Thermal Reduction of Co^{III}(pn)$_2$Cl(L)$^{2+}$-Fe(II) Ions in Aqueous-Organic Solvent Medium *via* Outer-Sphere Electron Transfer Approach

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Medium imparts changes in redox reactions of metal complexes. That is, solvent plays an important role in trapping the exchanging electron on one site similar to that of intramolecular structural changes. Especially in ionic reactions, ion can be thought of creating a polarization field in the surrounding solvent. The rationality behind the proposal of the kinetics was detailed by fit the data in correlation equation involving linear and multiple Grunwald-Winstein plot, Swain's dual linear relationship and Kamlet-Taft's equations. The kinetic inferences of outer-sphere electron transfer reactions of cobalt(III) aryl amine complexes (Co^{III}(pn)$_2$Cl(L)$^{2+}$ where L = RC$_6$H$_5$NH$_2$, R = *m*-OCH$_3$, *p*-F and H) with MeOH/dioxane solvent content were explored at different temperatures.

Keywords: Solvation, Electron transfer reactions, Energy dynamics, Regression analysis.

INTRODUCTION

At the molecular level there are three ways that the solvent molecules respond to the electrostatic field of the ion: (1) orientation of permanent solvent dipoles, (2) electrostatically induced structural distortions within the molecule and (3) induced electrostatic polarization of electronic clouds including bonding and nonbonding electron density. The strength of the ion-solvent interaction depends on the charge on the ion. When electron transfer occurs, changes must also occur in the orientation of the surrounding solvent dipoles since the electron transfer acts as the polarization fields when the reactants are interchanged [1-3].

For an outer-sphere reaction there are three factors, which play a role in determining the rate of electron transfer. The first is the approach of the reactants to be sufficiently close proximity to create an electronic interaction, which provides a basis for the 'delocalization' of the exchanging electron [4-6]. The second is a barrier to electron transfer that is created by the equilibrium structural differences between reactants and products. The third is an additional barrier that is created in the surrounding solvent by the change in charge distribution associated with the electron transfer act [7].

In the present communication, the effect of water-methanol/1,4-dioxane on the outer sphere electron transfer rate between Co^{III}(pn)$_2$Cl(L)$^{2+}$ (where L = RC$_6$H$_5$NH$_2$, R = *m*-OCH$_3$, *p*-F and H)complexes and [Fe(CN)$_6$$^{4-}$] is reported. Both the aprotic solvents with spattered relative permittivities and dipole moments will mount typically aqueous blends with water. 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 imitates long range ion-solvent interactions for a mixture of solvents with different temperature which was desired [8-12].

EXPERIMENTAL

Co^{III}(pn)$_2$Cl(L)$^{2+}$ where L = RC$_6$H$_5$NH$_2$, R = *m*-OCH$_3$, *p*-F and H) were prepared from *trans*-Co^{III}(pn)$_2$Cl$_2$$^+$ by literature method [13-15].

UV-visible spectra were recorded on a Shimadzu UV 420 spectrophotometer with the cell compartment thermostated at 25 °C. Electrochemical experiments at scan rate of 100 mV s^{-1} was performed using potentiostat (CHI 643 B, Texas, USA) controlled by general purpose electrochemical systems and N Graph Software. Concentrations of all complex-ion solutions

were typically 1.0×10^{-3} M and 0.1 M KCl. X-ray powder data for the finely ground sample were collected by means of X'PERT PRO-PANalytical XRD diffractometer. The X-ray source was a rotating anode operating at 40 kV and 25 mA with a copper target and graphite monochromatic radiation (λ = 1.5406 Å). Data were collected between 10° to 90° in 2θ with a step size of 0.02° and a scan step time of 0.5 s by continuous scan and a peak picking was conducted.

Data analysis: The electron transfer rate constants, k_{et}, between $Fe(CN)_6^{4-}$ and $Co^{III}(pn)_2Cl(L)^{2+}$ in varying compositions of binary mixtures [5-30 % (v/v) MeOH/dioxane in water] can be probed through various solvent empirical parameters. It is postulated that the solvent effect on a physicochemical quantity can be represented as a linear function of multiple parameters as in equation; $Y_s = Y_0 + a_1X_1 + a_2X_2 + a_3X_3 \ldots a_nX_n$. That is, suitable selection of bulk and molecular properties of solvents such as ε_r, Y, A, B, π^*, α and β constitute linear or multiple regression analysis model. To determine relative importance of different "effects" of explanatory variables, as given by the above equation may be statistically quantified into percentage contribution [P(X_i)]. In order to achieve this, the regression coefficients, which emerge from multiple regression equations are corrected to numerical range between 0-100. Therefore percentage contribution of P(X_i) of a solvent parameter in a multiple regression equation is quantified [15] as in equation P(X_i) = 100 $|a_i|/\Sigma^n_{i=1}|a_i|$ where a_i is the coefficient of ith parameter.

RESULTS AND DISCUSSION

The electronic absorption spectra of $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ in water at 27 °C are shown in Fig. 1. The repetitive scan spectra for the reduction of $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ by $Fe(CN)_6^{4-}$ at 27 °C in 10 % methanol solution are shown in Fig. 2. The first peak is displaced from 274.12 to 278.32 nm (for all other complexes there is a shift of 2.0 to 7 nm in λ_{max} towards longer wavelength, as expected.

