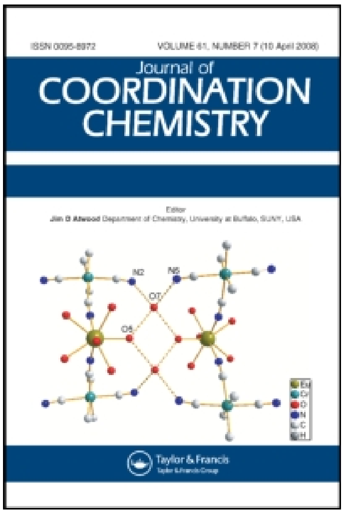

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Solvent and structural effects on the electro- and photo-reduction of <i>cis</i>-<i>β</i>-Co(trien)($RC_6H_4NH_2$)Cl]Cl_2 type complexes in water/1,4-dioxane media

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Solvent and structural effects on the electro- and photo-reduction of *cis*-β-[Co(trien)($RC_6H_4NH_2$)Cl]Cl_2 type complexes in water/1,4-dioxane media

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The electro- and photo-reduction of a series of cobalt(III) complexes of the type *cis*-β-[Co(trien)($RC_6H_4NH_2$)Cl]Cl_2 where R=H, *p*-OMe, *p*-OEt, *p*-Me, *p*-Et, *p*-F and *m*-Me has been studied in 1,4-dioxane/water. The redox potential ($E_{1/2}$) and photo-reduction quantum yield ($\phi_{Co(II)}$) data were correlated with solvent and structural parameters to shed light on the mechanism of these reactions. Correlation of $E_{1/2}$ and $\phi_{Co(II)}$ with macroscopic solvent parameters *viz*. relative permittivity indicates that the reactivity is influenced by both specific and non-specific solute-solvent interactions. The Kamlet-Taft solvatochromic comparison method was used to separate and quantify these effects. Increasing the percentage of organic co-solvent in the medium enhances both reduction processes; there exists good correlation between $E_{1/2}$ and $\phi_{Co(II)}$ suggesting a similar solvation in these redox processes.

Keywords: Cobalt(III) complexes; Photo-reduction; Electrochemistry; Solvent effect; Hammett equation

1. Introduction

Influence of solvent and structure on the reactions of cobalt(III) complexes in mixed solvents and correlation of reaction rates with various solvent and structural parameters affords important mechanistic information. Accumulated information on the correlation of reaction rates with solvent properties through Linear Solvation Energy Relationships (LSER) has led to significant results [1–6]. Solvent characteristics, such as hydrophobic effects, preferential solvation, anion and cation solvating tendencies, hydrogen bond donor-acceptor properties, etc., influence the kinetics and energetics of the reaction of cobalt(III) complexes.

Even though single empirical parameters can be used as good approximations of solvent polarity, no single macroscopic physical parameter accounts for the multitude of solute-solvent interactions on the microscopic level [7]. Thus, bulk solvent properties like relative permittivity [8], solvent ionizing power [9] and/or dipolarity/polarizability [10] poorly describe the microenvironment around the reacting species, which governs the stability of the intermediate and hence the rate of the reaction. A variety of attempts

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have been made to quantify different aspects of solvent polarity and then to use the resultant parameters to interpret the solvent effects on reactivity through multiple regression analysis. Various treatments for solvent-solvent-solute interactions based on LSER have been developed [11]. Although separation of solvent effects into various solvent-solvent-solute interaction is purely formal, the multi-parameter approach to solvent effects has been shown to work well [12].

Structural variation studies give much better insight into the nature of the transition state and the mechanism of redox reactions. Most of the work in this area has dealt with pentammine complexes, emphasis being placed on the dependence of reaction rates upon the nature of the sixth ligand [13]. Further, it is of interest to study electro- and photo-reduction in binary solvent mixtures which are more complex than pure solvents due to varying degrees of solute-solvent interactions. In a pure solvent the composition of the microsphere of solvation of a solute, the so called cybotatic region, is the same as in the bulk solvent, but in binary mixtures the composition in this microsphere can be different. The solute can interact to different degrees with the components of the mixture, and this difference in the interactions is reflected in the composition of the microsphere of solvation. The effect of varying the composition of the mixture from the bulk solvent to the solvation sphere is called preferential solvation [14].

The main objective of the present work is to study the substituent and solvent effects on the electro- and photo-reduction of a series of Co(III)-aryl amine complexes of the type $[Co(trien)(RC_6H_4NH_2)Cl]Cl_2$, in water/1,4-dioxane mixtures of varying compositions and correlation analysis of the data using linear free energy relationships to get better insight into the mechanisms.

