Correlation Analysis of Reactivity in the Photo- and Electro-Reduction of Cobalt(III) Complexes in Binary Organic Solvent/Water Mixtures

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The photo- and electro-reduction of a series of cobalt(III) complexes of the type *cis*-β-[Co(trien)($RC_6H_4NH_2$)Cl]Cl_2 with R = H, *p*-OMe, *p*-OEt, *p*-Me, *p*-Et, *p*-F, and *m*-Me has been studied in binary propan-2-ol/water mixtures. The redox potential ($E_{1/2}$) and photo-reduction quantum yield ($\Phi_{\text{Co(II)}}$) data were correlated with solvent and structural parameters with the aim to shed some light on the mechanism of these reactions. The correlation of $E_{1/2}$ and $\Phi_{\text{Co(II)}}$ with macroscopic solvent parameters, viz. relative permittivity, indicated 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: An increase in the percentage of organic co-solvent in the medium enhances both reduction processes, and there exists a good linear correlation between $E_{1/2}$ and $\Phi_{\text{Co(II)}}$, suggesting a similar solvation of the participants in these redox processes.

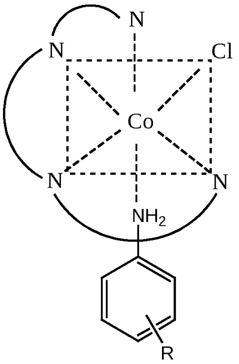
Key words: Cobalt(III) Complexes; Photo-Reduction; Electrochemistry; Solvent Effect; Hammett Equation.

1. Introduction

The study of the influence of solvent and structure on the reactions of cobalt(III) complexes in mixed solvent media and the correlation of reaction rates with various solvent and structural parameters afford important mechanistic information. Accumulated information on the correlation of reaction rates with the properties of the solvent through linear solvation energy relationships (LSER) has led to some significant results [1 – 6]. The general belief is that solvent characteristics, such as hydrophobic effects, preferential solvation, anion- and cation-solvating tendencies, and hydrogen-bond donor-acceptor properties, influence the kinetics and energetics of the reaction of cobalt(III) complexes and are important in the elucidation of reaction mechanisms.

In spite of the observation that single molecular-microscopic empirical parameters can often be used as good approximations of solvent polarity, no single macroscopic physical parameter could possibly account for the multitude of solute-solvent interactions on the molecular-microscopic level [7]. Thus, bulk solvent properties like relative permittivity [8], solvent ionizing power [9], and/or dipolarity/polarizability [10] will poorly describe the microenvironment around the reacting species, which also governs the stability of the activated complex and hence the rate of reaction. Therefore, during the recent past a variety of attempts has been made to quantify different aspects of solvent polarity, and then to use the resultant parameters to interpret the solvent effects on the reactivity through multiple regression analysis. Various treatments for the above solute-solvent-solvent interactions based on LSER have been developed [11]. Although the separation of solvent effects into various solute-solvent-solvent interaction mechanisms is purely formal, the multiparameter approach to solvent effects has been shown to work well [12].

Structural variation studies also give a much better insight into the nature of the activated complex and the mechanism of redox reactions. Most of the work in this area has dealt with complexes of the pentammine class, with emphasis on the dependence of reaction rates upon the nature of the sixth ligand [13]. Further, it is of much 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



Compound	R
1	H
2	*p*-OMe
3	*p*-OEt
4	*p*-Me
5	*p*-Et
6	*m*-Me
7	*p*-F

Fig. 1. Chemical structure of compounds **1**–**7**.

so called cybotactic region, is the same as in the bulk solvent, but in binary solvent mixtures the composition of this microsphere can be different. The solute can interact to a different degree 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 solvent mixture from the bulk solvent to the solvation sphere is called preferential solvation [14].

The main objective, therefore, of the present work was to study the substituent and solvent influence on the photo- and electro-reduction of a series of Co(III)-aryl amine complexes of the type *cis*-β-[Co(trien)($RC_6H_4NH_2$)Cl]Cl_2 (Fig. 1) in propan-2-ol/water mixtures of varying compositions and to analyze the correlation of the data obtained using LSER to get a better insight into the mechanism of such reactions. This binary solvent mixture was chosen so that small additions of alcohol to water enhanced its internal structure. Such water is more polar and has a larger hydrogen-bond donor (HBD) capability, but a smaller hydrogen-bond acceptor (HBA) ability than common pure water [14].

2. Results and Discussion

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

Table 1. Electrochemical data (E_p, V) from CV for the cobalt(III) complexes, measured in pure water at 25 °C.