Structure refinement: From the X-ray diffraction methods, it is possible to obtain information about different structural characteristics as solid phase, lattice parameters, crystallite size, microstrain, or defect concentration. First of all, the diffraction powder pattern can be qualitatively analyzed comparing the pattern obtained with the ICDD database of known compounds, with it being possible to identify the phase, multiphase mixtures are analyzed and polymorphic mixtures are identified.
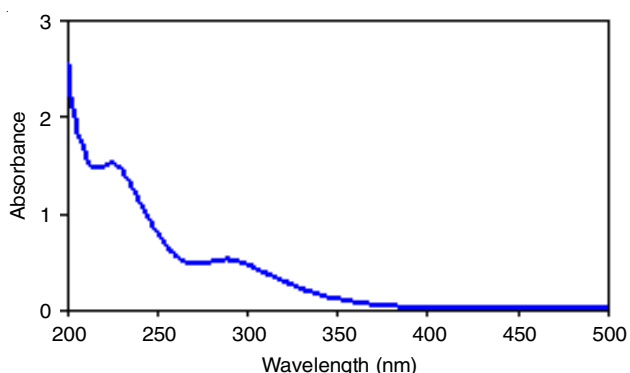

Fig. 1.　Electronic absorption spectra of $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ in water at 27 °C
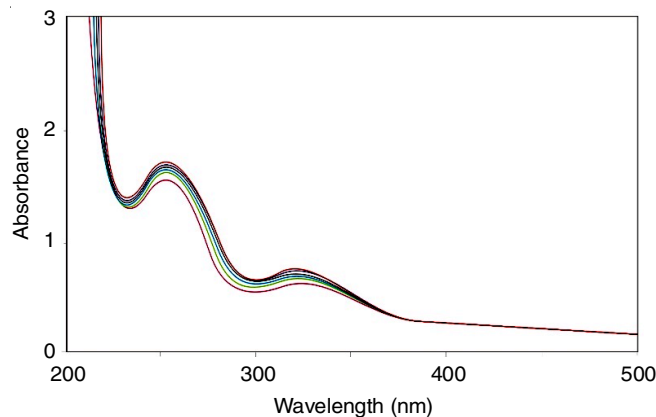
Fig. 2.　Repetitive scan spectra for the reduction of $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ by $Fe(CN)_6^{4-}$ at 27 °C in 10 % methanol solution, (Cycle time: 60 s)

X-ray diffraction pattern of $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ is shown in Fig. 3 as a representative complex. The replacement of H in $C_6H_5NH_2$ with $m\text{-}OCH_3$, p-F and H alters all unit cell parameters. X-ray diffraction study of the cobalt(III) complexes provided evidence regarding the geometry around cobalt(II) ion, distortions in symmetry and configuration effect of ligand $C_6H_5NH_2$ in $Co^{III}(pn)_2Cl(RC_6H_4NH_2)^{2+}$. The structure of $Co^{III}(pn)_2Cl(RC_6H_4NH_2)^{2+}$ was found to be a distorted monoclinic due to organic $RC_6H_4NH_2$ group in the coordination site. Unit cell parameters for $Co^{III}(pn)_2Cl(L)^{2+}$ where L = $RC_6H_5NH_2$, R = $m\text{-}OCH_3$, p-F and H) complexes are presented in Table-1 and are based on our experimental observations.
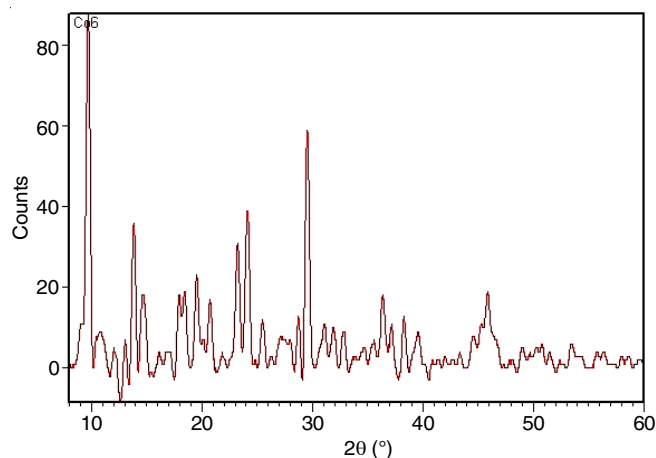
Fig. 3.　XRD pattern for $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ ion containing pattern range (2θ), deg = 5-75 and step scan increment (2θ), deg = 0.02, with step scan time = 1 s using generator settings = 30 mA, 40 kV

Cyclic voltammetry: The voltammograms of Co(III) complexes show the two peaks which correspond to two single electron transfer processes [16]. There is both oxidation and reduction waves appearing in this potential range, suggesting that the complexes are inert. It is also clear that the reactions are indeed dominated by diffusion control. Hence, present results confirmed that the electrochemical reduction is an irreversible diffusion controlled processes.

Therefore the data obtained from the study measurements refer to the E_{pc}, the relative potential at maximum diffusion current for the Co^{III}/Co^{II} and Co^{II}/Co^{I} couple according to the reaction [17].

TABLE-1
UNIT CELL PARAMETERS FOR Co^{III}(pn)$_2$Cl(L)$^{2+}$ WHERE L = RC$_6$H$_5$NH$_2$, R = m-OCH$_3$, p-F AND H) COMPLEXES

R in aniline	a	b	c	β	a*	b*	c*	β *	Volume (Å^3)
m-OCH$_3$	16.29	15.56	20.42	84.53	0.0617	0.0643	0.0492	95.47	5152.51
p-F	10.30	10.39	8.86	79.33	0.0988	0.0963	0.1149	100.67	931.13
H	14.94	13.47	9.35	93.56	0.0670	0.0743	0.1071	86.44	1878.70

The reduction peaks of Co^{III}(pn)$_2$Cl(L)$^{2+}$ are indicating the electron accepting/donating abilities of R of L ligand, that is, m-OCH$_3$ to H in aqueous solution. The electrochemical behaviour of Co(III) complexes is due to the Co^{III}/Co^{II} couples and the negative potential indicates that metal centered reduction [18]. The peak towards negative direction corresponds to Co^{III}/Co^{II} processes, which are irreversible processes.

