors were also employed in order to arrive at the solvation effect in terms of specific solvation or short range solvation effects (Reinhardt, 1988). These solvent property indices were intended to unravel and correlate solvent effects on the aquation rate constant of Chromium (III) –alkyl/aryl amine complexes in various solvent mixtures.

EXPERIMENTAL

The complexes $[Cr(en)_2Cl_2]Cl$,$[Cr(tn)_2Cl_2]Cl$, $[Cr(tetren)Cl]Cl_2$, $[Cr(pn)_2Cl_2]Cl$, $[Cr(trien)Cl_2]Cl$ and $[Cr(dien)Cl_3]$ were prepared according to standard literatures procedures (Anbalagan and Rajendran, 2006). The purity of the complexes was checked by comparing the absorption spectrum with a spectrum reported in their respective literatures. MeOH, 1, 4-dioxane and $HClO_4$ were generally used as supplied without further purification and water was triply distilled from alkaline potassium permanganate.

Kinetic measurements

The kinetics of substitution reactions of all the complexes [complex concentration=1×10^{-2} M, $[HClO_4]$ =0.1 M; pH = 1.2] was carried out by spectrophotometric method using a Shimadzu-240 UV-visible double beam spectrophotometer in various aqueous solutions of MeOH or 1,4-dioxane(5,10,15,20,25 and 30% (v/v) of organic co solvent) at different temperatures such as 303, 313, 323 and 333K , the control being ± 0.1℃ .First order rate constants, k, for each run were evaluated from the plots of time versus $\log(A_t-A_\alpha)$ were A_t and A_α are the absorbances at time t and infinity respectively. Activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ were evaluated from the slope and intercept respectively of linear Eyring plot of logk/T verses 1/T. All the values recorded are reproducible with a precesion of ca ±3%. Correlation analyses were made using computer software. The goodness of fit was established using the correlation coefficient (r), standard deviation (sd) and Exner's statistical parameter (ψ). The relative importance (on a percentage scale) of different solvation effects were analyzed using various empirical solvent parameters. The percentage contribution of a parameter to the total effect of reactivities was determined using Equations 1 and 2. To calculate this value, the regression coefficient of each parameter is statistically quantified as follows:

$$Y=a_0+a_1x_1+a_2x_2+\ldots\ldots\ldots\ldots\ldots\ldots+a_nx_n \qquad (1)$$

$$P(X_i)=100|a_i|/\Sigma^n_{i=1}|a_i| \qquad (2)$$

RESULTS AND DISCUSSION

Aquation of $[Cr(N)_xCl_y]^{(3-y)+}$ takes place smoothly in water-methanol (1,4 - dioxane) solutions as shown by a progressive shift of the solution absorption maxima to a shorter wavelength (Equations 3 and 4).

$$[Cr(en)_2Cl_2]^+ + H_3O^+ \rightarrow [Cr(en)_2(H_2O)_2Cl_2]^+ + enH_2^{2+} \qquad (3)$$

$$[Cr(en)_2(H_2O)_2Cl_2]^+ \rightarrow [Cr(en)_2(H_2O)_2Cl]^+ + Cl^- \qquad (4)$$

The electronic spectrum of $[Cr(en)_2Cl_2]^+$ ion in water-organic co solvent is displayed in Figure 1.

The first LF maximum is displaced from 529.5 to 532.9 nm (for all other complexes, there is a shift of 3.2 to 4.6 nm in λ_{max}) towards longer wavelength, as expected on the basis of the lower spectra chemical position of H_2O relative to en (or Cl^-). It is worthwhile to note from Tables 1 to 4, that $[Cr(N)_xCl_y]^{(3-y)+}$ cation undergoes aquation rate that is significantly dependent on the concentration of the organic co solvent component. As x_2 of the medium increases, k_{obs}, either increases or decreases in value. For instance, the velocity of the reaction is enhanced in parallel with x_2 of the medium for $[Cr(tn)_2Cl_2]^+$ but retarded for [Cr(en or pn)$_2$Cl$_2$]$^+$ in methanolic solutions. In short, rate increases for $(tn)_2$ (in methanol) and $(pn)_2$, (dien) and (trien) complexes (in dioxane), but decreases for $(en)_2$, $(pn)_2$, (dien), (trien) and (tetren) (in methanol) and $(en)_2$, $(tn)_2$, and (tetren) (in dioxane) complexes. Also, at a given acidity, the reaction rates changed markedly in binary solvent media as shown in Tables 1 to 4.

The immediate finding is that the reaction is strongly solvent assisted, this can be accounted from the following mechanism. In addition, free amine ligand was identified from change in pH; however, chloride was found to be negligible, which was ensured by estimating chloride-using $AgNO_3$. These results are consistent with a predominant loss of amine ligand but loss of chloride is to a lesser extent. These pathways consist nucleophilic attack of H_2O at the Cr (III) center followed by solvent reorganization. Ultimately, the seven-coordinated intermediate is converted into product or reactant according to the solvent shell influence (Equations.5, 6 and 7).

$$[Cr(en)_2Cl_2]^+ + H_3O^+ \leftrightarrow [Cr(en)_2\,Cl_2(H_2O)]^+ \quad K \qquad (5)$$

$$[Cr(en)_2\,Cl_2(H_2O)]^+ + H_3O^+ \rightarrow [Cr(en)\,(enH)\,Cl_2\,(H_2O)]^{2+}\,k \qquad (6)$$

$$[Cr(en)\,(enH)\,Cl_2(H_2O)]^{2+} \rightarrow [Cr(en)Cl_2(H_2O)_2]^+ + enH_2^{2+} \qquad (7)$$

According to the above, the experimental data, k_{obs}, are related to Equation 8.

$$k_{obs} = (k_0 + k\,K\,[cosol]) / (1+K\,[cosol]) \qquad (8)$$

At low x_2 values the K [cosol] product can be neglected with respect to unity and k_{obs} becomes a linear function of [co sol]. Linear dependence of k_{obs} on the concentration of organic co solvent is in fact, observed. Figure 2 is the typical representative plot, which illustrates the change of rate constant with the change in mole-fraction of the organic co solvent.

The reaction exhibits a linear dependence on the variable like solvent composition, thereby allows making study with regression analysis more effectively based on linear free energy relationships (LFER). Figures 3 and 4 are the typical isokinetic plots between log k_{obs} at 313 K and log k_{obs} at 303 K in methanolic and 1,4-dioxane

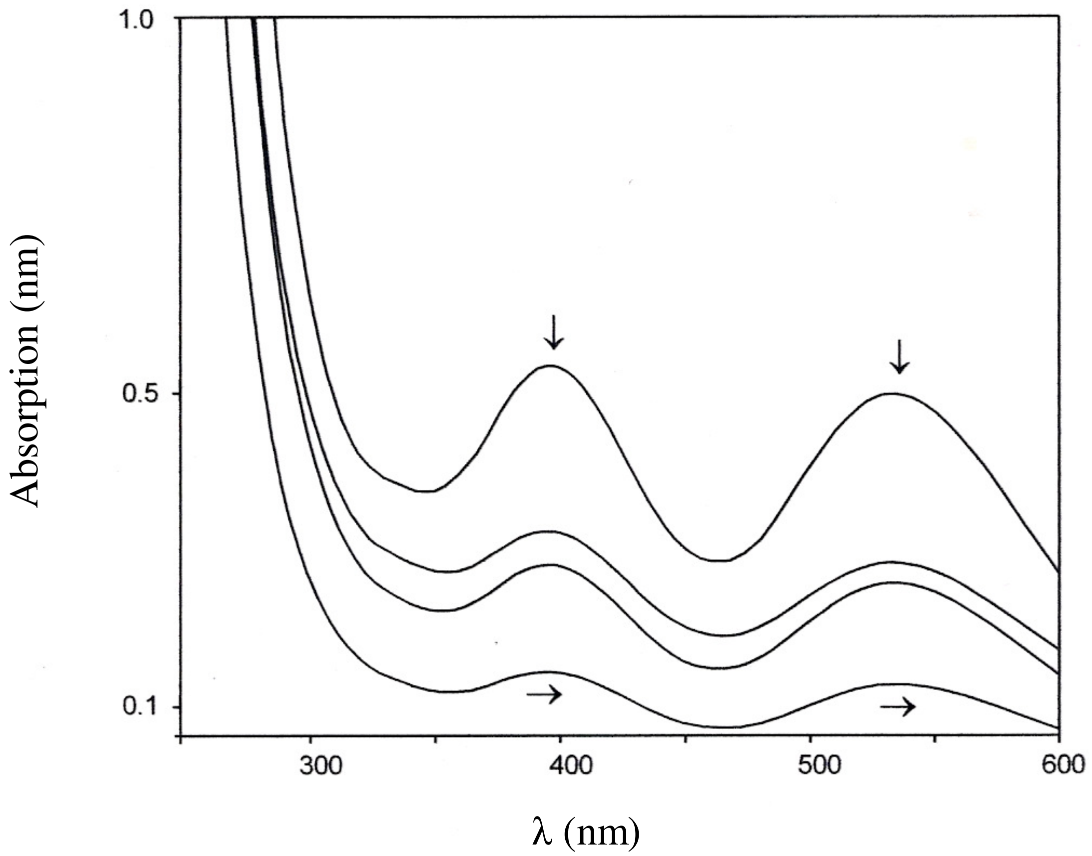


Figure 1. UV –Vis spectra of $[Cr(en)_2Cl_2]Cl$ as a function of different time intervals (0, 10, 15 min respectively). Experimental conditions: complex = 1×10^{-2} M, ionic strength, pH = 1.2, Temp = 303K

solutions respectively. Isokinetic relationship is an essential requirement for the validity of LFER. Linear isokinetic relationships allow the applicability of linear free energy relationships (Atkins, 1998).

It also implies that all reactions correlated here follow a similar mechanism. Table 5 and 6 present equilibrium constant $K^{\#}$. Based on the variation of the rate constant with the mole fraction of the mixed solvent, the change in the chemical potential $\Delta\mu^{\#}$ for the formation of an activated complex, at a given temperature for a specified process can be calculated (Atkins, 1998). It is given by the mathematical expression as $\ln k = \ln 2.08 \times 10^6 T - \Delta\mu^{\#} (n_1 + n_2) / RT$, where n_1 and n_2 are the mole fractions of organic solvent and water respectively. A plot of log k versus $(n_1 + n_2)$ should be linear with the slope giving the change in the chemical potential. The molar Gibbs function is given by the chemical potential, that is, $G_m = \mu^{\#}$ and hence $\Delta G^*m\ \Delta\mu^{\#}_m = - RT \ln K^{\#}$ where $K^{\#}$ is the equilibrium constant of the reactant / activated complex equilibrium (Atkins, 1998).

Tables 5 and 6 represent the calculated values of $K^{\#}$ (from the computed values of $\Delta\mu^{\#)}$ for the aquation reaction of complexes of chromium (III) in the solvent mixtures studied at four different temperatures and found to be close to each other. This result confirms the aquation of chromium (III) complexes follow associative mechanism.

For the $[Cr(N)_xCl_y]^{(3-y)+}$ $[(N)_x = (en)_2, (pn)_2, (tn)_2$, (dien), (trien) and (tetren)] complexes the activation values were evaluated and presented are in Tables 7 and 8. The activation parameters for the aquation of the chromium (III) complexes in water / organic co solvent calculated $\Delta H^{\#}$ and $\Delta S^{\#}$ may be taken to be the composites of the reaction component and the solvent component ($\Delta X^{\#}_{overall} = \Delta H^{\#}_R + \Delta X^{\#}_S$). There is a small change in $\Delta H^{\#}$ values, the energetic role of the solvent co sphere of the transition state in indirectly influencing the development of the polar transition state. It is presumed that there are significant changes in solvation as the coordinated water molecules are replaced by methanol / 1, 4-dioxane molecules or perhaps likely a more significant release of steric strain dissociation of the water-coordinated metal center of the transition state. This implies that the co-solvent is beginning to play an important role in the solvation of the activated complex at this point, and a more ordered transition state is now possible compared to that formed in pure water.