2. Experimental

2.1. *Materials*

All chemicals used were of high purity analytical grade (Aldrich, Merck, India). The cobalt(III) complexes, *cis*-β-$[Co(trien)(RC_6H_4NH_2)Cl]Cl_2$ where R=H, *m*-Me, *p*-Me, *p*-Et, *p*-OMe, *p*-OEt and *p*-F were prepared and purified as described [15]. The organic co-solvent, 1,4-dioxane, was spectroscopic grade (Merck, India) and was used as received. Doubly-distilled water was used throughout the work.

2.2. *Electrochemical experiment*

Solutions of cobalt(III) complexes were prepared with double distilled water. All electrochemical experiments were performed at 25°C using a standard three-electrode, two compartment configuration with a glassy carbon (GC–3 mm) working electrode, a spiral platinum counter electrode and a Ag|AgCl (KCl sat.) reference electrode. The carbon electrodes were polished between experiments with alumina (0.5 μm) paste. The cyclic voltammetric experiments were carried out with a computer-controlled electrochemical system (CHI643B Electrochemical Analyzer) at $50\,mV\,s^{-1}$. All solutions were deoxygenated thoroughly by purging with nitrogen for 15–20 min before measurement.

2.3. *Photolysis experiment*

Solutions for photolysis contained the Co(III) complex (4×10^{-3} M), and $NaNO_3$ (0.1 M). All solutions contained binary solvents of varying compositions: 1,4-dioxane in water [0–40% (v/v) of co-solvent]. Steady photolysis experiments were carried out using a low pressure mercury vapor pen-ray quartz lamp (254 nm). Air-equilibrated solutions were used for photolysis and the temperature control was maintained at $25 \pm 1°C$. For quantum yield determinations, photolysis was carried out to within less than *ca.* 15% of the total reaction. The incident light intensities were measured by potassium ferrioxalate actinometry [16]. Quantum yields were calculated, estimating Co(II) formed by Kitson's method [17]. All absorption measurements were carried out using a Shimadzu UV–Vis (UV 240 Graphicord) double beam spectrophotometer.

2.4. *Linear free energy relationships*

The effect of solvent macroscopic property, the relative permittivity, ε_r, on reactivity can be described by the equation of Laidler and Erying [8]:

$$\mathrm{d}\ \ln k/\mathrm{d}(1/\varepsilon_r) = e^2 Z^2 (1/r - 1/r^*)/2\mathrm{kT} \tag{1}$$

where k is the rate constant ($E_{1/2}$ in the case of electro-reduction or $\phi_{Co(II)}$ in the case of photo-reduction), Z the net-charge, r the effective radius and r^* the radius of the activated species. The data were also correlated with donor number which has proven very useful in coordination chemistry, correlated with other physical observables such as redox potentials [7].

As stated above, both specific and nonspecific solute-solvent-solvent interactions can influence the reactivity. Hence, the data were analyzed using the Kamlet-Taft solvatochromic comparison method equation (2), which incorporates both types of interactions.

$$\log \mathrm{k} = A_0 + \mathrm{s}\pi^* + a\alpha + b\beta \tag{2}$$

where π^* is an index of solvent dipolarity/polarizability measuring the ability of the solvent to stabilize a charge or dipole by virtue of its dielectric effect, α is the solvent hydrogen bond donor (HBD) acidity which describes the ability of the solvent to donate a proton, β is the solvent hydrogen bond acceptor (HBA) basicity which provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond, and A_0 is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients s, a and b measure the relative susceptibilities of the solvent dependent solute property $\log \mathrm{k}(E_{1/2}$ or $\phi_{Co(II)}$ in the present study) to the indicated solvent parameter. These solvatochromic parameters for the aqueous organic mixtures used in the present study were calculated as described [12].

The effect of substituent on reactivity was tested using the Hammett equation [11]:

$$\log k = \log k^0 + \rho\sigma \tag{3}$$

where k is the rate constant ($E_{1/2}$ or $\phi_{Co(II)}$ in the present study). The symbol k^0 denotes the statistical quantity corresponding approximately to k for the unsubstituted compound, σ is characteristic of the substituent (in a given position, *meta* or *para*) and independent of the reaction, whereas ρ is determined by the reaction and its conditions (reagent, solvent, catalyst, temperature) and is independent of the substituent.

2.5. *Data analysis*

Correlation analyses were carried out using Microcal origin (version 6) computer software. The goodness of the fit was discussed using correlation co-efficient (r in the case of simple linear regression and R in the case of multiple linear regression) and standard deviation (sd) [11]. In case of multiple correlation analysis, the percentage contribution ($\mathbf{P}_X$) of a parameter to the total effect on reactivity was computed as reported earlier [18].

