RASĀYAN *J. Chem.*
Vol. 11 | No. 1 |155-165 | January - March | 2018
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SOLVENT EFFECTS ON OUTER-SPHERE ELECTRON TRANSFER BETWEEN $Co^{III}(L)_3^{3+}$-Fe(II) IONS IN AQUEOUS-ORGANIC SOLVENT MEDIA: A SPECIATION APPROACH

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ABSTRACT

The solvent plays an important role in determining the magnitudes of electron transfer rate constants through the dynamics of changes in solvent dipole orientations. The logic behind the design of the kinetics was detailed by fit the data in correlation equation involving linear and multiple Grunwald-Winstein plots, Swain's dual linear relationship and Kamlet-Taft's equations. The kinetic implications of outer-sphere electron transfer reactions of cobalt(III) alkylamine complexes $[Co^{III}(NH_3)_6]Cl_3$, $[Co^{III}(en)_3]Cl_3$, $[Co^{III}(pn)_3]Cl_3$, $[Co^{III}(tn)_3]Cl_3$, and $[Co^{III}(bn)_3]Cl_3$with MeOH/ Diox solvent content were explored at different temperatures.

Key Words: Solvation, Charge-transfer Reactions, Energy Dynamics, Regression effects.

INTRODUCTION

Studies of the kinetics and mechanism of charge-transfer reactions in condensed phase is an important and intensively developing branch of theoretical chemistry. Electron transfer (ET), the simplest process of this kind, displays in the purest way the role of solvation effects in chemical kinetics. The effect of the solvent on complex equilibria in solution is significantly affected by the donor-strengths of the solvent molecules, and by the properties of the solvate complexes in solution, primarily their stabilities.[1] It is usual to give the donor strengths of the solvent molecules on the basis of the stabilities of the solvate complexes formed with various reference acceptors, their heats of solvation, or the equilibrium constant for the formation of the solvate complex.[2-7] The rate of electron transfer from donor to the acceptor in the solvent is controlled by several factors such as the donor-acceptor separation distance, polarity of the solvent, dynamic property of the solvent, and temperature.[8] Studies on the reduction of $Co^{III}(L)_3^{3+}$ (where L = $(NH_3)_2$, en, pn, tn, and bn) complexes in mixed aqueous-organic cosolvent seems to support the mechanistic trend of electron-transfer of the Co(III)-Fe(II) system through a solvent modified process.

In the present note, the effect of water- methanol/1,4-dioxane on the electron transfer rate between $Co^{III}(L)_3^{3+}$ (where L = $(NH_3)_2$, en, pn, tn, and bn) complexes and $[Fe(CN)_6^{4-}]$ is reported. Both the aprotic solvents with speckled relative permittivities and dipole moments will frame typically aqueous mixtures with water.[9,10] Methanol is a better hydrogen bond donor, HBD, as well as a hydrogen bond acceptor, HBA, solvent; 1,4- dioxane is a better HBA solvent. The relative permittivity reflects long range ion-solvent interactions for a mixture of solvents directly.[11-15]

EXPERIMENTAL

Materials

Cobalt (III) complexes, $Co^{III}(L)_3^{3+}$ (where L = $(NH_3)_2$, en, pn, tn, and bn) were prepared according to the method described in the literature.[16-17] The cobalt (III) complex was first dissolved in doubly distilled water and subsequently, the desired volumes of $NaClO_4$ and $Na_2(H_2\,EDTA)$ were added to obtain 1×10^{-3} M, 0.01 M and 5×10^{-5} M concentrations respectively in the experimental solution. An equimolar solution of $K_4[Fe(CN)_6]$ of 0.05-0.175 M was added to the cell instantaneously using a syringe. The absorbance at 420 nm (an absorption maximum for the formed product $Fe(CN)_6^{3-}$) was recorded as a

http://dx.doi.org/10.7324/RJC.2018.1111770

function of time. All chemicals were of analytical grade and used without further purification. Ultrapure water was used for the preparation of all solutions. The pH was adjusted in the range 6.5-8.0. Pure nitrogen gas was bubbled through the reaction solutions to remove dissolved oxygen. Oxidant solutions were shielded from light with aluminium foil. When not in immediate use, solutions were stored at 4°C in the dark.

Instrumentation

UV-visible spectra were recorded on a Shimadzu UV 420 spectrophotometer with the cell compartment thermostated at 25°C. Electrochemical experiments were performed using potentiostat (CHI 643 B, Texas, USA) controlled by general purpose electrochemical systems and N Graph Software.

RESULTS AND DISCUSSION

Electrochemistry

Concentrations of all complex-ion solutions were typically 3.88×10^{-3} M to 5.60×10^{-3} M and 0.1 M KCl. For all measurements, the three-electrode cell configuration consisted of a 3.0 mm glassy carbon electrode (GCE) disk working electrode, a 1.0 mm platinum wire auxiliary electrode, and an Ag/Ag^+ (0.01 M) reference electrode. The solutions were deoxygenated with solvent-saturated nitrogen before sealing the high-pressure cell. The temperature for all electrochemical measurements was 27.0 ± 0.2°C. The electrochemical method is a useful complement to investigate the reduction character of the metal center of transition metal complexes due to coordination. Figure-1 is the successive cyclic peaks of the cyclic voltammograms of $Co^{III}(tn)_3^{3+}$ in water and in 0.1 M KCl ($\upsilon = 100$ mVs^{-1}). The shift of the redox potential of the complexes from simple NH_3 ligand to longer chain bn indicates a binding interaction and the constraints due to coordination make complexes less readily reducible.[18,19] It indicates the behavior of metallic ion that it is very sensitive to coordination surrounding of the metal center. On this basis, it can be interpreted that $Co^{III}(L)_3^{3+}$ is reduced to give $Co^{II}(L)_3^{2+}$and further reduction is not occurring. The latter observation can be explained due to subsequent lability of the $Co^{II}(L)_3^{2+}$ species.

$$Co^{III}(L)_3^{3+} \quad + \quad e^- \quad \leftrightarrow \quad Co^{II}(L)_3^{2+} \quad \leftrightarrow \quad \text{Products} \qquad (1)$$

A careful analysis of the above results suggests that the electron transferred in reaction 1 is localized on metal showing pronounced changes due to coordinated ligands such as NH_3 to bn.

