Measurement of Solvent Dynamics Effects on the Electron Transfer Reaction of $Co(NH_3)_4ox^+$ in Mixed Solvents: A Quantitative Approach

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For reactions involving electron transfer or nucleophilic attack on the transition state/excited state of metal complex in aquo-organic solvent mixtures, a linear relationship between logarithms of rate constant and solvent empirical parameters can be derived. The relationship, $Y_S = Y_0 + a_1X_1 + a_2X_2 + ... + a_nX_n$, fits well for both the measured quantity in a solvent and solvent dependent property. From the quantitative estimation of the coefficients, the dominant solvent stoichiometric and other substantial medium effects on reactivities can be confirmed. Electron-transfer reaction of $Co(NH_3)_4ox^+$ complex with $Fe(CN)_6{}^{4-}$ in six different water−cosolvent binary mixtures have been investigated (cosolvent: methanol or 1,4-dioxane 5−30% (v/v)) and the respective k_{et} and K_{IP} values have been experimentally determined. The k_{et} values evaluated in mixed solvents show linearity with x_{org} and $\epsilon_r{}^{-1}$, reflecting the individuality of the cosolvent and thereby suggesting that the relative stability of the ion pair is governed by the preferential solvation effect. The thermodynamic parameters ($\Delta H^\#$, $\Delta S^\#$, and $\Delta G^\#$) are sensitive to the structural changes in the bulk solvent phase. Likewise, irradiation (at 254 nm) of the charge-transfer bands of $Co(NH_3)_4ox^+$ in varying compositions of water−methanol/1,4-dioxane mixtures results in reduction of Co(III) to Co(II); with respect to x_{org}, $\phi_{Co(II)}$ increases up to 1.6-fold (organic cosolvent 5−30% (v/v)). The predominance of Co(II) formation at higher x_{org} is due to solvent-assisted reduction in mixture solvents. There is a linear relationship between $\phi_{Co(II)}$ with $\epsilon_r{}^{-1}$ of the medium indicating the solvational contributions. The experimentally determined k_{et} and $\phi_{Co(II)}$ are well correlated through multiple regression equations based on proposed models to understand the consequences of short range and long-range solvation effects. A quantitative estimation of relative importance of the components is attempted. A number of empirical solvent parameters are used in the multiple regression equations. The correlation analysis reveals significant information on the effect of solvent−solvent and solvent−solute interactions on reactivities. The investigation is a novel attempt to understand the “solvent tuning” of reactions and to obtain a quantitative measure of the relative importance of the influences of solvents.

Introduction

The interest in the theoretical understanding and description of outer-sphere electron-transfer (OSET) reactions of transition metal complexes in mixed solvents has increased significantly in recent years.[1−2] This can partly be ascribed to an improved ability to describe such processes theoretically and partly to the application of new techniques with which additional experimental information has become available. In electron-transfer reactions, the solvent plays an essential role that is well understood since the seminal papers of Marcus, Hush, and others. Recently, Anbalagan et al. reported electron-transfer reactions of a series of mixed ligand complexes of alkylamine−cobalt(III) and arylamine−cobalt(III) complexes in aqueous organic solvent mixtures.[3−7] It was established that the method of linear solvation energy relationship (LSER) is a generalized treatment of solvation effects and can very well be used to understand the influence of solvent on reaction rates, provided some classical considerations are taken into account.[8] In essence, there are three types of interactions: (i) nonspecific, long-range intermolecular forces, solvent−solute interactions, (ii) specific, short-range intermolecular forces, solvent−solute interactions, and (iii) solvent−solvent interactions from the cavity effect. These solute−solvent interactions are used to determine the solvation property, hence from a practical point of view, it would seem expedient to take “solvent polarity” to mean the overall solvation ability of a solvent. It is presumed that empirical parameters of solvent polarity can generally provide a more comprehensive measure of the overall solvation ability of the solvent.[2,9] Empirical correlations of the reactivities are usually linear relationships involving logarithms of rate or equilibrium constants or the absorption maxima.[8−10] To through light on the above experimentally determined quantities, the rate constant k or photo reduction quantum yield ϕ may be subjected to regression analyses. There is often a reasonable linear correlation between a solvent dependent property (log k or log ϕ) and a single solvent parameter, the first one is Laidler and Eyring reciprocal relationship,[11] that is with $\epsilon_r{}^{-1}$ the reciprocal of relative permittivity of the medium, and the second one is Grunwald−Winstein mY plot,[12] where Y is the measure of “solvent−ionising power”.

In another attempt, the solvent dependent property may also be subjected to multiple regression analysis using various solvent empirical parameters, which rationalize solvent effects in terms of properties of the medium. Therefore, a number of other polarity scales of wider applications were used for instance, Swain’s solvent vectors[13] A and B, where A is an anion

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solvating tendency (acity) and B is cation solvating tendency (basity). Second, Dimroth and Reichardt's normalized dimensionless Lewis acidity solvent polarity parameter[9–11] E_T^N which was calculated from solvatochromic studies of pyridinium-*N*-phenoxide betaine dye. Gutmann's normalized donor number DN^N is chosen as a measure of solvent Lewis basicity, where DN^N is the negative enthalpy of formation of adducts between the uncharged Lewis acid $SbCl_5$ and a given solvent molecule as Lewis base in dilute 1,2-dichloroethane solvent.[9,10] Third, Kamlet−Taft's solvatochromic[14] parameters π^*, α, and β, in which π^* is a scale index of solvent dipolarity/polarizability, α is a scale of solvent HBD (hydrogen-bond donor) acidity, and β is a scale of HBA (hydrogen-bond acceptor) basicity.

In the present work, $Fe(CN)_6^{4-}$ reduction of $Co(NH_3)_4ox^+$ and ligand to metal charge transfer (LMCT) excited-state redox reaction of $Co(NH_3)_4ox^+$ were studied in varying compositions of aqueous mixtures of methanol (MeOH) and 1,4-dioxane (Diox). The resulting data were subjected to vigorous statistical analysis to understand the solvation effects on reactivities of the complexes.

Experimental Section

Materials. $[Co(NH_3)_4ox]Cl$ was prepared by a modified literature procedure to increase the overall yield.[15] The complex was purified through recrystalization from acidified water and the purity was checked using UV−vis spectral data (throughout λ in nm, ϵ in M^{-1} cm^{-1}), 510 (80.6) and 358 (112.5), compare favorably with those reported in the literature.[16] $K_4[Fe(CN)_6]$, organic solvents, and EDTA (disodium salt) AR grade were obtained from Merck. All of the solutions were prepared with deionized water (conductivity $< 10^{-8}$ S m^{-1}).

Kinetics. In all kinetic runs, the ionic strength was maintained as constant by adding sodium perchlorate to make the solutions 0.3 mol dm^{-3} in this salt. The concentration of the cobalt complex was always 2×10^{-4} mol dm^{-3}, and six hexacyanoferrate(II) concentrations were employed, ranging from 1×10^{-2} to 3.5×10^{-2} mol dm^{-3}. All kinetic runs were carried out in varying solvent compositions range from 5% to 30% (v/v) of methanol or 1,4-dioxane. Addition of $Na_2(H_2EDTA)$ was necessary to prevent precipitation[17] of $Co_2Fe(CN)_6$. The reaction was followed spectrophotometrically at 420 nm, where the hexacyanoferrate(III) produced in the reaction absorbs.[17,18] Pseudo-first-order rate constants were obtained from the slopes of the linear plots of $\log(A_i - A_t)$ vs time, and the temperature control was 300 K. These plots were linear for atleast three half-lives. Activation parameters, linear regression, and multiple regression analyses were carried out using a computer program.