3. Results and discussion

The solvent and substituent effects on the electro- and photo-reduction of a series of Co(III)-aryl amine complexes of the type *cis*-β-[Co(trien)($RC_6H_4NH_2$)Cl]Cl_2, where R=H, *p*-OMe, *p*-OEt, *p*-Me, *p*-Et, *p*-F and *m*-Me, in varying concentrations of 1,4-dioxane in water were investigated. Attempts have been made to analyze the effect of solvent and structure on the redox potentials ($E_{1/2}$) and photo-reduction quantum yields ($\phi_{\mathrm{Co(II)}}$) of the complexes using simple and multiple regression equations.

3.1. *Electro-reduction study*

Cyclic voltammetric behavior of Co(III)-aryl amine complexes were examined in varying percentage of 1,4-dioxane in water containing sodium perchlorate (0.1 M) as supporting electrolyte at a scan rate of $50\,\mathrm{mV\,s^{-1}}$. The redox potential data for all the complexes in water is given in table 1. Generally the redox potentials are better expressed by $E_{1/2}$ than by the anodic peak E_{pa} or cathodic peak E_{pc} potentials, because both E_{pa} and E_{pc} change with scan rate, whereas $E_{1/2}$ is independent of the scan rate [19]. The redox potential ($E_{1/2}$) of the Co(III)/Co(II) couple was determined from equation (4) [20].

$$E_{1/2} = \frac{(E_{pa} + E_{pc})}{2} \tag{4}$$

Table 1. Electrochemical data (E_p, V) from CV for cobalt(III) complexes in water.

Substituent in aniline moiety	E_{pa}(III/IV)	E_{pc}(II/I)	E_{pc}(III/II)	E_{pa}(II/III)	ΔE_p
H	0.923	−0.218	0.288	0.270	18
p-OMe	0.864	−0.392	−0.198	−0.344	146
p-OEt	0.861	−0.365	−0.213	−0.316	103
p-Me	0.860	−0.360	−0.192	−0.308	116
p-Et	0.852	−0.342	−0.195	−0.125	70
m-Me	0.834	−0.330	0.220	0.193	27
p-F	0.820	−0.092	0.254	0.229	25

A representative cyclic voltammogram is shown in figure 1 and all other complexes exhibit similar cyclic voltammograms. Cyclic voltammograms of these complexes show one well-defined redox peak corresponding to the Co(III)/Co(II) couple. Similar observations were made by Vasilevskis *et al.* [21] and Ortiz *et al.* [22] for cobalt(III) complexes. An irreversible cathodic peak is observed for all complexes at negative potentials, due to reduction of Co(II) to Co(I). The irreversible anodic peak at 0.9 V may be due to oxidation of the aniline [5, 23]. The ΔEp values (table 1) show the reversible (H, *m*-Me and *p*-F) and quasi-reversible (*p*-OMe, *p*-OEt, *p*-Me and *p*-Et) nature of Co(III)/Co(II) redox couple [24].

The anodic and cathodic potential data indicate the sensitivity of the Co(III)-aryl amine complexes to the nature of the sixth ligand, previously described in the electrochemistry of cobaloximes [25]. The ratio (RIp) of the anodic peak current to the cathodic peak current is close to unity ($0.8 < \mathrm{RIp} < 1$) indicating the reversibility or quasi-reversibility of the Co(III)/Co(II) couple. The ratio is independent of the scan rate in the investigated solvent media and the peak currents were essentially constant for several cycles, indicating that there were no chemical reactions coupled with the electron transfer [19]. Furthermore, the reduction potential E_{pc} was found to depend on scan rate. The correlation of log scan rate *versus* E_{pc} is linear ($r = 0.986$, $\mathrm{sd} = 0.006$). The rate of reduction computed from the slope of the straight line for [Co(trien)(p-$FC_6H_4NH_2$)Cl]Cl_2 in water was 0.2554 s^{-1}.