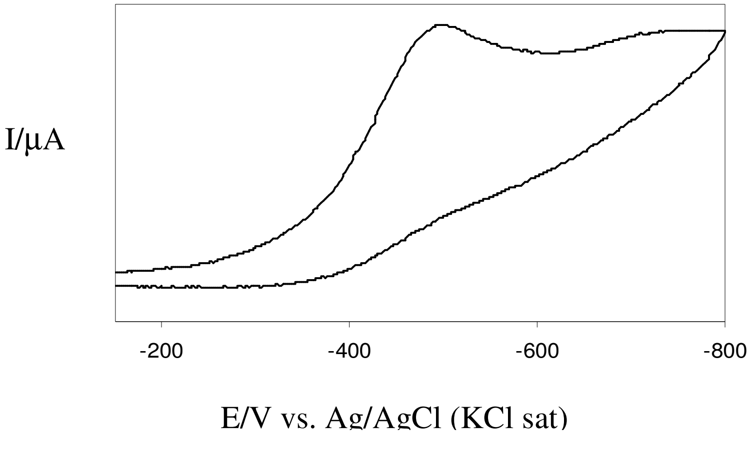

Fig.-1: Cyclic voltammograms obtained at a 3.0 mm glassy carbon electrode for $[Co^{III}(tn)_3]Cl_3$ in 0.1 M KCl with water at 100 mVs^{-1} as a scan rate.

Electronic Absorption

The Spectral changes observed upon the reduction of $Co^{III}(en)_3^{3+}$ by $[Fe(CN)_6^{4-}]$ in 10% methanol solution during the repetitive scan are illustrated in Fig.-2. The rates of reduction of $[Co^{III}(NH_3)_6]Cl_3$, $[Co^{III}(en)_3]Cl_3$, $[Co^{III}(pn)_3]Cl_3$, $[Co^{III}(tn)_3]Cl_3$, and $[Co^{III}(bn)_3]Cl_3$ complexes by $[Fe(CN)_6^{4-}]$ were measured in various water-methanol and water-1,4-dioxane mixtures (0, 5, 10, 15, 20, 25, and 30% (v/v) organic cosolvent) over three temperatures (286, 293 and 300K). Tables 1 and 2 give the pseudo-first-order rate constants, k_{obs}, for $[Co^{III}(en)_3]Cl_3$ in water-methanol/1,4-dioxane. Table 3 gives the pseudo-first-order rate constants, k_{et}, and K_{IP} for the $[Co^{III}(en)_3]Cl_3$ system studied as a function of cosolvent percentage and temperature.

The pseudo first-order rate constant k_{obs} and the electron transfer rate constant, k_{et}, for all the complexes in both the aquo-organic solvent mixtures at three different temperatures increases with increase in mole fraction of the cosolvent in the mixture. The K_{IP} values observed do not show any systematic behavior with the amount of cosolvent. This is a situation often found and the reason is the compensative behavior of the two factors influencing this parameter: (i) the decrease of the dielectric constant would bring about an increase of the K_{IP} values on increasing the amount of organic cosolvent, and (ii) the activity coefficient factor varies causing a change in K_{IP} in the opposite direction. The magnitude of K_{IP} illustrates ion pair formation. More important for the mechanistic interpretations are the values of k_{et} and the associated activation parameters.

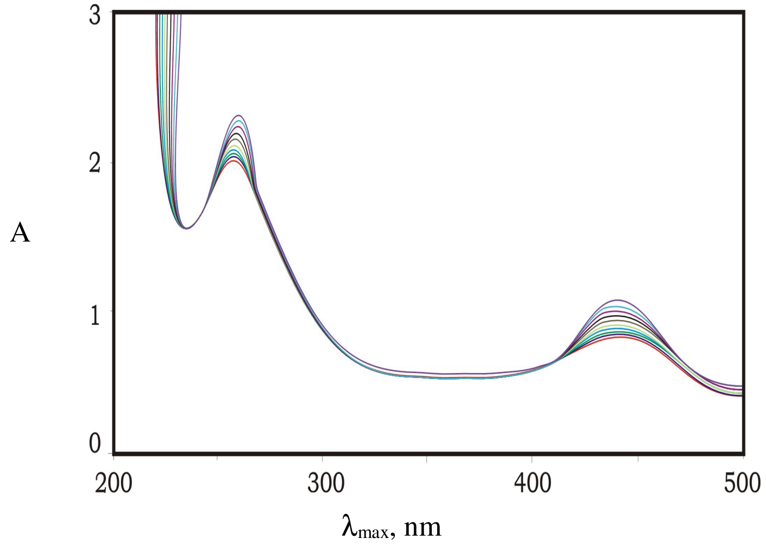

Fig.-2: Repetitive scan spectra for the $[Fe(CN)_6^{4-}]$ reduction of $[Co(en)_3]Cl_3$ in 10% methanolic at 27°C (λ_{max} = 254nm)