Photolysis Experiment. The light source was a low pressure 254 nm lamp with a reactor vessel. Intensity of incident light was measured by ferrioxalate actinometry.[19] Solutions of $Co(NH_3)_4ox^+$, approximately 3.5×10^{-3} mol dm^{-3}, were irradiated to a conversion of less than 10% in all cases. The photolyte solutions were prepared using 5−30% [(v/v) methanol/1,4-dioxane] aqueous organic solvent mixtures. Temperature was maintained at 300 K by means of a thermostated water flowing system. Ionic strength was maintained constant with 0.1 mol dm^{-3} $NaNO_3$, and all of the photolyte solutions were air-equilibrated. The solution was magnetically stirred, and a necessary correction was given for thermal component. The Co(II) formed was determined[20] via spectrophotometric analysis of $Co(SCN)_4^{2-}$ in acetone at 620 nm. In all analytical procedures, photolyzed solutions were compared to identically treated unphotolyzed ones. The difference in analysis was attributed to the photolysis.

Analysis of Data. The electron-transfer rate constant, k_{et}, between $Fe(CN)_6^{4-}$ and $Co(NH_3)_4ox^+$ as well as the LMCT reduction quantum yield, $\phi_{Co(II)}$, in varying compositions of binary mixtures (5−30% (v/v) methanol/1,4-dioxane in water) can be probed through various solvent empirical parameters. Therefore, it is assumed that a quantitative allowance for the solvent effect on reaction rates/quantum yield of reactions consist in establishing eq 1

$$Y_S = f(X_1, X_2, X_3, ...) \quad (1)$$

where Y_S is the physicochemical quantity and X_1, X_2, X_3 are independent but complementary empirical parameters characterizing the properties of the medium. These parameters are based on nonspecific and specific solvation effects such as relative permittivity, hydrogen bonding, and electron pair donor/acceptor complexation. Hence, appropriate equations correlating rate constant/quantum yield with medium properties are derived on the basis of experimentally justified models in order to take into account one, two, or more aspects of solvation and linear regression approach works well.

The Model. It is postulated in general that the solvent effect on a physicochemical quantity Y_S can be represented as a linear function of multiple parameters as in eq 2

$$Y_S = Y_0 + a_1X_1 + a_2X_2 + a_3X_3 + ... + a_nX_n \quad (2)$$

The variable Y_S is the solvent dependent property ($\log k_{et}$ or $\log \phi$) in a given solvent, Y_0 is the statistical quantity (intercept term) corresponding to the value of the property in the reference solvent, and a_1, a_2, a_3, etc. are the regression coefficients as determined by a least squares procedure. The setting-up of scales X_1, X_2, X_3, etc. (explanatory variables) depend on the assumption that capability of solvent effecting various interactions on reactants/ion pair. That is, suitable selection of bulk and molecular properties of solvents such as ϵ_r, Y, A, B, E_T^N, DN^N, π^*, α, and β constitute linear or multiple regression analysis model. Thus, it is assumed that the solvent effect on property Y_S can be described using explanatory variables X_1, X_2, X_3, etc., in terms of regression line (a single solvent parameter, X_1), regression plane (two solvent parameters, X_1 and X_2), and regression tetragonal (three solvent parameters, X_1, X_2, and X_3). The first one describes nonspecific solvent−solute interactions, second one explains specific solvent−solute interactions, and the third one includes both of the above.

In general, the explanatory variables X_1, X_2, etc. do not vary by the same amounts in a given data set. Thus, it is not possible to obtain a quantitative measure of the relative importance of solvent effect for a given physicochemical quantity just by examining the regression coefficients a_1, a_2, a_3, etc. To determine the relative importance of the solvent parameters, the regression coefficients are defined in terms of percentage value. The relative importance of different "effects" of explanatory variables as dictated by multiple regression eq 2 may be statistically quantified into percentage contribution $[P(X_i)]$. This is an analytical model, based on statistical weighting, which may not exhibit absolute status, but definitely, it is presumed that, given an immediate indication of the relative importance of the various effects in terms of percentage basis and in order to achieve this, the regression coefficients which emerge from multiple regression equations are corrected to numerical range 0−100. Therefore, percentage contribution, $P(X_i)$, of a solvent parameter in a multiple regression equation is quantified[21] as in eq 3

$$P(X_i) = \frac{100|a_i|}{\sum_{i=1}^{n}|a_i|} \tag{3}$$

Thus, $P(X_i)$ may be regarded as an estimate of the percentage contributions from solvent property to the observed solvent effect. Because $P(X_i)$ is in a single scale, comparison of relative importance of solvent property can easily be described. All of the calculations were performed using a computer program.

Results and Discussion

Iron(II) Reduction. The oxalatotetramminecobalt(III), $Co(NH_3)_4ox^+$, exists as a single positive species in various compositions of water−methanol and water−1,4-dioxane mixtures, which was verified through repetitive scan spectra of the complex. The overall redox reaction followed the same pattern as in pure water.[22−24] Analysis of products and stoichiometric determinations indicate the overall reaction may be expressed[22,24] as in eq 4

$$Co(NH_3)_4ox^+ + Fe(CN)_6^{4-} \rightarrow Co^{2+}_{aq} + Fe(CN)_6^{3-} + 4NH_3 + C_2O_4^{2-} \quad k_{obs} \tag{4}$$

$Co(NH_3)_4ox^+$ is reduced to Co(II) by $Fe(CN)_6^{4-}$, which was confirmed by the increased concentration of $Fe(CN)_6^{3-}$ as the reaction proceeds.[17,22] Therefore, the reaction was analyzed by monitoring the production of $Fe(CN)_6^{3-}$ at 420 nm.

The reduction of $Co(NH_3)_4ox^+$ by $Fe(CN)_6^{4-}$ in varying solvent compositions of water−methanol and water−1,4-dioxane mixtures (5−30% (v/v) MeOH or Diox) merits special attention with respect to solvent effect. The most favorable mechanism for the outer-sphere electron transfer (OSET) reaction[25] of $Co(NH_3)_4ox^+$ consists of three elementary steps given in eqs 5−7, viz, outer-sphere precursor formation (K_{IP})

$$Co(NH_3)_4ox^+ + Fe(CN)_6^{4-} \rightleftarrows \{Co(NH_3)_4ox^+; Fe(CN)_6^{4-}\} \quad K_{IP} \tag{5}$$

$$\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\} \rightarrow \{Co(NH_3)_4ox; Fe(CN)_6^{3-}\} \quad k_{et} \tag{6}$$

$$\{Co(NH_3)_4ox;Fe(CN)_6^{3-}\} \rightarrow \text{products.} \qquad \text{fast} \tag{7}$$

rate-determining electron transfer (k_{et}), precursor formation, and successor dissociation are diffusion controlled processes, of which only the precursor formation process affects the observed pseudo-first-order rate constant, k_{obs}, in a thermodynamic way. The rate law derived from the above mechanism is given[24] in eq 8

$$k_{obs} = \frac{k_{et}K_{IP}[Fe(CN)_6^{4-}]}{\{1 + K_{IP}[Fe(CN)_6^{4-}]\}} \tag{8}$$

All of the observed pseudo-first-order rate constants, k_{obs}, measured as a function of mole fraction, x_2, of added methanol or 1,4-dioxane and temperature are collected in Tables 1 and 2.