The electro-reduction of Co(III) complexes has been studied in 1,4-dioxane in water ranging from 0 to 40% v/v of co-solvent. The electrochemical data as a function of co-solvent percentage are collected in table 2. A representative cyclic voltammogram for the reduction of [Co(trien)($C_6H_5NH_2$)Cl]Cl_2 with increasing percentage of 1,4-dioxane in water is depicted in figure 2. The general pattern of the curves remains unaltered with change in the composition of the solvent, indicating that the co-solvent does not alter

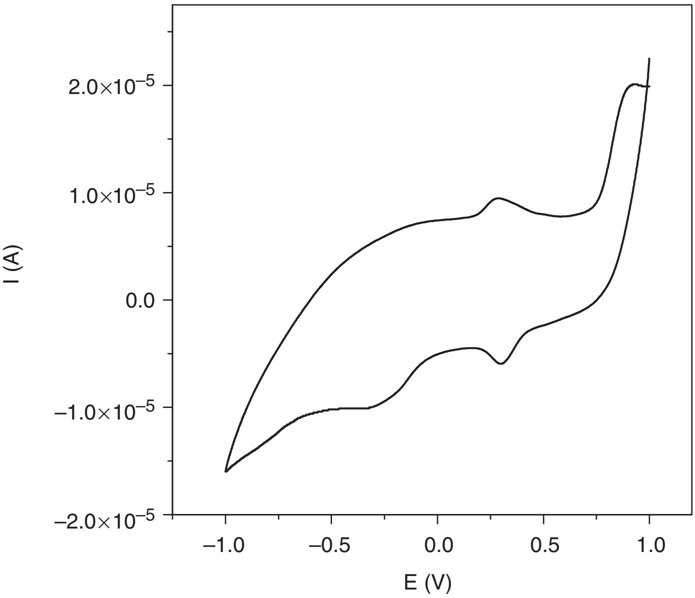

Figure 1. Cyclic voltammogram of [Co(trien)($C_6H_5NH_2$)Cl]Cl_2 in water at a scan rate of 50 mV s^{-1}.

Table 2. Electrochemical data ($E_{1/2}$, V) from CV for Co(III) complexes in varying percentage of 1,4-dioxane in water.

Substituent in aniline moiety	% of dioxane								
	0	5	10	15	20	25	30	35	40
H	0.279	0.270	0.278	0.286	0.290	0.294	0.295	0.297	0.302
p-OMe	−0.271	−0.270	−0.267	−0.262	−0.254	−0.246	−0.238	−0.233	−0.227
p-OEt	−0.265	−0.256	−0.253	−0.250	−0.244	−0.238	−0.231	−0.221	−0.213
p-Me	−0.250	−0.240	−0.223	−0.211	−0.195	−0.186	−0.176	−0.166	−0.154
p-Et	−0.160	−0.153	−0.150	−0.143	−0.141	−0.138	−0.134	−0.132	−0.125
m-Me	0.207	0.265	0.266	0.272	0.273	0.274	0.274	0.275	0.276
p-F	0.260	0.266	0.269	0.270	0.270	0.274	0.281	0.286	0.282

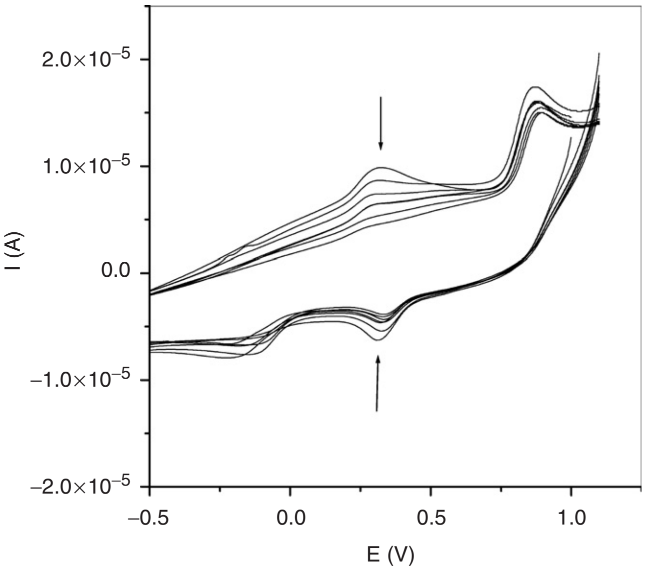

Figure 2. The cyclic voltammogram of $[Co(trien)(C_6H_5NH_2)Cl]^{2+}$ in varying percentage (0–40%) of dioxane in water.

the mechanism of the reduction. However, change in composition of the solvent influences the ease of the reduction process. For all the complexes, correlation of $E_{1/2}$ with inverse of relative permittivity of the medium is just satisfactory ($0.98 \geq r \geq 0.85$). The positive slopes (figure not shown) indicate that $E_{1/2}$ increases with increase in concentration of the co-solvent in the mixture. Thus, the addition of 1,4-dioxane in the mixture makes the reduction of Co(III) to Co(II) easier.