It has been noted that $\Delta G^{\#}$ is generally a well-behaved

Table 1. Observed rate constants for the medium assisted aquation of chromium (III) complexes in water-methanol mixtures.

Complex	k_{obs} (10^{-5}) s^{-1} x_{MeOH}							
	Temp (K)	**0**	**0.0229**	**0.0471**	**0.0728**	**0.1001**	**0.1292**	**0.1602**
$[Cr(en)_2Cl_2]Cl$	303	6.39	19.96	18.60	12.45	9.58	4.64	3.35
	313	17.44	36.78	32.43	27.23	18.23	6.48	5.51
	323	25.42	62.22	56.20	53.61	33.16	14.33	7.15
	333	38.98	96.77	88.36	87.56	56.16	30.28	10.58
$[Cr(pn)_2Cl_2]Cl$	303	6.15	4.06	1.89	0.92	0.73	0.49	0.34
	313	8.59	7.35	3.18	1.48	1.04	0.99	0.92
	323	11.34	9.89	6.33	1.96	1.94	1.48	1.47
	333	18.85	13.42	7.46	3.73	3.12	2.55	1.94
$[Cr(tetren)\,Cl\,Cl_2$	303	3.55	6.29	9.62	14.12	30.96	36.42	50.17
	313	8.96	13.22	32.13	36.39	37.18	50.51	57.99
	323	20.83	29.35	34.05	39.78	49.69	123.93	138.97
	333	29.54	33.54	49.02	49.58	53.69	144.39	175.66
$[Cr(dien)Cl_3]$	303	7.31	5.53	3.19	2.59	1.83	1.34	0.87
	313	8.79	8.87	7.43	5.90	4.88	2.74	2.01
	323	16.46	11.89	10.94	7.47	6.96	4.55	3.27
	333	29.65	22.72	20.60	14.25	13.95	6.24	4.49
$[Cr(trien)Cl_2]Cl$	303	6.12	3.43	1.93	1.84	1.58	1.41	1.08
	313	7.62	7.52	3.80	3.39	3.12	2.93	1.44
	323	11.21	12.56	11.08	8.50	6.18	5.97	2.75
	333	17.52	25.85	18.93	16.66	16.44	10.91	6.28
$[Cr(tetren)\,Cl]\,Cl$	303	26.06	23.87	25.75	30.64	33.67	34.52	37.48
	313	47.49	32.50	43.77	50.10	64.26	72.00	82.76
	323	97.64	35.07	73.50	78.64	79.79	105.84	119.77
	333	149.1	59.55	97.05	131.68	134.60	135.04	153.06

Spectrophotometric method at 529.5, 544, 526.5, 482, 591.5 and 488 nm. Mean of 2 to 3 determinations.$[Cr(III)] = 1\times10^{-2}$ M, $[HClO_4] = 0.1$ M.

function, that is, it usually changes smoothly and gradually as the solvent composition changes (Lewis, 1987). The more negative values of $\Delta S^{\#}$ observed for the aquation process agree with a greater degree of solvation. Moreover, the changes in $\Delta S^{\#}$ values range from -137 to -246 JK^{-1} mol^{-1} in water-methanol media and from - 95.9 to - 287 JK^{-1} mol^{-1} in water - 1,4 -dioxane media for the entire 5 to 30% (v/v) range supports the view that there are changes in the coordination sphere occupation and general solvation. The $\Delta S^{\#}$ values are all clearly negative, $\Delta S^{\#}$ = - 246 to -125 JK^{-1} in water / MeOH and -287 to - 95.9 JK^{-1}mol in water /Diox, indicate an associately activated substitution. Taking into account all the mechanistic considerations about electrostriction and aquation of complexes, the results as a whole are quite a good indicator of the mechanistic shifts that can be obtained for subtle changes in the systems (Kosewer, 1968). This is consistent with a more solvated species formation in the activated state. This general observation is taken to indicate that the solvation components of the activation parameters are sensitive to solvent structural perturbations. It is also worthy to note that the variations in $\Delta S^{\#}$ and $\Delta H^{\#}$ indicate that the overall solvation on these activation parameters are mutually compensatory (Poonkodi and Anbalagan, 2001). The large negative value of $\Delta S^{\#}$ is consistent with associative mechanism and retention of steric configuration of the parent complex.

Influence of binary solvent mixtures on reactions

Mixed solvent effects on reactions of metal complexes are of prime importance owing to their applications in structure - function studies (Balzani and Carassiti, 1970). However, the interpretations of results in these solvents

Table 2. Observed rate constants for the medium assisted aquation of chromium (III) complexes in water-1, 4 dioxane mixtures.

Complex	k_{obs} **(10^{-5}) s^{-1} x_{Diox}**							
	Temp (K)	**0**	**0.0019**	**0.0229**	**0.0359**	**0.0502**	**0.0659**	**0.0831**
$[Cr(en)_2Cl_2]Cl$	303	6.39	6.22	5.93	3.45	1.83	1.29	0.69
	313	17.44	12.76	8.81	6.35	5.90	2.89	1.19
	323	25.42	21.66	18.75	13.73	12.15	5.43	2.00
	333	38.98	38.46	37.03	29.22	28.36	14.81	5.43
$[Cr(pn)_2Cl_2]Cl$	303	6.15	7.15	13.64	19.54	38.71	43.57	49.81
	313	8.59	10.14	19.13	29.78	65.65	85.61	95.94
	323	11.34	17.22	28.46	40.46	90.47	109.55	126.34
	333	18.85	28.44	35.20	62.61	118.33	133.73	149.15
$[Cr(tn)_2Cl_2]Cl$	303	3.55	2.19	1.36	0.87	0.62	0.39	0.31
	313	8.96	3.73	2.57	1.43	0.81	0.57	0.41
	323	20.83	5.49	4.83	4.16	1.29	0.79	0.14
	333	29.54	9.75	7.97	6.69	3.00	1.67	1.25
$[Cr(dien)Cl_3]$	303	7.31	14.29	28.49	30.49	32.37	46.88	60.66
	313	8.79	21.08	32.19	36.63	55.81	62.80	71.77
	323	16.46	32.56	35.69	45.69	67.31	76.47	91.04
	333	29.65	39.85	41.82	45.87	91.24	92.03	101.45
$[Cr(trien)Cl_2]Cl$	303	6.12	9.20	12.92	17.47	36.63	43.07	60.00
	313	7.62	9.88	14.10	28.73	52.03	59.44	62.03
	323	11.21	13.06	18.69	37.31	56.43	68.89	72.84
	333	17.52	19.44	28.17	51.88	74.95	87.86	105.96
$[Cr(tetren)Cl]Cl_2$	303	46.06	45.71	33.24	16.91	13.09	10.19	08.28
	313	47.49	93.44	86.27	34.82	26.19	15.38	12.89
	323	97.64	149.93	134.55	67.38	51.81	26.54	25.25
	333	149.1	211.63	178.30	151.12	72.30	63.72	61.58

Spectrophotometric method at 529.5, 544, 526.5, 482, 591.5 and 488 nm. Mean of 2 to 3 determinations. [Cr(III)) = 1 x 10^{-2} M, $[HClO_4]$ = 0.1 M.

are complicated for several reasons. Secondly, solvent effects are specific depending upon the mixtures under study. In spite of the above difficulties, solvent mixtures are useful in continuously changing the macroscopic properties. A series of water-methanol and water - 1, 4 - dioxane binary solvent mixtures were used in this study. Most probably the organic co solvent exerts two types of opposite effects on the reaction rate. The first type of effect may be due to the greater solvation of the transition state and the increase of the water molecules from water clusters. The second type of effect responsible for decreasing the rate constant is due to (i) decrease of the bulk dielectric constant of the medium and (ii) decrease in the polarity of the solvent. From an electrostatic viewpoint, a rate decrease might be expected because of destabilization of the polar transition state when the bulk dielectric constant is lowered by successive addition of the organic co solvent. Since the highly polar transition state is more strongly solvated relative to that of the solvent polarity decrease, hence, the reaction rate decreases.

Investigations on the change of aquation rate constant with the change in mole fraction of the organic co solvent vividly suggest that the aquation kinetics strongly depends on the mole fraction (x_2) of the organic co solvent. Figure 6 depicts a typical plot of log k_{obs} vs x_2 (mole fraction of the organic co solvent) for the complex $[Cr(en)_2Cl_2]Cl$, in both water- methanol (1,4 - dioxane) mixtures, which yields the following relationships (Equations 25 and 26).

$\log k_{obs}=-3.488-6.077x_2$;(water-methanol,
r=0.982,sd=0.067,Ψ=0.14,
n=6, Temp.=303K) (25)

$\log k_{obs}$ = - 3.988 to 13.948 x_2 ; (water-1,4 -dioxane, r = 0.990, sd = 0.060, Ψ= 0.11,n=6,Temp.=303K) (26)

Thus, the rate acceleration or deceleration is essentially due to the concentration of MeOH / Diox in the medium. As x_2 is progressively increased from 0 to 30% (v/v), the added organic co solvent imparts some effect leading to

Table 3. Statistical results coefficients and weighted contributions of solvent parameters in Swain's equation for the aquation reaction of Cr(III) complexes in water – methanol mixtures at different temperatures.

Complex	Statistical parameter								
	Temp (K)	R^2	Sd	Ψ	a	b	P(A)	P(B)	intercept
$[Cr(en)_2Cl_2]Cl$	303	0.981	0.056	0.15	-1571	778	67	33	769
	313	0.935	0.118	0.03	-1853	941	66	34	909
	323	0.901	0.155	0.34	-202	115	64	36	84
	333	0.862	0.179	0.41	945	-459	67	33	-488
$[Cr(tn)_2Cl_2]Cl$	303	0.958	0.094	0.22	131	-360	27	73	225
	313	0.934	0.915	0.28	31934	17504	65	35	-40519
	323	0.920	0.106	0.31	-211	489	30	70	-281
	333	0.886	0.126	0.37	-76	156	33	67	-83
$[Cr(tetren) Cl]Cl_2$	303	0.939	0.025	0.27	72.8	-39.3	65	35	-37
	313	0.971	0.033	0.19	-438.9	213.8	67	33	222
	323	0.899	0.099	0.35	-1716.1	849.8	67	33	863
	333	0.842	0.099	0.56	-489.0	239.6	67	33	246
$[Cr(pn)_2Cl_2]Cl$	303	0.944	0.121	0.26	-220	125	64	36	90
	313	0.805	0.205	0.48	229	-102	69	31	-131
	323	0.825	0.192	0.46	-2233	1129	66	34	1099
	333	0.907	0.124	0.33	-250	119	64	36	92
$[Cr(trien)Cl_2]Cl$	303	0.921	0.061	0.31	1311.1	-649.8	67	33	-666
	313	0.909	0.089	0.33	2199.7	-1092.3	67	33	-1112
	323	0.939	0.076	0.33	1182.2	-582.6	67	33	-603
	333	0.914	0.081	0.32	379.7	-182.0	62	38	-201
$[Cr(dien) Cl_3]$	303	0.992	0.037	0.98	906.2	-442.4	67	33	-468
	313	0.976	0.050	0.17	-757.6	388.7	66	34	365
	323	0.945	0.079	0.15	-2710.7	1365.7	67	33	1341
	333	0.969	0.068	0.19	-2659.7	1341.9	66	34	1314

R2 = Coefficient of multiple determination; sd = standard deviation; Ψ = Exner's statistical parameter; a and b = coefficients of A and B in Equation 7; P(A) and P(B) = weighted percentage contributions.

solvent dependent aquation. To examine the concentration effect due to co solvent, the rate data was correlated with relative permittivity of the medium. For ion-ion reactions, electrostatic interactions generally make the greatest contribution to the activation free energy. The solvent parameter widely used as a measure of the electrostatic interactions between solute and solvent is the relative permittivity and recently, the ionizing power and bipolarity / polarizability.