The observed peak potentials strongly depend on the donor strength of the substituted aniline ligands, since electron affinity of the Co(III) complexes are significantly altered by ligand Lewis base. The cyclic voltammogram of Co^{III}(pn)$_2$(p-FC$_6$H$_4$NH$_2$)Cl^{2+} complex in Fig. 4.

Linear regression: The outer sphere electron transfer between [Co^{III}(pn)$_2$Cl(RC$_6$H$_4$NH$_2$)]$^{2+}$ (where R = m-OCH$_3$, p-F, H, m-CH$_3$, p-CH$_3$, p-OC$_2$H$_5$ and p-OCH$_3$) and Fe(CN)$_6^{4-}$ is delineated as follows:

$$Co^{III}(pn)_2Cl(L)^{2+} + Fe(CN)_6^{4-} \xrightarrow{K_{IP}}$$

$$\{Co^{III}(pn)_2Cl(L)^{2+}:Fe(CN)_6^{4-}\} \qquad (1)$$

$$\downarrow k_{et}$$

$$\{Co^{II}(pn)_2Cl(L)^{2+}:Fe(CN)_6^{3-}\} \qquad (2)$$

$$\downarrow fast$$

$$Co^{II}(pn)_2Cl(L)^{2+} + Fe(CN)_6^{3-} \qquad (3)$$
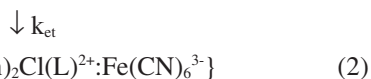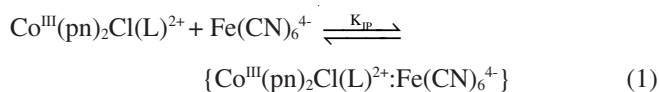
The reduction was found to be very fast, therefore, the reaction was followed under second order conditions. The observed second-order rate constant (k$_{et}$) for the above mechanism is given by eqn. 4:

$$k_2 = k_{et} K_{IP}[Co^{III}(pn)_2Cl(RC_6H_4NH_2)^{2+}] [Fe(CN)_6^{4-}] \qquad (4)$$
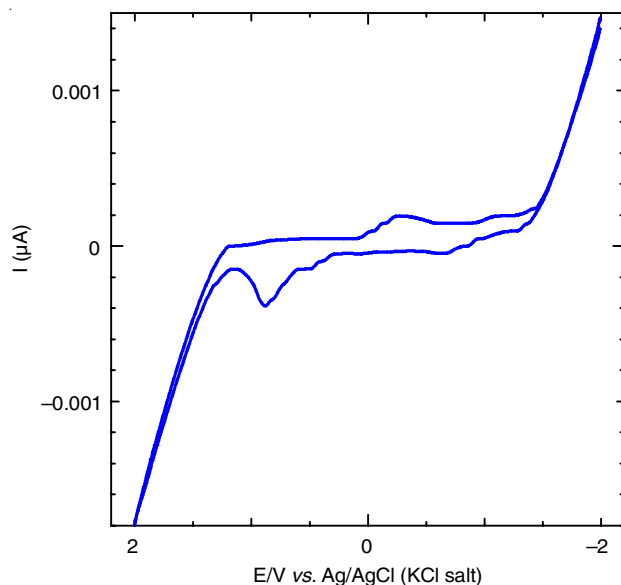
Fig. 4. Cyclic voltammograms obtained at a 3.0 mm glassy carbon electrode for Co^{III}(pn)$_2$(p-FC$_6$H$_4$NH$_2$)Cl^{2+} in 0.1 M KCl with water at 100 mV s^{-1} as a scan rate

Rates were followed in water-methanol and water-1,4-dioxane mixtures at three different temperatures with six different concentrations of [Fe(CN)$_6^{4-}$]. The choice of methanol and 1,4-dioxane were on the basis of their inherent property to be a better HBD/HBA and HBA solvent respectively. The values of rate constants (k$_{et}$) in both water-methanol/dioxane mixtures for model Co^{III}(pn)$_2$Cl(p-FC$_6$H$_4$NH$_2$)$^{2+}$ complex is given in Tables 2-4.

TABLE-2
PSEUDO FIRST ORDER RATE CONSTANTS (10^{2}k$_2$, dm^3 mol^{-1} s^{-1}) FOR [Fe(CN)$_6^{4-}$] REDUCTION OF
Co^{III}(pn)$_2$Cl(p-FC$_6$H$_4$NH$_2$)$^{2+}$ ION IN WATER-METHANOL MIXTURES AT DIFFERENT TEMPERATURES

[Fe(CN)$_6^{4-}$] (M)	Temp. (K)	Methanol % (v/v)						
		0	5	10	15	20	25	30
0.050		1.2421	1.2917	1.3108	1.3537	1.4249	1.4648	1.5017
0.075		1.2708	1.3249	1.3795	1.4249	1.4605	1.5103	1.5562
0.100	286	1.3259	1.5908	1.6966	1.8308	1.9924	2.0568	2.1603
0.125		1.3663	1.6703	2.3326	2.5880	2.9206	3.0321	3.2321
0.150		1.4122	2.2232	3.2394	3.6778	3.8655	4.1649	4.4346
0.175		1.4605	2.4716	3.4795	3.8926	4.2937	4.6577	4.8356
0.050		2.1472	2.5088	2.7137	3.0075	3.1676	3.3535	3.5398
0.075		2.5240	2.7367	2.9525	3.3124	3.4542	3.7679	4.0177
0.100	293	2.7465	3.3478	3.7256	4.3725	4.9529	5.3248	6.1576
0.125		2.8193	4.0048	4.9554	6.0901	6.2617	6.7249	7.3855
0.150		3.0331	4.7125	5.6054	6.4641	7.0225	7.3046	7.6220
0.175		3.4941	4.8685	6.3776	6.9204	8.1037	9.7561	10.1317
0.050		4.8685	5.3362	5.7241	6.4599	7.2098	7.7580	9.0171
0.075		5.1706	5.6529	6.3939	7.3046	8.5837	9.1408	10.1317
0.100	300	5.4735	6.0459	6.9979	8.2102	9.1182	11.5741	13.4953
0.125		5.8754	6.4558	7.9051	9.5329	10.3627	12.5471	14.3062
0.150		6.1690	6.6800	8.7032	10.3627	12.5945	14.2857	16.7224
0.175		6.3735	7.5415	9.8912	11.8765	14.2857	16.3132	19.4553