TABLE 1: Rate Data for the Reduction of $Co(NH_3)_4ox^+$ by $Fe(CN)_6^{4-}$ as a Function of Mole Fraction of Methanol in Water−Methanol Mixtures[a]

MeOH (vol %)	x_2	ϵ_r	$10^3\ k_{obs}$		
			293 K	300 K	308 K
5	0.02274	76.18	0.547	1.378	2.999
10	0.04683	73.8	0.647	1.921	3.508
15	0.07238	71.5	0.774	2.433	3.841
20	0.09959	69.2	0.931	3.318	4.767
25	0.12845	66.97	1.014	4.234	5.759
30	0.15931	64.68	1.535	6.366	7.749

[a] Ionic strength 0.3 mol dm^{-3} $NaClO_4$, [Co(III)] = 2 × 10^{-4} mol dm^{-3}, [Fe(II)] = 0.01 mol dm^{-3} and (Na_2H_2EDTA) = 5 × 10^{-4} mol dm^{-3}. Wavelength of analysis 420 nm. Each value is the mean of at least three kinetic runs.

TABLE 2: Rate Data for the Reduction of $Co(NH_3)_4ox^+$ by $Fe(CN)_6^{4-}$ as a Function of Mole Fraction of 1,4-dioxane in Water−1,4-dioxane Mixtures[a]

1,4-dioxane (vol %)	x_2	ϵ_r	$10^3\ k_{obs}$		
			293 K	300 K	308 K
5	0.01095	74.58	0.512	1.642	3.049
10	0.02283	70.77	0.712	2.140	3.714
15	0.0358	66.96	0.921	3.104	4.511
20	0.04994	63.15	1.084	4.006	5.405
25	0.0655	59.34	1.251	5.130	6.158
30	0.08267	55.53	1.687	6.739	8.013

[a] Ionic strength 0.3 mol dm^{-3} $NaClO_4$, [Co(III)] = 2 × 10^{-4} mol dm^{-3}, [Fe(II)] = 0.01 mol dm^{-3} and (Na_2H_2EDTA) = 5 × 10^{-4} mol dm^{-3}. Wavelength of analysis 420 nm. Each value is the mean of at least three kinetic runs.

TABLE 3: Value of k_{et} and K_{IP} for the Reduction of $Co(NH_3)_4ox^+$ by $Fe(CN)_6^{4-}$ in Water−Organic Cosolvent Mixtures at 300 K

cosolvent (vol %)	ϵ_r	$10^3\ k_{et}$ (s^{-1})		K_{IP} mol^{-1} dm^3	
		water−MeOH	water−Diox	water−MeOH	water−Diox
5	76.1	8.220	7.152	20.0	29.63
10	73.8	9.412	8.321	25.6	34.47
15	71.5	10.078	14.081	30.71	26.04
20	69.3	16.204	18.647	25.65	27.44
25	67.0	21.771	26.868	24.19	23.82
30	64.7	34.638	35.745	21.56	22.18

The k_{obs} values measured as a function of $Fe(CN)_6^{4-}$ concentrations were fitted in eq 8 (double reciprocal plot of $1/k_{obs}$ vs $1/[Fe(CN)_6^{4-}]$), and a very good fit was observed. From these plots, the first-order electron-transfer rate constants, k_{et}, and encounter complex formation constant, K_{IP}, could be calculated. The errors derived for the first-order rate constants were always in the 5−10% margin. Table 3 presents all k_{et} and K_{IP} values for the systems studied as a function of mole fraction of MeOH or Diox in the mixture. From standard Eyring plots, the thermal activation parameters were obtained and are summarized in Table 4. The pseudo-first-order electron-transfer rate constant, k_{et}, increases with increasing amount of organic cosolvent (Table 3). That is, rate constants exhibit[24] a distinct medium relative permittivity dependence.

The OSET reaction is characterized by a significant increase in negative $\Delta S^{\#}$ value and a slightly decrease in $\Delta H^{\#}$ value (Table 4) from 5% aqueous MeOH/Diox mixture to a 30% mixed solution. The thermal activation parameters ($\Delta H^{\#}$ and $\Delta S^{\#}$) are in close agreement with those reported for the corresponding reduction of $Co(NH_3)_4ox^+$ by Fe^{2+} in pure water (see ref 15 for a detailed summary of available data). The sensitivity of the $\Delta S^{\#}$ value for the reduction of $Co(NH_3)_4ox^+$

TABLE 4: Activation Enthalpy, Entropy, and Free Energy Data for the Iron(II) Reduction of $Co(NH_3)_4ox^+$ in Various Water−Organic Cosolvent Mixtures

cosolvent (vol %)	water−methanol			water−dioxane		
	$\Delta H^\#$ (kJ mol^{-1})	$-\Delta S^\#$ (JK^{-1} mol^{-1})	$\Delta G^\#$ (kJ mol^{-1})	$\Delta H^\#$ (kJ mol^{-1})	$-\Delta S^\#$ (JK^{-1} mol^{-1})	$\Delta G^\#$ (kJ mol^{-1})
5	82.491	25.484	90.136	86.347	12.290	90.034
10	81.699	26.300	89.589	79.722	32.162	89.371
15	77.118	40.157	89.165	76.371	41.04	88.683
20	78.531	33.454	88.567	77.145	36.802	88.186
25	83.578	15.229	88.147	76.366	37.953	87.752
30	77.618	31.981	87.212	74.580	41.588	87.056

TABLE 5: Quantum Yields for the Charge-Transfer Photolysis of $Co(NH_3)_4ox^+$ in Water−Organic Cosolvent Mixtures[a]

cosolvent	organic cosolvent (vol %)	ϵ_r	$10^2\phi_{co(II)}$
methanol	5	76.11	5.14 ± 0.03 (3)
	10	73.82	5.55 ± 0.04 (4)
	15	71.54	5.74 ± 0.02 (4)
	20	69.25	6.39 ± 0.04 (3)
	25	66.97	7.25 ± 0.03 (3)
	30	64.68	8.06 ± 0.01 (5)
1,4-dioxane	5	74.58	5.38 ± 0.05 (4)
	10	70.77	5.74 ± 0.02 (5)
	15	66.96	6.31 ± 0.04 (4)
	20	63.15	7.04 ± 0.03 (4)
	25	59.34	7.84 ± 0.04 (4)
	30	55.53	8.44 ± 0.02 (3)

[a] Complex concentration 3.5×10^{-3} mol dm^{-3}, ionic strength 0.1 mol dm^{-3} $NaNO_3$, wavelength of excitation 254 nm and temperature 300 K. Number of determinations in parentheses. $\phi_{Co(II)} = 0.0372$ in neat water.

with increase in the mole fraction of MeOH/Diox suggests that ion pair formation involving approach of $Fe(CN)_6^{4-}$ to $Co(NH_3)_4ox^+$ is facilitated at higher concentrations of organic cosolvent in the media. In other words, the electron-transfer (ET) is “entropy controlled”, and charge reduction in reaction 6 results in electrostriction[24,25] with increase of x_2 of MeOH/Diox of the medium and is accompanied by a significant decrease in entropy, indicating that the transition state is more structured[12,24] in the media under study. The higher negative $\Delta S^\#$ values observed for the reduction of $Co(NH_3)_4ox^+$ from 5% to 30% ((v/v) MeOH/Diox) in the mixture can be interpreted on the basis of an increase in solvation due to charge distribution in going from the precursor ion pair (+1, −4) to the successor ion pair (0, −3) in various mixtures. The near constancy of $\Delta G^\#$ for the reduction in all of the binary mixtures indicate the similarity in mechanism through ion pair formation.