Linear regression approach

It is hardly surprising that a single parameter fails to sum up the complexities of solvation. Due to limitations of dielectric constant, different solvent parameters have been developed which are based on actual solvent sensitive chemical or physical processes. Majority of these are based on linear free energy relationships involving empirical solvatochromic parameters. Univariate linear solvation energy relationships (LSERs) may possess the conventional form $Y = a_0 + a_1X_1$ where a_1 is the characteristic of the reaction and X_1 is the function ($1 / \varepsilon_r$ or Y) of the solvent. According to electrostatic theory, the dependence of the rate constant, k_{obs}, with the relative permittivity, ε_r, for the reaction between an ion of charge Z_A and a dipole of dipole moment μ_B at a distance, r, can be expressed as given by the equation;

$\log (k / k_\alpha) = Z_A e\mu_B / 4 \pi \varepsilon_0 k_B Tr^2 \varepsilon_r$, where k_α is the rate constant in a medium relative permittivity (ε_r) of infinite magnitude, and other symbols have their usual meanings (Balzani and Carassiti, 1970).

The influence of solvent relative permittivity (ε_r) on the rate of the reaction was studied at six different water -

Table 4. Statistical results coefficients and weighted contributions of solvent parameters in Swain's equation for the aquation reaction of Cr (III) complexes in water – 1, 4-dioxane mixtures at different temperatures.

Complex	**Statistical parameter**								
	Temp (K)	**R2**	**Sd**	**Ψ**	**a**	**b**	***P(A)***	***P(B)***	**Intercept**
[Cr(en)2Cl2]Cl	303	0.980	0.069	0.15	53.5	-89.2	37	63	32
	313	0.942	0.114	0.26	-12.0	69.9	15	85	-62
	323	0.913	0.148	0.32	-6.3	56.9	10	90	-54
	333	0.843	0.167	0.43	-79.9	230.4	26	74	-153
[Cr(tn)2Cl2]Cl	303	0.989	0.058	0.15	196.3	-447.4	30	70	246
	313	0.978	0.072	0.16	177.7	-395.5	31	69	213
	323	0.914	0.155	0.32	-237.5	628.5	27	73	-395
	333	0.965	0.090	0.20	-154.2	420.9	27	73	-270
[Cr(tetren) Cl]Cl2	303	0.952	0.083	0.24	416.3	-992.7	29	71	573
	313	0.982	0.062	0.14	7743.9	-1790.9	29	71	1044
	323	0.962	0.087	0.12	1474.5	-3594.5	29	71	2117
	333	0.898	0.100	0.35	-141.4	373.8	27	73	-235
[Cr(pn)2Cl2]Cl	303	0.904	0.133	0.34	86.5	-248.5	26	74	158
	313	0.926	0.138	0.29	3.9	-52.1	7	93	44
	323	0.931	0.119	0.28	95.8	-274	26	74	174
	333	0.914	0.117	0.32	-217.8	502.9	30	70	-289
[Cr(trien)Cl2]Cl	303	0.968	0.075	0.19	174.9	-466.2	27	73	287
	313	0.890	0.146	0.36	-358.5	846.1	30	70	-492
	323	0.909	0.121	0.33	-418.0	995.5	30	70	-581
	333	0.930	0.099	0.29	-292.8	689.0	30	70	-410
[Cr(dien)Cl3]	303	0.892	0.091	0.36	114.1	-303.5	27	73	186
	313	0.939	0.065	0.27	151.0	-393.5	28	72	239
	323	0.966	0.043	0.20	-14.6	15.6	48	52	-5
	333	0.874	0.089	0.39	223.2	-569.5	28	72	343

R2 = Coefficient of multiple determination; sd = standard deviation; Ψ = Exner's statistical parameter; a and b = coefficients of A and B in Equation 7 ; P(A) and P(B) = weighted percentage contributions.

methanol / 1, 4 - dioxane mixtures at four different temperatures. It was found that the first order rate constants (k_{obs}) either increase or decrease with the change in polarity of the medium. The influence of ε_r on the rate constant can be described by the Equation (4) of Lailder and Eyring $d\ \ln k\ d\ (1/\varepsilon_r) = e^2Z^2\ (1/r - 1/r^*)/2kT$, where k is the rate constant, Z the net charge, r the effective radius and r* is the radius of the activated species (Equation 24).

The correlation coefficient r of theplots is in the range of 0.900 to 0.992 and Exner's statistical parameter (Ψ) indicates the best fit of the data plotted in the range of 0.43 to 0.10 and standard deviation lies in the range of 0.408 to 0.023 for the complexes in water-methanol medium (Table 9) (Equation 25). A similar trend was observed in water-1,4 -dioxane medium, (r = 0.900 to 0.991, sd = 0.369 to 0.040, Ψ = 0.38 to 0.11, n = 6) (Table 10).

If the relative permittivity of the medium predominates on reaction rate then there should be a linear relationship. Figures 5 and 6 are the typical plots of log kversus 1 / ε_r, in methanolic and 1, 4-dioxane media respectively. The slopes of the plots confirm the substantial contribution of relative permittivity in rising or lowering of the aquation rate. For this reaction the large driving force is the relative permittivity of the medium and suggests that the transition state formation $[Cr(N)_xCl_y(H_2O)]^{(3-y)+}$ is enhanced and in some cases reduced due to solvent ordering. Such an effect is indeed reflected in the large negative entropy values observed.

The solvent effect was also analyzed using the Grunwald - Winstein equation:

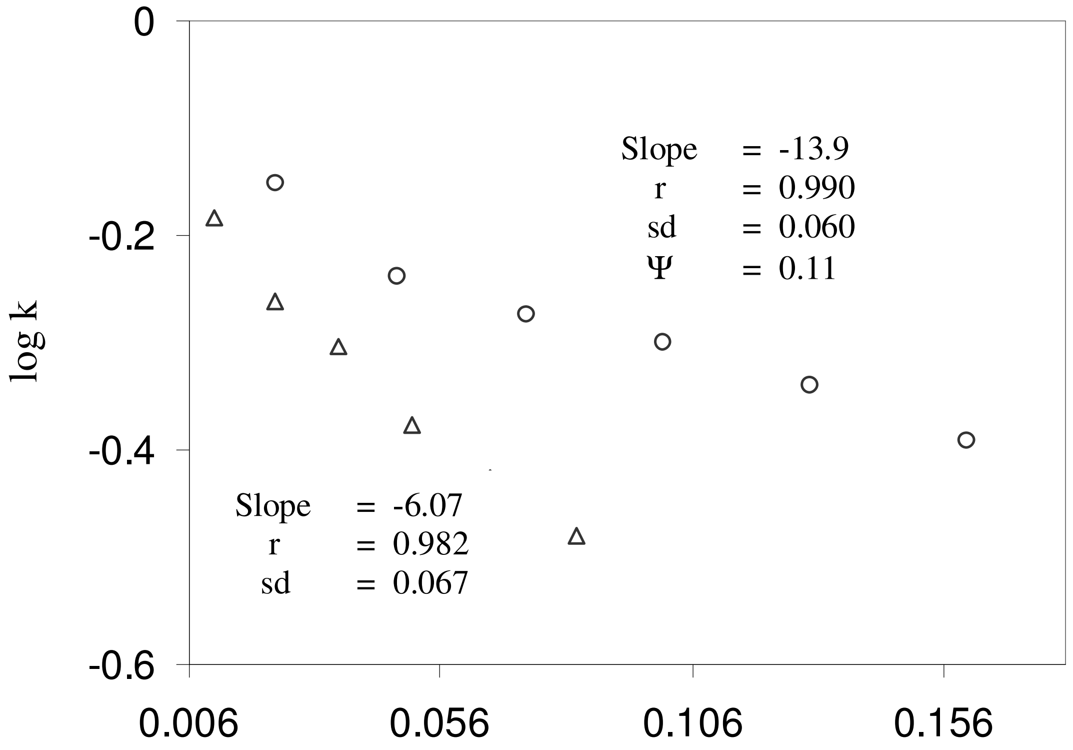


Figure 2. Plot of log k versus mole fraction of co solvent, x_2 , for the aquation of $[Cr(en)_2Cl_2]Cl$ at 303K in water – methanol(o) and water-1,4-dioxane (Δ).

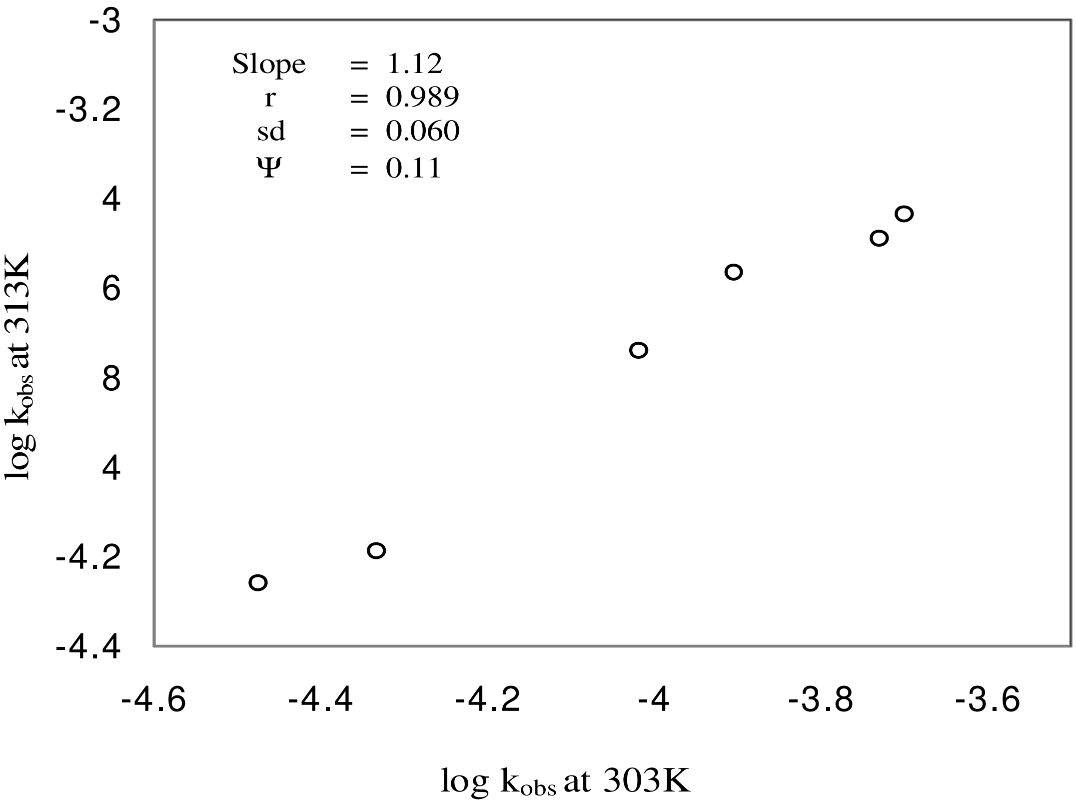


Figure 3. Isokinetic plot of log k_{obs} at 313K versus log k_{obs} at 303K for the aquation of $[Cr(en)_2Cl_2]Cl$ in water –methanol.

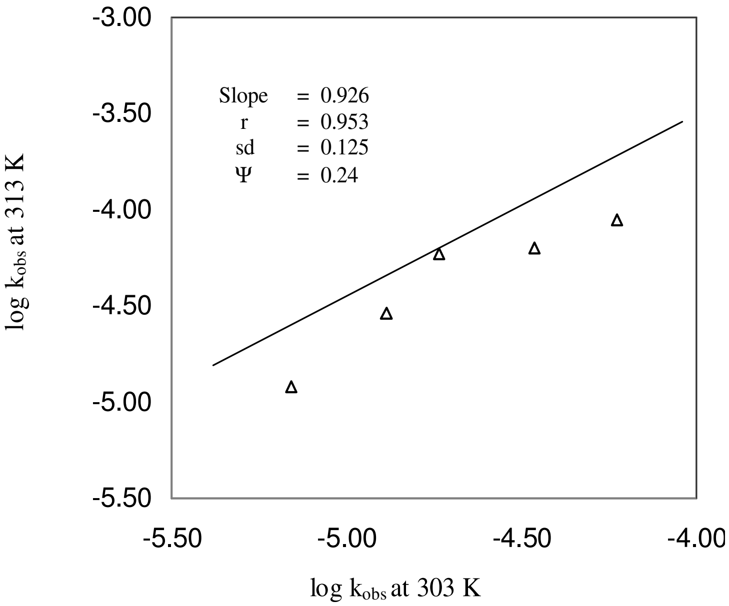


Figure 4. Isokinetic plot of log k_{obs} at 313 K versus log k_{obs} at 303 K for the aquation of $[Cr(en)_2Cl_2]Cl$ in water- dioxane.

