Differential Pulse Voltammetric Studies of Some Mixed-ligand Co(III) Complexes in Aquo-Organic Solvent Media Possessing Different Hydrogen Bonding Properties

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The electro-reduction of a series of Co(III) complexes of the type *cis*-β-[Co(trien)(4-R-Py)Cl]Cl_2, where trien = triethylenetetramine and R = H, Me, Et, *t*-Bu, COMe, and CN, has been studied in propan-2-ol/water and 1,4-dioxane/water binary mixtures. The redox potential ($E_{1/2}$) data were correlated with solvent and structural parameters with an aim to shed some light on the mechanism of these reactions. Correlation of $E_{1/2}$ with macroscopic solvent parameters indicated that the reactivity is influenced by both specific and non-specific solute-solvent interactions. The reduction of Co(III) to Co(II) in these complexes was observed to become increasingly easier with an increase in the dipolarity/polarizability of the medium as evidenced by the Kamlet-Taft correlation. The difference in the relative lenience of the reduction has been explained using the difference in H-bonding properties of the medium.

Key words: Cobalt(III) Complexes, Electrochemistry, Solvent Effect, Reduction, Solvation

Introduction

Recently, the research on the effect of solvents on various phenomena has become a topic of interest because many solvents can change the solvation energy of the molecules under investigation and consequently the mechanism of the phenomena. As a result, the rate and mechanistic pathway of a corresponding chemical reaction may be affected. The alteration in the rate of a reaction depends on the characteristics of the solvents such as, among others, hydrophobic effects, preferential solvation, anion and cation solvating tendencies and hydrogen bond donor-acceptor properties [1 – 7].

It was established that the molecular macroscopic properties of the solvents such as relative permittivity, solvent ionizing power, and/or dipolarity/polarizability can, in the majority of the incidences, poorly describe the microenvironment around the reacting species, which governs the stability of the intermediate and hence the rate of the reaction [8]. So, multiple regression analysis of solvent-solute interactions based on linear solvation energy relationships (LSER) has been developed [9]. Although the separation of solvent effects into various solute-solvent interaction mechanisms is purely formal, the multiparameter approaches to solvent effects were shown to work well [10].

During recent past we have been interested in the study of solvent effects on the reactivity, in general, and the photo- and electro-reduction of cobalt(III) complexes in particular [11, 12]. As a part of our research work in this line, here in this article, we report the solvent hydrogen bonding influences on the electro-reduction of cobalt(III) complexes of the type *cis*-β-[Co(trien)(4-R-Py)Cl]Cl_2 in propan-2-ol/water and 1,4-dioxane/water mixtures of varying compositions. Attempts were made to analyze the experimental data using the technique of correlation analysis with an aim to get a better insight into the mechanism of such reactions. The selection of the organic co-solvent is based on the fact that propan-2-ol is a typical hydrogen bond donor (HBD) solvent while 1,4-dioxane is a hydrogen bond acceptor (HBA) solvent, and both these solvents when added to water enhance its structure and alter its hydrogen bonding properties to a larger extent. Further, it is of much interest to study such electrochemical redox processes in binary solvent mixtures, which are more complex than pure solvents owing to varying degrees of solute-solvent interactions. In a pure solvent the composition of the microsphere of solvation of a solute, the so-called cybotactic region, is the same as in the bulk solvent, but in binary mixtures the composition of this microsphere can be different.

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Table 1. Electrochemical data ($E_{1/2}$, V) from DPV for the Co(III) complexes *cis*-β-[Co(trien)(4-R-Py)Cl]Cl_2 in water at 25 °C.

X^a	E_{pc} (III/II)	E_{pa} (II/III)	$E_{1/2}$	ΔEp
H	−0.053	−0.163	−0.108	110
Me	−0.168	−0.240	−0.204	72
Et	−0.176	−0.280	−0.228	104
t-Bu	−0.164	−0.256	−0.210	92
COMe	−0.140	−0.231	−0.185	91
CN	−0.080	−0.144	−0.112	64

[a] Substituent of the pyridine co-ligand.