Substituent of aniline	E_{pa} (III/IV)	E_{pc} (II/I)	E_{pc} (III/II)	E_{pa} (II/III)	ΔEp
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

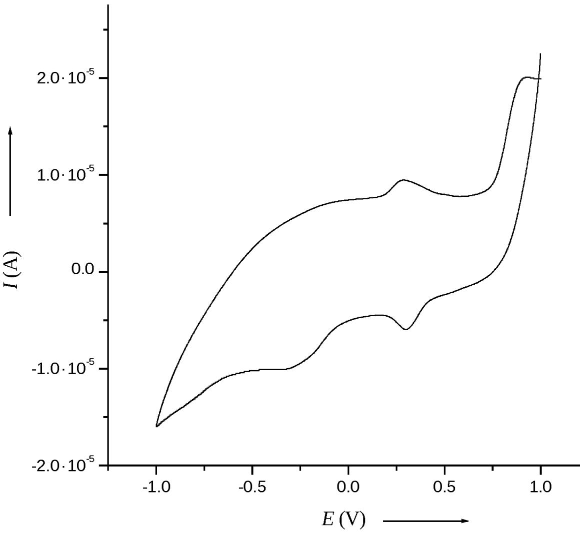


Fig. 2. Cyclic voltammogram of [Co(trien)($C_6H_5NH_2$)Cl] Cl_2 in water at a scan rate of 50 mV s^{-1}.

2.1. Electro-Reduction Study

The cyclic voltammetric behaviour of Co(III)-aryl amine complexes was examined in propan-2-ol/water mixtures with varying percentage of propan-2-ol, containing sodium perchlorate (0.1 mol/L) as supporting electrolyte, at a scan rate of 50 mV s^{-1}. The redox potential data of all the complexes measured 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 the scan rate, whereas $E_{1/2}$ is independent of the scan rate [15]. The redox potential of the Co(III)/Co(II) couple was determined according to the equation [16]

$$E_{1/2} = (E_{pa} + E_{pc})/2. \quad (1)$$

A representative cyclic voltammogram is shown in Fig. 2, and all other complexes exhibit similar cyclic voltammogrames under the same experimental condi-

Table 2. Electrochemical data ($E_{1/2}$, V) from CV for the cobalt(III) complexes in varying percentage of propan-2-ol in water.

Substituent of aniline	$E_{1/2}$ Vol.% of propan-2-ol 0	5	10	15	20	25	30	35	40
H	0.279	0.321	0.330	0.346	0.348	0.356	0.360	0.369	0.376
p-OMe	−0.271	−0.171	−0.161	−0.151	−0.142	−0.121	−0.104	−0.086	−0.128
p-OEt	−0.265	−0.190	−0.182	−0.178	−0.166	−0.162	−0.154	−0.146	−0.119
p-Me	−0.250	−0.238	−0.210	−0.198	−0.186	−0.184	−0.183	−0.185	−0.181
p-Et	−0.160	−0.132	−0.122	−0.112	−0.103	−0.082	−0.065	−0.047	0.036
m-Me	0.207	0.217	0.229	0.238	0.240	0.244	0.246	0.255	0.270
p-F	0.260	0.284	0.314	0.321	0.322	0.323	0.328	0.332	0.333

tions. The cyclic voltammograms of these complexes exhibit one well-defined redox peak corresponding to the Co(III)/Co(II) couple. Similar observations were also made by Vasilevkis and Olson [17] and Ortiz and Park [18] for cobalt(III) complexes. An irreversible cathodic peak was observed for all complexes at negative potentials, which may probably be due to the reduction of Co(II) to Co(I). On the positive side an irreversible oxidation corresponding to a Co(III) to Co(IV) transition was observed around 0.8 to 0.9 V [19]. 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 the Co(III)/Co(II) redox couple [20].

The anodic and cathodic potential data indicate the sensitivity of the Co(III)-aryl amine complexes to the nature of the sixth ligand. A similar phenomenon was described in the electrochemistry of cobaloximes [21]. The ratio (*RIp*) of the anodic peak current to the cathodic peak current is close to unity $(0.8 < RIp < 1)$, which again indicates the reversibility or quasi-reversibility of the Co(III)/Co(II) couple. Further, the ratio is independent of the scan rate in all investigated solvents. It was also found that the peak currents are essentially constant for several cycles. These results indicated that there are no chemical reactions coupled with the electron transfer [15]. Furthermore, the reduction potential E_{pc} was found to depend on the scan rate. The correlation of log scan rate versus E_{pc} was found to be linear ($r = 0.986$, $sd = 0.006$). The rate of reduction computed from the slope of the straight line for $[\text{Co(trien)}(p\text{-FC}_6\text{H}_4\text{NH}_2)\text{Cl}]\text{Cl}_2$ in water was found to be $0.2554\ \text{s}^{-1}$.

2.2. Solvent-Reactivity Correlation

The electro-reduction of Co(III)-complexes has been studied in propan-2-ol/water mixtures with a varying amount of propan-2-ol ranging from 0 to 40% v/v of organic 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 $[\text{Co(trien)}(p\text{-FC}_6\text{H}_4\text{NH}_2)\text{Cl}]\text{Cl}_2$ with increasing percentage of propan-2-ol in water is depicted in Figure 3. The general pattern of the curves remained unaltered with changes in the composition of the solvent mixture, which indicates that the added organic co-solvent does not alter the nature of the reduction mechanism. However, changes in the composition of the solvent mixture influence the lenience of the reduction process.