Table 5. Statistical results of K and $\Delta\mu^{\#}$ for the aquation reaction of $[Cr(N)_xCl_y]^{(3-y)+}$ complexes in water - methanol mixtures at different temperatures.

$(N)_x$	methanol % (v/v)					
	Temp (K)	**r**	**sd**	**Ψ**	**K**	$\Delta\mu^{\#}$
$(en)_2$	303	0.976	0.078	0.17	0.13	5116
	313	0.950	0.128	0.24	0.18	4454
	323	0.935	0.151	0.28	0.20	4309
	333	0.909	0.175	0.33	0.16	4990
$(pn)_2$	303	0.980	0.088	0.15	0.19	4127
	313	0.916	0.162	0.32	0.18	4514
	323	0.910	0.165	0.33	1.00	4552
	333	0.980	0.094	0.15	0.13	5608
$(tn)_2$	303	0.986	0.067	0.13	4.89	-4002
	313	0.902	0.108	0.34	14.11	-6889
	323	0.954	0.106	0.23	8.55	-5765
	333	0.939	0.120	0.27	8.33	-5869
dien	303	0.994	0.035	0.08	0.10	5823
	313	0.978	0.058	0.16	0.08	6690
	323	0.988	0.109	0.12	0.10	6296
	333	0.949	0.107	0.25	0.13	5746
trien	303	0.946	0.061	0.25	0.02	9312
	313	0.920	0.100	0.30	0.07	6886
	323	0.953	0.082	0.24	0.07	7100
	333	0.945	0.080	0.26	0.05	8065
tetren	303	0.976	0.018	0.17	2.32	-2119
	313	0.989	0.020	0.11	1.54	-1130
	323	0.930	0.100	0.29	12.46	-6776
	333	0.976	0.082	0.17	1.46	-1057

R = correlation coefficient, sd = standard deviation, Ψ = Exner's statistical parameter.

Table 6. Statistical results of K and $\Delta\mu^{\#}$ for the aquation reaction of $[Cr(N)_xCl_y]^{(3-y)+}$ complexes in water - 1, 4 - dioxane mixtures at different temperatures.

$(N)_x$	**1, 4 dioxane % (v/v)**					
	Temp (K)	**r**	**sd**	**Ψ**	**K**	**$\Delta\mu^{\#}$**
$(en)_2$	303	0.985	0.074	0.21	0.09	6172
	313	0.957	0.120	0.40	0.09	6376
	323	0.935	0.153	0.60	0.10	6169
	333	0.900	0.165	0.84	0.08	7144
$(pn)_2$	303	0.967	0.095	0.31	15.63	-6927
	313	0.976	0.095	0.25	10.52	-6124
	323	0.976	0.085	0.25	13.80	-7050
	333	0.966	0.089	0.31	19.09	-8167
$(tn)_2$	303	0.989	0.032	0.19	18.71	7380
	313	0.988	0.043	0.19	0.08	6507
	323	0.954	0.139	0.41	0.27	3536
	333	0.981	0.091	0.24	0.08	6882
dien	303	0.950	0.066	0.24	1.52	-1058
	313	0.978	0.086	0.16	1.58	-1188
	323	0.986	0.168	0.12	1.56	-1363
	333	0.930	0.082	0.29	1.58	-1264
trien	303	0.987	0.058	0.12	18.10	-7291
	313	0.946	0.112	0.23	14.10	-6891
	323	0.963	0.094	0.21	18.60	-7854
	333	0.975	0.073	0.17	23.60	-8756
tetren	303	0.979	0.066	0.16	0.42	7980
	313	0.978	0.086	0.16	12.70	6606
	323	0.901	0.168	0.34	0.01	6641
	333	0.953	0.082	0.24	0.69	1026

r = correlation coefficient, sd = standard deviation, Ψ = Exner's statistical parameter.

$$\log k = \log k_0 + mY$$

where Y is an empirical parameter (solvent ionizing power) characteristic of the given solvent and m is a substrate parameter measuring the substrate sensitivity to changes in the ionizing power of the medium. Figure 7, is the plot of log k_{obs} vs Y (Grunwald-Winstein polarity parameter) correspond to $[Cr(en)_2Cl_2]Cl$ aquation in water-methanol (r = 0.983, sd = 0.066, Ψ = 0.14, n = 6 ; Temp. = 303 K in water - dioxane (r = 0.990, sd = 0.060, Ψ = 0.11, n = 6, Temp. = 303 K). For all the complexes at the four different temperatures studied, the plots of log k_{obs} versus Y were linear (r = 0.900 to 0.992, sd = 0.179 to 0.022, Ψ = 0.37 to 0.10, n = 6, Temp. = 303 – 333 K, water - methanol mixture). For water - 1, 4-dioxane mixture, r = 0.900 – 0.990, sd = 0.371 to 0.034, Ψ = 0.37 – 0.11, n = 6, Temp. 303 to 333K) with negative slopes (Tables 11 and 12). The negative m values indicate a transition state which is less polar than the reactants and that the present complexes undergo aquation by an associative mechanism.

It is well known that, in an associative reaction between two oppositely charged ions, the transition state is more easily attained in the medium of lower relative permittivity (Amis and Hinton, 1973). Therefore, it may be concluded that the reactants attain the transition state more easily; hence, the increase in rate with decrease in relative permittivity of the medium. Moreover, the near similarity in m values indicates that a similar mechanism is operating throughout the series. Ultimately the conventional dielectric continuum models on reaction rates provide some description of the role of solvent. These models presume essentially the overall solvent reorganization that dictates the formation and stability of an

Table 7. Activation parameters for the aquation reaction of [Cr(N)xCly](3-y)+ complexes in water - methanol mixtures.

(N)x		**methanol % (v/v)**						
	ΔX#	**0**	**5**	**10**	**15**	**20**	**25**	**30**
	ΔH#	42.9	41.6	41.2	52.3	46.9	50.9	47.7
(en)2	-ΔS#	182	178.0	180.0	147.0	167.0	161.0	159.0
	ΔG#	98.2	95.7	95.9	96.8	97.6	99.8	95.9
	ΔH#	27.8	30.1	37.8	55.0	38.9	42.5	45.5
(pn)2	-ΔS#	234	229.0	210	157.0	215.0	206.0	198.0
	ΔG#	98.8	99.6	101.0	103.0	104.0	104.0	105.0
	ΔH#	58.1	46.5	39.3	30.1	27.1	41.7	36.2
(tn)2	-ΔS#	137	171.0	190.0	218.0	229.0	174.0	189.0
	ΔG#	99.9	98.4	96.9	96.1	96.4	94.4	93.7
	ΔH#	37.6	35.3	47.6	42.3	51.6	40.5	42.7
dien	-ΔS#	201	210.0	173.0	193.0	165.0	204.0	200.0
	ΔG#	98.6	99.1	100.2	100.7	101.5	102.3	103.3
	ΔH#	26.9	52.5	63.8	60.4	61.9	54.8	46.6
trien	-ΔS#	237.5	157.0	125.0	137.0	133.0	157.0	188.0
	ΔG#	98.9	100.1	101.7	101.9	102.3	102.4	103.5
	ΔH#	47.4	20.9	35.2	37.8	34.1	35.2	36.2
tetren	-ΔS#	157	246.0	197.0	188.0	198.0	194.0	190.0
	ΔG#	95.1	95.4	95.0	94.7	94.3	94.1	93.8

ΔH# in kJ mol^{-1}, ΔS# in JK^{-1} mol^{-1} and ΔG# in kJ mol^{-1}at 300K, [Cr(III)] = 1 x 10^{-2} M, [HClO4] = 1 x 10^{-1} M, pH = 1.2

Table 8. Activation parameters for the aquation reaction of [Cr(N)$_x$Cl$_y$]$^{(3-y)+}$ complexes in water - 1,4 - dioxane mixtures

(N)$_x$		**1,4-dioxane % (v/v)**					
	ΔX$^{\#}$	**5**	**10**	**15**	**20**	**25**	**30**
	ΔH$^{\#}$	47.7	49.6	57.5	72.5	63.8	53.6
(en)$_2$	-ΔS$^{\#}$	168.0	163.0	141.0	95.9	128.0	168.0
	ΔG$^{\#}$	98.6	99.1	100.0	101.0	103.0	104.0
	ΔH$^{\#}$	36.5	24.6	29.2	28.3	27.9	27.5
(pn)$_2$	-ΔS$^{\#}$	204.0	237.0	219.0	216.0	216.0	216.0
	ΔG$^{\#}$	98.5	96.7	95.8	93.9	93.5	93.1
	ΔH$^{\#}$	38.2	47.2	57.7	40.7	38.5	41.1
(tn)$_2$	-ΔS$^{\#}$	282.0	182.0	152.0	211.0	222.0	215.0
	ΔG$^{\#}$	101.0	102.0	103.0	104.0	105.0	106.0
	ΔH$^{\#}$	26.9	7.9	9.6	25.1	16.1	12.4
dien	-ΔS$^{\#}$	229.0	287.0	280.0	228.0	255.0	265.0
	ΔG$^{\#}$	96.5	94.9	94.6	94.4	93.5	92.9
	ΔH$^{\#}$	18.4	19.2	27.0	16.1	16.6	12.8
trien	-ΔS$^{\#}$	262.0	257.0	227.0	257.0	254.0	265.0
	ΔG$^{\#}$	61.2	97.1	95.9	94.1	93.7	93.2
	ΔH$^{\#}$	40.1	43.7	57.9	46.3	47.8	53.3
tetren	-ΔS$^{\#}$	176.0	166.0	126.0	166.0	165.0	148.0
	ΔG$^{\#}$	93.5	94.1	96.3	96.7	97.7	98.3

ΔH# in kJ mol^{-1}, ΔS# in JK^{-1} mol-1 and ΔG# in kJ mol^{-1}at 300 K, [Cr(III)]= 1x10-2 M, [HClO4]= 1x 10^{-1} M, pH = 1.2.

Table 9. Statistical results of Laidler-Eyring plot for the aquation reaction of $[Cr(N)_xCl_y]^{(3-y)+}$ complexes in water methanol mixtures at different temperatures.

$(N)_x$	Statistical parameter					
	Temp (K)	**r**	**sd**	**Ψ**	**Slope**	**Intercept**
$(en)_2$	303	0.982	0.066	0.15	-360.1	1.1
	313	0.958	0.116	0.22	-397.9	1.9
	323	0.950	0.125	0.24	-418.9	2.4
	333	0.928	0.146	0.29	-402.3	2.4
$(pn)_2$	303	0.966	0.114	0.20	-427.1	1.1
	313	0.910	0.187	0.37	-356.4	0.4
	323	0.900	0.408	0.38	-349.6	0.4
	333	0.946	0.167	0.26	-332.4	0.4
$(tn)_2$	303	0.976	0.087	0.17	389.1	-9.3
	313	0.900	0.118	0.37	222.6	-6.6
	323	0.952	0.098	0.23	310.2	-7.7
	333	0.939	0.111	0.27	304.2	7.5
dien	303	0.992	0.040	0.10	-315.1	-0.2
	313	0.985	0.046	0.13	-281.9	-0.3
	323	0.934	0.105	0.28	-273.2	-0.2
	333	0.959	0.096	0.22	-323.9	-0.7
trien	303	0.937	0.066	0.28	-177.1	-2.2
	313	0.927	0.097	0.30	-238.2	-1.1
	323	0.969	0.066	0.19	-257.8	-0.5
	333	0.963	0.064	0.21	-230.9	-0.5
tetren	303	0.963	0.023	0.21	82.6	-4.7
	313	0.977	0.058	0.16	164.4	-5.6
	323	0.936	0.096	0.28	254.7	-6.7
	333	0.900	0.090	0.43	143.9	-5.0

r = correlation coefficient, sd = standard deviation, Ψ = Exner's statistical parameter.

intermediate.

