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Photoreactivity differences of $[Cr^{III}(N–N)_3]^{3+}$ and $[Cr^{III}(N–N)_2RCl]^{2+}$ complex ions in aquo-methanol/1,4-dioxane binary mixtures

K. Anbalagan*, A. Rajendran

Department of Chemistry, Gandhigram Rural Institute-Deemed University, Gandhigram 624 302, Tamil Nadu, India

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Abstract

Photoaquation of $[Cr^{III}(N–N)_3]^{3+}$ ((N–N) = en, pn and tn) and $[Cr^{III}(N–N)_2RCl]^{2+}$ (R = $C_6H_5NH_2$, *o*-$MeC_6H_4NH_2$ and *p*-$MeC_6H_4NH_2$) complexes in water/methanol (MeOH) and water/1,4-dioxane (Diox) binary solutions (composition: water/methanol (1,4-dioxane) are 20/0, 19/1, 18/2, 17/3,16/4, 15/5, 14/6, v/v) have been followed and quantum yields were estimated. The measured photoefficiencies vary linearly with molefraction, x_2, of cosolvent and Φ is found to either increase or decrease. It is determined to attain an upper limit regularly or a lower limit as the $x_2: x_{MeOH}/x_{Diox}$ of the medium is increased from 0.0229/0.019 to 0.1602/0.0831. The nature of solvation has notable effects on Φ describing a logarithmic relationship to between quantum yield and empirical solvent scales like ε_r, Y, $E_T{}^N$, DN^N, α, β and π^*. A correlation equation of the form $Y_S = Y_0 + \sum_{n=1}^{\infty} a_i X_i$ is useful in understanding the role of solvent in terms of both qualitative and quantitative manner. The unprecedented change in quantum yield and the influence of solvent as a mediating agent are discussed.

Keywords: Photochemistry of alkyl amine-chromium(III); Chromium(III)-arylamine photoreactions; Mixed solvent effect; Correlation analysis

1. Introduction

Transition metal excited states have considerable potential for use as chemical reagents or as key elements in optoelectronic system [1–4]. The photochemistry of chromium(III) complexes has been one of the most studied aspects of modern inorganic photochemistry and continues to be one of the areas most actively investigated [5,6]. The photochemistry of octahedral chromium(III) complexes is almost always ligand substitution or racemization, charge-transfer (CT) excited states of transition metal complexes arise from the radial movement of electron density between metal and ligands (or solvent), and this charge distribution should be inherently sensitive to changes in the solvent. The commonly observed solvatochromism of CT absorption and luminescence bands, for example, results from dielectric and/or hydrogen bonding interactions between the complex and the solvent [5]. Chromium(III) complexes nicely illustrate the problems involved since the decay of the lowest energy excited state ^2E Cr(III), is spin forbidden and does not involve a change of orbital electronic population [1]. The thermal quenching of excited state chromium(III) complexes largely depends upon the nature of the solvent [7]. It should be possible to find complex solvent pairs in which the transition from slow to fast motion can be observed. In order to identify such systems, it is necessary to use solvents for which independent measures of solvent mobility are available.

Many studies have been reported [8,9] on the effect of solvents mainly pure solvents on quantum yield of chromium(III) complexes. However, photoaquation reaction in binary aqueous mixtures are limited. Investigations in mixed solvents, which are common in studies of reaction kinetics, have been hampered due to non-availability of solvatochromic parameters for the binary aqueous solvent mixtures [10]. We have undertaken a detailed program of investigations on the effect of diverse solvent on the photoaquation of some chromium(III)-alkyl/aryl complexes, $[Cr^{III}(N–N)_3]^{3+}$ and $[Cr^{III}(N–N)_2RCl]^{2+}$, in order to establish the possible mechanistic pathways involved. The present work is also aimed at making a quantitative correlation between quantum yield for the photoaquation of chromium(III) complexes and macroscopic/microscopic properties [11] such as: relative permittivity ε_r/Grunwald–Winstein solvent ionizing power *Y*, close range indices Reichardt's micropolarity parameter

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* Corresponding author. Tel.: +91 451 2452371; fax: +91 451 2454466.
E-mail address: anbal4@yahoo.co.in (K. Anbalagan).

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E_T^N/Gutmann's donor number DN^N as well as variable solvatochromic parameters dipolarity-polarizability π^*/hydrogen bond donor acidity α/hydrogen bond acceptor basicity β, which is still an elusive exercise. One, two and three parametric equations involving different combinations have been attempted with a view to finding out an efficient correlation. Moreover, quantification of solvation influence is attempted using model equation.