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

$$\mathrm{d}\ln k/\mathrm{d}(1/\varepsilon_\text{r}) = e^2 Z^2 (1/r - 1/r^*)/2kT, \qquad (2)$$

where k is the rate constant ($E_{1/2}$ in the case of electro-reduction or $\Phi_{\text{Co(II)}}$ in the case of photo-reduction), Z the net charge, r the effective radius, and r^* the radius of the activated species. For all complexes, the correlation of $E_{1/2}$ with the inverse of the relative permittivity of the medium is just satisfactory $(0.95 \geq r \geq 0.80)$. The positive slopes (figure not shown) indicate that $E_{1/2}$ increases with an increase in the content of the co-solvent in the mixture. Thus, the addition of propan-2-ol to the mixture makes the reduction of Co(III) to Co(II) easier.

Likewise, the data were also correlated with the normalized donor number, DN^N, of Gutmann [7], which is an empirical semiquantitative measure of the nucleophilic properties of electron pair donor solvents. Since the donor number has proven to be very useful in coordination chemistry, it can be correlated with other physical observables like redox potentials for such reactions [7]. The $E_{1/2}$ value also correlates satisfactorily with the normalized donor number of the solvent mixture $(0.97 \geq r \geq 0.82)$ with positive slope. The DN^N values employed in the present study were calculated as described earlier [22]. A representative plot is shown in Figure 4. For a given complex, $E_{1/2}$ shifts towards more positive potentials with an increase in DN^N. In

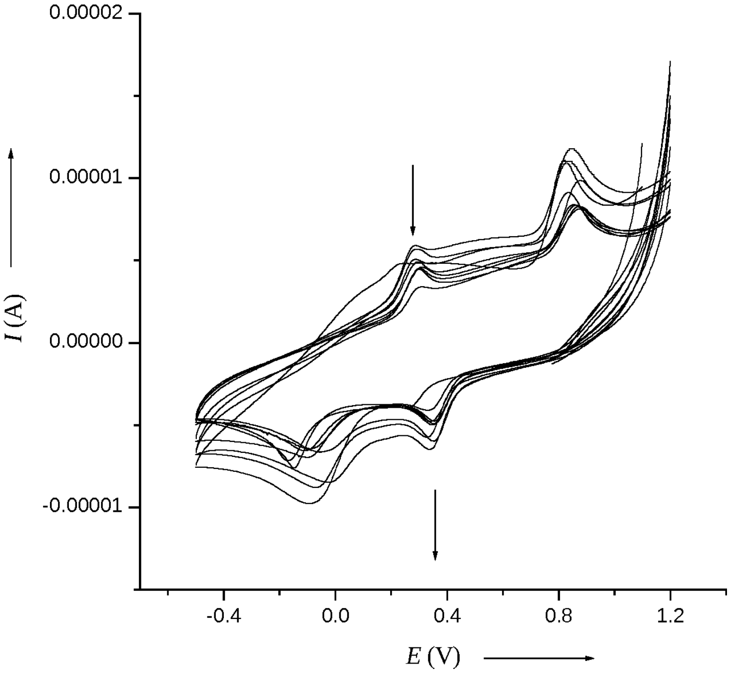


Fig. 3. Cyclic voltammogram of [Co(trien)(p-$FC_6H_4NH_2$)Cl]$^{2+}$, measured in propan-2-ol/water mixtures with varying percentage of propan-2-ol (0 – 40% v/v).

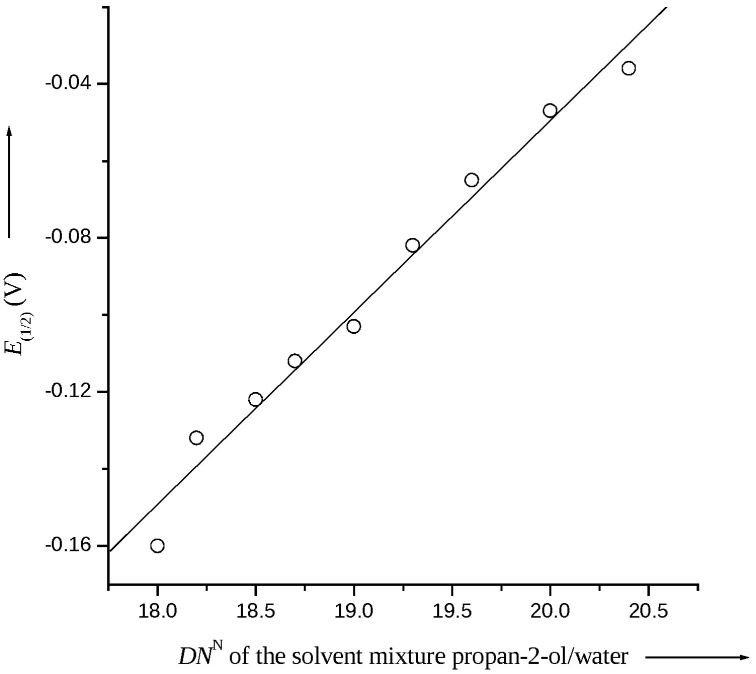


Fig. 4. Plot of log $E_{(1/2)}$ versus DN^N for [Co(trien)(p-$EtC_6H_4NH_2$)Cl]Cl_2.

other words, with rise in the content of the organic co-solvent in the mixture the reduction of Co(III) to Co(II) becomes easier [15].