Photoreduction. Monochromatic irradiation, $\lambda_{exc} = 254$ nm, of $Co(NH_3)_4ox^+$ in air-equilibrated water-methanol and water-1,4-dioxane mixtures (5−30% (v/v) organic cosolvent) led to the formation of the Co(II) ion. This product was spectrophotometrically detected[20] by Kitson’s method when conversions to such products remained below 10%. Although the Co(II) concentration increased linearly with mole fraction of methanol in alcoholic solutions, a slow increase of Co(II) was measured in water−dioxane mixtures. Table 5 shows that there is a regular increase in reduction quantum yield $\phi_{Co(II)}$ with increase in the mole fraction of methanol or dioxane in the medium. The linearity between $\phi_{Co(II)}$ and the x_2 of the organic cosolvent in the media is related to the effect of medium on reactant/excited state of the complex.[24] In accordance with this experimental evidence and the known photochemistry of Co(II) complexes,[26−30] it is proposed that ligand to metal charge transfer and solvent to metal charge-transfer excited states undergo conversions to the indicated Co(II) products as in eqs 9−11

$$^*Co^{III}(NH_3)_4ox^+ \xrightarrow{ox \rightarrow Co} [Co^{II}(NH_3)_4^{\;2+}, ox^-] \qquad (9)$$

$$\xrightarrow{N \rightarrow Co} [Co^{II}(NH_3)_3ox, NH_3^{\;+}] \qquad (10)$$

$$\xrightarrow{S \rightarrow Co} [Co^{II}(NH_3)_4ox, S^+] \qquad (11)$$

where S is the solvent and the radical-ion pairs are known to undergo recombination or separation in aqueous solutions within a nano second.[31]

The larger yield of complex in methanolic and dioxane solutions at higher x_2 appears to reflect more a medium-dependent photochemistry, i.e., a medium dependence of the quantum yield. In the redox-mediated reactions discussed by Endicott,[32] which follow charge-transfer excitation, the changes of yield tend to respond to the solvent environment. The photoaquation quantum yield of $[Co(NH_3)_6]^{3+}$ and *cis*-$[Coen_2Cl_2]^+$ in water−glycerol mixture was found to respond to solvent viscosity and polarity.[33] The medium dependence of $\phi_{Co(II)}$ can lie in the probability of dissociation of the caged radicals, and the main solvent effect can be in competition between dissociation and trapping leading to the product. It is, however, important to remember that the role of the solvent occurs very early in this process, specifically, faster than exchange between primary and secondary coordination spheres (~1 ns). That is, it occurs before the solvent can diffuse into the radical cage. Hence, it may be concluded that the solvent effects are not due simply to the inclusion of the solvent into the radical cage and the formation of a solvent adduct[34] (i.e., the penta coordinate species plus one solvent molecule).

The results of the $Fe(CN)_6^{4-}$ reduction of $Co(NH_3)_4ox^+$ and photoreduction at the LMCT band of the $Co(NH_3)_4ox^+$ experiments are listed in Tables 1−5. These results exhibit several interesting features: it is found that there is increase in k_{et} over a factor of 4.2 to 5.0 and photoreduction yield $\phi_{Co(II)}$ 1.6 to 1.5 in the composition 5% to 30% (v/v) of organic cosolvent in water−methanol and water−1,4-dioxane mixtures, respectively. Thus, arguments based on long and short range solvent−solute interactions offer viable explanations. Consequently, a model is formulated for the origin of solvent participation in reduction behaviour of this complex. Suppose the role of solvent is the specific promotion of rate/quantum yield ϕ, the reaction scheme can be written as:

$$(CoNH_3)_4ox^+ + Fe(CN)_6^{\;4-} \overset{K_{IP}}{\rightleftharpoons} \{(CoNH_3)_4ox^+; Fe(CN)_6^{\;4-}\} \qquad (12)$$

$$Co(NH_3)_4ox^+ \xrightarrow{h\nu} \{Co(II); \text{Ligand radical}\} \qquad (13)$$

Evidently, the increase in rate/quantum yield in a medium of lower relative permittivity is due to disruption of solvent structure accompanying effective solvation of solute/ion-pair/excited state. The solvation fruitfully stabilizes and assists the dissociation of intermediates into products. Therefore, it is

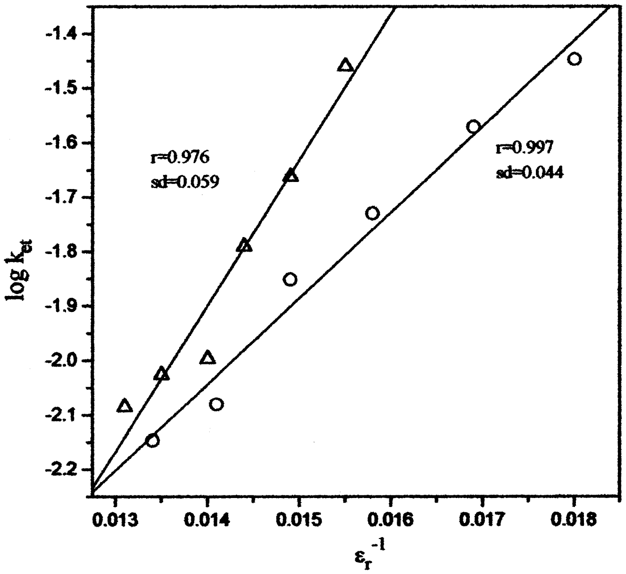

Figure 1. Plots of electron transfer rate constants, log k_{et}, as a function of solvent relative permittivity, ϵ_r^{-1}, for the reduction of $Co(NH_3)_4(ox)^+$ by $Fe(CN)_6^{4-}$ in water−methanol (△) and water−1,4-dioxane (○) mixtures at 300 K.

tempted to study the solvation effects in detail using multiparameter approach.

Influence of Solvation Effects

Solvent−Solvent−Solute Interactions. The solvent effects on chemical reactivity consists a few mechanisms based on the solvent−solute interactions. The three types of interactions are (i) nonspecific, solvent−solute interations. This may by understood by the macroscopic physical parameter of the solvent, such as relative permittivity, refractive index, etc. Thus, the solvent effect on rate/quantum yield data can be presumed to form a linear relationship such as $Y_S = Y_0 + a_1X_1$, where X_1 is an empirical parameter (in this case ϵ_r) of solvent. It is assumed that the linear relationship constitutes the regression line model. Likewise, (ii) specific, solvent−solute interactions can be represented by linear functions of two independent but complementary parameters such as $Y_S = Y_0 + a_1X_1 + a_2X_2$, describes regression plane model. Last, a regression tetragonal model contains three parameters such as $Y_S = Y_0 + a_1X_1 + a_2X_2 + a_3X_3$, which dictates both nonspecific and specific solvent contributions. Third type of interaction (iii) solvent−solvent contribution on rates is more complex and needs theoretical models. Therefore, log(k_{et} or $\phi_{Co(II)}$) values are fitted in model equations to obtain physical meaning of solvent influences. This approach provides excellent descriptions of solvent effects.[35]