TABLE-3
PSEUDO FIRST ORDER RATE CONSTANTS ($10^2 k_2$, dm³ mol⁻¹ s⁻¹) FOR [Fe(CN)$_6^{4-}$] REDUCTION OF
Co^{III}(pn)$_2$Cl(p-FC$_6$H$_4$NH$_2$)$^{2+}$ ION 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
0.050	286	1.2421	1.2752	1.3189	1.3189	1.3663	1.4142	1.4548
0.075		1.2708	1.3259	1.3843	1.3843	1.4049	1.4370	1.4872
0.100		1.3259	1.6202	1.9952	1.9952	2.1013	2.1801	2.2941
0.125		1.3663	1.7117	2.5069	2.5069	2.7122	3.0139	3.2373
0.150		1.4122	2.1749	3.6206	3.6206	3.8625	4.0502	4.1719
0.175		1.4605	2.3883	3.7258	3.7258	4.1339	4.3215	4.5086
0.050	293	2.1472	2.5694	2.8082	3.0084	3.0432	3.3135	3.4795
0.075		2.5240	2.8058	3.0111	3.1827	3.2712	3.4916	3.7679
0.100		2.7465	3.4518	3.9777	4.3535	4.8900	5.3648	5.8343
0.125		2.8193	4.3122	4.6104	5.4318	5.7405	5.9207	6.3012
0.150		3.0331	4.8450	6.1538	7.0028	7.3260	8.3752	9.0253
0.175		3.4941	5.0916	6.7249	7.6923	8.0128	9.3110	9.9900
0.050	300	4.8685	5.7208	5.8928	6.5617	7.3638	7.7101	9.5329
0.075		5.1706	6.0459	6.9832	7.7700	8.8968	9.4429	10.3627
0.100		5.4735	6.2578	7.3260	8.5911	10.7643	12.0627	12.7877
0.125		5.8754	7.1582	8.6356	9.7656	12.0337	12.9199	16.6113
0.150		6.1690	7.7042	9.5969	11.3766	13.9860	15.1745	18.7266
0.175		6.3735	8.4818	10.1215	12.5786	14.3266	16.3399	20.0803

TABLE-4
PSEUDO-FIRST ORDER ELECTRON TRANSFER RATE CONSTANTS ($10^3 k_{et}$, s⁻¹) AND THE ION PAIR
FORMATION CONSTANTS (K_{IP}, mol⁻¹ dm³) FOR [Fe(CN)$_6$]$^{4-}$ REDUCTION OF [Co(pn)$_2$Cl(p-FC$_6$H$_4$NH$_2$)]Cl$_2$
IN WATER-METHANOL/1,4-DIOXANE MIXTURES AT DIFFERENT TEMPERATURES

	Temp. (K)	Methanol % (v/v)						
		0	5	10	15	20	25	30
K_{et}	288	1.5163	2.9967	6.9784	10.2775	13.2626	16.6113	21.4592
K_{IP}		81.4198	13.2421	4.0710	2.6878	2.1180	1.7006	1.3276
K_{et}	293	3.6271	7.3746	11.4416	14.6413	18.6916	23.2019	26.9542
K_{IP}		38.8313	9.4167	5.6387	4.7431	3.7413	3.1232	2.7895
K_{et}	300	7.0225	8.0192	11.8624	15.1976	19.0114	25.3165	29.9401
K_{IP}		41.8822	36.6767	17.2041	13.7083	11.6889	8.4042	7.9524
		1,4-Dioxane % (v/v)						
K_{et}	288	1.5163	3.0048	7.2886	10.9649	14.8810	18.9036	23.4742
K_{IP}		81.4198	13.1024	3.7901	2.4450	1.7968	1.4297	1.1736
K_{et}	293	3.6271	7.9936	11.8483	16.1031	20.0803	23.8663	28.0112
K_{IP}		38.8313	8.6875	5.5894	4.1126	3.2549	2.9097	2.5870
K_{et}	300	7.0225	9.2507	13.1406	16.9779	22.9358	28.0112	33.1126
K_{IP}		41.8822	29.2162	15.5036	12.0204	9.0833	7.4375	7.3658

Activation parameters: Variation of the rate constant with the mole fraction of the mixed solvent and 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. The relationship can be expressed mathematically 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 number of moles 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 chemical potential *i.e.*, Gm = $\mu^{\#}$ and hence $\Delta G^* = \Delta\mu^{\#} = -$ RT ln K$^{\#}$, where K$^{\#}$ is the equilibrium constant of the reactant/activated complex equilibrium. This is estimated from the computed values of $\Delta\mu^{\#}$ for the [Fe(CN)$_6^{4-}$] reduction of cobalt(III)aryl amine complexes in water-methanol/1,4-dioxane solvent mixtures at 286, 293 and 300 K. Table-5 illustrate the values of K, which are found to be greater than unity giving a strong evidence of associative mechanism.