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 physical solvent parameters. In reality, satisfactorily quantitative descriptions of medium effects have taken into account all non-specific and specific solute-solvent-solvent interactions. The separation of solvent polarity into non-specific and specific solute-solvent-solvent interaction mechanisms is purely formal, but if this separation can be reasonably done, the resultant parameters can be used to interpret solvent effects through such multiple correlations, thus providing information about the type and magnitude of interactions with the solvent [7].

This kind of dual dependency of reactivity on solvent composition is illustrated by the Kamlet-Taft solvatochromic comparison method [10]. This method can be used to unravel, quantify, correlate, and rationalize multiple interacting solvent effects on reactivity. The data were analyzed using the most celebrated Kamlet-Taft solvatochromic comparison method

$$\log k = \log k_0 + s\pi^* + a\alpha + b\beta, \quad (3)$$

which incorporates both types of interactions. π^* 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, α is the solvent HBD acidity, which describes the ability of the solvent to donate a proton to a hydrogen bond, β is the solvent HBA basicity, which provides a measure of the solvent ability to accept a proton (donate an electron pair) in a solute to solvent hydrogen bond, and $\log k_0$ is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients s, a, and b measure the relative susceptibilities of the solvent-dependent solute property $\log k$ ($E_{1/2}$ or $\Phi_{\mathrm{Co(II)}}$ 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 in [12]. 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 measured in the binary solvent mixtures investigated show an excellent correlation with the Kamlet-Taft parameters with an observed variance of ca. 97%. 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 reduction potential ($E_{1/2}$) of Co(III/II) with Kamlet-Taft's solvatochromic parameters α, β, and π^*.

Substitutent of aniline	$100R^2$	sd	a	b	s	P_α	P_β	P_{π^*}
H	95	0.008	6.07	0.54	−4.78	45	04	52
p-OMe	93	0.009	18.07	5.72	−10.34	47	13	40
p-OEt	96	0.009	1.31	−5.60	−5.59	09	35	56
p-Me	99	0.003	2.40	−5.83	−6.01	15	32	53
p-Et	99	0.006	0.74	1.18	−1.24	20	29	50
m-Me	96	0.005	−0.47	−1.83	−1.46	11	39	50
p-F	98	0.003	6.18	0.25	−4.66	47	02	52

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 governing the reactivity of the cobalt complexes. (ii) The sign of the coefficients a and b of the triparametric equation is randomly observed, that is, all the 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/activated complex [1]. (iii) The contribution of the solvent dipolarity/polarizability towards reactivity is found to be dominant, and it alone accounts for nearly 50% of the observed solvent effects. The sign of the coefficients of this term is negative. Hence, the value of $E_{1/2}$ increases with a decreasing dipolarity/polarizability of the medium. Thus, the reduction of Co(III) to Co(II) becomes easier with an increase of the amount of organic co-solvent in the binary solvent mixture.

2.3. Structure-Reactivity Correlation

The effect of substituents of the aniline moiety on the redox potential of the Co(III)/Co(II) couple was studied with seven substituted anilines as ligands in propan-2-ol/water mixtures. The redox potentials measured are given in Table 2. $E_{1/2}$ correlates linearly with Hammett's substituent constants and a typical plot is shown in Figure 5. The statistical results for these plots are given in Table 4. The positive value of the reaction constant, ρ, indicates that electron-donating substituents shift the redox potential to a more cathodic potential [23]. The reaction constants for metal reduc-

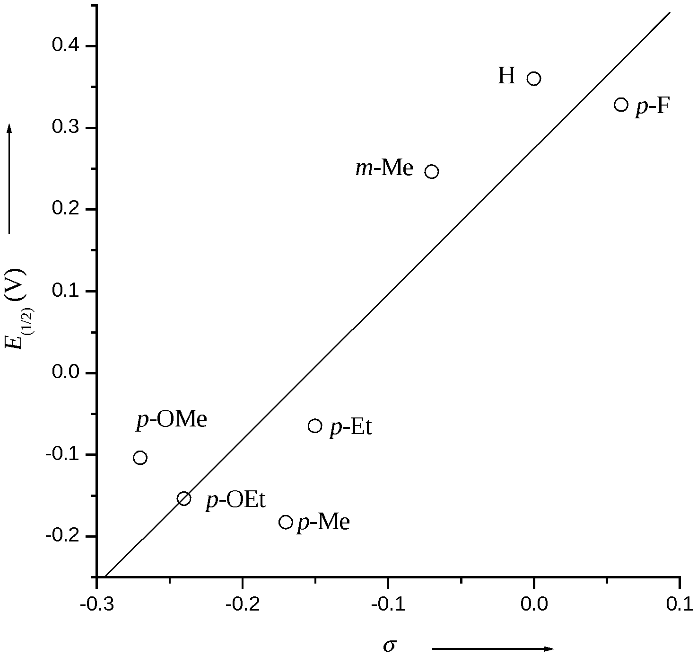


Fig. 5. Plot of $E_{(1/2)}$ versus σ, determined in a propan-2-ol/water mixture (30% v/v of propan-2-ol).

