SHORT PAPER

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Stoichiometric solvation effects on the reduction reactions of a cobalt(III) complex in aquo-organic solvents[†]

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Solvent effects on the reduction of $Co(NH_3)_4ox^+$ in water-methanol/1,4-dioxane mixtures have quantitatively been analysed in terms of linear solvation energy relationships. The experimentally determined rate constants/quantum yield values are well correlated with solvent empirical parameters through an equation of the form $Y=a_0+a_1X_1+a_2X_2+...+a_n X_n$, wbich revealed significant information on the solvent–solvent–solute interactions

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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 $[Coen_2X_2]$ (X=Cl, Br) and $[Coen_2(RC_6H_4NH_2)Cl]^{2+}$ complexes in aqueous organic solvent mixtures.[1–5] It was established that the method of linear solvation energy relationship (LSER) is a generalised treatment of solvation effects, and can be used to understand the influence of solvent on reaction rates, provided some classical considerations are taken into account.[6] There is often a reasonable linear correlaton[7] between a solvent-dependent property (log k or log ϕ) and a single solvent parameter, the first one is Laidier and Eyring reciprocal relationship,[8,9] that is with, ε_r^{-1} the reciprocal of relative permittivity of the medium and the second one is Grunwald–Winstein mY plot,[10] where Y is the measure of "solvent-ionising power". In another attempt, a number of other polarity scales of wider application were used, for instance, Swain's solvent vectors[11] A and B, where A is the anion solvating tendency (acity) and B is the cation solvating tendency (basity). Secondly, Dimroth and Reichardt's normalised, dimensionless, Lewis acidity solvent polarity parameter[7–9] E_T^N which was calculated from solvatochromic studies of pyridinium-N-phenoxide betaine dye, Gutmann's normalised 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 solvent.[7,8] Thirdly, Kamlet–Taft's solvatochromic[12] parameters π^*, α, and β, in which the π^* scale is an index of solvent dipolarity/polarisability, 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.

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.

The model: It is postulated in general that the solvent effect on a physicochemical quantity Y can be represented as a linear function of multiple parameters as in equation (1).

$$Y= a_o+a_1X_1+a_2X_2+a_3X_3+............+a_nX_n \qquad (1)$$

The variable Y is the solvent dependent property (log k_{et}, log ϕ, *etc.*,) in a given solvent, a_o is the statistical quantity (intercept term) corresponding to the value of the property in the reference solvent; 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) depends on the assumption of solvent effecting various interactions of the reactants/ion pair. That is, suitable selection of bulk and molecular properties of solvents such as ε_r, Y_{GW}, A, B, E_T^N, D_N^N, π^*, α and β constitute a linear or multiple regression analysis model.

The relative importance of different 'effects' of explanatory variables as dictated by multiple regression equation (1) may be statistically quantified into a percentage contribution $[P(X_i)]$. Therefore, the percentage contribution, $P(X_i)$, of a solvent parameter in a multiple regression equation is quantified[6,13] as in equation (2):

$$P(X_i) = \frac{100|a_i|}{\Sigma^n_{i=1}|a_i|} \qquad (2)$$

Thus, $P(X_1)$ may be regarded as an estimate of the percentage contributions from the solvent property to the observed solvent effect. Since $P(X_i)$ is in a single scale, comparison of the relative importance of the solvent property can easily be described. Multiple regression analysis was carried out using a commercially available microcal origin version 3.5 software runs on a Pentium model computer.

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% to 30% (v/v) MeOH or Diox) merits special attention with respect to solvent effect. The k_{obs} values, measured as a function of $[Fe(CN)_6]^{4-}$ concentrations, were fitted in double reciprocal plot of $1/k_{obs}$ *vs* $1/[Fe(CN)_6^{4-}]$ and the first-order electron-transfer rate constants, k_{et} and encounter

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Table 1 Values of k_{et} and K_{IP} for the reduction of $Co(NH_3)_4ox^+$ by $Fe(CN)_6^{4-}$ in water–organic co-solvent mixtures at 300K

Cosolvent		10^3k_{et} (S^{-1})		K_{IP}/mol/dm^3	
(vol%)	ε_r	Water–MeOH	Water–Diox	Water–MeOH	Water–Diox
5	76.1	8.220	7.152	20.00	29.63
10	73.8	9.412	8.321	25.60	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

Table 2 Quantum yields for the charge-transfer photolysis of $Co(NH_3)_4ox^+$ in water–organic cosolvent mixtures. 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 300K

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)