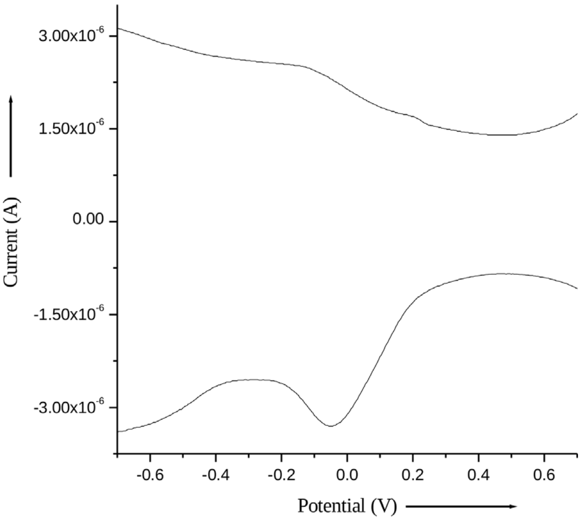


Fig. 1. Differential pulse voltammogram of *cis*-β-[Co(trien)(Py)Cl]Cl_2 in water.

The solute can interact to a different degree with the components of the mixture, and such an effect is called preferential solvation [13].

Results and Discussion

The solvent and substituent effects on the electroreduction of a series of Co(III) complexes of the type *cis*-β-[Co(trien)(4-R-Py)Cl]Cl_2, where R = H, Me, Et, *t*-Bu, COMe, and CN, in varying concentrations of organic co-solvents (propan-2-ol and 1,4-dioxane) in water was investigated. Attempts have been made to analyze the effect of solvent and structure on the redox potentials ($E_{1/2}$) of the complexes using simple and multiple regression equations.

The differential pulse voltammetric (DPV) technique was used to study the redox behavior of these complexes. A representative DPV curve is shown in Fig. 1. All the other Co(III) complexes exhibit a similar DPV pattern under the given experimental conditions. The redox potential data for all the complexes in water are 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 [14]. The redox potential ($E_{1/2}$) of the Co(III)/Co(II) couple was determined according to Eq. 1 [15].

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

The voltammograms of all the Co(III) complexes exhibit a reversible cathodic and anodic peak in the −0.05 to −0.3 V range which is probably due to the Co(III)/Co(II) couple. The separation values between the anodic and cathodic peak potentials (ΔEp) show the quasi-reversible nature of the Co(III)/Co(II) redox couple [14, 15].

Effect of solvent

The electroreduction of the Co(III) complexes has been studied in varying amounts of the organic co-solvent 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 Tables 2 and 3. The results indicate that in both the solvent mixtures the $E_{1/2}$ value for the Co(III)/Co(II) couple becomes more positive with an increase in the co-solvent concentration in the mixture. Also this increase was found to be relatively larger in a water/propan-2-ol mixture than in the reference solution. The general pattern of the voltammograms remains unaltered with the change in the composition of the solvent mixture which indicates that the added organic co-solvent does not alter the nature of the mechanism of the redox reaction. However, the change in composition of the solvent mixture influences the lenience of the redox process. The variation of $E_{1/2}$ with the mole fraction of the organic co-solvent (x_2) in the binary mixture is depicted in the following correlation relations (Eqs. 2, 3).

$$E_{1/2}(\mathrm{V}) = 0.55x_2 - 0.10 \tag{2}$$

(Co-solvent = propan-2-ol; R = H; $r = 0.96$; sd = 0.007)

$$E_{1/2}(\mathrm{V}) = 0.31x_2 - 0.11 \tag{3}$$

(Co-solvent = 1,4-dioxane; R = H; $r = 0.99$; sd = 0.002)

The difference in the observed slope values indicates a difference in the participation of the co-solvents in the solvation process.

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

X^{a}	— % of propan-2-ol —								
	0	5	10	15	20	25	30	35	40
H	−0.108	−0.093	−0.080	−0.066	−0.055	−0.051	−0.045	−0.040	−0.026
Me	−0.204	−0.195	−0.188	−0.172	−0.167	−0.159	−0.154	−0.149	−0.144
Et	−0.228	−0.217	−0.212	−0.208	−0.200	−0.194	−0.187	−0.181	−0.175
t-Bu	−0.210	−0.198	−0.187	−0.180	−0.166	−0.162	−0.138	−0.126	−0.116
COMe	−0.185	−0.161	−0.144	−0.131	−0.118	−0.110	−0.100	−0.091	−0.076
CN	−0.112	−0.108	−0.104	−0.098	−0.092	−0.088	−0.082	−0.077	−0.071

[a] Substituent of the pyridine co-ligand.

Table 3. Electrochemical data ($E_{1/2}$, V) from DPV for the Co(III) complexes for varying percentages of 1,4-dioxane in water.