2. Experimental

Metal complexes $[Cr(en)_3]Cl_3$, $[Cr(pn)_3]Cl_3$, $[Cr(tn)_3]Cl_3$, $[Cr(en)_2(C_6H_5NH_2)Cl]Cl_2$, $[Cr(en)_2(o\text{-}MeC_6H_4NH_2)Cl]Cl_2$ and $[Cr(en)_2(p\text{-}MeC_6H_4NH_2)Cl]Cl_2$ were prepared [12,13] according to the standard literature procedures. The purity of the complexes was ascertained by comparing the absorption spectrum with the spectrum reported in their respective literatures. Methanol, 1,4-dioxane and $HClO_4$ were of AnalaR Grade and water was triply distilled from alkaline potassium permanganate. All photo reactions were carried out in water-methanol (1,4-dioxane) (20/0, 19/1, 18/2, 17/3, 16/4, 15/5, 14/6, v/v) air-saturated mixed solvents (concentration of the complex = 1×10^{-2} M in 0.1 M $HClO_4$ at pH 1.2). Solid complex was instantaneously dissolved and transferred into a cylindrical cell (path length = 3 cm, inner dia = 2.5 cm, volume = 15.5 cm^3) made up of corning glass.

Photoirradiation was carried out with ELH lamp, 120 V, 300 W, Kondo-Japan with a three-compartment filter for 436 nm light source [14]. The lamp intensity was in the range of 2.98×10^{-8} to 5.63×10^{-8} $Einsteins^{-1}$ as measured by ferrioxalate actinometry [14]. An aliquot of the solution was maintained in the dark at the same temperature in order to provide a correction for the thermal component. During irradiation, these solutions were stirred magnetically. After 5–10 min irradiation, the light beam was interrupted and the irradiated solution was analyzed spectrophotometrically using a Shimadzu-240 UV-visible double beam spectrophotometer. After suitable irradiation periods, the samples were brought to spectrophotometer and absorptions were measured at specific wavelengths for estimation. To avoid problems with secondary photolysis, the solutions were photolysed to less than 5% concentration. To obtain more information about the reaction mechanism of excited state chromium(III) complexes, the following experiments were also carried out.

2.1. Analytical procedures

The free chloride content of photolysis mixtures was measured by potentiometric titration with 0.002 M silver nitrate. The aliquots (2–3 ml) were kept in an ice bath in order to minimize possible thermal reaction effects. Blank experiments showed that the results were not affected by the presence of complexes in solution. Photoreleased en/pn/tn was identified as proton uptake, according to published method [15]. pH change was ascertained by using a Systronics digital pH meter 335 and pH differences between dark and irradiated samples were monitored using glass electrode. At the experimental pH, fractions of deprotonated en/pn/tn is negligible. Absorption peaks were detected for the irradiated solutions of all the complexes using a Shimadzu-240 UV-Visible double beam spectrophotometer. This has been done in order to find out whether these complexes experience red shift or blue shift during photoaquation reaction. Absorption at a wavelength of 455.7 nm (462, 464.4, 454, 506 and 459 nm) for $[Cr(en)_3]Cl_3$, ($[Cr(pn)_3]Cl_3$, $[Cr(tn)_3]Cl_3$, $[Cr(en)_2(C_6H_5NH_2)Cl]Cl_2$, $[Cr(en)_2,(o\text{-}MeC_6H_4NH_2)Cl]Cl_2$ and $[Cr(en)_2(p\text{-}MeC_6H_4NH_2)Cl]Cl_2$) complexes was monitored for quantum yield measurement.

Regression analysis most probably the organic co-solvent exerts two types of opposite effects on the rate. The first type of effect due to which the photoefficiencies is enhanced is the greater solvation of the transition state and the increase of true water molecules from water clusters while the other type of effects responsible for decrease in the photoaquation yield; (i) decrease of the bulk dielectric constant of the medium and (ii) decrease in the polarity of the solvent [11]. It is hardly surprising that a single parameter fails to sum up the complexities of solvation. Due to the limitations of dielectric constant, different solvent parameters have been developed which are based on actual solvent sensitive chemical or physical processes. Majority of these are based on linear free energy relationship (LFER) and empirical parameters. Linear solvation energy relationships (LSER) are used as a diagnostic tool of understanding the reaction pathway. The influence of solvent effect on a single solute/excited state obeys the relationship [16–18] as given in eq. (1).

$$Y_S = Y_0 + \sum_{i=1}^{n} a_1 X_i \tag{1}$$

The variable Y_S is the solvent dependent property ($\log \Phi_{Cr(III)}$) in a given solvent or mixture of solvents, Y_0 is the statistical quantity representing the value of the property in the reference solvent, X_1, X_2, X_3, etc., (explanatory variables) represent independent but complementary solvent parameters which account for the solute-solvent interaction mechanisms: a_1, a_2, a_3, etc., are the regression coefficients describing the sensitivity of property Y_S to the different solute/solvent interaction mechanisms.