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

Vol.% of propan-2-ol in water	100*r*	*sd*	*ρ*
0	94	0.10	2.013 ± 0.34
5	92	0.11	1.897 ± 0.37
10	92	0.11	1.872 ± 0.36
15	92	0.11	1.880 ± 0.36
20	92	0.11	1.845 ± 0.35
25	91	0.11	1.811 ± 0.36
30	91	0.11	1.782 ± 0.36
35	90	0.11	1.762 ± 0.38
40	91	0.11	1.809 ± 0.36

tions are always smaller when compared to simple ligands as observed herein [5].

2.4. Photo-Reduction Study

The photo-reduction of the cobalt(III) complexes under investigation, which can be generally delineated as follows, has been carried out in propan-2-ol/water mixtures with varying contents of the organic co-solvent with the aim to investigate the influence of solvent and structure of the complex on its reactivity:

$$\mathrm{Co^{III}L_6} \xrightarrow{+h\nu\ (254\ \mathrm{nm})} {}^{*}\mathrm{Co^{III}L_6} \longrightarrow \mathrm{Co^{II}} + \text{other products.} \tag{4}$$

The quantum yields, $\Phi_{\mathrm{Co(II)}}$, measured at $\lambda = 254$ nm for the photo-reduction of the cobalt(III)-aryl amine complexes in various propan-2-ol/water mixtures, are collected in Table 5. It is evident that $\Phi_{\mathrm{Co(II)}}$ increases as the mole fraction of the organic co-solvent increases in the mixture. This may be due to the reduction of the metal centre by the ligand (LMCT) and the solvent (solvent-to-metal charge transfer). This argument is in line with that suggested by Weit et al. [24] for the photo-reduction of cobalt(III)-am(m)ine complexes. Therefore, attempts have been made to analyze the influence of solvent and substitution on the photo-reduction quantum yields of cobalt(III)-aryl amine complexes using linear and multiple regression equations.

Table 5. Quantum yields ($10^2\Phi_{\mathrm{Co(II)}}$) for the photo-reduction of [Co(trien)($\mathrm{RC_6H_4NH_2}$)Cl]$\mathrm{Cl_2}$ in air-equilibrated propan-2-ol/water mixtures at (25 ± 1) °C.

Substituent of aniline	Quantum yield Propan-2-ol (%) (v/v) 0	5	10	15	20	25	30	35	40
H	7.01	7.18	7.27	7.52	7.60	7.87	7.96	8.18	8.40
p-OMe	4.71	4.75	4.81	4.88	4.93	5.23	5.33	5.42	5.56
p-OEt	4.46	4.55	4.63	4.64	4.68	4.89	5.14	5.21	5.33
p-Me	4.81	4.83	4.85	4.99	5.38	5.95	6.36	6.55	6.48
p-Et	5.26	5.60	5.66	5.76	5.97	6.10	6.11	6.39	6.58
m-Me	3.16	3.17	3.18	3.19	3.27	3.39	3.45	3.48	3.59
p-F	4.56	4.86	5.04	5.11	5.18	5.41	5.52	5.57	5.71

The correlation of photo-reduction quantum yields with the inverse of the relative permittivity of the

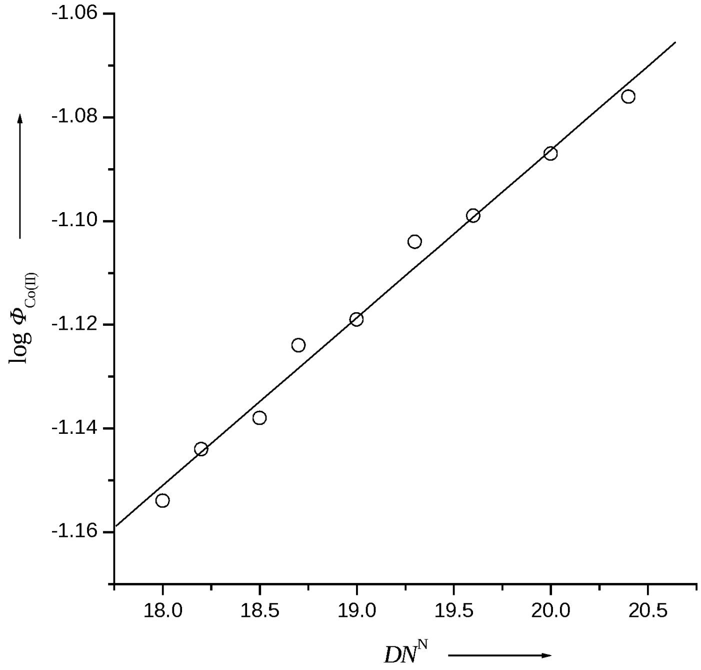


Fig. 6. Plot of $\log \Phi_{Co(II)}$ versus DN^N for $[Co(trien)(C_6H_5NH_2)Cl]Cl_2$.