X^{a}	— % of 1,4-dioxane —								
	0	5	10	15	20	25	30	35	40
H	−0.108	−0.101	−0.100	−0.093	−0.090	−0.086	−0.080	−0.073	−0.070
Me	−0.204	−0.202	−0.197	−0.189	−0.184	−0.179	−0.177	−0.172	−0.167
Et	−0.228	−0.224	−0.220	−0.215	−0.213	−0.207	−0.205	−0.201	−0.195
t-Bu	−0.210	−0.204	−0.199	−0.195	−0.190	−0.186	−0.185	−0.181	−0.177
COMe	−0.185	−0.172	−0.159	−0.144	−0.136	−0.122	−0.111	−0.102	−0.089
CN	−0.112	−0.108	−0.104	−0.100	−0.094	−0.090	−0.086	−0.079	−0.078

[a] Substituent of the pyridine co-ligand.

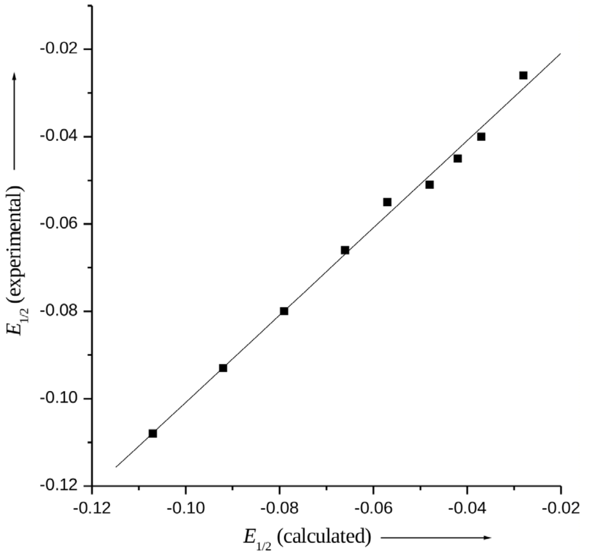


Fig. 2. Experimentally determined redox potential values in propan-2-ol/water mixtures for the complex *cis*-*β*-[Co(trien)(Py)Cl]Cl_2 plotted against the corresponding values estimated using the Kamlet-Taft relationship given in Table 4.

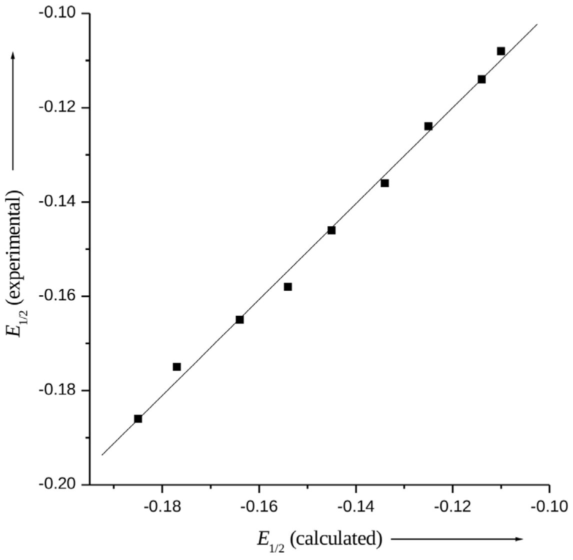


Fig. 3. Experimentally determined redox potential values in 1,4-dioxane/water mixtures for the complex *cis*-*β*-[Co(trien)(Py)Cl]Cl_2 plotted against the corresponding values estimated using the Kamlet-Taft relationship given in Table 5.

For all the complexes, in both the aquo-organic solvent media, the correlation of $E_{1/2}$ with the inverse of the relative permittivity of the medium is satisfactory ($0.98 \geq r \geq 0.91$; not shown) with positive slopes. In both propan-2-ol/water and 1,4-dioxane/water media the positive slopes of the correlation indicate that $E_{1/2}$ increases with an increase in concentration of the cosolvent in the mixture. Thus, the addition of propan-2-ol or 1,4-dioxane to the mixture makes the reduction of Co(III) to Co(II) easier. Likewise, the correlation of $E_{1/2}$ values with the normalized donor number, DN^{N}, of the solvent mixture is also satisfactory ($0.99 \geq r \geq 0.96$ for propan-2-ol/water and $0.99 \geq r \geq 0.92$ for 1,4-dioxane/water medium). The DN^{N} values employed in the present study were calculated as described earlier [16].

Satisfactory quantitative descriptions of medium effects should take all nonspecific and specific solvent-solute interactions into considerations. This kind of dual dependency of reactivity on solvent composition is illustrated by the Kamlet-Taft solvatochromic comparison method [17]. This method may be used to unravel, quantify, correlate, and rationalize multiple interacting solvent effects on reactivity. Thus, the exper-

Table 4. Statistical results and weighted percentage contributions for the correlation of the redox potential ($E_{1/2}$) for the Co(III/II) couple with Kamlet-Taft's solvatochromic parameters α, β and π^* in propan-2-ol/water.