Such an equation can be applied only to data for a large number of well chosen solvent empirical parameters, and its success must be examined by proper statistical methods [9–11]. When we encounter a multiparametric equation, which is said to be successful in correlating a set of reactivity data, it is natural to inquire into the physical significance of the various terms in relation to the reaction mechanism. Multiparametric equations provide a better quantitative description of the solvent effect on chemical reactions. The relative importance of different effects of explanatory variables as dictated by multiple regression may be statistically quantified into percentage contribution, $P(X_i)$ factor as in Eq. (2)

$$P(X_i) = 100|a_i| / \sum_{i=1}^{n} |a_i| \tag{2}$$

Thus, $P(X_i)$ may be regarded as an estimate of the percentage contribution of solvent property on the observed solvent effect. Since $P(X_i)$ is in a single scale, comparison of relative importance of solvent property can easily be described.

Table 1
Quantum yields for the photo aquation of chromium(III) complexes in air-equilibrated water–methanol mixtures at 303 K

(N–N)/R	$\Phi \times 10^{-2}$ mole fraction of methanol						
	0	0.0229	0.0471	0.0728	0.1001	0.1292	0.1602
	$[Cr^{III}(N–N)_3]^{3+}$						
en	11.49	33.70	31.53	27.79	24.06	21.47	14.4
pn	22.43	21.33	19.12	16.92	15.81	14.70	12.49
tn	37.61	32.38	29.04	27.61	26.56	22.85	19.04
	$[Cr^{III}(N–N)_2LCl]^{2+}$						
$C_6H_5NH_2$	76.70	70.69	57.90	53.39	50.38	45.87	40.71
o-$MeC_6H_4NH_2$	56.84	57.93	54.26	51.67	49.09	45.64	43.49
p-$MeC_6H_4NH_2$	42.79	50.53	49.63	48.96	48.23	47.87	46.06

3. Results and discussion

The absorption spectra of the complexes studied exhibit three LF bands. The photoreactivity was investigated using $\lambda = 436$ nm light irradiation of the complexes. An initial pH of ∼1.2 was chosen for the samples to be photolyzed, so as to neglect spectral changes due to deprotonation of $[Cr^{III}(N–N)_3]^{3+}$ and $[Cr^{III}(N–N)_2RCl]^{2+}$, complexes with water. For the complexes, $[Cr^{III}(N–N)_3]^{3+}$ and $[Cr^{III}(N–N)_2RCl]^{2+}$ essentially the closely resembling spectral variations occur upon 436 nm light irradiation. Identification of products reveals that amine is released predominantly than chloride for $[Cr^{III}(N–N)_2RCl]^{2+}$ (amine release for $[Cr^{III}(N–N)_3]^{3+}$). This observation indicates that the photoreaction is aquation of amine as illustrated in Eqs. (3)–(5).

$$[Cr^{III}(N–N)_2RCl]^{2+} \rightarrow {}^*[Cr^{III}(N–N)_2RCl]^{2+} h\nu \quad (3)$$

$$\begin{aligned} &{}^*[Cr^{III}(N–N)_2RCl]^{2+} + H_3O^+ \\ &\quad \rightarrow [Cr^{III}(N–N)RCl(H_2O)]^{2+} + (N–N)H_2{}^{2+} \end{aligned} \quad (4)$$

$$\begin{aligned} &{}^*[Cr^{III}(N–N)_2RCl]^{2+} + H_3O^+ \\ &\quad \rightarrow [Cr^{III}(N–N)_2R(H_2O)]^{3+} + Cl^- \end{aligned} \quad (5)$$