Table-1: Pseudo first-order rate constants (10^3 k_{obs}, s^{-1}) for the $[Fe(CN)_6^{4-}]$ reduction of $[Co^{III}(en)_3]Cl_3$ in water-methanol mixtures at different temperatures

$[Fe(CN)_6^{4-}]$ M	Temp (K)	Methanol % (v/v)						
		0	5	10	15	20	25	30
0.05	286	1.309	1.550	1.590	1.620	1.640	1.710	1.772
0.075		1.6711	1.787	1.845	1.878	1.965	2.054	2.088
0.1		1.9062	2.055	2.493	2.887	3.040	3.127	3.243
0.125		2.073	2.329	2.581	3.317	3.768	4.018	4.373
0.15		2.379	2.587	2.730	3.455	3.863	4.352	4.573
0.175		2.595	3.224	3.318	3.574	4.307	4.845	5.089
0.05	293	2.595	2.746	2.901	3.086	3.274	3.487	3.719
0.075		3.042	3.396	3.671	3.926	4.378	5.028	5.394
0.1		3.513	3.722	4.012	4.373	4.955	5.571	5.923
0.125		3.849	4.378	4.833	5.376	6.293	7.310	8.410
0.15		4.373	4.769	5.429	6.219	7.003	7.905	8.636

0.175		5.285	6.035	6.854	7.962	9.050	10.010	11.261
0.05	300	3.894	4.228	4.431	4.883	5.356	6.143	6.807
0.075		4.367	4.787	5.336	6.031	7.003	7.278	7.849
0.1		4.958	5.336	6.013	6.935	7.728	8.446	8.597
0.125		5.371	6.028	7.023	7.770	9.443	10.384	11.211
0.15		6.079	6.794	7.758	9.355	11.186	13.263	14.837
0.175		6.716	8.410	10.132	12.690	16.722	27.624	33.670

Table-2: Pseudo first-order rate constants (10^3 k_{obs}, s^{-1}) for the [$Fe(CN)_6^{4-}$] reduction of [$Co^{III}(en)_3$]Cl_3 in water-1,4-dioxane mixtures at different temperatures

[$Fe(CN)_6^{4-}$] M	Temp (K)	1,4-dioxane % (v/v)						
		0	5	10	15	20	25	30
0.05	286	1.309	1.335	1.362	1.385	1.429	1.481	1.514
0.075		1.6711	1.727	1.798	1.891	2.044	2.256	2.3445
0.1		1.9062	2.030	2.090	2.189	2.333	2.524	2.585
0.125		2.073	2.469	2.786	3.042	3.373	3.650	3.909
0.15		2.379	2.568	3.031	3.317	3.455	3.729	3.983
0.175		2.595	2.786	3.373	3.685	3.771	3.858	4.314
0.05	293	2.595	2.819	3.064	3.274	3.489	3.761	4.078
0.075		3.042	3.138	3.455	3.745	4.057	4.476	4.885
0.1		3.513	3.768	4.057	4.355	4.955	5.414	6.046
0.125		3.849	4.170	4.888	5.420	5.889	6.964	7.758
0.15		4.373	4.948	6.250	6.734	7.880	9.461	10.582
0.175		5.285	5.727	7.384	8.897	10.560	12.285	14.045
0.05	300	3.894	4.054	4.417	4.85	5.336	6.181	7.032
0.075		4.367	4.359	4.780	5.336	5.910	6.321	6.826
0.1		4.958	5.092	5.737	6.402	7.210	8.006	8.734
0.125		5.371	6.090	7.418	9.200	10.363	11.442	12.674
0.15		6.079	6.748	8.425	10.373	13.351	16.750	20.040
0.175		6.716	7.758	9.399	11.468	18.215	21.368	26.738

Activation Parameters

The thermal activation parameters for the reaction of $Co^{III}(en)_3^{3+}$ with [$Fe(CN)_6^{4-}$] in different aqueous-organic solvent medium (methanol/1,4-dioxane) are assembled in Table 4, and are derived from the primary data compiled. The rate was studied at three different temperatures viz., 286, 293 and 300 K in order to obtain the thermodynamic parameters for the reaction between $Co^{III}(L)_3^{3+}$ and Fe(II) in water-methanol/(1,4-dioxane) mixtures and the values are; $\Delta H^{\#}$ = 3.431 to 36.699(5.023 to 34.154) kJ mol^{-1}; -$\Delta S^{\#}$ = 66.43 to 185.85(75.09 to 173.13) $JK^{-1}mol^{-1}$; $\Delta G^{\#}$ = 19.892 to 55.752(25.522 to 51.934) kJ mol^{-1}. For model $Co^{III}(pn)_3^{3+}$ towards methanol as seen from the values, the decrease in $\Delta H^{\#}$ with increasing solvent compositions was due to the electrostatic attraction between the reactant species. The pseudo first-order kinetics and the large negative $\Delta S^{\#}$ obtained for the reduction of $Co^{III}(L)_3^{3+}$ are consistent with ion-pair formation mechanism. The decrease in the values of the enthalpy and entropy of activation with decreasing polarity of the medium can be explained by the fact that a medium of lower relative permittivity enhances rate favoring the outer sphere association between the reactants. It is worth emphasizing that the sign and magnitude of activation entropy and enthalpy are consistent with an associative/ion-pair formation mechanism in the transition state. The sensitivity of $\Delta S^{\#}$ value suggests that ion-pair formation involving approaching of $Fe(CN)_6^{4-}$ to $Co^{III}(L)_3^{3+}$ is facilitated at higher concentration of organic co-solvent in the media. In other words, the electron transfer is "entropy controlled". Moreover the higher negative $\Delta S^{\#}$ values[21] observed in this reduction reaction can be interpreted on the basis of an increase in solvation due to charge distribution in going from the precursor ion-pair to the successor ion-pair.