medium through the Laidler-Erying [8] equation is not very satisfactory ($0.98 \geq r \geq 0.94$). The positive slope indicates that the excited state is less polar than the ground state of the reactant. Such an excited state will more easily be attained in a medium of lower relative permittivity, and hence an increase in quantum yield with an increase in the proportion of organic co-solvent is observed. Similarly, the experimental data also correlate satisfactorily with the normalized donor number ($0.98 \geq r \geq 0.95$) with a positive slope. A representative plot is shown in Figure 6.

As solvent macroscopic parameters fail to completely explain the solvent dependency of reactivity, it is assumed that the photo-reduction of Co(III) complexes can also be influenced by both specific and nonspecific solute-solvent interactions due to the same reasons as spelt in the electro-reduction earlier in this article. The dual dependency of reactivity on the solvent composition was tested using the Kamlet-Taft equation. The $\Phi_{Co(II)}$ values in various propan-2-ol/water mixtures showed an excellent correlation via (3) with an observed variance of ca. 99%. The statistical results of the correlation and weighted percentage contributions of the solvatochromic parameters are given in Table 6.

The results indicate that: (i) The specific solute-solvent interactions, as indicated by P_α and P_β, play a major role in governing the reactivity of cobalt(III) complexes. The contribution of the solvent HBD acidity, α, to the solvent effects is dominant. This is due to the fact that the addition of propan-2-ol to water enhances its structure, and the enhanced water structure has a larger HBD capability than the common water structure [14]. (ii) The sign of the coefficients *a*, *b*, and *s* of the triparametric equation is randomly observed. This is probably due to the fact that the medium may interact in a complex manner with the reactant/excited state [1].

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^*.

Substitutent of aniline	$100R^2$	*sd*	*a*	*b*	*s*	P_α	P_β	P_{π^*}
H	99	0.002	1.82	2.13	−0.89	61	29	10
p-OMe	97	0.006	−2.33	−0.34	0.43	90	05	05
p-OEt	97	0.006	−4.35	−1.71	0.94	81	13	06
p-Me	99	0.002	2.22	6.84	0.67	42	54	04
p-Et	97	0.007	2.41	1.79	−1.61	66	20	14
m-Me	97	0.007	−4.41	−2.72	0.54	77	20	03
p-F	95	0.006	−0.46	−4.12	−3.30	15	52	33

The influence of the ligand structure on $\Phi_{Co(II)}$ was studied by changing the substituent in the aniline moiety. The experimentally measured quantum yields for all cobalt(III) complexes as a function of percentage

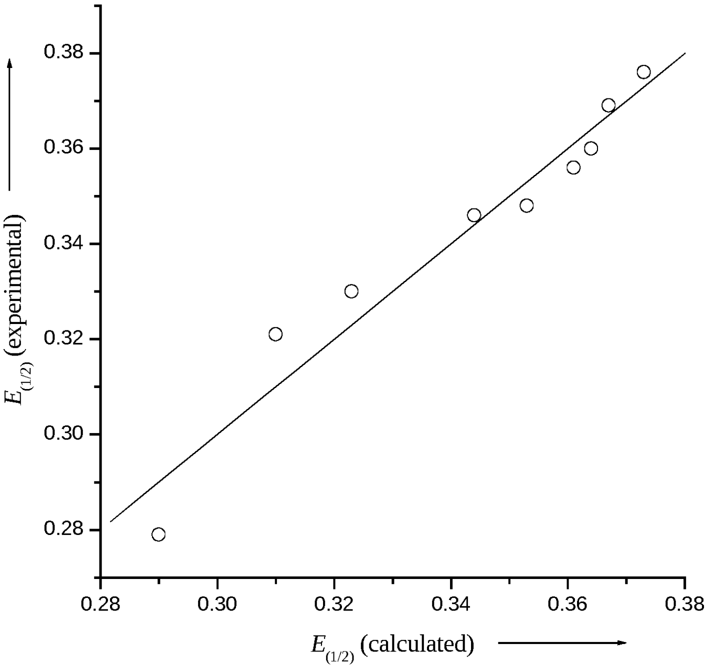


Fig. 7. Experimentally determined redox potentials of $[Co(trien)(C_6H_5NH_2)Cl]Cl_2$ plotted against the corresponding values estimated using the Kamlet-Taft relationship given in Table 3.

of organic co-solvent are given in Table 5. The $\Phi_{Co(II)}$ values fail to conform to the usual 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 be due to the fact that the substituents of the aniline ligand have no significant effect on the photo-reduction of these complexes [25].