The activation parameters such as the $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ for the [Fe(CN)$_6^{4-}$ reduction of cobalt(III) aryl amine complexes

in water-methanol/water-1,4-dioxane were calculated from the slopes and intercept respectively of the Laidler-Eyring plot of log k/T *versus* 1/T and are listed in Table-6. 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}(pn)$_2$Cl(L)$^{2+}$ and Fe(II) in water-methanol mixtures and the values are; $\Delta H^{\#}$ = 6.330 to 60.580 kJ mol⁻¹; $-\Delta S^{\#}$ = 16.95 to 165.05 JK⁻¹ mol⁻¹; $\Delta G^{\#}$ = 17.206 to 138.707 kJ mol⁻¹. For model [Co(pn)$_2$Cl(p-FC$_6$H$_4$NH$_2$)]Cl$_2$, as seen from the values, the decrease in $\Delta H^{\#}$ with increasing in the 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}(pn)$_2$Cl(L)$^{2+}$ 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 the rate favouring the outer sphere association between the reac-

TABLE-5
STATISTICAL RESULTS OF K AND $\Delta\mu^{\#}$ FOR THE THERMAL REDUCTION OF COBALT(III) ARYLAMINE
COMPLEXES IN AQUEOUS - METHANOL MIXTURES AT DIFFERENT TEMPERATURES

R in aniline	Temp. (K)	R^2	sd	ψ	$\Delta?^{\#}$	K
m-OCH$_3$	286	0.9913	0.0017	0.162	-299	1.386
	293	0.9840	0.0023	0.219	-488	1.669
	300	0.9739	0.0029	0.280	-476	1.755
p-F	286	0.9593	0.0036	0.349	-359	1.477
	293	0.9855	0.0022	0.209	-544	1.766
	300	0.9935	0.0015	0.140	-538	1.774
H	286	0.9877	0.0020	0.192	-388	1.469
	293	0.9742	0.0029	0.278	-531	1.710
	300	0.9811	0.0025	0.238	-665	1.992

R^2 – Correlation coefficient, sd – standard deviation, ψ – Exner's statistical parameter

TABLE-6
ACTIVATION PARAMETERS FOR $Fe(CN)_6^{4-}$ REDUCTION OF COBALT(III)
COMPLEXES IN DIFFERENT WATER- METHANOL MIXTURES

R in aniline	$\Delta X^{\#}$	Methanol % (v/v)					
		5	10	15	20	25	30
m-OCH$_3$	$\Delta H^{\#}$	27.774	28.566	21.729	18.880	13.684	11.266
	$-\Delta S^{\#}$	92.68	94.75	57.43	123.62	140.32	148.01
	$\Delta G^{\#}$	27.774	28.395	17.206	37.067	42.083	44.392
p-F	$\Delta H^{\#}$	20.146	10.631	7.682	6.993	8.199	6.330
	$-\Delta S^{\#}$	123.03	153.63	162.708	164.25	159.32	165.05
	$\Delta G^{\#}$	36.890	46.079	48.805	49.268	47.786	49.513
H	$\Delta H^{\#}$	60.580	23.486	21.561	15.968	13.403	12.254
	$-\Delta S^{\#}$	16.95	110.03	115.56	133.72	141.84	145.21
	$\Delta G^{\#}$	5.025	32.985	34.647	40.099	42.539	43.552

$\Delta H^{\#}$ (kJ mol^{-1}), $\Delta S^{\#}$ (JK^{-1}) and $\Delta G^{\#}$ (kJ mol^{-1}) at 300 K; [Co(III)] = 1 × 10^{-3} M [Fe(II)] = 0.05 – 0.175 M, {NaClO$_4$} = 0.01 M, [Na$_2$(H$_2$EDTA)] = 5 × 10^{-5} M

tants. It is worth emphasizing that the sign and magnitude of activation entropy and enthalpy are consistent with an associative/ion-pair formation mechanism and a net increase in bond order in transition state [19,20]. The sensitivity of $\Delta S^{\#}$ value suggests that ion-pair formation involving approaching of $Fe(CN)_6^{4-}$ to $Co^{III}(pn)_2Cl\,L^{2+}$ 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 observed in this reduction reaction can be interpreted on the basis of an increase in solvation due to charge distribution in moving from the precursor ion-pair to the successor ion-pair.

The thermal activation parameters were obtained for $Co^{III}(pn)_2Cl(L)^{2+}$ in water-1,4-dioxane mixtures for and the values are as follows. $\Delta H^{\#}$ = 6.026 to 27.621 KJ mol^{-1}; $\Delta S^{\#}$ = -97.97 to –170.47 JK^{-1} mol^{-1} and $\Delta G^{\#}$ = 29.363 to 51.134 KJ mol^{-1}.

The nonlinear variation of $\Delta S^{\#}$ is a criterion of specific solvation. The $\Delta S^{\#}$ values are negative for all the complexes at all solvent compositions. This means a more ordered systems exists for $Co^{III}(pn)_2Cl(L)^{2+}$ complexes which may be attributed to the presence of R group in aniline moiety. Here arises the effect of increasing hydrophobicity in increasing the stability of the individual complex at low x_2. The excess of R groups present in aniline moiety show their hydrocarbon ends as principal contact areas between the complex cation and the solvent and the structure forming capacity of the organic groups in aqueous organic solutions usually results in more negative values in $\Delta S^{\#}$. Moreover, the highly negative $\Delta S^{\#}$ support the formation of intermediate ion-pair complex, hence the electro-