The overall values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ may be taken to be composites of the reaction components ($\Delta X^{\neq}_{overall} = \Delta X^{\neq}_{R} + \Delta X^{\neq}_{S}$). The low $\Delta H^{\neq}$ values and large negative $\Delta S^{\neq}$ values suggested an associative mechanism. It has been noted that $\Delta G^{\neq}$ changes smoothly and gradually as the solvent composition changes. This behavior contradicts with those of $\Delta H^{\neq}$, $\Delta S^{\neq}$ because these quantities often vary in an erratic manner, but usually changes so as to minimize changes in $\Delta G^{\neq}$. The entropy of activation is believed to reflect ordering of solvent molecules in the transition state relative to that of the initial state.[21]

Table-3: Pseudo-first order electron transfer rate constants ($10^3 k_{et}, s^{-1}$) and the ion pair formation constants (K_{IP}, $mol^{-1}\ dm^3$) for the $[Fe(CN)_6]^{4-}$ reduction of $[Co(en)_3]Cl_3$ in water-methanol/1,4-dioxane mixtures at different temperatures

	Temp (K)	Methanol % (v/v)						
		0	5	10	15	20	25	30
k_{et}	286	3.897±0.01	4.192±0.03	4.987±0.03	8.539±0.05	15.220±0.06	22.286±0.07	27.855±0.08
K_{IP}		9.984±0.03	10.940±0.03	8.950±0.05	4.486±0.06	2.313±0.07	1.579±0.08	1.286±0.09
k_{et}	293	6.958±0.01	8.326±0.04	10.309±0.04	13.315±0.05	18.450±0.06	25.510±0.07	33.783±0.08
K_{IP}		11.226±0.03	9.456±0.04	7.519±0.05	5.776±0.06	4.201±0.06	3.161±0.07	2.446±0.08
k_{et}	300	8.305±0.01	10.245±0.02	13.927±0.03	18.726±0.04	29.154±0.06	44.642±0.06	53.821±0.08
K_{IP}		16.493±0.02	13.013±0.03	8.864±0.04	6.675±0.05	4.287±0.06	2.909±0.08	2.616±0.09
1,4-dioxane% (v/v)								
k_{et}	286	3.897±0.01	4.945±0.04	7.622±0.04	10.416±0.05	12.091±0.05	14.388±0.07	20.920±0.07
K_{IP}		9.984±0.03	7.326±0.04	4.245±0.05	3.009±0.05	2.667±0.06	2.332±0.07	1.582±0.09
k_{et}	293	6.958±0.01	7.758±0.03	11.350±0.04	13.966±0.04	19.342±0.06	29.761±0.06	39.525±0.08
K_{IP}		11.226±0.03	10.479±0.04	6.725±0.04	5.593±0.05	4.039±0.06	2.666±0.07	2.126±0.09
k_{et}	300	8.305±0.01	10.152±0.04	14.471±0.04	21.231±0.05	44.843±0.06	53.475±0.06	67.567±0.07
K_{IP}		16.493±0.03	12.012±0.04	7.942±0.05	5.352±0.05	2.423±0.06	2.253±0.07	1.973±0.08

$[Co(III)] = 1 \times 10^{-3}$ M, $[Na_2(H_2EDTA)] = 5 \times 10^{-5}$ M, $[NaClO_4] = 0.01$

Relative Permittivity

Generally, in ion-ion reaction, the electrostatic interactions formulate the utmost contribution[22] to the activation free energy. The relative permittivity (ε_r) was the solvent parameter widely used to measure the electrostatic interactions between the solute and solvent.[23] The influence of solvent relative permittivity on the rate of the reaction was considered in six different water-methanol/1,4-dioxane mixtures (5-30% v/v organic cosolvent) at three different temperatures with six different $Fe(CN)_6^{4-}$ concentrations. It was observed that k_{et} increases with a decrease in relative permittivity of the medium. It is in good agreement with the fact that, the possibility of an association between the charged reactants is favored due to increase in organic component of the medium.

The correlation of log k_{et} versus the inverse of ε_r is satisfactory giving straight lines with positive slopes in both water-methanol/1,4-dioxane mixtures for three different temperatures studied. The statistical results of these plots are given in Table-5, and typical plots are shown in Fig.-3. The positive slope favors an associative mechanism (r*>r).