The $E_{1/2}$ also correlates with normalized donor number, DN^N, of the solvent mixture ($0.96 \geq r \geq 0.83$) with negative slope. The DN^N values employed in the present study were calculated as described earlier [26]. A representative plot is shown in figure 3. For a given complex, the $E_{1/2}$ shifts toward more positive potentials with decrease in DN^N, with rise in concentration of the organic co-solvent. The shift of $E_{1/2}$ can be explained by donor-acceptor Lewis-type interactions. Increasing organic co-solvent in the mixture may stabilize Co(II) and consequently makes the reduction easier [19].

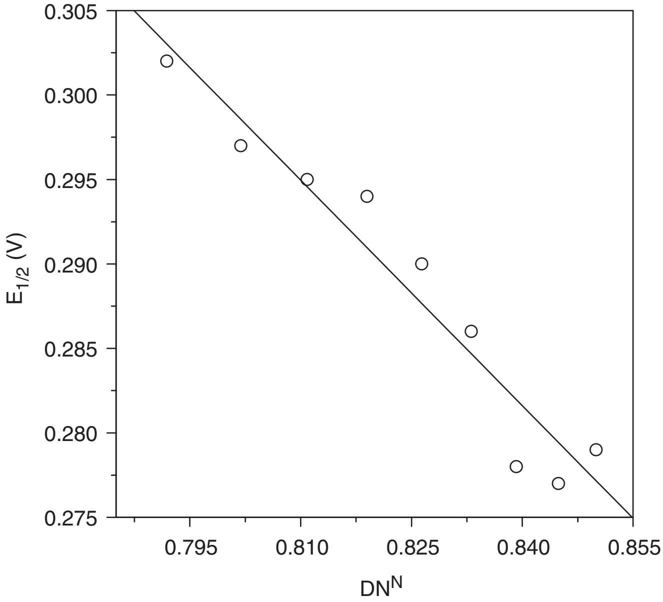

Figure 3. Plot of $E_{1/2}$ *vs.* DN^N for $[Co(trien)(C_6H_5NH_2)Cl]Cl_2$.

The simplicity of idealized electrostatic models for the description of solvation of ions and dipolar molecules, considering solvents as non-structured continua, has led to the use of physical constants, such as relative permittivity, ε_r, refractive index, n, or functions thereof, as macroscopic solvent parameters for the evaluation of medium effects. However, solute-solvent interactions take place on a molecular microscopic level within a structured discontinuum consisting of individual solvent molecules, capable of mutual solvent-solvent interactions. For this reason, and because of neglecting specific solute-solvent interactions, the electrostatic approach to medium effects often failed in correlating observed solvent effects with solvent parameters. Satisfactory quantitative descriptions of medium effects take into account all nonspecific and specific solvent-solvent-solute interactions. The separation of solvent polarity into nonspecific and specific solvent-solvent-solute interactions is purely formal, but, if this separation can be reasonably done, the resultant parameters may be used to interpret solvent effects through such multiple correlations, providing information about the type and magnitude of interactions with the solvent [7].

Dual dependency of reactivity on solvent composition is illustrated by the Kamlet-Taft solvatochromic comparison method [10], which may be used to quantify, correlate and rationalize multiple interacting solvent effects on reactivity. Thus, the experimentally measured redox potential values, $E_{1/2}$, for the Co(III)/Co(II) couple were correlated with the solvatochromic parameters α, β and π^*. The $E_{1/2}$ values in the solvent mixtures investigated show excellent correlation with Kamlet-Taft parameters with an observed variance of ca. 98%. The statistical results of the correlation and weighted percentage contributions of the solvatochromic parameters are presented in table 3.

Table 3. Statistical results and weighted percentage contributions for the correlation of redox potential ($E_{1/2}$) of Co(III/II) with Kamlet-Taft's solvatochromic parameters α, β and π^*.

Substituent in aniline moiety	$100R^2$	sd	*a*	*b*	*s*	P_α	P_β	P_{π^*}
H	93	0.004	06	−94	−46	14	36	50
p-OMe	99	0.002	20	−24	−53	42	08	50
p-OEt	99	0.001	−04	32	−19	22	29	49
p-Me	99	0.005	44	−130	−143	34	16	50
p-Et	96	0.003	−03	−27	−03	34	49	17
m-Me	92	0.004	38	−48	−100	27	06	67
p-F	94	0.008	36	02	−77	50	00	50

The observation of this multiple regression analysis leads to the following preliminary conclusions: (i) The weighted percentage contributions indicate that both specific and non-specific solute-solvent interactions play an almost equal role in the reactivity of the complexes. (ii) The sign of the coefficients a and b of the triparametric equation is randomly observed; all observations of a particular set of experiments do not result in values with similar sign. This means that the medium interacts in a complex manner with the reactant/excited state [1]. (iii) The signs of the coefficients of the dipolarity/polarizability term are negative. Hence, the value of $E_{1/2}$ increases with decreasing dipolarity/polarizability of the medium. Thus, the reduction of Co(III) to Co(II) becomes relatively easier with increase in organic co-solvent.