static field is much stronger in the vicinity of this intermediate ion-pair and exerts a strong orienting force on the surrounding polar solvent molecules and hence the degree of ordering around this intermediate complex ion is higher than that for the initial state leading to highly negative $\Delta S^{\#}$ [21]. The overall values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ may be taken to be composites of the reaction components ($\Delta X^{\neq}_{overall} = \Delta X^{\neq}_R + \Delta H^{\neq}_S$). 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 behaviour contradicts with those of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ because these quantities often vary in 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. It is evident from the data that the solvent structure and preferential solvation might contribute to solvent ordering in the microenvironments of the initial and transition state. However, the solvent effects on the solvation components of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are mutually compensatory. This indicates that there is no change in the mechanism. As the charge separation takes place in the transition state, the charged end becomes highly solvated. The near constancy of $\Delta H^{\neq}$ and the strong dependence of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ on the solvent composition clearly predicts compensatory. The negative $\Delta S^{\neq}$ observed for the reduction process agree with a greater degree of solvation. It also favours the associative mechanism, that is, ion pair formation take place between cobalt(III) aryl amine complexes and $Fe(CN)_6^{4-}$.

Relative permittivity: Normally, in ion-ion reactions, the electrostatic interactions make the greatest contribution [22] to the activation free energy. The solvent parameter which is widely used as a measure of the electrostatic interactions between the solute and solvent is relative permittivity (ε_r) [23]. The influence of solvent relative permittivity on the rate of the reaction was studied 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 the decrease in relative permittivity of the medium. It is in good agreement with the fact that, the possibility of association between the charged reactants is favoured due to an increase in the organic component of the medium.

Fig. 5 represents a linear least-squares plot of log k_{et} *versus* the reciprocal of the bulk relative permittivity of the medium ($1/\varepsilon_r$) (Table-7). In the present study, it has been observed that the plot of log k_{et} *versus* $1/\varepsilon_r$ is a straight line with a positive slope, which indicates ion-ion type interaction. It also implies that the strong ion-pairing effect is influenced with the decrease in the relative permittivity of the medium. Positive values of slopes from Table-7 ($r^2 = 0.947$-0.9871, slope $= 189.71$-432.12, sd $= 0.032$-0.110, $\psi = 0.120$-0.252 and Temp $= 286$, 293 and 300 K) for all cobalt(III)-aryl amine complexes indicate that the reaction proceeds *via* an associative reduction path ($r^* > r$).
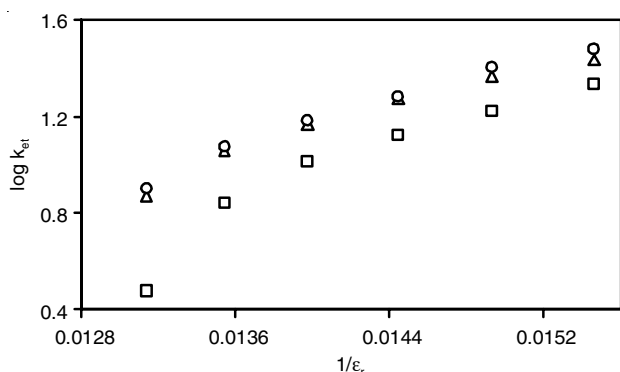

Fig. 5. Plot of log k_{et} *versus* $1/\varepsilon_r$ for the $Fe(CN)_6^{4-}$ reduction of $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)Cl_2$ complex in water-methanol mixtures at three different temperatures

The addition of small amount of methanol or 1,4-dioxane causes an increase in the rate constant. This situation is clearly understood by using solvent ionizing power [24] index Y. There is a good correlation between the log k_{et} and the Grunwald-Winstein's, Y, parameter [25], as shown in Fig. 6, which is the plot of log k_{et} *versus* Y. It is a measure of solvent ionizing power. Thus the slopes of Gruwnald-Winstein's plot, log $k_2 =$ log $k_o + mY$, are negative as presented in Table-8, m = -0.521 to -1.808 in water-methanol and m = -0.348 to -1.162 in water-1,4-dioxane media for the iron(II) reduction of cobalt(III)-aryl amine complexes. These values support an associative pathway and the transition state is less polar. Plot of log k_{et} *versus* Y (Fig. 6) for $[Co^{III}(pn)_2Cl(RC_6H_4NH_2)]^{2+}$ in water-methanol and water-1,4-dioxane mixtures show distinct lines. The slopes of the two lines are different, they correspond to dispersion phenomenon. The occurrence of dispersion phenomenon is due to the fact that a different blend of non-specific and specific solvent influences interact with the solute for each solvent.
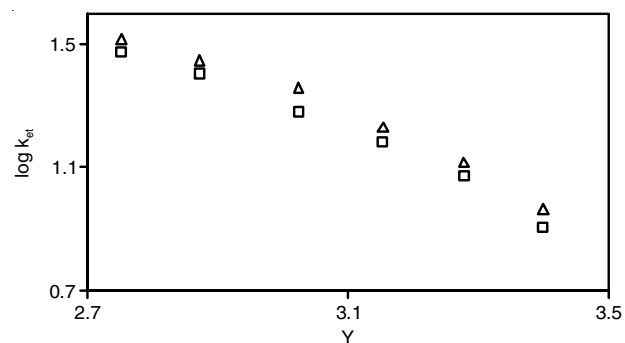

Fig. 6. Plot of log k_{et} *versus* Y for the $Fe(CN)_6^{4-}$ reduction of $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ ion at 300 K in water-methanol (□) and water-1,4-dioxane (△) mixtures showing dispersion phenomenon