Further, systematic analysis on the variations of rate in mixed solvent media of different compositions should provide valuable information about solvation shell participation. From idealized theories, the solvent relative permittivity is often predicted to serve as a quantitative measure of solvent polarity. However, this approach is often inadequate since these theories regard solvents as a non-structured continuum, not composed of individual solvent molecules with their own solvent - solvent interactions, and they take into account specific solute-solvent interactions such as hydrogen bonding and electron pair donor-electron pair acceptor interactions, which often play a dominating role in solute-solvent interactions. No single macroscopic physical parameter could possibly account for the multitude of solute-solvent interactions on the molecular microscopic level.

Thus, bulk solvent properties like the relative permittivity, the ionizing power and/or bipolarity /polarizability will poorly describe the micro–environment around the reacting species, which governs the stability of the intermediate reaction complex and hence the rate of aquation reaction. Hence, during the recent past, a variety of attempts have been made to quantify different aspects of solvent polarity and then to use the resultant parameters to interpret solvent effects on reactivity through multiple regressions.

Multiple regression approach

The solvational properties of solvent appear to control the reactivity of the complex which is not taken care of in the solvent effect relationship stated as:

Table 10. Statistical results of Laidler-Eyring plot for the aquation reaction of $[Cr(N)_xCl_y]^{(3-y)+}$complexes in water - 1, 4 - dioxane mixtures at different temperatures.

$(N)_x$	**Statistical parameter**					
	Temp (K)	**r**	**sd**	**Ψ**	**Slope**	**Intercept**
$(en)_2$	303	0.991	0.058	0.11	-219.2	-1.2
	313	0.974	0.093	0.18	-209.5	-1.1
	323	0.960	0.120	0.22	-215.2	-0.7
	333	0.925	0.134	0.30	-176.0	-0.9
$(pn)_2$	303	0.944	0.123	0.26	183.7	-6.5
	313	0.957	0.128	0.23	218.5	-6.8
	323	0.959	0.111	0.22	196.4	-6.3
	333	0.949	0.110	0.25	171.1	-5.8
$(tn)_2$	303	0.987	0.062	0.13	-354.9	0.1
	313	0.986	0.062	0.13	-414.9	0.9
	323	0.949	0.369	0.25	-433.5	1.5
	333	0.978	0.079	0.16	-409.9	1.4
dien	303	0.940	0.082	0.27	117.1	-5.3
	313	0.961	0.063	0.22	113.4	-5.1
	323	0.981	0.040	0.15	104.9	-4.9
	333	0.925	0.082	0.30	103.8	-4.8
trien	303	0.980	0.073	0.16	183.9	-6.5
	313	0.931	0.139	0.29	185.2	-6.4
	323	0.938	0.121	0.27	169.8	-6.1
	333	0.954	0.098	0.24	161.8	-5.8
tetren	303	0.961	0.090	0.22	-163.5	-1.2
	313	0.968	0.150	0.20	-205.2	-0.3
	323	0.900	0.183	0.38	-176.5	-0.5
	333	0.942	0.091	0.26	-133.2	-0.9

r = correlation coefficient, sd = standard deviation, Ψ = Exner's statistical parameter.

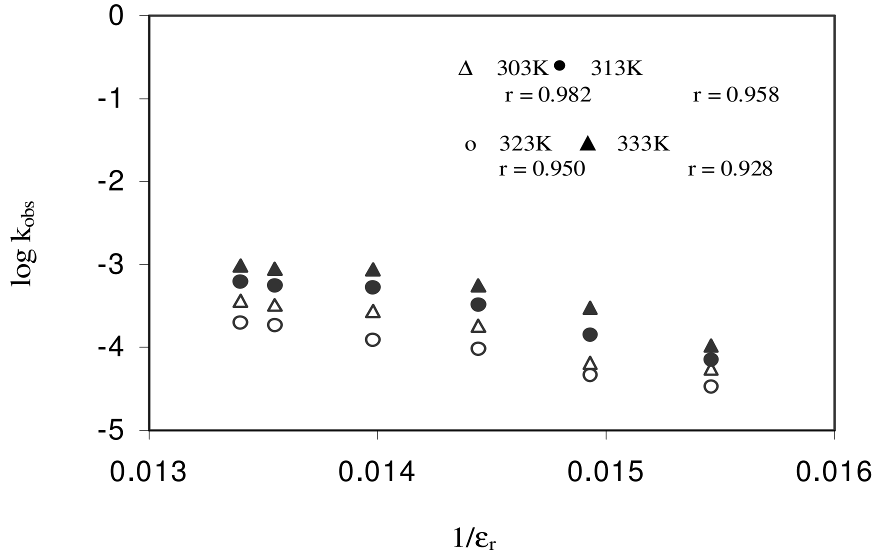


Figure 5. Plot of log k_{obs} versus $1/\varepsilon_r$ for the aquation of $[Cr(en)_2Cl_2]Cl$ in water-methanol at four different temperatures.

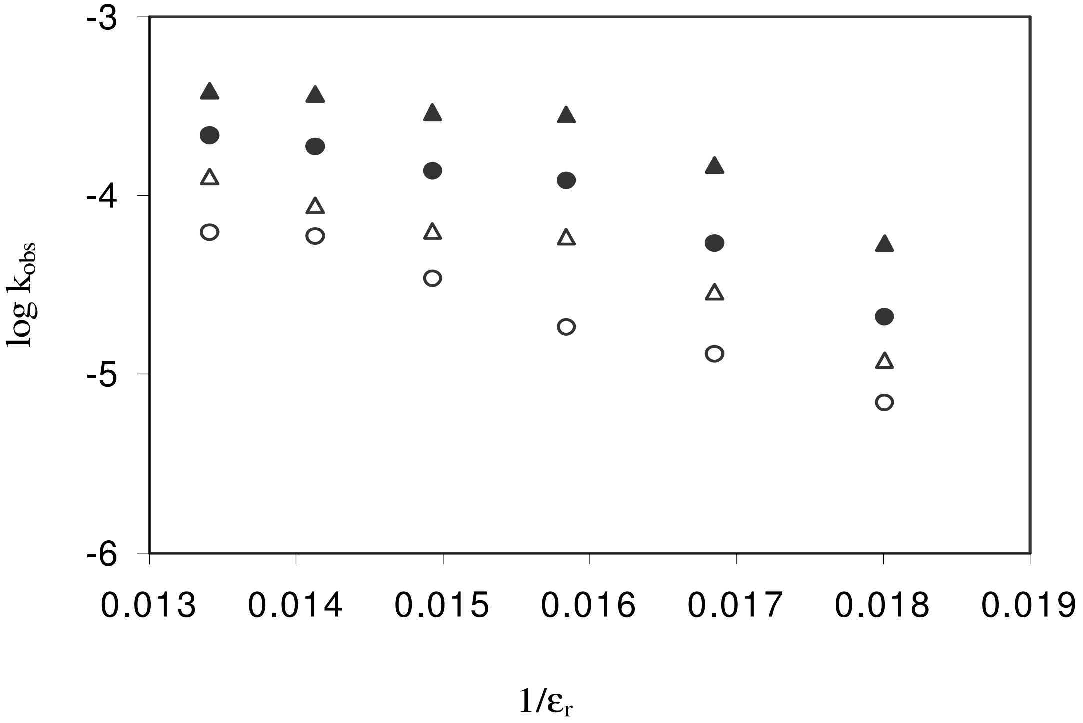


Figure 6. Plot of log k_{obs} versus $1/\varepsilon_r$ for the aquation of $[Cr(en)_2Cl_2]Cl$ in water - 1,4-dioxane at four different temperatures

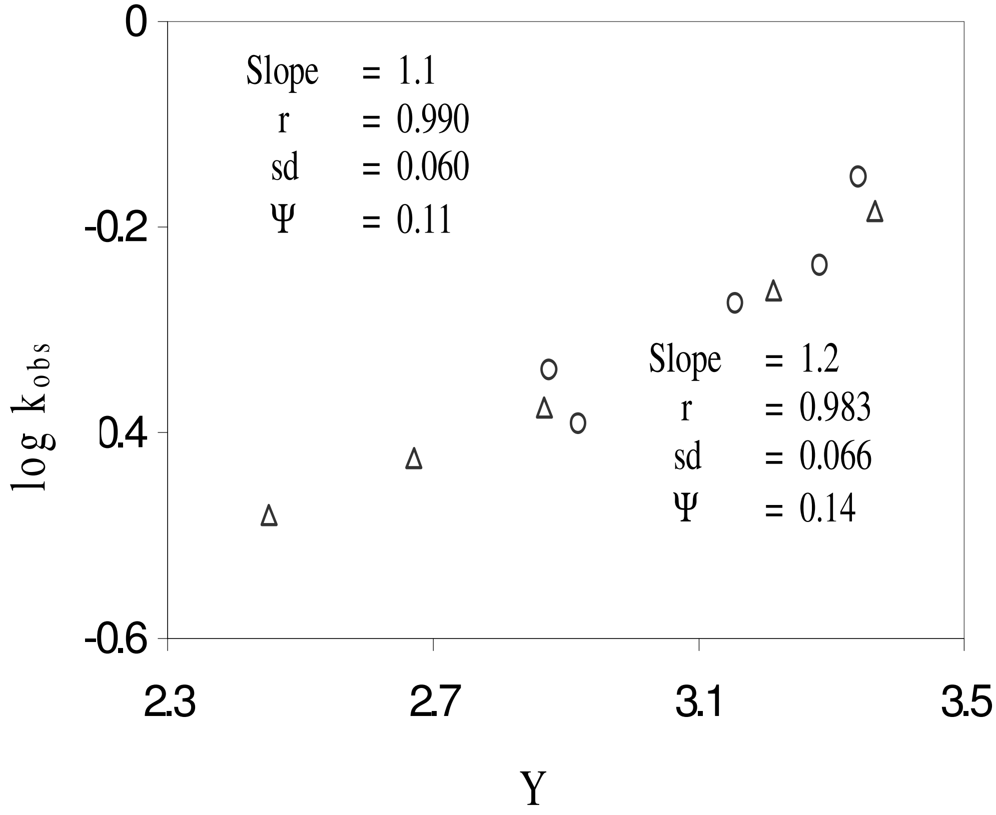


Figure 7. Plot of log k_{obs} versus Grunwand-Winstein parameter, Y for the aquation of $[Cr(en_2)Cl_2]Cl$ in water- methanol (o) and water - 1, 4 - dioxane (Δ) mixtures at 303K.

Table 11. Statistical results of Grunwald-Winstein plot for the aquation reaction of $[Cr(N)_xCl_y]^{(3-y)+}$ complexes in water - methanol mixtures at different temperatures.

$(N)_x$	Statistical parameter					
	Temp (K)	**r**	**sd**	**Ψ**	**Slope**	**Intercept**
$(en)_2$	303	0.983	0.066	0.14	1.2	-7.8
	313	0.958	0.115	0.22	1.4	-7.9
	323	0.951	0.133	0.24	1.4	-7.9
	333	0.928	0.157	0.29	1.4	-7.5
$(pn)_2$	303	0.971	0.106	0.19	1.5	-9.6
	313	0.900	0.179	0.35	1.3	-8.6
	323	0.900	0.179	0.36	1.2	-8.4
	333	0.951	0.168	0.24	1.2	-7.9
$(tn)_2$	303	0.981	0.078	0.15	-1.4	0.1
	313	0.900	0.116	0.37	-1.0	0.8
	323	0.954	0.097	0.23	-1.1	0.1
	333	0.938	0.112	0.27	-1.1	0.1
dien	303	0.992	0.039	0.10	1.1	-8.1
	313	0.986	0.048	0.13	1.0	-7.3
	323	0.934	0.105	0.28	0.9	-7.1
	333	0.960	0.097	0.22	1.1	-7.4
trien	303	0.938	0.066	0.27	0.6	-6.7
	313	0.920	0.101	0.31	0.8	-7.0
	323	0.961	0.074	0.22	0.9	-6.9
	333	0.956	0.071	0.23	0.8	-6.3
tetren	303	0.968	0.022	0.20	-0.3	-2.6
	313	0.982	0.053	0.15	-0.6	-1.5
	323	0.930	0.100	0.29	-0.9	-0.3
	333	0.915	0.088	0.12	-0.6	-1.0

r = correlation coefficient, sd = standard deviation, Ψ = Exner's statistical parameter.