Number of determinations in parenthesis

complex formation constant, K_{IP} were calculated (Table 1). Monochromatic irradiation, λ_{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 Co(II) ion. Table 2 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 linear least squares plot of log k_{et} (or log $\phi_{co(II)}$) vs ε_r^{-1} shows a good correlation (r = 0.996-0.998 for water–MeOH and r = 0.996–0.997 for water–1,4-dioxane mixtures). 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 non-specific and specific interactions of solvent are proposed.[2,3] Likewise, log k_{et} (or log $\phi_{co(II)}$) were fitted in the well known Grunwald–Winstein relationship, $\log k = \log k_0 + m\, Y_{GW}$, where Y_{GW} is the solvent ionising power. The plots are linear yielding negative slopes, which indicates that the transition state is less polar than the reactants. Moreover, log k_{et} values were subjected to Swain's dual solvent vector relationship, $\log k_{et} = aA + bB + c$ and log $\phi_{co(II)}$ in the Krygowski and Fawcett relationship $Q = Q_0 + a\, E_T^N + b\, DN^N$ (where $Q = \log \phi_{co(II)}$). It is 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 as due to 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 mixtures, in which the solvational effect is mainly due to the cation solvating tendency[3] on the ion pair, $\{[Co(NH_3)_4ox]^+[Fe(CN)_6]^{4-}\}$

It is also apparent that $P(E_T^N)$ and $P(DN^N)$ obtained in the case of water–methanol mixtures are 63% and 37%, but in water–dioxane solutions 94% and 6% respectively. This result can be attributed to the formation of agglomerates or ion pairs, that is {Co(II); ligand radical}, in mixed solvents so that $\phi_{co(II)}$ is influenced by both solvent Lewis acidity and Lewis basicity. The Lewis acidity interaction is high (63% and 94%) and occurs at the negative part of the {Co(II) ligand radical} pair. The presence of a positive charge on the radical pair is more significant, that is, $\{[Co^{11}(NH_3)_4]^{2+}ox\}$ $\{[Co^{11}(NH_3)_3ox,NH_3]^+\}$ or $\{[Co^{11}(NH_3)_4ox,S]^+\}$ 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[5] acidity/basicity of the solvent, the greater the solvation, and the more the $\phi_{co(II)}$ yield. The rate/quantum yield of the reduction of $[Co(NH_3)_4ox]^+$ data were also correlated by forming a set of simultaneous equations of the form developed by Kamlet–Taft.

log k_{et} (or log $\phi_{co(II)}$) $= A_0 + s\pi^* + a\alpha + b\beta$. The weighted values of $P(X_i)$ (equation(2)) indicates the relative importance of the solvent property. It is evident that the reduction of $[Co(NH_3)_4\ ox]^+$ by $[Fe(CN)_6]^{4-}$ is 23–24% affected by bulk or non-specific solvent properties and 77–76% by specific solvent properties in water–MeOH and water–Diox mixtures respectively. Similarly, the photoreduction yield is 32–37% affected by bulk solvent properties and 68–63% by specific solvent properties.

The structural characteristics of the mixtures of water–MeOH/Diox emerge from the reported studies, MeOH is a protic EPD (electron pair donor) solvent with self associating ability although it contains hydrophobic head group. In the water–methanol system both constituents are capable of hydrogen bonding. Hence, it is suggested[4] 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 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 the rate as compared to fully aqueous medium in the present reaction and the enhancement is well increased in the binary solvents under study.

Dioxane is a partially hydrophobic cosolvent. Therefore, addition of Diox to the medium brings about marked structural changes in the prevailing water structure by causing 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 facilitates the precursor complex/CT excited state formation due to specific local electrostatic interaction.[5] Therefore, our results suggest that; 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 ion pair formation and stabilisation of geminate radical pair. The reaction is influenced by non-specific, long-range effects as analysed by ε_r, Y_{GW}, and π^* parameters of the solvent. 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 analysed by independent quantities like the *A*, *B*, α, and β set of empirical solvent parameters.

Experimental

Kinetics: In all kinetic runs the ionic strength was maintained 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 ranging (from 5% to 30% (v/v) of methanol or 1,4-dioxane. Addition of $Na_2(H_2EDTA)$ was necessary to prevent precipitation[14] of $Co_2Fe(CN)_6$. The reaction was followed spectrophotometrically at 420 nm, where the hexacyanoferrate(III) produced in the reaction absorbs. 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 was 300K. These plots were linear for at least three half-lives. Linear regression and multiple regression analyses were carried out using commercially available Microcal origin version 3.5 software runs on a Pentium model computer.

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. 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 300K by means of thermostated water flowing system. Ionic strength was maintained constant with 0.1 mol/dm^3 $NaNO_3$ and all the photolyte solutions were air equilibrated. The solution was magnetically stirred and necessary correction was made for the thermal component. The Co(II) formed was determined[15] via spectrophotometric analysis of $[Co(SCN)_4]^{2-}$ in acetone at 620 nm. In all analytical procedures, photolysed solutions were compared to identically treated unphotolysed ones. The difference in analysis was attributed to the photolysis.

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