3. Conclusions

The foregoing results and discussion indicate that the electro- and photo-reduction of cobalt(III) complexes are highly influenced by the solvent and structural changes. The electro- and photo-reduction of Co(III) to Co(II) in these complexes becomes easier with an increase in the percentage of the organic co-solvent, propan-2-ol, in the propan-2-ol/water mixture. The solvent effects on the redox properties of these complexes can be quantitatively described by the Kamlet-Taft relationship. The electro-reduction of these complexes depends linearly on structural changes in the aniline ligand, while there seems to be no significant influence of substituents on the photo-reduction.

It is well established that a dynamic exchange of solvent molecules exists between the solvation shell of the ground and excited state and the bulk solvent [26]. As the organic co-solvent content increases in the binary solvent mixture, more and more organic solvent molecules are introduced into the solvation shell, thereby increasing the hydrophobic environment of the excited state. An increase in hydrophobicity of the medium stabilizes the excited state (which is less polar than the reactant in the ground state, as indicated by the Laidler-Erying correlation) through specific solute-solvent interactions, and consequently increases the redox potential and quantum yield as the organic co-solvent proportion in the mixture increases. This is demonstrated by the observation, that plots of the experimentally determined parameters ($E_{1/2}$ and $\Phi_{Co(II)}$) against the corresponding values estimated by means of the Kamlet-Taft multiparameter equation give satisfactorily straight lines, as shown in Figs. 7 and 8. As can be seen, this relationship successfully describes the solvent dependence on the Co(III) to Co(II) reduction both by electrochemical and by photochemical paths. For all Co(III) complexes under investigation, the $E_{1/2}$ and $\Phi_{Co(II)}$ values increase with increase in the mole fraction of the organic co-solvent (Fig. 9), as expected. Further, there exists a good correlation ($r = 0.92$, $sd = 0.01$) between $E_{1/2}$ and $\Phi_{Co(II)}$ with a positive slope (Fig. 10), suggesting similar types of activated complex and mode of solvation of the reactant/activated

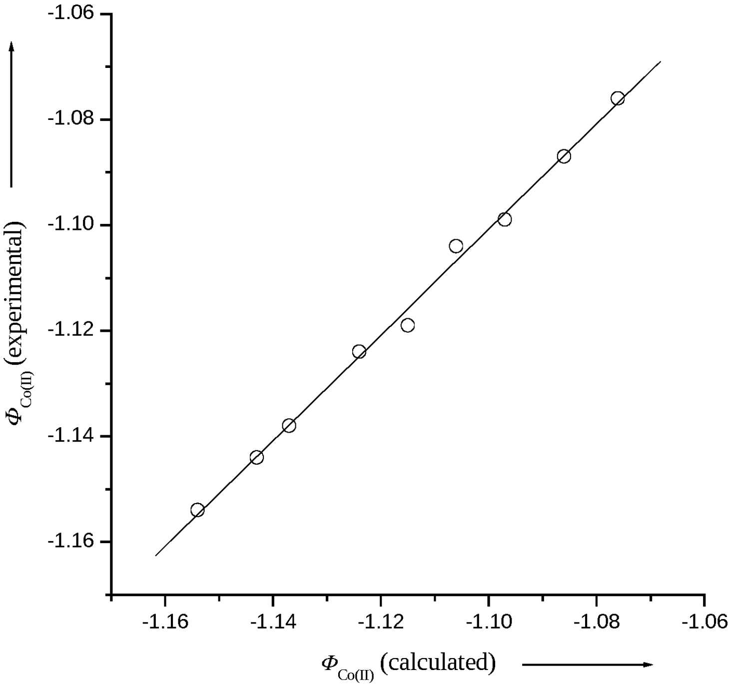


Fig. 8. Experimentally determined quantum yields of [Co(trien)($C_6H_5NH_2$)Cl]Cl_2 plotted against the corresponding values estimated using the Kamlet-Taft relationship given in Table 6.

complex during the electro- and photo-reduction of these complexes.

4. Experimental

4.1. Materials

The chemicals used were of high purity (Aldrich, Merck, India). The cobalt(III) complexes, *cis*-β-[Co (trien)($RC_6H_4NH_2$)Cl]Cl_2 with R = H, *m*-Me, *p*-Me, *p*-Et, *p*-OMe, *p*-OEt, and *p*-F, were prepared and purified as described in [27]. The organic co-solvent, propan-2-ol, was of spectroscopic grade (Merck, India) and was used as received. Doubly distilled water was used throughout the work.

4.2. Electrochemical Experiment

Solutions of the electrolyte, cobalt(III) complexes, were prepared with doubly distilled water. All electrochemical experiments were performed at 25 °C using a standard three-electrode, a two-compartment configuration with a glassy carbon (GC–3 mm) working electrode, a spiral platinum counter electrode, and an Ag | AgCl (KCl sat.) reference electrode. The carbon electrodes were polished between the 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 gas for 15 – 20 min before commencement of the measurement.