Table-4: Activation Parameters for the $Fe(CN)_6^{4-}$ reduction of Cobalt (III) complexes in different water-methanol mixtures

Complex	$\Delta X^{\#}$	Methanol % (v/v)					
		5	10	15	20	25	30
$[Co(NH_3)_6]Cl_3$	$\Delta H^{\#}$	3.431	7.403	4.151	7.645	20.054	16.424
	$-\Delta S^{\#}$	185.85	164.88	175.27	162.60	118.96	130.73
	$\Delta G^{\#}$	55.752	49.457	52.576	48.771	35.668	39.203
$[Co(en)_3]Cl_3$	$\Delta H^{\#}$	18.176	20.873	15.767	12.831	13.663	12.912
	$-\Delta S^{\#}$	128.97	118.98	135.19	143.70	139.59	141.37
	$\Delta G^{\#}$	38.673	35.673	40.541	43.096	41.862	42.399
$[Co(pn)_3]Cl_3$	$\Delta H^{\#}$	29.209	21.545	21.677	16.923	10.507	6.562
	$-\Delta S^{\#}$	91.32	115.88	114.15	129.40	150.50	163.44
	$\Delta G^{\#}$	27.367	34.744	34.224	38.804	45.139	49.026
$[Co(tn)_3]Cl_3$	$\Delta H^{\#}$	36.699	25.305	15.332	10.317	10.137	5.645
	$-\Delta S^{\#}$	66.43	103.87	136.20	151.84	151.54	166.02
	$\Delta G^{\#}$	19.892	31.137	40.844	45.542	45.452	49.799
$[Co(bn)_3]Cl_3$	$\Delta H^{\#}$	29.360	20.910	22.790	22.704	20.581	17.776
	$-\Delta S^{\#}$	92.29	119.85	112.30	111.26	116.45	125.00
	$\Delta G^{\#}$	27.657	35.933	33.668	33.356	34.915	37.481
		1,4-dioxane % (v/v)					
$[Co(NH_3)_6]Cl_3$	$\Delta H^{\#}$	12.416	5.533	5.023	6.472	9.594	13.121
	$-\Delta S^{\#}$	149.27	172.03	173.13	167.71	156.39	143.68
	$\Delta G^{\#}$	44.770	51.605	51.934	50.307	46.907	43.091
$[Co(en)_3]Cl_3$	$\Delta H^{\#}$	14.525	12.835	14.199	26.424	26.523	23.554
	$-\Delta S^{\#}$	141.34	145.80	140.12	97.01	95.80	104.93
	$\Delta G^{\#}$	42.387	43.726	42.023	29.078	28.713	31.456
$[Co(pn)_3]Cl_3$	$\Delta H^{\#}$	25.375	19.235	16.436	11.559	11.928	9.039
	$-\Delta S^{\#}$	104.59	124.23	132.36	147.74	145.50	154.23
	$\Delta G^{\#}$	31.352	37.250	39.691	44.312	43.637	46.260
$[Co(tn)_3]Cl_3$	$\Delta H^{\#}$	34.154	17.993	16.484	13.309	12.460	5.371
	$-\Delta S^{\#}$	75.09	128.00	131.86	141.56	143.46	166.73
	$\Delta G^{\#}$	22.491	38.381	39.542	42.453	43.026	50.015
$[Co(bn)_3]Cl_3$	$\Delta H^{\#}$	31.405	26.025	26.178	23.592	18.841	13.231
	$-\Delta S^{\#}$	85.18	101.97	99.90	107.27	122.14	139.88
	$\Delta G^{\#}$	25.522	30.566	29.944	32.159	36.624	41.951

$\Delta H^{\#}$ in kJ mol^{-1}, $\Delta S^{\#}$ in JK^{-1} and $\Delta G^{\#}$ in kJ mol^{-1} at 300 K, [Co(III)] = 1 x 10^{-3} M [Fe(II)] = 0.05 – 0.175 M, $[NaClO_4]$ = 0.01 M, $[Na_2(H_2EDTA)]$ = 5 x 10^{-5} M

To test the significance of relative permittivity in the $Fe(CN)_6^{4-}$ reduction of $[Co^{III}(en)_3]Cl_3$ in water-methanol (eq 2) /water-1,4-dioxane (eq 3), regression analysis was carried out at 300 K with $1/\varepsilon_r$.

$$\log k_{et} = -3.271 + 326.29\ 1/\varepsilon_r \qquad (2)$$

($r^2 = 0.9937$, sd = 0.036, $\Psi = 0.087$, n = 6 and Temp = 300K)

$$\log k_{et} = -1.477 + 188.53\ 1/\varepsilon_r \quad (3)$$
($r^2 = 0.9709$, sd = 0.089, $\Psi = 0.187$, n = 6 and Temp = 300K)

Table-5: Statistical results of the Laidler-Eyring's plot for the $[Fe(CN)_6]^{4-}$ reduction of cobalt(III) - alkylamine complexes in water-methanol mixtures at different temperatures

Complex	Temp (K)	r^2	sd	Ψ	X	I
$[Co(NH_3)_6]Cl_3$	286	0.9432	0.050	0.261	145.93	-0.9833
	293	0.9871	0.032	0.124	206.09	-1.8829
	300	0.9785	0.074	0.161	363.19	-3.9618
$[Co(en)_3]Cl_3$	286	0.9864	0.063	0.128	387.42	-4.4825
	293	0.9990	0.012	0.035	268.82	-2.6205
	300	0.9937	0.036	0.087	326.29	-3.2706
$[Co(pn)_3]Cl_3$	286	0.9847	0.064	0.135	369.52	-4.1975
	293	0.9640	0.082	0.208	306.22	-3.1651
	300	0.9467	0.058	0.253	175.31	-1.0450
$[Co(tn)_3]Cl_3$	286	0.9631	0.138	0.210	507.34	-6.2034
	293	0.9871	0.052	0.124	328.67	-3.4529
	300	0.9857	0.041	0.131	248.93	-2.1482
$[Co(bn)_3]Cl_3$	286	0.9950	0.043	0.077	438.39	-5.4044
	293	0.9920	0.045	0.098	363.41	-4.0745
	300	0.9909	0.048	0.104	366.60	-3.9019

r^2 = correlation coefficient, sd = standard deviation, Ψ = Exner's statistical parameter