Plot of log k_{et} *versus* Y (Fig. 6) for $[Co^{III}(pn)_2Cl(RC_6H_4NH_2)]^{2+}$ in water-methanol and water-1,4-dioxane mixtures show distinct lines. The following eqns. 5 and 6 represent Grunwald-Winstein's relationship for $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ ion in water-methanol and water-1,4-dioxane mixtures respectively,

$$\log k_{et} = 3.866\text{-}0.859\ Y \quad \text{(water – methanol)} \quad (5)$$
($R^2 = 0.9917$, sd $= 0.031$, $\psi = 0.100$, n $= 6$ and Temp. $= 300$ K)

$$\log k_{et} = 3.048\text{-}0.604\ Y \quad \text{(water – 1,4-dioxane)} \quad (6)$$
($R^2 = 0.9829$, sd $= 0.043$, $\psi = 0.143$, n $= 6$ and Temp. $= 300$ K)

Multiparametric regressions

Swain model: Bulk solvent property like relative permittivity will poorly describe the micro environment around the reacting species, which governs the stability of the intermediate and hence the rate of electron transfer. Therefore, specific solvent

TABLE-7
STATISTICAL RESULTS OF LAIDLER-EYRING'S PLOT FOR $[Fe(CN)_6]^{4-}$ REDUCTION OF
$[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}$ ION IN WATER-METHANOL MIXTURES AT DIFFERENT TEMPERATURES

R in aniline	Temp. (K)	r^2	sd	ψ	Slope	I
m-OCH₃	286	0.9841	0.076	0.138	432.12	-5.2585
	293	0.9744	0.058	0.175	260.24	-2.5772
	300	0.9628	0.071	0.211	260.76	-2.3765
p-F	286	0.9470	0.110	0.252	334.91	-3.7711
	293	0.9769	0.050	0.166	234.29	-2.1452
	300	0.9879	0.037	0.120	241.39	-2.2198
H	286	0.9798	0.066	0.156	330.45	-3.8020
	293	0.9629	0.064	0.211	233.63	-2.2143
	300	0.9714	0.045	0.185	189.71	-1.3873

$\Delta H^{\#}$ (kJ mol⁻¹), $\Delta S^{\#}$ (JK⁻¹) and $\Delta G^{\#}$ (kJ mol⁻¹) at 300 K; [Co(III)] $= 1 \times 10^{-3}$ M [Fe(II)] $= 0.05 – 0.175$ M, {NaClO₄} $= 0.01$ M, [Na₂(H₂EDTA)] $= 5 \times 10^{-5}$ M

TABLE-8
STATISTICAL RESULTS OF GRUNWALD-WINSTEIN PLOT FOR $[Fe(CN)_6]^{4-}$ REDUCTION OF
$[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}$ ION IN WATER-METHANOL MIXTURES AT DIFFERENT TEMPERATURES

R in aniline	Temp. (K)	R^2	sd	ψ	Slope	ψ
m-OCH₃	286	0.9887	0.064	0.116	-1.539	5.6399
	293	0.9805	0.051	0.153	-0.928	3.9908
	300	0.9686	0.065	0.194	-0.930	4.2041
p-F	286	0.9522	0.105	0.239	-1.194	4.6791
	293	0.9817	0.044	0.148	-0.835	3.7644
	300	0.9917	0.031	0.100	-0.859	3.8662
H	286	0.9845	0.058	0.136	-1.177	4.5327
	293	0.9681	0.059	0.196	-0.833	3.6801
	300	0.9760	0.041	0.170	-0.676	3.3976

effect was analyzed using the empirical solvent parameters of Swain *et al.* [26]. The most important properties of solvents, affecting the chemical reactivity in processes are anion-solvating and cation-solvating tendencies [27,28]. The appropriate expression is log k₂ = aA + bB + c. The pseudo first-order reduction rate constants (log k_{et}) of all the cobalt(III)-aryl amine complexes in both the solvent mixtures show an excellent correlation with solvent acidity (A) and basicity (B) terms. The rate of reduction of cobalt(III)-aryl amine complexes by $[Fe(CN)_6]^{4-}$ in water-methanol/1,4-dioxane mixtures show an excellent correlation in Swain's eqns. 7 and 8. In the case of $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ ion:

$$\log k_{et} = 3.04 \text{ A} - 9.70 \text{ B} - 7.50 \text{ (water – methanol)} \quad (7)$$
$(R^2 = 0.9800, sd = 0.039, \psi = 0.173, n = 6 \text{ and Temp.} = 300 \text{ K})$

$$\log k_{et} = -26.49 \text{ A} + 42.09 \text{ B} + 14.66 \text{ (water – 1,4-dioxane)} \quad (8)$$
$(R^2 = 0.9800, sd = 0.050, \psi = 0.225, n = 6 \text{ and Temp.} = 300 \text{ K})$

The statistical results are listed in Table-9. In water-methanol system, the percentage contribution of anion-solvating tendency P(A) (1-39) and the percentage contribution of cation-solvating tendency P(B) (61-99) and in water-1,4-dioxane mixed solvent media, P(A) (11-39) and P(B) (61-89), give some indication that the cation solvating tendency is more dominant than anion-solvating ability of the solvents.

Kamlet-Taft model: The solvatochromic comparison method may be used to unravel, quantify, correlate and rationalize multiple interacting solvent effects on many types of physico-chemical properties and reactivity. The specific solvation effects are further discussed using Kamlet-Taft's relationship [29], which is intended to provide a rationalization of solvent effects on many types of chemical and spectroscopic properties

and reactivity parameters [30]. The rate constants k_{et} in water-methanol/1,4-dioxane were correlated in terms of linear solvation energy relationship of Kamlet *et al.* [29] (eqns. 9 and 10). The results of correlation analyses for $Co^{III}(pn)_2Cl(p\text{-}FC_6H_4NH_2)^{2+}$ ion, in water-methanol and water-1,4-dioxane are given below:

$$\log k_{et} = 611.37 - 141.69 \, \pi^* - 338.57\alpha - 333.10\beta \text{ (water – methanol)} \quad (9)$$
$(R^2 = 0.9894, sd = 0.035, \psi = 0.146, n = 6 \text{ and Temp.} = 300 \text{ K})$

$$\log k_{et} = 2092.36 - 2337.99 \, \pi^* + 723.20\alpha - 2161.64\beta \text{ (water – 1,4-dioxane)} \quad (10)$$
$(R^2 = 0.9911, sd = 0.031, \emptyset = 0.133, n = 6 \text{ and Temp.} = 300 \text{ K})$