$\log k_{obs} = aA + bB + c$

where A and B represent the anion-solvating power and cation-solvating power of the solvent respectively and c is the intercept term. In order to throw light on solvation effect, the bi-parametric equation employing Swain's solvent vectors A and B were used. To test the significance of anion-solvating and cation-solvating tendencies in the aquation reaction of $[Cr(en)_2Cl_2]Cl$ in water-methanol (Equation 27) and in water - 1,4 – dioxane (Equation 28), multiple linear regression analysis was carried out at 303 K .

$$\log k_{obs} = - 1571\ A + 778\ B + 769.5 \qquad (27)$$

($R^2 = 0.981$, sd = 0.056, $\Psi = 0.15$, n = 6, Temp. = 303 K, water-methanol)

$$\log k_{obs} = 53.5\ A - 89.2\ B + 31.8 \qquad (28)$$

($R^2 = 0.980$, sd = 0.069, $\Psi = 0.15$, n = 6, Temp. = 303 K, water - 1, 4 -dioxane)

Therefore, the properties A and B appear to mimic the solvation effects in the reaction rate better than does the bulk property ε_r. The statistical results are presented in Tables 13 and 14, which contain estimates of the percentage contributions by solvent through anion-solvating and cation - solvating abilities. In majority of the cases, the value of P(A) ≈ 56% (27 to 69) and P(B) ≈ 44% (31 to 73) presumably indicate specific solvation effects, which appear to be important at all temperatures under study. The values of P(A) are consistent with the fact that the stabilizing effect of the medium on the transition state is much greater due to anion-solvating

Table 12. Statistical results of Grunwald-Winstein plot for the aquation reaction of $[Cr(N)_xCl_y]^{(3-y)+}$ complexes in water - 1,4 - dioxane mixtures at different temperatures.

$(N)_x$	Statistical parameter					
	Temp (K)	r	sd	Ψ	Slope	Intercept
$(en)_2$	303	0.990	0.060	0.11	1.1	-7.9
	313	0.971	0.099	0.19	1.1	-7.4
	323	0.955	0.128	0.23	1.1	-7.2
	333	0.918	0.145	0.31	0.9	-6.3
$(pn)_2$	303	0.950	0.116	0.24	-0.9	-0.9
	313	0.962	0.120	0.31	-1.1	-0.2
	323	0.964	0.104	0.20	-0.9	-0.3
	333	0.953	0.105	0.24	-0.7	-0.6
$(tn)_2$	303	0.989	0.054	0.11	0.9	-7.9
	313	0.988	0.269	0.12	1.0	-8.1
	323	0.954	0.371	0.24	1.1	-8.0
	333	0.981	0.081	0.15	1.1	-7.6
dien	303	0.943	0.080	0.26	-0.6	-1.7
	313	0.966	0.059	0.20	-0.6	-1.7
	323	0.983	0.034	0.14	-0.5	-1.7
	333	0.927	0.081	0.30	-0.5	-1.6
trien	303	0.910	0.068	0.33	-0.8	-1.3
	313	0.938	0.133	0.27	-0.9	-0.7
	323	0.944	0.115	0.26	-0.9	-0.9
	333	0.959	0.092	0.22	-0.8	-0.9
tetren	303	0.966	0.085	0.20	0.8	-6.2
	313	0.971	0.151	0.19	1.0	-6.5
	323	0.900	0.179	0.37	0.9	-5.9
	333	0.945	0.089	0.26	0.7	-4.9

r = correlation coefficient, sd = standard deviation, Ψ = Exner's statistical parameter.

ability.

The positive or negative values of the coefficients a and b indicate either direct or indirect interactions of solvent on reactants / transition state. On the contrary, the stabilization of seven coordinated intermediate is influenced by solvation due to cation - solvating strength of solvent as found from P(B) ≈ 73% (52 to 93) and P(A) = 27 % (7 to 48) in water-1,4-dioxane binary mixtures.

The change in the activation barrier $\delta\Delta G^{\#}$ for the complexes from water to water-organic co solvent can be interpreted using a familiar multivariate LSER as in Equation 29. It seems reasonable to use the excess Gibbs free energy (G^E) of the mixtures as an adequate solvent parameter to consider the influence of the disruption and reorganization of the solvent-solvent interactions on reactivity.

Thus, we use the following multiparameter regression to rationalize the observed medium effects. All the complexes show good correlation as given by Equation 29.

$$\delta\Delta G^{\#} = a\delta A + b\delta B + cG^E \qquad (29)$$

where $\delta\Delta G^{\#} = \Delta G^{\#}_{\text{mixture}} - \Delta G^{\#}_{\text{pure water}}$, $\delta A = A_{\text{mixture}} - A_{\text{pure water}}$, $\delta B = B_{\text{mixture}} - B_{\text{water}}$.

The Gibb's excess free energy function G^E, often taken as an indicative of the solvent structure, exhibits a satisfactory linear plot with log k_{obs}. The correlation points the role of significance of structure on reactant, $[Cr(N)_xCl_y]^{(3-y)+}$ / transition state, $[Cr(N)_xCl_y(H_2O)]^{(3-y)+}$. Thus values of G^E for the water-methanol/ 1,4 -dioxane mixtures, used in the present study, were calculated as described in the literature. The $\delta\Delta G^{\#}$ values evaluated for

Table 13. Statistical results coefficients and weighted contributions of solvent parameters in Swain's equation for the aquation reaction of $[Cr(N)_xCl_y]^{(3-y)+}$ complexes in water- methanol mixtures at different temperatures.

$(N)_x$	Statistical parameter								
	Temp (K)	R^2	**sd**	**Ψ**	**a**	**b**	**P(A)**	**P(B)**	**Intercept**
$(en)_2$	303	0.981	0.056	0.15	-1571	778	67	33	769.5
	313	0.935	0.118	0.03	-1853	941	66	34	909.6
	323	0.901	0.155	0.34	-202	115	64	36	83.8
	333	0.862	0.179	0.41	945	-459	67	33	-488.2
$(pn)_2$	303	0.944	0.121	0.26	-220	125	64	36	90.4
	313	0.805	0.205	0.48	229	-102	69	31	-131.2
	323	0.825	0.192	0.46	-2233	1129	66	34	1099.5
	333	0.907	0.124	0.33	-250	119	64	36	91.6
$(tn)_2$	303	0.958	0.094	0.22	131	-360	27	73	225.6
	313	0.934	0.915	0.28	31934	17504	65	35	-40519
	323	0.920	0.106	0.31	-211	489	30	70	-281.2
	333	0.886	0.126	0.37	-76	156	33	67	-83.4
dien	303	0.992	0.037	0.98	906	-442	67	33	-468.0
	313	0.976	0.050	0.17	-758	389	66	34	365.0
	323	0.945	0.079	0.15	-2711	1366	67	33	1341.2
	333	0.969	0.068	0.19	-2660	1342	66	34	1314.3
trien	303	0.921	0.061	0.31	1311	-650	67	33	-665.8
	313	0.909	0.089	0.33	2200	-1092	67	33	-1111.5
	323	0.939	0.076	0.33	1182	-583	67	33	-603.4
	333	0.914	0.081	0.32	380	-182	62	38	-201.2
tetren	303	0.939	0.025	0.27	73	-39	65	35	-37.1
	313	0.971	0.033	0.19	-439	214	67	33	221.5
	323	0.899	0.099	0.35	-1716	850	67	33	862.9
	333	0.842	0.099	0.56	-489	240	67	33	246.2

R2 = coefficient of multiple determination; sd = standard deviation; Ψ =Exner's statistical parameter; a and b = coefficients of A and B in equation 6; P(A) and P(B) = weighted percentage contributions.

the aquation of chromium (III) - alkyl amine complexes in both the binary mixtures were analyzed using the above equation and the statistical results are presented in (Table 15).

The positive or less negative coefficient of G^E over the entire range of composition in mixed solvent is destabilized relative to pure solvents. It may be inferred that the destabilization of solvent structure results in rate acceleration. The transition state is less hydrophilic than the initial state hence, more stabilized resulting in rate acceleration. Such a transition state will more easily be attained with increase in mole fraction of organic solvent in the mixture; hence, the observed increase in rate with increase in proportion of added organic co solvent.

This is in line with the results of Grunwald - Winstein's mY plot. The signs of the coefficients a and b of the parameters A and B could be explained on the basis of influence of acidity / basicity of the medium on reaction rate. In order to test the reliability of this analysis $\Delta G^{\#}_{cal}$, calculated from the correlation parameters, were plotted against $\Delta G^{\#}_{exp}$ as illustrated in Figure 8. A good linear correlation has been obtained, with a slope near unity (Table 15).

In order to obtain a deeper insight into the specific co solvent interactions, which influence reactivity, we have tried to adopt the solvatochromic comparison method developed by Kamlet and Taft. The kinetic data were correlated with the solvatochromic parameters α, β and π^* characteristic of the different mixtures in the form of a linear solvation energy relationship:

$$\log k = A_0 + s\pi^* + a\alpha + b\beta$$

Table 14. Statistical results coefficients and weighted contributions of solvent parameters in Swain's equation for the aquation reaction of $[Cr(N)_xCl_y]^{(3-}$complexes in water - 1, 4 -dioxane mixtures at different temperatures.

Complex	**Statistical parameter**								
	Temp (K)	**R^2**	**sd**	**Ψ**	**a**	**b**	**P(A)**	**P(B)**	**Intercept**
$(en)_2$	303	0.980	0.069	0.15	54	-89	37	63	31.8
	313	0.942	0.114	0.26	-12	70	15	85	-61.6
	323	0.913	0.148	0.32	-6	57	10	90	-54
	333	0.843	0.167	0.43	-80	230	26	74	-153
$(pn)_2$	303	0.904	0.133	0.34	87	-249	26	74	158
	313	0.926	0.138	0.29	4	-52	7	93	44.1
	323	0.931	0.119	0.28	96	-274	26	74	174.3
	333	0.914	0.117	0.32	-218	503	30	70	-289
$(tn)_2$	303	0.989	0.058	0.15	196	-447	30	70	246
	313	0.978	0.072	0.16	178	-396	31	69	213
	323	0.914	0.155	0.32	-238	629	27	73	-395
	333	0.965	0.090	0.20	-154	421	27	73	-270
dien	303	0.892	0.091	0.36	114	-304	27	73	185.6
	313	0.939	0.065	0.27	151	-394	28	72	238.9
	323	0.966	0.043	0.20	-15	16	48	52	-4.6
	333	0.874	0.089	0.39	223	-570	28	72	342.8
trien	303	0.968	0.075	0.19	175	-466	27	73	287.1
	313	0.890	0.146	0.36	-359	846	30	70	-491.7
	323	0.909	0.121	0.33	-418	996	30	70	-581.4
	333	0.930	0.099	0.29	-293	689	30	70	-410.0
tetren	303	0.952	0.083	0.24	416	-993	29	71	573.1
	313	0.982	0.062	0.14	7744	-1791	29	71	1044.1
	323	0.962	0.087	0.12	1475	-3594	29	71	2117.1
	333	0.898	0.100	0.35	-141	374	27	73	-235.0

R^2 = coefficient of multiple determination; sd = standard deviation; Ψ = Exner's statistical parameter; a and b = coefficients of A and B in Equation 6 ; P(A) and P(B) = weighted percentage contributions.

where, π^* is an index of solvent bipolarity/polarizability which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is the solvent HBD (hydrogen bond donor) acidity which describes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond, β is the solvent HBA (hydrogen bond acceptor) basicity which provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond, and A_0 is the regression value of the solute property in the reference solvent cyclohexane.