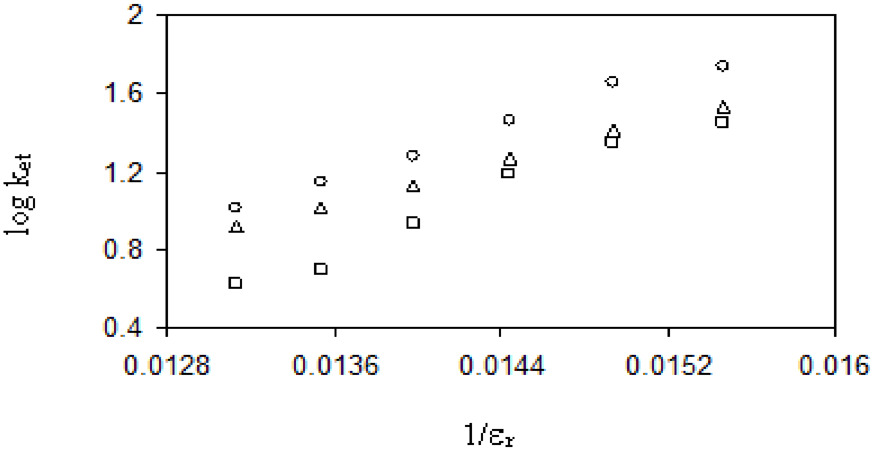

Fig.-3: Plot of $\log k_{et}$ versus $1/\varepsilon_r$ for the $Fe(CN)_6^{4-}$ a reduction of $Co^{III}(en)_3Cl_3$ complex in water-methanol mixtures at three different temperatures.

Specific Solvent Effects

Grunwald-Winstein relations have recently been interpreted as specific solvent effects according to effective nucleophilic participation by solvent molecules from the rear side in the transition state (TS). These results have been evaluated by the extended Grunwald-Winstein equation[24] considering nucleophilic assistance from a solvent. For all the cobalt(III)-alkyl amine complexes at three different temperatures in both the solvent mixtures studied the plots of log k_{et} versus Y are linear with negative slopes (Table-6). The negative value of m indicates a transition state which is less polar than the reactants and narrates associative process for the present complexes which undergo reduction. This type of transition state will simply be established in a medium with lower ionizing power, hence, the increase in k_{et} with an increase in the amount of organic cosolvent added. When log k_{et} values of a cobalt(III)-alkyl amine complex in two binary mixtures of solvents studied are correlated using Grunwald-Winstein equation, the phenomenon of dispersion is observed, that is, lines of different slopes (Fig.-4) are observed for water-methanol and water-1,4-dioxane systems. The occurrence of dispersion phenomenon is due to the different unify of specific/non-specific solvent influences interaction with the solute for the individual solvent pair. The satisfactory correlation of k_{et} with ε_r^{-1} and Y may be understood in terms of solvation phenomenon. The above solvent effect equations involve only one solvent vector, ε_r or Y which appears to be insufficient for the linear free energy correlation in the present context, hence, multiparameter correlation studies are attempted.

Figure-4 is a plot for log k_{et} vs Y (Grunwald-Winstein polarity parameter), corresponds to $[Co^{III}(en)_3]Cl_3$ reduction with $Fe(CN)_6^{4-}$ in water-methanol (eq.-4) /water-1,4-dioxane (eq.-5), regression analysis was carried out at 300 K with Y.

$$\log k_{et} = 4.953-1.160\ Y \text{ (water – methanol)} \quad (4)$$
$(r^2 = 0.9968$, sd = 0.026, $\Psi = 0.062$, n = 6 and Temp = 300K)

$$\log k_{et} = 4.258-0.956\ Y \text{ (water – 1,4-dioxane)} \quad (5)$$
$(r^2 = 0.9746$, sd = 0.084, $\Psi = 0.175$, n = 6 and Temp = 300K)

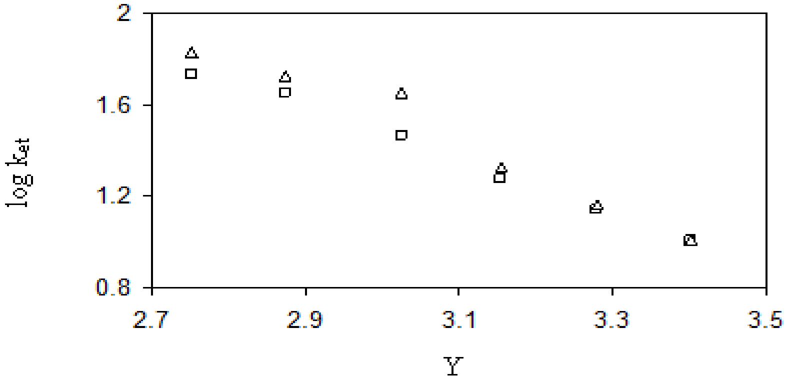

Fig.-4: Plot of log k_{et} versus Y for the $Fe(CN)_6^{4-\,a}$ reduction of $[Co^{III}(en)_3]Cl_3$ complex at 300K in water-methanol (□) and water-1,4-dioxane (Δ) mixtures showing dispersion phenomenon.