Table-10 listed the statistical results of Kamlet-Taft's solvent parameters. It is observed that the reduction of cobalt(III)-aryl amine complexes in water-methanol, P(α) (19-47) and P(β) (39-47), hence β play a major role when compared to α. The solvent polarity/dipolarizability P(π*) (13-34), accounts the macroscopic effect and for water-1,4-dioxane system P(α) (9-15), P(β) (39-53) and P(π*) (38-46) respectively.

In water-methanol system, the sign of coefficients of both α and β terms are negative indicating better solvation of the reactants than the transition state. Since, the specific interaction between the transition state and the solvent is less in this mixture. In water-1,4-dioxane system, the sign of coefficient (a), the solvent HBD acidity term α is positive showing better solvation of the transition state through HBD interaction, while that of b, coefficient of HBA basicity β is negative indicating solvation of the reactants is dominant through HBA interaction. Since 1,4-dioxane can act as a HBD as well as a HBA solvent, the transition state is effectively solvated than the reactants resulting in larger rate constant values in the mixture.

TABLE-9
STATISTICAL RESULTS, THE COEFFICIENTS AND WEIGHTED CONTRIBUTIONS OF SOLVENT
PARAMETERS IN SWAIN'S EQUATION FOR $[Fe(CN)_6]^{4-}$ REDUCTION OF $[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}$
ION IN WATER- METHANOL MIXTURES AT DIFFERENT TEMPERATURES

R in aniline	Temp. (K)	Statistical parameters							Intercept
		R^2	sd	ψ	a	b	P(A)	P(B)	
m-OCH₃	286	0.9686	0.087	0.217	-0.07	-14.34	1	99	14.668
	293	0.9515	0.066	0.269	0.96	-9.19	9	91	8.973
	300	0.9372	0.076	0.307	5.41	-11.64	32	68	7.162
p-F	286	0.9178	0.114	0.351	10.77	-17.05	39	61	6.736
	293	0.9621	0.052	0.238	4.01	-9.99	29	71	6.813
	300	0.9800	0.039	0.173	3.04	-9.70	24	76	7.503
H	286	0.9655	0.070	0.227	3.76	-13.07	22	78	9.706
	293	0.9289	0.073	0.327	1.31	-8.49	13	87	7.945
	300	0.9507	0.049	0.272	3.00	-7.57	28	72	5.983

TABLE-10
STATISTICAL RESULTS, THE COEFFICIENTS AND WEIGHTED CONTRIBUTIONS OF SOLVENT
PARAMETERS IN KAMLET-TAFT'S EQUATION FOR $[Fe(CN)_6]^{4-}$ REDUCTION OF $[Co(pn)_2Cl(RC_6H_4NH_2)]^{2+}$
ION IN WATER-METHANOL MIXTURES AT DIFFERENT TEMPERATURES

R in aniline	Temp. (K)	R^2	sd	ψ	s	a	b	P(π*)	P(α)	P(β)	Intercept
					$XYZ = XYZ_o + s\pi^* + a\alpha + b\beta$						
m-OCH$_3$	286	0.9920	0.054	0.126	-254.77	-878.54	-746.12	14	47	39	1440.107
	293	0.9941	0.028	0.109	-206.72	-746.11	-627.00	13	47	40	1211.836
	300	0.9792	0.054	0.204	-475.21	-580.91	-835.80	25	31	44	1349.006
p-F	286	0.9655	0.090	0.263	-953.42	-548.58	-1347.69	34	19	47	1924.105
	293	0.9872	0.037	0.160	-303.12	-440.03	-568.41	23	34	43	948.328
	300	0.9894	0.035	0.146	-141.69	-338.57	-333.10	17	42	41	611.369
H	286	0.9951	0.032	0.099	-322.86	-759.90	-761.13	18	41	41	1378.384
	293	0.9836	0.043	0.181	-457.33	-522.69	-785.19	26	30	44	1252.105
	300	0.9883	0.029	0.153	-342.53	-356.20	-568.28	27	28	45	893.408

Conclusion

$Co^{III}(pn)_2Cl(L)^{2+}/[Fe(CN)_6^{4-}]$ with MeOH/dioxane were found to show interesting outcome with regression analysis. Activation parameters (K), the rate constant found to be greater than unity giving a strong evidence of associative mechanism. The decrease in $\Delta H^{\#}$ with increasing in the solvent compositions narrates the electrostatic attraction between the reactant species and the decrease in the values of the enthalpy and entropy of activation with decreasing polarity of the medium explains that a medium of lower relative permittivity enhances the rate favouring the outer sphere association between the reactants. The higher negative $\Delta S^{\neq}$ values observed confirmed an increase in solvation due to charge distribution in moving from the precursor ion-pair to the successor ion-pair were inveterate by activation parameters. The low $\Delta H^{\neq}$ values and large negative $\Delta S^{\neq}$ values suggested an associative mechanism. Multiple regression models with solvatochromic parameters (α, β and π*) confirms the convolution of cation/anion solvation of ion-pair. A quantitative analysis (P(α), P(β) and P(π*)) stated the relative solvatochromic ability of specific-non-specific interactions. It indicates that the cation solvating tendency is more dominant than anion-solvating ability of the solvents. By distinct correlation methods, the solvation effect on ion-pair/transition state can effectively be explained.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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