Regression Line Model

The influence of solvent on the rate of reduction of $Co(NH_3)_4ox^+$ by $Fe(CN)_6^{4-}$ in varying compositions of binary mixtures of water−MeOH (Diox) was analyzed by means of relative permittivity, ϵ_r, of the medium. Figure 1 is a plot of log k_{et} vs ϵ_r^{-1} and examines how rate constants in various media vary with changes in ϵ_r^{-1} as caused by addition of MeOH or Diox. According to electrostatic theory, the dependence of the rate constant k on the relative permittivity, ϵ_r, can be expressed by the Laidler−Eyring relationship[11] as in eq 14

$$d \ln k/d(1/\epsilon_r) = [e^2z^2(1/r - 1/r^*)/2kT] \qquad (14)$$

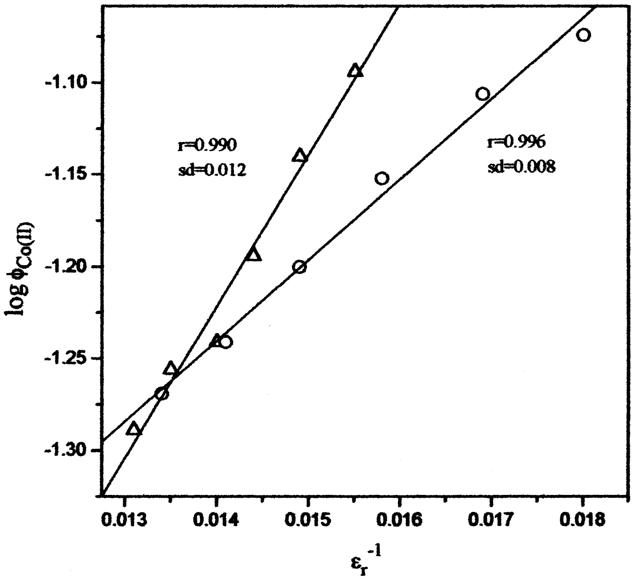

Figure 2. Plots of photoreduction quantum yield, log $\phi_{Co(II)}$, as a function of solvent relative permittivity, ϵ_r^{-1}, for photoreduction of $Co(NH_3)_4(ox)^+$ in water−methanol (△) and water−1,4-dioxane (○) mixtures at 300 K.

where k is the reaction constant, z is the net charge, r is the effective radius, and r^* is the relative radius of the activated species. The linear-least squares plot of log k_{et} vs ϵ_r^{-1} shows a reasonable correlation (correlation coefficient, $r = 0.976$ for water−MeOH and $r = 0.997$ for water−1,4-dioxane mixtures). The goodness of the fit was established using Exner's statistical parameter, ψ, which indicates the best fit of the data plotted showing a decreased correlation from 0 upward on a numerical scale.[8] The plots yield positive slopes for both the lines indicating $r^* > r$, which suggests that the electron transfer between $Co(NH_3)_4ox^+$ and $Fe(CN)_6^{4-}$ proceeds through an associative path or ion pair formation. The heterogeneous electron-transfer rate constant of tris(bipyridine) cobalt(III) was found to show[36] strong ion-pairing effect with varying relative permittivity of the medium. The increase in rate in 5% aqueous organic mixture to 30% mixture is the result of greater stabilization of the ion pair, $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}$, in relation to that of the reactants. Moreover, the charge-transfer transition causes an inward flow of electron density that decreases the dipole moment of the $Co(NH_3)_4ox^+$ complex. Figure 2 illustrates a good relationship between log $\phi_{Co(II)}$ and ϵ_r^{-1}. The increase in mole fraction of MeOH/Diox, which are less polar, in water destabilizes the ground state (decreases its solvation energy) more than the excited state/{Co(II); ligand radical} pair and this lowers the transition energy. Solvent relative permittivity arguments explain the higher yield in hydroxylic solvents (methanolic solutions) and lower yield in non-hydroxylic solvents (dioxane solutions). A specific association between the complex and solvent must be involved, therefore, both nonspecific and specific interactions of solvent are proposed.

Grunwald−Winstein Solvent Polarity Scale. Reaction rates can be strongly affected by solvent polarity; therefore, introduction of solvent scale using suitable solvent-sensitive chemical reactions was obvious. One of the most ambitious attempts to correlate reaction rates with empirical parameters of solvent polarity is that of Grunwald−Winstein[12] relationship as in eq 15

$$\log k = \log k_0 + mY \qquad (15)$$

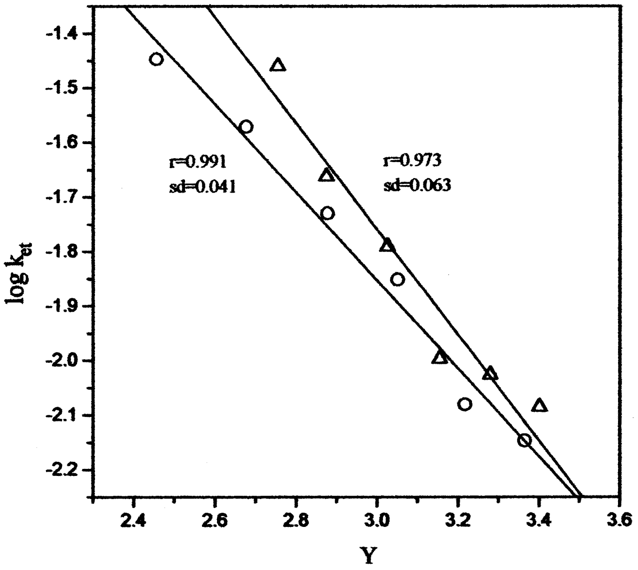

Figure 3. Plots of electron transfer rated constants, log k_{et}, as a function of solvent ionising power, *Y*, for the reduction of $Co(NH_3)_4(ox)^+$ by $Fe(CN)_6^{4-}$ in water−methanol (△) and water−1,4-dioxane (○) mixtures at 300 K.

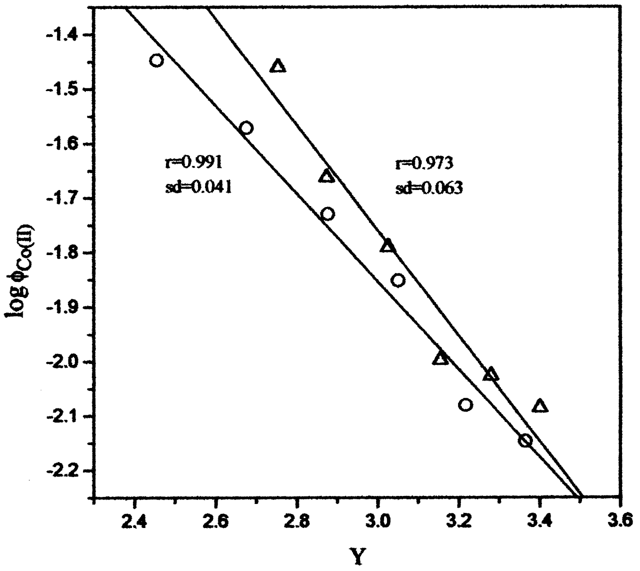

Figure 4. Plots of photoreduction quantum yield, log $\phi_{Co(II)}$, as a funtion of solvent ionising power, *Y*, for the photoreduction of $Co(NH_3)_4(ox)^+$ in water−methanol (△) and water−1,4-dioxane (○) mixtures at 300 K.