Multiparametric Regressions

Swain's Model

The bi-parametric equation employing Swain's solvent vectors A and B narrates solvation effect.[25] The significance of anion solvating and cation-solvating tendencies in the $[Fe(CN)_6^{4-}]$ reduction of $[Co^{III}(en)_3]Cl_3$ in water-methanol (eq.-6) and in water-1,4-dioxane (eq.-7) tested with multiple linear regression analysis was carried out at 300 K along A and B.

$$\log k_{et} = -1.23\ A - 10.19\ B + 12.32 \text{(water – methanol)} \quad (6)$$
$(R^2 = 0.9883$, sd = 0.040, $\Psi = 0.132$, n = 6 and Temp = 300K)

$$\log k_{et} = 61.66A - 188.33\ B + 127.57 \text{ (water – 1,4-dioxane)} \quad (7)$$
$(R^2 = 0.9507$, sd = 0.096, $\Psi = 0.272$, n = 6 and Temp = 300K)

The statistical results are presented in Table-7 comprises the percentage contributions of solvent through anion/cation solvating abilities. For both water-methanol/1,4-dioxane, the stability of ion-pair is influenced by solvation due to the cation-solvating strength of solvent was originate from *P(B)* (43-99) in water-methanol and *P(B)* (50-79) in water-1,4-dioxane >> *P(A)* (1-57) in water-methanol and *P(A)* (21-50) in water-1,4-dioxane mixtures. Hence, ion pairing of $Co^{III}(L)_3^{3+}$ with $[Fe(CN)_6^{4-}]$ is electrostatically more favorable in a binary mixture of water-methanol/1,4-dioxane solutions.

Kamlet-Taft Model

The solvatochromic comparison method may be used to unravel, enumerate, associate and diminish multiple solvent interaction effects on several types of physicochemical properties and reactivities. The specific solvation effects are further discussed using Kamlet-Taft's relationship,[26] which is intended to provide a rationalization of solvent effects on several types of chemical and spectroscopic properties and reactivity parameters, here log k_{et}. The log k_{et} values were interrelated with the solvatochromic parameters (α, β, and π^*).

Table-6: Statistical results of the Grunwald - Winstein plot for the $[Fe(CN)_6]^{4-}$ reduction of cobalt(III) - alkylamine complexes in water-methanol mixtures at different temperatures

Complex	Temp(K)	R^2	sd	Ψ	X	I
$[Co(NH_3)_6]Cl_3$	286	0.9496	0.047	0.246	-0.521	2.7006
	293	0.9804	0.040	0.153	-0.726	3.2893
	300	0.9832	0.066	0.142	-1.294	5.1991
$[Co(en)_3]Cl_3$	286	0.9894	0.055	0.113	-1.378	5.2821
	293	0.9989	0.012	0.036	-0.953	4.1456
	300	0.9968	0.026	0.062	-1.160	4.9534
$[Co(pn)_3]Cl_3$	286	0.9882	0.056	0.119	-1.315	5.1179
	293	0.9711	0.074	0.186	-1.094	4.5672
	300	0.9529	0.055	0.238	-0.626	3.3803
$[Co(tn)_3]Cl_3$	286	0.9679	0.129	0.196	-1.808	6.5943
	293	0.9888	0.048	0.116	-1.167	4.8258
	300	0.9899	0.035	0.110	-0.886	4.1292
$[Co(bn)_3]Cl_3$	286	0.9974	0.031	0.056	-1.558	5.6418
	293	0.9912	0.047	0.103	-1.287	5.0696
	300	0.9938	0.040	0.086	-1.303	5.3374

R^2 = correlation coefficient, sd = standard deviation, Ψ = Exner's statistical parameter

The rates of reduction of all cobalt(III)-alkyl amine complexes studied, in both the solvent mixtures at three different temperatures, show excellent correlation with solvent (Table-8). This kind of correlation relationship is an indication of the existence of both non-specific and specific solvent-solvent-solute interactions. In this work LSER is applied on reaction rate data, for instance, log k_{et} of $[Co^{III}(en)_3]Cl_3$ in methanolic (eq.-8) and in 1,4-dioxane (eq.-9) mixtures at 300 K are illustrated.

$$\log k_{et} = 389.04 + 281.71\,\pi^* - 594.51\alpha + 1.94\beta \text{ (water – methanol)} \tag{8}$$
$$(R^2 = 0.9988,\ sd = 0.015,\ \Psi = 0.049,\ n = 6 \text{ and Temp} = 300K)$$

$$\log k_{et} = 5002.98 - 5742.31\,\pi^* + 1838.05\alpha - 4962.85\beta \text{ (water – 1,4-dioxane)}$$
$$(R^2 = 0.9987,\ sd = 0.019,\ \Psi = 0.051,\ n = 6 \text{ and Temp} = 300K) \tag{9}$$

Table-7: Statistical results, the coefficients and weighted contributions of solvent parameters in Swain's equation for the $[Fe(CN)_6]^{4-}$ reduction of cobalt(III) – alkylamine complexes in water-methanol mixtures at different temperatures

Complex	Temp. (K)	Statistical Parameters							Intercept
		R^2	sd	ψ	a	b	P(A)	P(B)	
$[Co(NH_3)_6]Cl_3$	286	0.9348	0.044	0.312	7.27	-8.83	45	55	2.415
	293	0.9756	0.037	0.191	-2.63	-5.41	33	67	8.800
	300	0.9569	0.086	0.254	-2.60	-10.65	20	80	13.937
$[Co(en)_3]Cl_3$	286	0.9850	0.054	0.150	-9.80	-7.53	57	43	17.834
	293	0.9985	0.012	0.047	-1.64	-8.05	17	83	10.505
	300	0.9883	0.040	0.132	-1.23	-10.19	11	89	12.316
$[Co(pn)_3]Cl_3$	286	0.9795	0.060	0.175	7.48	-16.40	31	69	9.401
	293	0.9311	0.094	0.321	-1.66	-9.29	15	85	11.696
	300	0.9473	0.066	0.281	-0.05	-5.86	1	99	7.007
$[Co(tn)_3]Cl_3$	286	0.9288	0.158	0.327	-0.18	-16.79	1	99	17.245