The effect of substituents on aniline on the redox potentials of Co(III)/Co(II) couple was studied with seven substituted anilines as ligands. The redox potentials are given in table 2. The $E_{1/2}$ correlates linearly with the Hammett's substituent constants and a typical plot is shown in figure 4. The statistical results for these plots are given in table 4. Positive values of the reaction constant, ρ, indicate that electron-donating substituents shift the redox reaction to a more cathodic potential [27]. The reaction constants for metal reductions are always smaller than for simple ligands, as observed herein [5].

3.2. *Photo-reduction study*

The quantum yields, $\phi_{\mathrm{Co(II)}}$, measured at 254 nm for photoreduction of all the cobalt(III)-aryl amine complexes in various water/1,4-dioxane mixtures, are collected in table 5. $\phi_{\mathrm{Co(II)}}$ increased as the mole fraction of the organic co-solvent increased, due to reduction of metal center by the ligand (LMCT) and the solvent (solvent-to-metal charge transfer). This argument is in line with that suggested by Kutal *et al.*, for photoreduction of cobalt(III)-am(m)ine complexes [28]. Therefore, attempts have been made to analyze the effect of solvent and substitution on the photo-reduction quantum yields of the cobalt(III)-aryl amine complexes using linear and multiple regression equations.

The correlation of photo-reduction quantum yields with inverse of relative permittivity of the medium through Laidler-Erying [8] equation is only satisfactory ($0.99 \geq r \geq 0.87$). The positive slope indicates the excited state is less polar than the reactant. Such an excited state will more easily be attained in a medium of lower

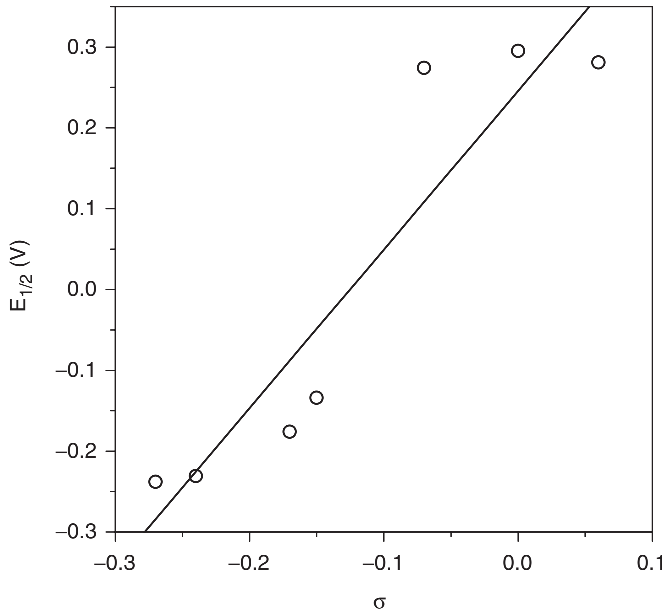

Figure 4. The plot of $E_{1/2}$ *vs.* σ in 30% dioxane.

Table 4. Simple linear correlation of the redox potential data, $E_{1/2}$, with substituent constants.

% of 1,4-dioxane in water	100*r*	sd	ρ
0	93	0.10	1.977 ± 0.35
5	92	0.11	2.024 ± 0.38
10	93	0.11	2.022 ± 0.37
15	93	0.11	2.017 ± 0.37
20	93	0.11	1.991 ± 0.36
25	93	0.11	1.978 ± 0.36
30	93	0.10	1.963 ± 0.35
35	93	0.10	1.949 ± 0.34
40	93	0.10	1.918 ± 0.34

relative permittivity. Similarly, the experimental data also correlate with donor number ($0.98 \geq r \geq 0.84$) with negative slope. A representative plot is shown in figure 5.

As solvent macroscopic parameters fail to completely explain the solvent dependency of reactivity, it is assumed that photo-reduction of Co(III) complexes may also be influenced by both specific and non-specific solute-solvent interactions as described earlier in this article for electro-reduction. The dual dependency of reactivity on solvent composition was tested using the Kamlet-Taft equation. The $\phi_{\mathrm{Co(II)}}$ values in different 1,4-dioxane/water mixtures show excellent correlation via equation (2) with an observed variance of ca. 98%. The statistical results of the correlation and weighted percentage contributions of the solvatochromic parameters are given in table 6.