The availability of a large body of Grunwald−Winstein parameter, *Y*, provides an opportunity to scruitnise possible linear correlations of log k_{et} with *Y* in the binary mixtures. The parameter *Y* represents solvent ionising power, which is the ability of the solvent to transform the covalent bond into an ionic bond. The parameter is based on kinetic data for the dissociative solvolysis of *tert*-butyl chloride in aqueous ethanol. Figure 3 shows the dependence of the log k_{et} on the Grunwald−Winstein parameter, *Y*, which are linear and show good correlations yielding negative slopes for water−MeOH and water−Diox mixtures, respectively. The negative value of m suggests that $Co(NH_3)_4ox^+$ is reduced by $Fe(CN)_6^{4-}$ by an associative process through similar mechanism in various compositions of water-MeOH/Diox mixtures. Moreover, the negative *m* values indicate a lesser degree of charge separation[37] in the transition state or the transition state is less polar than the reactants. This means that the rate is accelerated by the solvent with lower ionizing power, *Y*, suggesting that ion pair formation is more facilitated.

Therefore, precursor ion pair, $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}$, formation is facilitated with a decrease in polarity of the medium, and this enhances the rate. Further, a negative *m* value is the indication[38] of reactions in which one of the separating moieties is a negatively charged species containing several hydrophilic groups. It is a clear indication for the fast separation of $Fe(CN)_6^{3-}$ ion from transition state. Hence, it is the clear indication that reduction of $Co(NH_3)_4ox^+$ by $Fe(CN)_6^{4-}$ proceeds via an outer sphere electron transfer mechanism. Figure 3 shows two lines of slightly different slopes for water−MeOH and water−Diox systems. The difference in slope is known as the phenomenon of dispersion, which strongly indicates a different blend of solvation effects such as nonspecific and specific interactions. In other words, the substrate parameter *m* is solvent dependent in these cases. If eq 15 is strictly obeyed, all of the points should lie on a single straight line. These observations indicate that the reaction rate does depend not only on the ionising power of the solvent but also on the specific solvation effects, like nucleoplicity, etc. Bulk solvent property like relative permittivity will poorly describe the microenvironment around the reacting species, which governs the stability of the intermediate and hence the electron-transfer reactions in liquid phase, which is complex due to many possible intermolecular solute−solvent interactions. Another problem in deciding which characteristics of the solvent effects are to be considered when the effects of the solvent on thier reactivity is determined.

Table 5 and Figure 2 indicate the addition of small quantities of organic cosolvent to water solution strongly increase the yield of the LMCT reduction of $Co(NH_3)_4ox^+$. Figure 4 is the plot of log $\phi_{Co(II)}$ vs the Grunwald−Winstein polarity parameter, where *Y* (obtained from kinetic measurements) shows good correlation of data. The point corresponding to the $\phi_{Co(II)}$ in water is outside the correlation, which suggests, at first, that the deviation of the water point in the above cases can be related to a phenomenon of preferential solvation.[39] The difference in the slope values obtained for the two binary mixtures indicate a different blend of solvation effects.

The linear variation of log k_{et} or log $\phi_{Co(II)}$ with solvent composition for the mixed solvents suggests solvent structural effects. That is, a small addition of organic cosolvent modifies the structure of liquid water. To shed light on this question, we consider bi- and triparametric regression equations consisting of microscopically interacting but complementary empirical parameters. Therefore, rate constant or quantum yield data are correlated with these empirical solvent parameters in appropriate equations. This is based on experimentally justified models in order to take into account two or more aspects of solvation effects.[8−10]

Regression Plane Model

Swain Equation. The most important properties of solvents affecting the chemical reactivity in an ET process are their anion-solvating (acity A) and cation-solvating (basity B) tendencies. They are empirical solvent parameters representing solvent properties such as the specific local electrostatic interactions of solvents with polar center or ions of solutes. For water−MeOH and water−Diox mixtures 5%−30% (v/v), these solvent vectors were derived based on the assumptions,[40] which seems reasonable for water rich mixtures. In terms of these dual solvent vectors, the Swain‘s relationship is given in eq 16

$$\log k_{et} = aA + bB + c \qquad (16)$$

TABLE 6: Application of Multiparameter Linear Regression Analysis on the Complementary Description of Solvent Effects Using Empirical Solvent Parameters for the $Fe(CN)_6^{4-}$ Reduction of $Co(NH_3)_4ox^+$ in Binary Mixture Solvents[a]

cosolvent	percentage contribution $P(X_i)$	estimated value	SD	R²	ψ
	$\log k_{et} = aA + bB + c$				
methanol	$P(A)$	67	0.062	0.961	0.245
	$P(B)$	33			
dioxane	$P(A)$	30	0.027	0.994	0.095
	$P(B)$	70			
	$\log k_{et} = A_0 + s\pi^* + a\alpha + b\beta$				
methanol	$P(\alpha)$	70	0.025	0.999	0.041
	$P(\beta)$	7			
	$P(\pi^*)$	23			
dioxane	$P(\alpha)$	3	0.004	0.999	0.012
	$P(\beta)$	73			
	$P(\pi^*)$	24			

[a] The signs of $P(A)$ and $P(\pi^*)$ are negative (water−methanol). The signs of $P(A)$, $P(\alpha)$, and $P(\beta)$ are negative (water−1,4-dioxane). *R* is a coefficient of multiple correlation and ψ is Exner's statistical weight, ensure best fit of data points.

TABLE 7: Application of Multiparameter Linear Regression Analysis on the Complementary Description of Solvent Effects Using Empirical Solvent Parameters for 254 nm Photo Reduction of $Co(NH_3)_4ox^+$ in Binary Mixture Solvents[a]

cosolvent	percentage contribution $P(X_i)$	estimated value	SD	R^2	ψ
	$\log \phi_{Co(II)} = Q_0 + aE_T^N + bDN^N$				
methanol	$P(E_T^N)$	63	0.018	0.999	0.012
	$P(DN^N)$	37			
1,4-dioxane	$P(E_T^N)$	94	0.002	0.999	0.008
	$P(DN^N)$	6			
	$\log \phi_{Co(II)} = A_0 + s\pi^* + a\alpha + b\beta$				
methanol	$P(\alpha)$	39	0.005	0.999	0.009
	$P(\beta)$	24			
	$P(\pi^*)$	37			
1,4-dioxane	$P(\alpha)$	23	0.002	0.999	0.008
	$P(\beta)$	45			
	$P(\pi^*)$	32			

[a] The signs of $P(E_T^N)$ and $P(\alpha)$ are negative (water−methanol). The signs of $P(E_T^N)$, $P(DN^N)$, $P(\alpha)$, and $P(\beta)$ are negative (water−1,4-dioxane). *R* is coefficient of multiple correlation and ψ is Exner's statistical weight, ensure best fit of data points.

where coefficients *a* and *b* represent the sensitivity of the reaction to solvent acidity and basicity parameters and c is the predicted value[9,10] of $\log k_{et}$ for the reference solvent. The $\log k_{et}$ values for the reduction of $Co(NH_3)_4ox^+$ by $Fe(CN)_6^{4-}$ in various compositions of binary mixtures were subjected to multiple regression analysis using eq 16, which shows good correlation. The specific solvation property, which dominates in altering the rate is determined by statistically quantifying the coefficient of the property under consideration using eq 3. For instance, $P(A)$ and $P(B)$ may be regarded as estimates of the percentage contributions from solvent, anion-solvating tendency, and cation-solvating tendency, respectively.