4.3. Photolysis Experiment

Solutions for photolysis contained the Co(III) complex ($4 \cdot 10^{-3}$ M) and $NaNO_3$ (0.1 M). All solutions prepared contained binary solvents of varying compositions: propan-2-ol in water [0 – 40% (v/v) of co-solvent]. Steady photolysis experiments were carried out using a low pressure mercury vapour pen-ray quartz lamp (254 nm). Air-equilibrated solutions were used for photolysis, and the temperature control was maintained at (25 ± 1) °C. For quantum yield determinations, photolysis was carried out within less than ca. 15% of the total reaction. The incident light intensities were measured by potassium ferrioxalate actinometry [28]. Quantum yields were calculated, estimating Co(II) formed by Kitson's method [29]. All absorption measurements were carried out using a Shimaduz UV-Vis (UV 240 Graphicord) double-beam spectrophotometer.

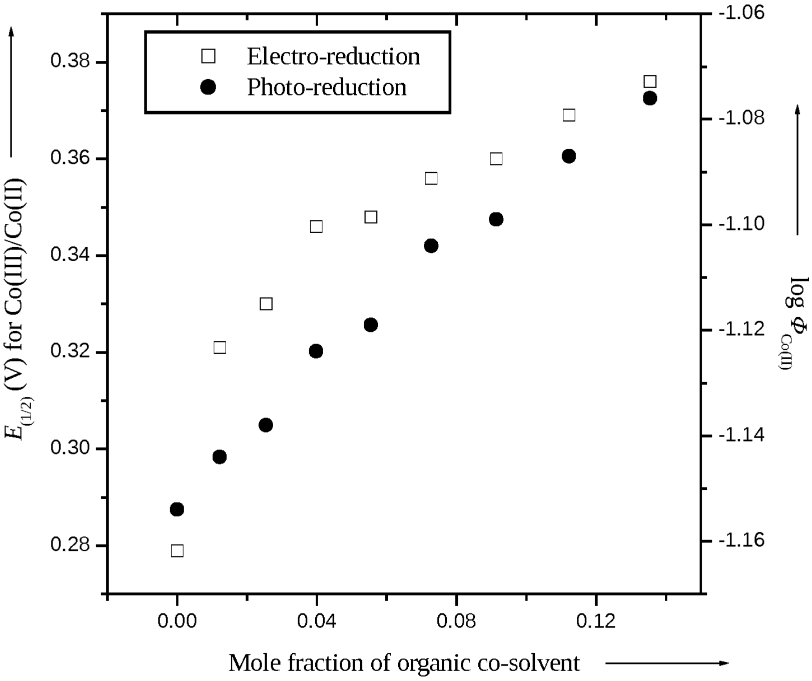


Fig. 9. Plot of $E_{(1/2)}$ for the electro-reduction and log $\Phi_{Co(II)}$ for the photo-reduction of [Co (trien)($C_6H_5NH_2$)Cl]Cl_2 versus the mole fraction of the organic co-solvent.

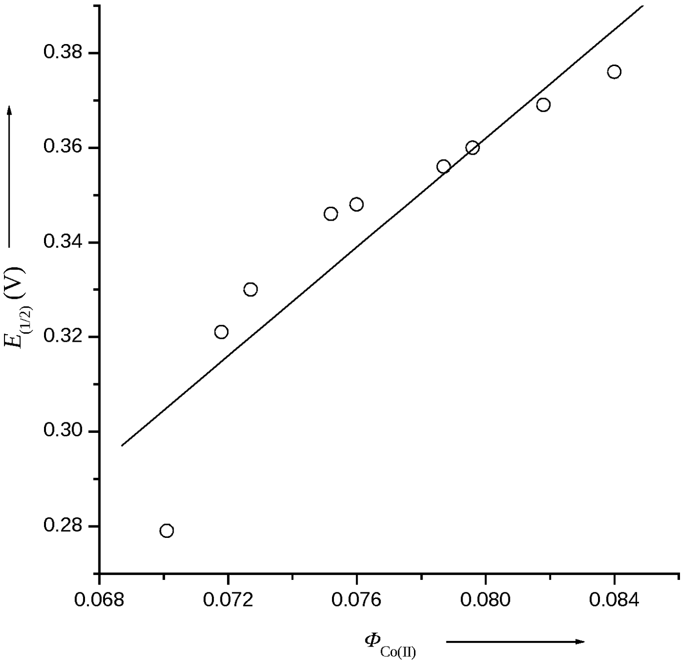


Fig. 10. Plot of $E_{(1/2)}$ versus $\Phi_{Co(II)}$ of [Co (trien)($C_6H_5NH_2$)Cl]Cl_2.

4.4. Linear Free Energy Relationships

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

$$\log k = \log k_0 + \rho\sigma, \qquad (5)$$

where k is the rate constant ($E_{1/2}$ or $\Phi_{Co(II)}$ in the present study), 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.

4.5. 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 (P_X) of a parameter to the total effect on reactivity was computed as reported earlier [30].

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