X[a]	100 R^2	sd	a	b	s	P_α	P_β	P_{π^*}
H	99	0.002	2	−1.2	−3	32	19	49
Me	99	0.001	3.9	2	−2.2	48	25	27
Et	99	0.001	0.28	−0.02	−0.82	25	02	73
t-Bu	98	0.004	−0.62	0.80	−0.24	37	48	15
COMe	99	0.003	1.5	−2.1	−3.5	21	30	49
CN	99	0.001	0.49	0.73	−0.39	31	45	24

[a] Substituent of the pyridine co-ligand.

Table 5. Statistical results and weighted percentage contributions for the correlation of the redox potential ($E_{1/2}$) for the Co(III/II) couple with Kamlet-Taft's solvatochromic parameters α, β and π^* in 1,4-dioxane/water.

X[a]	100 R^2	sd	a	b	s	P_α	P_β	P_{π^*}
H	98	0.001	−1.72	−26.8	−6.26	5	69	26
Me	99	0.001	5.47	−73.5	−38.3	4	52	44
Et	98	0.001	0.24	−19.4	−7.83	1	60	39
t-Bu	96	0.002	12.6	−45.5	−43.9	11	35	54
COMe	98	0.004	27.4	−92.3	−93.3	11	34	55
CN	99	0.001	−5.12	−3.22	9.37	24	13	63

[a] Substituent of the pyridine co-ligand.

imentally measured redox potential data, $E_{1/2}$, for the Co(III)/Co(II) couple were correlated with the solvatochromic parameters α, β and π^*. The $E_{1/2}$ values for the solvent mixtures investigated show an excellent correlation with Kamlet-Taft parameters with an observed variance of ∼ 98 % in both the solvent mixtures. The goodness of these fits was confirmed by the linearity of the plots of experimentally measured $E_{1/2}$ values *versus* calculated $E_{1/2}$ values (Figs. 2 and 3). The statistical results of the correlation and the weighted percentage contributions of the solvatochromic parameters are presented in Tables 4 and 5.

Such an excellent correlation of the experimental data with the Kamlet-Taft solvatochromic parameters indicates the operation of both specific and non-specific solute-solvent interaction mechanisms in the present system. The results shown in Tables 4 and 5 indicate that, in both the solvent mixtures, the non-specific contribution *i. e.* from dipolarity/polarizability of the medium towards the reactivity is found to be dominant, and it alone accounts for nearly 50 % of the observed solvent effect. In both the solvent mixtures the sign of the coefficients of this term are negative indicating that the value of $E_{1/2}$ would increase with a decreasing dipolarity/polarizability of the medium. As the concentration of organic co-solvent in the mixture increases the dipolarity/polarizability of the medium decreases [13] and thus, the reduction of Co(III) to Co(II) becomes relatively easier.

In aquo-organic solvent mixtures, at low organic solvent concentrations, water molecules tend to organize around the hydrophobic groups forming cages with enhancement of the structure of water. The reinforcement of the structure of water by small additions of organic solvents causes a larger variation (twice in the case of alcohols) in polarity than in hydrogen bonding properties [13]. Hence, in the present study, the contribution of dipolarity/polarizability of the medium was found to be the dominant force in governing the electro-reduction of the Co(III) complexes.

Further, the weighted percentage contributions indicate that in the case of the propan-2-ol/water medium both HBD and HBA properties play appreciable roles in governing the reactivity. The signs of the majority of the coefficients of the α and β terms are positive indicating that the solvation of the intermediate, through H-bonding properties, is greater than that of the reactant [18]. Hence, an increase in the concentration of the co-solvent in the mixture stabilizes the intermediate and consequently makes the reduction of Co(III) to Co(II) easier. On the other hand, in the case of the 1,4-dioxane/water medium, since 1,4-dioxane is a typical HBA solvent, its contribution towards reactivity was found to be appreciable, as indicated by the β term. The sign of the coefficients of this term was observed to be negative indicating better solvation of the reactant than of the intermediate through dioxane's HBA properties. Hence an increase in the concentration of the co-solvent in the mixture should have made the reduction of Co(III) to Co(II) more difficult. However, the appreciable contribution of the dipolarity/polarizability of the medium makes the reduction easier. Owing to these two opposite effects the increase in the $E_{1/2}$ values in this mixture is observed to be less.