Table 6 is a computer generated table that lists quantified overall percentage contribution values $P(A)$ and $P(B)$ of *A* and *B*. The data were evaluated statistically by the familiar coefficient of multiple correlation *R* and also by Exner's ψ. Finally, it should be noted that the sign associated[41−44] with *a* or *b* indicates either direct (+) or reverse (−) proportionality between the solvent effects and *A* or *B*, respectively. The results of applying eq 16 to $\log k_{et}$ are summarized in Table 6. It is immediately apparent that $P(A)$ is 67 in water−methanol mixtures, whereas $P(B)$ is 70 in water−1,4-dioxane mixtures. These results can be attributed to the influence by solvent through anion-solvating tendency as well as cation-solvating tendency on the agglomerate or ion pair. In water−methanol media, the solvent as anion−solvator interacts chiefly with the $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}$ ion pair. The same effect is not observed in water−dioxane mixture, in which the solvational effect is mainly due to the cation-solvating tendency on the ion pair, $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}$.

It is assumed that the solvent effect on property *Q* (i.e., $\log \phi_{Co(II)}$) can be described in terms of the regression plane,[42] as described by Krygowski and Fawcett relationship (eq 17)

$$Q = Q_0 + aE_T^N + bDN^N \tag{17}$$

a and *b* are constants describing the sensitivity of the property *Q* to Lewis acidity and Lewis basicity of the solvent. The normalized, dimensionless Dimroth−Reichardt parameter, E_T^N, is chosen as a measure of Lewis acidity, which were evaluated for binary mixtures from the solvatochromic property of pyridinium-*N*-phenoxide dye.[41−43] Similarly, normalized Gutmann Donor number DN^N is chosen as a measure of solvent Lewis basicity, where DN^N is the negative enthalpy of formation of adducts between the uncharged Lewis acid $SbCl_5$ and a given solvent molecule as Lewis base in dilute 1,2-dichloro ethane solutions.[42]

The results of applying eq 17 to $\phi_{Co(II)}$ data are summarized in Table 7. It is immediately apparent that $P(E_T^N)$ and $P(DN^N)$ obtained in the case of water-methanol mixtures are 63 and 37, whereas in water−dioxane solutions, their values are 94 and 6, respectively. This result can be attributed to the formation of agglomerates or ion pairs, that is, {Co(II);ligand radical}, at mixed solvents, so that $\phi_{Co(II)}$ is influenced by solvent Lewis acidity and Lewis basicity. The Lewis acidity interaction is high (63 and 94) and occurs at the negative part of {Co(II);ligand radical} pair. The presence of a positive charge on the radical pair is more significant; that is, $\{Co(NH_3)_4^{2+};ox^-\}$, $\{Co(NH_3)_3ox;NH_3^+\}$, or $\{Co(NH_3)_4ox;S^+\}$ are the more probable pairs. Therefore, the solvent as a Lewis base (37 and 6) also interacts chiefly at the positive part of the pairs. In both water−methanol/1,4-dioxane solutions, $P(E_T^N)$ is large and in agreement with established ideas regarding anionic part solvation. The greater Lewis acidity/basicity of solvent, greater the solvation, and more the $\phi_{Co(II)}$ yield.

It should be noted that the value of Q_0, the predicted $\phi_{Co(II)}$ in the absence of solvent interactions ($E_T^N = DN^N = 0$), is low, whereas a larger value is observed in methanolic solutions ($\phi_{Co(II)} = 8.06 \times 10^{-2}$). This comparison gives some indication of the important role of the magnitude of solvent effect on this quantity.

Regression Tetragonal Model

Interrelation of Solvation Effects. The inclusion of a dipolarity/polarizability term (π^*) in regression plane makes easier the correlation in prediction of the extent of short range and long range solvation effects. Accordingly, combining our findings with a triparametric equation covering a different range of the property studied yields a characteristic intercept and coefficients of the independent variables. A number of workers have recognized the possibility that various solvation effects on solutes in reactions may be resolved into individual components, when we include the additional term, there was, indeed a seemingly significant improvement in statistical goodness of fit. The three parameter correlation was proposed[14] by Kamlet–Taft.

Kamlet–Taft Equation. The above discussion is directly pertinent to the problem of deciding the specific interaction of solvent in solute–solvent interactions. Presumably, to measure both the nonspecific and specific solvent effects on reaction, it is proved that Kamlet–Taft's relationship works well. The experimental rate constants, log k_{et}, from Tables 1 and 2 were also correlated by forming a set of simultaneous equation of the form in eq 18

$$\log k_{et} = A_0 + s\pi^* + a\alpha + b\beta \qquad (18)$$

The solvatochromic parameters were evaluated on the common mole fraction composition scale.[40] The π^* scale is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. The α scale of solvent HBD (hydrogen bond donor) acidity describes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond. The β scale of HBA (hydrogen bond acceptor) basicity provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond. The coefficients s, a, and b are constants describing the sensitivity of log k_{et} to π^*, α, and β scales. The relative importance of the solvent parameters are defined in the statistics of multiple linear regression by the relationships in eqs 1 and 2. The coefficients are normalized to estimate the percentage contributions from solvent polarizability, HBD and HBA ability, respectively. The weighted values are $P(\pi^*)$, $P(\alpha)$, and $P(\beta)$, which are on the same scale, comparison of these parameters gives an estimate of the relative importance of solvent property. It is evident from Table 6 that the bulk solvent effect, that is, nonspecific contribution, is 23 and 24 in water–MeOH and water–Diox mixtures, respectively. The weighted regression coefficient $P(\alpha) = 70$ and $P(\beta) = 7$ in water–MeOH, whereas $P(\alpha) = 3$ and $P(\beta) = 73$ in water–Diox mixtures, indicating that almost all of the explained variation can be attributed to specific effect, that is HBD or HBA ability of water–MeOH or water–Diox mixture. From the above, it may be concluded that solvent–solute and solute–medium dipolarity/polarizability interactions covary so strongly that they can be properly apportioned to measure solvation effects.

Electron-transfer process is presumed to consist a partial reorientation of the solvent molecules in the first solvation shell of the precursor ion pair followed by fast electron transfer. The rate/$\phi_{Co(II)}$ is increasing with respect to x_2 of MeOH or Diox and is in line with an observed behavior for cobalt(III)–amine systems. The anionic compartment of $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}$ is predominantly solvated because of anion-solvating tendency ($P(A) = 67$) and is supported by the HBD ability of solvent mixtures ($P(\alpha) = 70$) in water–methanol mixtures, and conversely, the cationic compartment of $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}$ is predominantly solvated because of the cation-solvating tendency ($P(B) = 70$), which is confirmed by the HBA ability ($P(\beta) = 73$) in water–Diox mixtures. The positive value of $P(X_i)$ in the mixtures is interpreted as indicating the amount of destruction to solvent structure accompanying solvation. Thus, the chemical linkage between transition state and the solvent molecules of first solvation shell is very rapid. On the other hand, the negative value of $P(X_i)$ indicates that the bond formation between the transition state and the solvent molecules is very late comparing the earlier case. As x_2 of cosolvent increases in various mixtures, MeOH or Diox interacts with the water structure or interstitially into the cavities; therefore, microheterogeneity sets in. Such interactions can affect the ion pair $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}$ modifying the solvation shell of the ion-pair, in which the microheterogeneous effect because of the cosolvent is pronounced. This stabilizes the ion pair, which leads to enhanced rate at higher x_2 values.