	293	0.9801	0.053	0.173	-4.55	-8.46	35	65	13.771
	300	0.9728	0.047	0.202	-2.33	-7.01	25	75	10.375
$[Co(bn)_3]Cl_3$	286	0.9928	0.042	0.104	4.81	-17.22	22	78	12.579
	293	0.9833	0.053	0.158	2.62	-13.51	16	84	11.444
	300	0.9871	0.047	0.140	-6.71	-8.52	44	56	16.037

Majority of experimental observations measured in water-methanol mixtures showed that the sign of the coefficient α is positive showing better solvation of ion-pair through HBD interaction, while that of β is negative indicating solvation of the reactants is dominant through HBA interaction. However, all the results do not have a similar sign, there are few deviations. The percentage contribution values calculated from the coefficients of α, β, and π* make it clear that the ion-pair is effectively solvated than the reactants resulting in the larger rate constant values. Though methanol is good HBD as well as a HBA solvent, the results are in favor of better solvation of transition state than reactants through HBD interactions. Similarly, the sign of coefficients values of the π* is both positive and negative indicating the interaction between the solvent and the reactants are more than ion-pair-solvent interactions.

Table-8: Statistical results, the coefficients and weighted contributions of solvent parameters in Kamlet-Taft's equation for the $[Fe(CN)_6]^{4-}$ reduction of cobalt(III) – alkylamine complexes in water-methanol mixtures at different temperatures

Complex	Temp (K)	R^2	sd	Ψ	s	a	b	*P(π*)*	*P(α)*	*P(β)*	Intercept
$XYZ = XYZ_o + s\pi^* + a\alpha + b\beta$											
$[Co(NH_3)_6]Cl_3$	286	0.9216	0.060	0.396	-262.79	-193.62	-392.53	31	23	46	584.498
	293	0.9919	0.026	0.127	-201.92	490.39	50.56	27	66	7	-362.016
	300	0.9970	0.028	0.077	1042.67	1819.77	727.66	40	32	28	-307.68
$[Co(en)_3]Cl_3$	286	0.9939	0.042	0.110	319.93	-977.91	-162.24	22	67	11	825.076
	293	0.9994	0.009	0.035	133.20	-124.96	90.47	38	36	26	-14.461
	300	0.9988	0.015	0.049	281.71	-594.51	1.94	32	67	1	389.044
$[Co(pn)_3]Cl_3$	286	0.9865	0.060	0.164	-375.94	-450.37	-649.91	25	31	44	1054.173
	293	0.9938	0.034	0.111	-268.30	-1089.91	-881.28	12	49	39	1726.968
	300	0.9826	0.034	0.187	-407.19	-524.89	-732.81	24	32	44	1191.022
$[Co(tn)_3]Cl_3$	286	0.9891	0.075	0.148	-1026.93	-1201.36	-1778.88	26	30	44	2845.341
	293	0.9874	0.051	0.159	252.05	-653.52	-63.16	26	67	7	501.979
	300	0.9937	0.027	0.112	-87.10	-530.34	-376.61	9	53	38	784.233
$[Co(bn)_3]Cl_3$	286	0.9929	0.051	0.119	160.37	-390.02	-17.32	28	69	3	284.8144
	293	0.9957	0.033	0.093	401.56	245.75	595.01	32	20	48	-831.744
	300	0.9991	0.015	0.042	579.47	-720.98	266.01	37	46	17	164.808

In water-1,4-dioxane mixtures, nearly half of the coefficients are showing negative values while the remaining are positive for the three parameters showing complexing interactions of the medium with the reactants/transition state. This is because 1,4-dioxane is a typical HBA solvent, which less effectively solvates the reactants/ion-pair through HBA interaction. Also, HBD solvation is hindered by HBA solvation resulting in lower k_{et} values in water-1,4-dioxane mixtures than that found in water-methanol mixtures.

CONCLUSION

A reasonable sensitivity to temperature was observed on the reaction medium ranging from 3-36 kJ mol^{-1} for the enthalpy of activation to the fused rate constant. The $\Delta S^{\neq}$ is having large negative values. The negative entropy of activation is not compatible with rate determining redox mechanism is the significant view in the overall process. Even though an analysis points further towards a rate determining redox reaction mechanism, a clear feature between that and addition rate determination from diffusion mechanism apart of the partners containing successor complex species is not decisively afford by the results. Linear regression model (ε_r and Y) analysis illustrates the implication of medium to that of preferential solvation effects. Multiple regression models (through dual solvent vectors (A and B), solvatochromic parameters (α, β, and π*)) confirms the intricacy of cation/anion solvation of ion-pair. A quantitative analysis (*P(α), P(β)* and *P(π*)*) narrates the relative solvatochromic ability of specific-non-specific solvation effects. By precise correlation methods, the solvation effect on ion-pair/transition state can successfully be explained.

ACKNOWLEDGEMENT

Dr LDS is obliged to the UGC, New Delhi for partial financial support in the form of Major Research Project.

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[RJC-1770/2017]