The regression coefficients, s, a, and b measure the relative susceptibilities of the solvent dependent solute property log k_{obs} to the indicated solvent parameter. In the present investigation, LSER is applied on the rate data, for example, log k_{obs} of $[Cr(en)_2Cl_2]Cl$ in aqueous methanolic (Equation 30) and 1,4-dioxane (Equation 31) mixtures at 303 K are illustrated.

$$\log k_{obs} = 1132.1 - 884\,\pi^* + 5.6\alpha - 995\,\beta \qquad (30)$$

R^2 = 0.998, sd = 0.019, Ψ = 0.04, n = 6, water-methanol, Temp. = 303 K

$$\log k_{obs} = 72.9 - 335\,\pi^* + 208\,\alpha + 253\,\beta \qquad (31)$$

R^2 = 0.982, sd = 0.081, Ψ = 0.14, n = 6, water-1, 4-dioxane, Temp. = 303 K

Tables 16 and 17 give the total influences of medium on the aquation of chromium (III)-alkyl amine complexes. A further observation on the rate of reaction in water-

Table 15. Multiple regression coefficients for the aquation reaction of [Cr(N)xCly](3-y)+ complexes in aqua-organic solvent mixtures

$(N)_x$	**$\delta\Delta G^{\#}_{exp} = a\ \delta A + b\delta B\ cG^{E}$**					
	a	**b**	**c**	**R^2**	**sd**	**Ψ**
water - methanol						
$(en)_2$	-23844	2072.44	-11.88	0.929	0.300	0.29
$(pn)_2$	-18596	-162.4	-9.697	0.971	0.551	0.19
$(tn)_2$	-13236	13518	-3.401	0.824	0.991	0.46
dien	3139.5	-3678.3	0.7077	0.997	0.132	0.06
trien	4988.5	-10459	-0.106	0.924	0.480	0.30
tetren	1559.7	914.61	1.0396	0.995	0.064	0.08
water - 1, 4-dioxane						
$(en)_2$	160.93	1677	0.1942	0.989	0.110	0.35
$(pn)_2$	-185.806	8988.5	0.7003	0.931	0.877	0.29
$(tn)_2$	22.766	-350.6	-0.007	0.996	0.193	0.07
dien	-34.233	1080.9	0.0729	0.912	0.581	0.32
trien	-124.234	4868.3	0.3671	0.947	0.707	0.25
tetren	-48.996	8487.2	0.7226	0.955	0.647	0.23

R2 = coefficient of multiple determinations; sd = standard deviation; Ψ = Exner's statistical parameter.

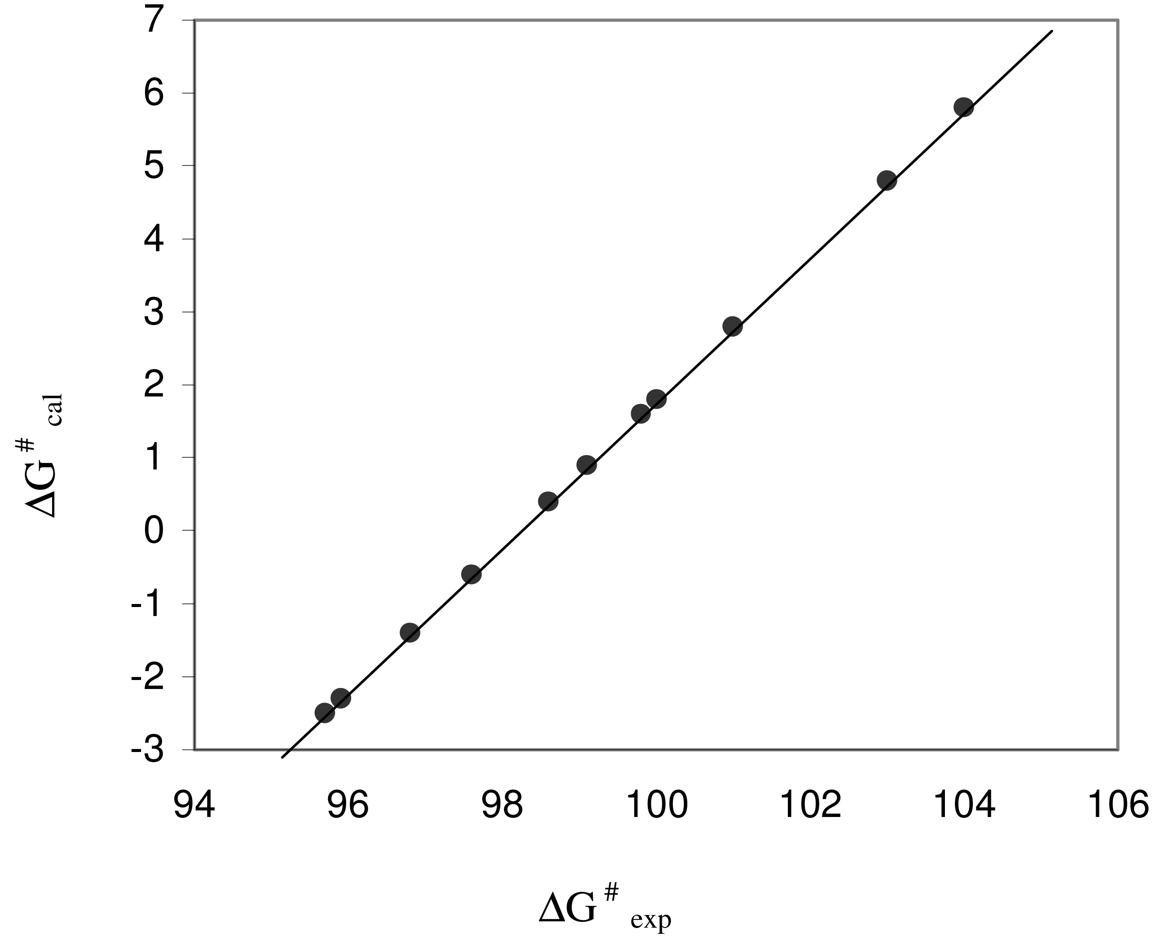


Figure 8. Plot of $\Delta G^{\#}_{cal}$ versus $\Delta G^{\#}_{exp}$ obtained from the aquation of $[Cr(en)_2Cl_2]Cl$ in water-methanol and water-1,4-dioxane mixtures.

Table 16. Statistical results, the coefficients and weighted contributions of solvent parameters in Kamlet - Taft's equation for the aquation of $[Cr(N)_xCl_y]^{(3-y)+}$ complexes in water - methanol mixtures.

$(N)_x$	Statistical parameter										
	Temp (K)	R^2	sd	Ψ	s	a	b	P(π*)	P(α)	P(β)	Intercept
$(en)_2$	303	0.998	0.019	0.04	-884	5.6	-995	47	1	52	1132.1
	313	0.995	0.038	0.07	-1606	255	-1665	46	7	47	1748.6
	323	0.988	0.067	0.12	-1058	-1133	-1812	27	28	45	2802.3
	333	0.982	0.079	0.15	-468	-2096	-1679	11	49	40	3201.0
$(pn)_2$	303	0.977	0.095	0.16	750	654	1174	29	25	46	-1797.7
	313	0.975	0.090	0.17	1252	1704	2309	24	32	44	-3778.6
	323	0.916	0.163	0.32	648	1771	1673	16	43	41	-3083.9
	333	0.972	0.084	0.18	832	730	1311	29	25	46	-2001.2
$[tn)_2$	303	0.992	0.049	0.09	-283	-933	-809	14	46	40	-1541.9
	313	0.984	0.055	0.14	-10168	37478	9207	18	66	16	-34428.5
	323	0.994	0.037	0.09	1326	-140	1412	46	5	49	-1539.2
	333	0.961	0.090	0.22	1087	378	1429	38	13	49	-1888.2
dien	303	0.992	0.040	0.10	401.8	-155.2	350.2	44	17	39	-323.6
	313	0.999	0.012	0.03	-540.2	-221.6	-723.2	36	15	49	976.1
	323	0.895	0.134	0.35	-660.4	199.7	-637.1	44	13	43	597.1
	333	0.978	0.071	0.16	-1072.3	-153.4	-1290.2	43	6	51	1577.0
trien	303	0.942	0.065	0.26	697.4	-194.0	663.6	45	12	43	-567.1
	313	0.972	0.061	0.18	1266.7	-1250.2	719.1	39	39	22	-51.6
	323	0.978	0.056	0.16	566.1	-1103.5	18.3	34	65	1	667.0
	333	0.989	0.035	0.11	121.0	-1132.4	-491.9	7	65	28	1278.1
tetren	303	0.985	0.015	0.13	-141.3	-191.3	-258.3	24	32	44	420.6
	313	0.994	0.020	0.09	-231.2	-275.9	-401.3	25	31	44	643.5
	323	0.942	0.092	0.26	-928.8	1201.9	-368.5	37	48	15	-331.0
	333	0.922	0.067	0.31	-848.6	-341.4	-1125.1	37	14	49	1523.6

R2 = correlation coefficient of multiple regression; sd = standard deviation; Ψ = Exner's statistical parameter; s, a and b = coefficients of Equations 8; P(π*), P(α) and P(β) -weighted percentage contributions.

methanol media may be made from the relative percentage contribution constant. Kamlet triparametric equation explains ≈ 98% of the effect of solvent on substitution. The major contribution is from HBD, and HBA ability of solvent P(α) ≈ 29% and P(β) ≈ 39% in methanol solution. They alone account for 68% of the data. The solvent polarity, P(π*) ≈ 32% plays a relatively minor role. Thus, log k_{obs} versus α, β and π* triparametric equation at various temperatures define solvent molecular and macroscopic properties in altering the rate with changing the concentration of methanol.

Similarly, both general medium and solvation effects in water-1, 4 -dioxane media remarkably influence the intermediate formation and stability. The percentage contribution scales of P(α) ≈ 19%, solvent acidity) and P(β) ≈ 39%, solvent basicity) indicate P(β) the solvent basicity plays more prominent than P(α) in stabilizing the intermediate in water-1, 4-dioxane media. The percentage contribution of π* values accounts P(π*) (≈ 42%, local polarity) relatively higher contribution in the phenolmenon of solvent influence. It means that the polarity of water-1, 4-dioxane solutions contribute extensively in altering the rate of aquation reaction as the mole fraction of 1, 4-dioxane changes. Figure 9 is a typical diagram which depicts the quantitative influence of solvation of transition state, $[Cr(N)_xCl_y(H_2O)]^{(3-y)+}$ due to various medium assistance.

The rate constant values presented in Tables 1 to 4 reveal that all the systems are not equivalent with respect to substitution rate. As a whole the rates of substitution of $[Cr(N)_xCl_y]^{(3-y)+}$ ($(N)_x$ = $(en)_2$, $(tn)_2$, tetren, $(pn)_2$, trien and dien) are quite good indicator of the medium dependence that was obtained for subtle changes in compositions of water-methanol and water-1, 4-dioxane

Table 17. Statistical results, the coefficients and weighted contributions of solvent parameters in Kamlet - Taft's equation for the aquation of $[Cr(N)_xCl_y]^{(3-y)+}$ complexes in water - 1,4 - dioxane mixtures.