Table 5. Quantum yields ($10\phi^2_{Co(II)}$) for photo-reduction of [Co(trien)($RC_6H_4NH_2$)Cl]Cl_2 in air-equilibrated 1,4-dioxane/water mixtures at 25 ± 1°C.

Substituent in aniline moiety	1,4-dioxane, % (v/v)								
	0	5	10	15	20	25	30	35	40
H	7.01	7.06	7.17	7.11	7.28	7.41	7.46	7.53	7.65
p-OMe	4.71	4.79	4.87	4.94	5.05	5.18	5.30	5.44	5.58
p-OEt	4.46	4.50	4.79	4.91	5.14	5.28	5.48	5.63	5.76
p-Me	4.81	4.88	4.95	5.02	5.07	5.15	5.23	5.29	5.41
p-Et	5.26	5.15	5.23	5.27	5.31	5.36	5.42	5.49	5.54
m-Me	3.16	3.25	3.34	3.43	3.52	3.53	3.54	3.86	3.89
p-F	4.56	4.62	4.65	4.77	4.83	4.91	5.01	5.08	5.14

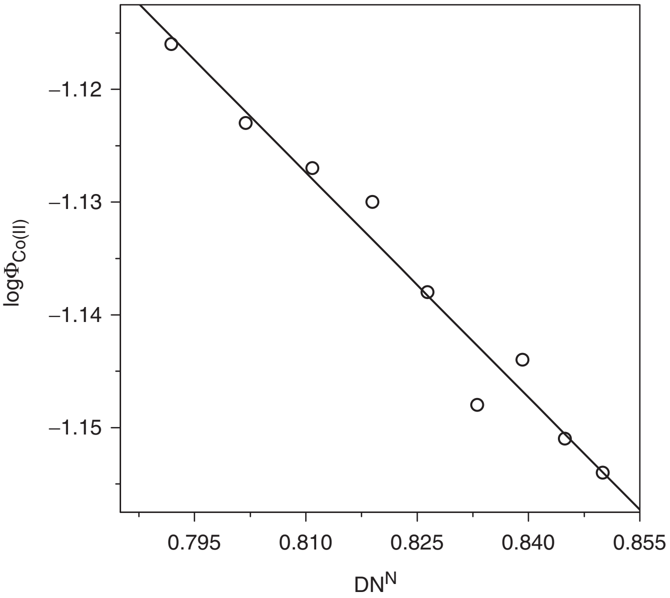

Figure 5. Plot of log $\phi_{Co(II)}$ *vs.* DN^N for [Co(trien)($C_6H_5NH_2$)Cl]Cl_2.

The results indicate: (i) The specific solute-solvent interactions, as indicated by P_α and P_β, play a major role in governing the reactivity of the complexes. (ii) The sign of the coefficients a and b of the triparametric equation is random due to the medium interacting in a complex manner with the reactant/excited state [1]. (iii) The dipolarity/polarizability of the mixture also plays an important role in the observed solvent effect as shown from percentage contribution values. The sign of the coefficient of this term is negative, showing that decrease in dipolarity/polarizability stabilizes the less polar excited state, and consequently increases the $\phi_{Co(II)}$. Parallel observations were made earlier for photo-reduction of cobalt(III) complexes in mixed solvent media [3].

The effect of structure of the ligand on $\phi_{Co(II)}$ was studied by changing the substituent in the aniline moiety (table 5). The $\phi_{Co(II)}$ failed to conform to the usual

Table 6. Statistical results and weighted percentage contributions for the correlation of photo-reduction quantum yield ($\phi_{Co(II)}$) with Kamlet-Taft's solvatochromic parameters α, β and π^*.

Substituent in aniline moiety	$100R^2$	sd	a	b	s	P_α	P_β	P_{π^*}
H	99	0.002	34	24	−66	50	06	44
p-OMe	99	0.001	11	02	−24	49	01	50
p-OEt	99	0.005	87	−169	−249	38	12	50
p-Me	99	0.002	06	−07	−17	42	07	51
p-Et	92	0.004	−0.3	−13	−04	07	48	45
m-Me	96	0.008	−50	−85	−77	50	14	36
p-F	94	0.007	−37	−191	−12	50	42	08