Mechanistic discussion for the observed photoreactions must account for the medium dependent quantum yields, that is, for the photoreduction of Co(III). It is attractive to assume that Co(II) is only formed by population of CT excited states. The reduction of Co(III) → Co(II) is consistent with the ligand → Co(III) CT band and solvent → Co(III) CT band assignments. The influences of the solvation effects on the relative $\phi_{Co(II)}$ can be probed through a consideration of Kamlet–Taft triparametric eq 19

$$\log \phi_{Co(II)} = A_0 + s\pi^* + a\alpha + b\beta \qquad (19)$$

A multiple linear regression to fit $\phi_{Co(II)}$ against α, β, and π^* (eq 19) is useful. The correlation coefficient, R, suggests that the observed photoreduction behavior is well expressed in terms of Kamlet–Taft parameters. The percentage contribution of the parameter on the solvent dependent reduction yield of $\phi_{Co(II)}$ indicates a dominant influence of HBD ability in water–methanol mixtures and HBA ability in water–dioxane mixtures on {Co(II);ligand radical pair}. The analysis afforded $P(\alpha) = 39$ and $P(\beta) = 45$ in water–methanol and water–dioxane, respectively. That is, hydrogen bond formation or the short range solvation is evident, which accounts nearly 63–68% in water–methanol/dioxane mixtures, whereas the long-range polarity/polarizability effect of solvent on the radical pair is 37–32% in the above mixtures. Recently, a laser photolysis study of a Cr(III) complex showed the presence of coordinated water hydrogen bonded to pyridine ligand.[44] These results suggest that the degree of hydrogen bond making by the primary radical pair in different compositions of solvent leads to a favorable reduction path. The $\phi_{Co(II)}$ values of $Co(NH_3)_4ox^+$ in the water–organic cosolvent mixtures vary as methanol > dioxane, an order that seemingly reflects both short and long range solvent properties on photoreduction.

The structural characteristics of the mixtures of water–MeOH/Diox emerge from reported studies, and MeOH is a protic EPD (electron pair donor) solvent with self-associating ability although it contains a hydrophobic headgroup. In the water–methanol system, both constituents are capable of hydrogen bonding, and a small addition of methanol to water causes contraction in volume[45] leading to enhanced water structure similar to that of a highly pressurized water,[46] a phenomenon commonly referrred as hydrophobic interaction. A recent neutron diffraction study[47] established the presence of a hydration shell of water molecule and MeOH molecule in the form of a disordered cage. Therefore, the presence of a solute induces a solute–solvent and solvent–solvent interaction leading to the formation of hydrogen bonded dimers/polymers of clatharates such as solvated complexes of differently composed microphases. Moreover, theoretical investigations on the structural aspects of $MeOH-H_2O$ mixtures by Kirkwood–Buff theory[48–51] indicate the existence of hydrophobic interaction effect.[52] Hence, it is suggested that CH_3OH from the solvation shell of the transition state interacts electrostatically through the –OH hydrophilic group along with the $-CH_3$ hydrophobic tail. On these grounds, the marked variation in reduction rate/quantum yield of $Co(NH_3)_4ox^+$ in solvents in the range $x_{MeOH} = 0.02-0.16$ is due to the hydrophobic environment of reactants, intermediate, or both. This is in line with earlier report;

Amis[53] and Cox et al.[54] established the preferential incorporation of organic solvent molecules into the solvation shell of simple ions. This preference in solvation can produce virtual inclusion of hydrophobicity in the solvation cosphere of the intermediate CT excited state by MeOH, which is not inconsistent with related literature opinions. Such a local specific effect of solvent facilitates the formation and stability of $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}/\{Co(II);ligand\ radical\}$ leading to increased rate/$\phi_{Co(II)}$ as x_{MeOH} increases. The hydrophobic effect does enhance as compared to the fully aqueous medium in the present reaction and the enhancement is well increased in binary solvents under study.

Dioxane is a partially hydrophobic cosolvent.[40] It has been noted that self-clustering of water is eliminated when Diox is present in lower compositions, viz., $x_{Diox} = 0.01-0.08$. This leads to microheterogeneity of the water−dioxane mixtures. In such cases, it has been found that α and β values measured for the lower x_{Diox} represent an average environment that a solute sees. In our systems under investigation, the limit of x_{Diox} is such that Diox can any longer be accommodated within the water structure[54] favoring the applicability of the concept of microheterogeneity to a lower range of compositions in the mixtures. In fact, Wahl and co-workers[55,56] point out in their redox studies with metal complexes that there is space between the coordinated ligands of each reactant to accommodate solvent molecules. To get a better insight into the effect of organic cosolvent on the reduction rates of $Co(NH_3)_4ox^+$, (Figures 1 and 2) organic cosolvent up to 30% (v/v) has been added, which resulted in a very marked effect in increasing the rate/$\phi_{Co(II)}$. This indicates that the addition of MeOH or Diox to the medium brings about marked structural changes in the prevailing water structure by making progressive desolvation between partners of the transition state/geminate radical pair which in all probability is highly solvated in the water medium.The influence of water−organic cosolvent mixtures during solvation of either $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}/\{Co(II);ligand\ radical\}$ or the incipient reactants directly or indirectly (Tables 6 and 7) facilitates the precursor complex/CT excited state formation because of specific local electrostatic interaction.[52] In the present system, only a stablizing effect due to solvation of water−methanol and water−dioxane is expected, and a higher K_{IP} is predicted (K_{IP} in water−methanol is 20−22 dm^3 mol^{-1} and in water−dioxane is 30−22 dm^3 mol^{-1}). The electrostatic interaction between the precursor complex and solvent mixtures should result in a net increase in the order of the system because of a reduction in the net charge and decreasing medium polarity. The relatively large negative value of $\Delta S^{\#}$ obtained (Table 4) suggests a highly ordered first solvation shell because of inclusion of organic solvent moieties, which is important in the formation and stability of precursor ion pair $\{Co(NH_3)_4ox^+;Fe(CN)_6^{4-}\}$ leading to products. Further, association of reactant ions and stabilization of a geminate radical pair are especially attractive in solvents with decreasing relative permittivity. Therefore, our result suggests the following: (I) The reduction rate/quantum yield of Co(II) formation of $Co(NH_3)_4ox^+$ is increased with increasing mole fraction of organic cosolvent, which facilitates formation and stabilization of ion pair or geminate radical pair. Low ϵ_r values lead to solute−solute interactions (ion pairing of unlike charged species) even in dilute solutions; this effect is strongly supported by thermodynamic parameters. (II) The positive sign of multiparametric coefficients suggests that the solvent mixture strongly solvates the transition state, and the negative sign of the coefficients shows the specific solvation of incipient reactants. (III) The reaction is influenced by nonspecific, long-range effects as analyzed by ϵ_r, Y, and π^* parameters of the solvent. (IV) Also, certain chemical properties of solvent mixtures such as hydrophobicity, described by specific local electrostatic effect of solute−solvent, may be very important in reaction rates. Such effects can be analyzed by independent quantities such as A, B, E_T^N, DN^N, α, and β set of empirical solvent parameters.

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