$(N)_x$	Statistical parameter										
	Temp (K)	R^2	sd	Ψ	s	a	b	P(π*)	P(α)	P(β)	Intercept
$(en)_2$	303	0.982	0.081	0.14	-335	208	253	42	26	32	72.9
	313	0.999	0.017	0.03	-6262	1974	-5734	45	14	41	5543.8
	323	0.995	0.042	0.07	-7821	2455	7217	45	14	41	6949.0
	333	0.990	0.096	0.11	-8865	2780	-8172	45	14	41	7878.2
$(pn)_2$	303	0.988	0.058	0.12	-7643	24589	-6553	46	15	39	6630.0
	313	0.996	0.039	0.07	-8007	2555	-6984	45	15	40	6991.6
	323	0.999	0.009	0.02	-7616	2479	-6345	46	15	39	6539.7
	333	0.998	0.019	0.04	-4809	1336	-5403	41	12	47	4647.1
$(tn)_2$	303	0.990	0.049	0.11	1679	-435	2042	41	10	49	-1693.7
	313	0.999	0.007	0.02	2772	-737	3282	41	11	48	-2754.5
	323	0.952	0.142	0.24	8265	-2909	5535	50	17	33	-6606.1
	333	0.974	0.096	0.18	3785	-1412	2008	52	20	28	-2839.9
dien	303	0.897	0.109	0.35	-1049.7	455.3	-143.3	64	27	9	633.5
	313	0.989	0.033	0.11	-4452.9	1513.8	-3313.7	48	16	36	3675.5
	323	0.990	0.028	0.11	-1942.5	589.1	-1866.3	45	13	42	1760.4
	333	0.950	0.068	0.25	-5441.5	71863.6	-3976.5	7	88	5	4463.2
trien	303	0.996	0.031	0.07	-5104.1	1700.7	-3992.7	47	16	37	4288.3
	313	0.998	0.024	0.05	-5429.3	1435.2	-6557.7	40	11	49	5415.3
	323	0.994	0.039	0.09	-3571.7	820.8	-5059.2	38	9	53	3839.8
	333	0.990	0.046	0.11	-2615.5	576.3	-3844.4	37	8	55	2864.9
tetren	303	0.991	0.043	0.10	806.6	68.6	2667.3	23	2	75	-1442.9
	313	0.996	0.036	0.06	-1314.5	903.6	1759.6	33	23	44	56.0
	323	0.969	0.096	0.19	-7312.3	3304.7	-510.7	66	30	4	4193.1
	333	0.982	0.051	0.14	6448.7	-2163.4	4987.4	47	16	37	-5398.4

R2 = correlation coefficient of multiple regression; sd = standard deviation; Ψ - Exner's statistical parameter; s, a and b = coefficients of Equations 8; P(π*), P(α) and P(β) = weighted percentage contributions.

solutions. For the complexes, the kinetic and activation data are completely in line with expected associativeness generally established for am(m)ine-chromium(III) complexes. Correlation analysis of the kinetic data illustrates the role of solvation effect in terms of local and long range. Solvent structural perturbations and hydrophobic effect of the organic cosolvent (-CH_3 of CH_3OH and $C_4H_8O_2$ of 1, 4-dioxane) on chemical reactivity. In the series of $[Cr(N)_xCl_y]^{(3-y)+}$ complexes, entropy of activation is more negative indicating ordering on going to the transition state; $\Delta S^\#$ = - 246 (- 287) to - 125 (- 95.9) $JK^{-1}mol^{-1}$ in water/methanol (1, 4-dioxane) solutions, values of $\Delta H^\#$ = 63.4 (63.8) to 20.9 (7.9) kJ mol^{-1} in water/ methanol (1, 4-dioxane) solutions indicate favorable aquation process, that is associatively activated substitution. It is expected that the activation enthalpy, $\Delta H^\#$ would approach the $H_2O....Cr^{III}....N$ bond energy for a predominantly associative process (Benzo et al., 1999). Increase in enthalpy of activation with the x_2 of the medium indicates the combination path. The close resemblance in $\Delta G^\#$ values: 93.7 (61.2) to 105 (106) kJ mol^{-1} illustrate a common mechanism in the substitution. High value of entropy of activation $\Delta G^\#$ and a shift of d-d transition band from λ_{max} at 529.5 to 532.99 nm are consistent with a sequential aquation via associative mechanism. The distinct red shift during the first aquation step indicates nucleophilic attack of water followed by the chelate ring opening which takes place at the Cr – N / Cr – Cl bond. It leads to cationic intermediate $[Cr(en)(enH)Cl_2]^{2+}$. The starting complex ion undergoes nucleophilic attack by water and exists as a seven coordinated intermediate $H_2O....Cr^{III}....$ L (where L is a leaving ligand), stability and concentration of this species is controlled by the solvation shell due to (Scheme 1) (i)

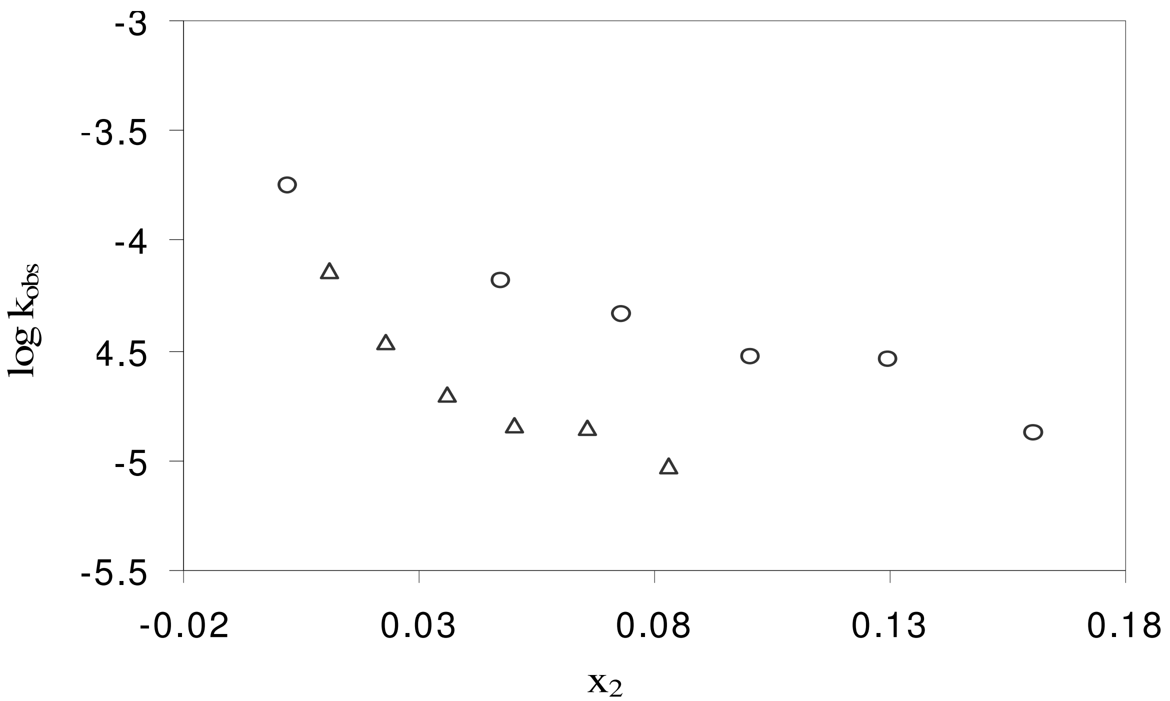
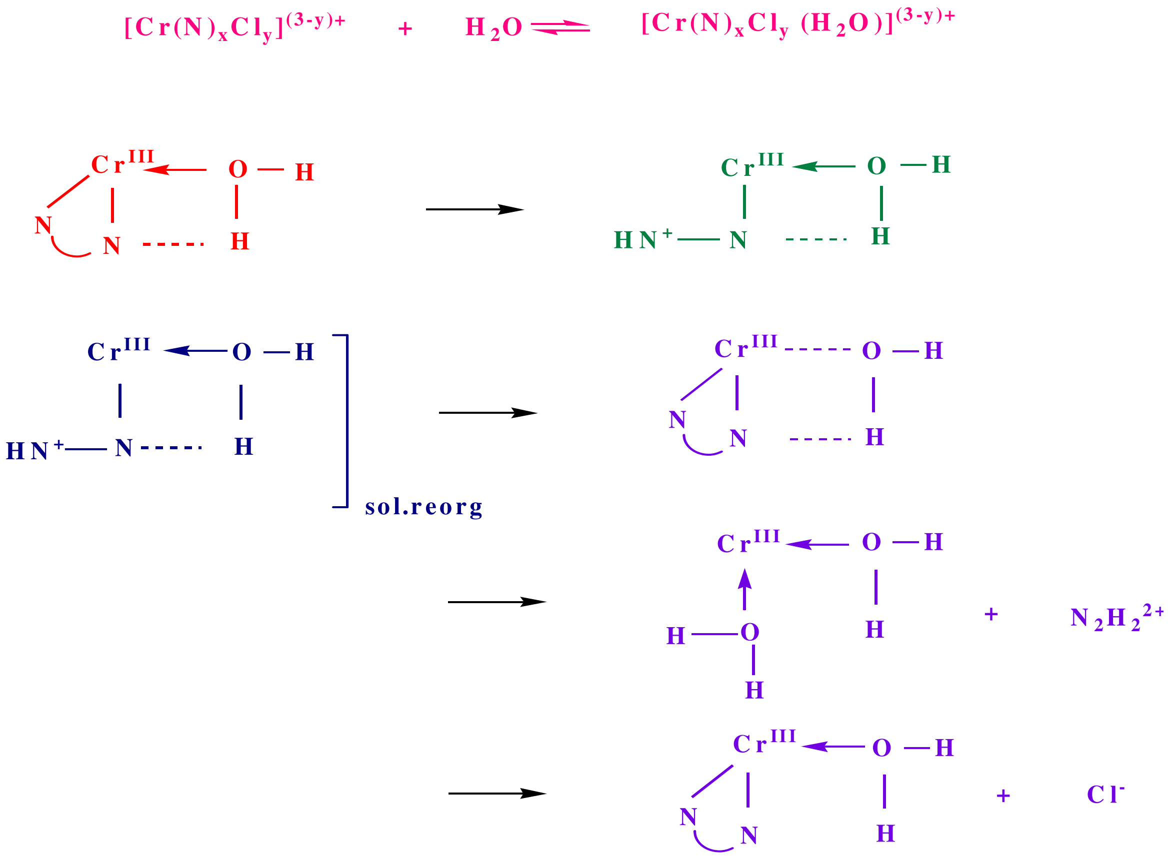


Figure 9. Plot of log k_{obs} versus mole fraction of cosolvent, x_2 , for the aquation of $[Cr(en)_2(C_6H_5NH_2)Cl]Cl_2$ at 303K in water - methanol (o) and water-1, 4-dioxane (Δ) mixtures.



Scheme 1. Probable product distribution from transition state due to concerted solvation shell reorganization.

non-specific, (ii) specific and (iii) hydrophobic effects upon raising the concentration of the organic co solvent in the medium (Tekkaya, 1992).

It can be established that physically concerted geometry of the transition state of the molecule in the solvation shell is either stabilized or destabilized. The intermediate is stabilized in a time scale within which the rupture of Cr^{III} – L bond and formation of Cr^{III} – O bond are facilitated; this results in acceleration of rate with an increase in x_2 of the medium. Conversely, the intermediate is stabilized by solvation effects, which is in equilibrium with the reactant complex ion; however, the steric and geometrical constraints do not afford the H2O....Cr^{III}.... L species to give products. That is, rupture of Cr^{III} – L bond interferes in the formation of Cr^{III} – O bond leading to the shift of equilibrium in such a manner reactant appears in higher concentration than product. Similar steric features were reported in the CO_2 and SO_2 uptake by $[Cr(C_2O_4)(L\text{-}L)(OH_2)_2]^+$ (where L-L denotes bidentate sugar derivative) in multistep reaction mechanism (Jacewicz et al., 2004).

Conclusion

The aquation of all complexes which has been studied in 0.1 M acid solution takes place via associative type mechanism. In case of complexes tn and tetren, the k values increase with the increase in concentration of organic co solvent, MeOH, while the k values decrease with the increase in concentration of 1, 4-dioxane. The other complexes such as pn, trien, and dien show decrease in k values with the increase in concentration of methanol while an opposite trend is observed in 1, 4-dioxane. It is surprising to note that the k values of aquation of the complex en decreases with increase in the concentration of both the solvents methanol and 1, 4-dioxane. No single macroscopic parameter could possibly account for the multitude of solute-solvent interactions on the molecular microscopic level. Thus, bulk solvent properties like the relative permittivity the ionizing power and/or dipolarity/polarizability will poorly describe the micro environment around the reacting species, which governs the stability of the intermediate reaction complex and hence the rate of substitution reaction. Hence during the recent past, a variety of attempts have been made to quantify different aspects of solvent polarity and then to use the resultant parameters to interpret solvent effects on reactivity through multiple regression this kind of aquation reaction is quiet common in biological systems too. Therefore this kind of study will surely be an eye opener for the researchers to carry out this kind of works with other complexes for *in vitro* and *in vivo* studies.

ACKNOWLEDGEMENTS

The author A.R thanks the Principal and the management of Sir Theagaraya College, Chennai-21 for their constant support and encouragement rendered.

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