There exists a dynamic exchange of solvent molecules between the solvation shell of the excited state and the bulk. As the concentration of organic co-solvent in the mixture increases, more organic solvent molecules are introduced into the solvation shell, increasing the hydrophobic environment of the excited state [19]. Increase in hydrophobicity of the medium stabilizes the intermediate through solute-solvent interactions (as enumerated in the Kamlet-Taft correlation) and consequently increases the redox potential, *i. e.* makes the reduction of Co(III) to Co(II) easier. This is demonstrated by the results of Eqs. 2 and 3. As the solute-solvent interaction varies in these mixtures, the extent of lenience of the reduction differs.

Effect of substituents

The effect of substituents at the pyridine co-ligand on the redox potentials of the Co(III)/Co(II) couple was studied with six 4-substituted Py ligands in propan-2-ol/water and 1,4-dioxane/water media. The $E_{1/2}$ values failed to conform to the usual Hammett or its modified equations [20]. The plot of $E_{1/2}$ *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 present in the *p*-position of the pyridine ligand have no significant effect on the eletroreduction of these complexes as they are far away from the metal center.

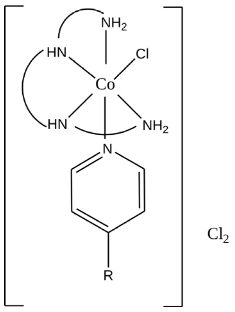
Conclusion

The foregoing results and their discussion have indicated that the electro-reduction of cobalt(III) complexes are highly influenced by the solvent properties. The electro-reduction of Co(III) to Co(II) becomes increasingly easier with an increase in the percentage of the organic co-solvent in the mixture. The solvent effects on the reduction of these complexes are conveniently described by the Kamlet-Taft relationship. The electro-reduction of these complexes indicates that there is no significant effect of *para*-substituents present in the pyridine co-ligand on the reactivity.

Experimental Section

Materials

All the chemicals used were of high-purity analytical grade (Aldrich, Merck, India) and were used as received. The cobalt(III) complexes, [Co(trien)(4-R-Py)Cl]Cl_2, where trien = triethylenetetramine and R = H, Me, Et, *t*-Bu, COMe and CN, were prepared and purified as described in the literature [20]. The structure of the complexes, with *cis*-β configuration, is given below.



R = H, Me, Et, *t*-Bu, COMe or CN

The organic co-solvents, propan-2-ol and 1,4-dioxane, were of spectroscopic grade (Merck, India) and were used without further purification. Doubly distilled water was used throughout the work.

Electrochemical experiments

The differential pulse voltammetric experiments were carried out with a computer-controlled electrochemical system (CHI643B electrochemical analyzer). Solutions of the electrolyte, the cobalt(III) complexes, were prepared with doubly 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 an Ag | AgCl (KCl sat.) reference electrode. The carbon electrodes were polished between the experiments with alumina paste (0.5 μm). All solutions were deoxygenated thoroughly by purging with nitrogen gas for 15 – 20 min before commencement of the measurement.

Linear Free Energy relationships

These relationships are formulated by using empirical constants and are linear with at least one variable, and on the other hand the linearity is not essential and is not strictly maintained in all known equations. In the present study, the effect of the solvent on the redox behavior was analyzed using solvent macroscopic properties such as the most popular relative permittivity, ε_r, [21] and the donor number [16]. The donor number has proven very useful in coordination chemistry, since it can be correlated with other physical observables such as redox potentials [8].

As it was established, both specific and nonspecific solute-solvent interactions can influence the reactivity [11 – 12]. Hence, the experimental data were analyzed using the most celebrated Kamlet-Taft solvatochromic comparison method which incorporates both types of interactions [17] (Eq. 4),

$$\log k = A_0 + s\,\pi^* + a\,\alpha + b\,\beta \tag{4}$$

where 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 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 k ($E_{1/2}$ 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 the literature [1].

The effect of a substituent on the reactivity was tested using the Hammett equation [20] (Eq. 5),

$$\log k = \log k^0 + \rho\sigma \tag{5}$$

where k is the rate constant ($E_{1/2}$ in the present study), and 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 not affected by the reaction, whereas ρ is determined by the reaction and its conditions (reagent, solvent, catalyst, temperature) and is independent of the substituent.

Data analysis

Correlation analyses were carried out using MICROCAL ORIGIN (version 6) computer software. The goodness of the fit was discussed using correlation co-efficients (r in the case of a simple linear regression, and R in the case of a multiple linear regression) and standard deviations (sd) [20]. 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].

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