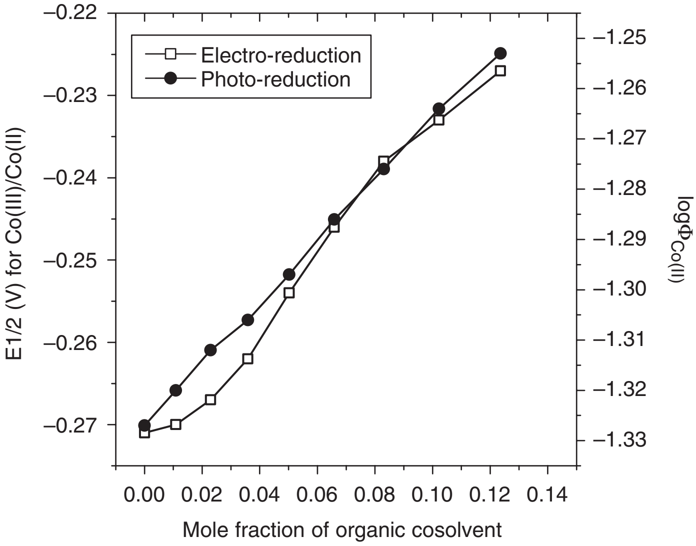

Figure 6. Plot of $E_{1/2}$ for the electro-reduction and $\phi_{Co(II)}$ for the photo-reduction for [Co(trien)(p-OMe-$C_6H_4NH_2$)Cl]Cl_2 *vs.* mole fraction of organic cosolvent.

Hammett equation. The plot of log $\phi_{Co(II)}$ *versus* Hammett's substituent constants, σ is a scatter gram. This deviation from Hammett's plot may indicate that the substituents or aniline have no significant effect on photo-reduction of these complexes [29].

4. Conclusion

Electro- and photo-reduction of the cobalt(III) complexes are highly influenced by solvent and structural changes. The electro- and photo-reduction of Co(III) to Co(II) in these complexes becomes easier with increase in the percentage of 1,4-dioxane in the mixture. The solvent effects on the redox properties of these complexes were quantitatively described by the Kamlet-Taft relationship. The electro-reduction of these complexes depends linearly on changes in the aniline ligand while there is no significant effect of substituents on the photo-reduction.

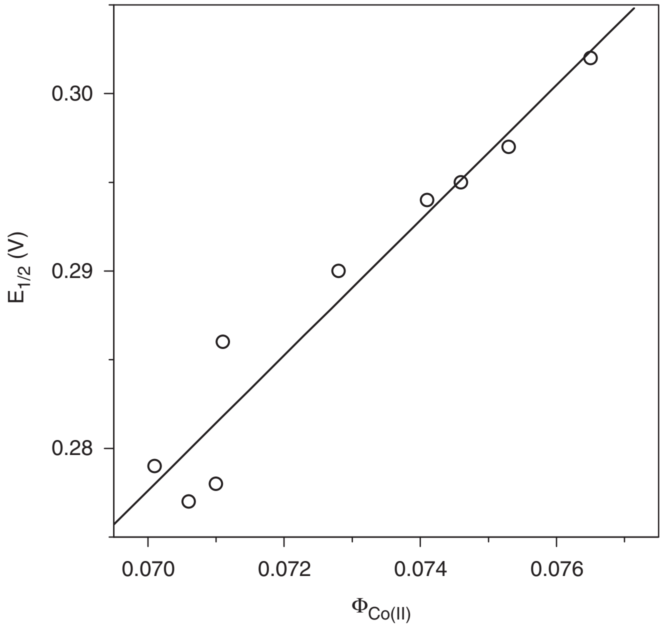

Figure 7. Plot of $E_{1/2}$ *vs.* $\phi_{Co(II)}$.

Dynamic exchange of solvent exists between the solvation shell of the excited state and the bulk [30]. As the organic co-solvent concentration increases, more organic solvent molecules are introduced into the solvation shell, increasing the hydrophobic environment of the excited state. Increase in hydrophobicity of the medium stabilizes the excited state (which is less polar than the reactant, as indicated by the Laidler-Erying correlation) through specific solute-solvent interactions and consequently increases the redox potential and reduction quantum yield as organic co-solvent proportion in the mixture increases. This is demonstrated by the observation that for all the Co(III) complexes under investigation, a plot of $E_{1/2}$ or $\phi_{Co(II)}$ *versus* mole fraction of the organic co-solvent is linear with positive slope (a representative plot is shown in figure 6). Further, there exists good correlation ($r = 0.967$, sd = 0.002) between $E_{1/2}$ and $\phi_{Co(II)}$ with positive slope (figure 7), suggesting similar types of transition state and solvation of the reactant/transition state during the electro- and photo-reduction of these complexes.

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