where (N–N) is en/pn/tn. Spectral measurements allow the calculation of the quantum yields in two mixed solvents which are collected in Tables 1 and 2. It seems then reasonable to infer that, to all the complexes, the quantum yield is dependent on the mole fraction of x_{MeOH}/x_{Diox} of the medium and the general prediction of the photoaquation is the efficiencies of aquation either is enhanced or retarded as the x_2 of the medium increases. Irradiation of $Cr^{III}(N–N)_3]^{3+}$ and $[Cr^{III}(N–N)_2RCl]^{2+}$ in the region of LF bands ($\lambda = 436$ nm) gave conversion to amine labilization by water molecule. The products were characterized by spectrophotometry, ligand estimation and pH measurements. It was concluded that two main products, for example $[Cr(pn)_2(pnH)(H_2O)]^{4+}$ and $[Cr(pn)_2(H_2O)_2]^{3+}$ were formed [19]. The understanding of the photochemical, photophysical and spectroscopic features and behaviours of chromium(III) octahedral-type complex ions in mixed solvent media has continued to challenge both the experimentalist and theoretician [20–23]. This sustained interest arises in part from a number of outstanding issues, including the relative chemical importance of the lowest electronically excited states, the types and roles of non-radiative processes, particularly the possible involvement of thermally activated back-intersystem crossing (bisc) from the lowest doublet to a low lying quartet state(s) ${}^4T_{2g}$ versus direct chemical reaction from the doublet excited state (^{2}Eg) and the occurrence of chemically reactive ground-state intermediates. Underlying all of these issues is the discernment of the roles of the surrounding media or environment (Table 3).

Irradiation of the LF bands of $[Cr^{III}(N–N)_3]^{3+}$ and $[Cr^{III}(N–N)_2RCl]^{2+}$ in binary mixed solvents (water-methanol/1,4-dioxane) follows pseudo-first order kinetics.

Table 2
Quantum yields for the photo aquation of chromium(III) complexes in air-equilibrated water-1,4-dioxane mixtures at 303 K

(N–N)/R	$\Phi \times 10^{-2}$ mole fraction of 1,4-dioxane						
	0	0.019	0.0229	0.0359	0.0502	0.0659	0.0831
	$[Cr^{III}(N–N)_3]^{3+}$						
en	11.49	13.85	17.35	19.28	22.28	25.58	27.11
pn	22.43	23.54	27.21	29.41	31.29	38.24	45.59
tn	37.61	43.80	56.18	69.51	79.99	89.72	92.40
	$[Cr^{III}(N–N)_2LCl]^{2+}$						
$C_6H_5NH_2$	76.70	65.42	54.89	49.63	42.11	37.60	33.09
o-$MeC_6H_4NH_2$	56.84	54.25	51.67	50.38	47.37	43.06	37.46
p-$MeC_6H_4NH_2$	42.79	38.81	37.35	35.18	33.08	31.80	29.90

Table 3
Statistical results coefficients and weighted contributions of solvent parameters in Krygowski–Fawcett equation for the photoaquation reaction of Cr(III) complexes in water–methanol mixtures at 303 K

(N–N)/R	Statistical parameter							
	R^2	S.D.	Ψ	α	β	$P(E_T^N)$	$P(D_N^N)$	Intercept
	$[Cr^{III}(N–N)_3]^{3+}$							
en	0.984	0.021	0.13	−9.41	97.78	9	91	74.18
pn	0.986	0.013	0.13	0.75	14.6	5	95	−13.80
tn	0.931	0.028	0.28	−7.25	70.9	9	91	−53.52
	$[Cr^{III}(N–N)_2LCl]^{2+}$							
$C_6H_5NH_2$	0.973	0.018	0.18	3.90	−8.05	33	67	2.83
o-$MeC_6H_4NH_2$	0.997	0.003	0.03	0.69	6.41	10	90	−6.35
p-Me$C_6H_4NH_2$	0.967	0.003	0.21	−0.44	6.44	6	94	−5.33

R^2–Coefficient of multiple determination; S.D.–standard deviation; Ψ–Exner's statistical parameter; α and β–coefficients of E_T^N and D_N^N in equation 10; $P(E_T^N)$ and $P(D_N^N)$–weighted percentage contributions.

It has been already reported [24–26] that the rate-controlling first step of the associative mechanism involves labilization of 1,2-diaminoethane (en). Therefore, the overall mechanism of the complexes [27–29] can be summarized as in the following steps; Eqs. (6)–(9):

$$[Cr^{III}(N–N)_3]^{3+} \rightarrow {}^*[Cr^{III}(N–N)_3]^{3+} h\nu \quad (6)$$

$$^*[Cr^{III}(N–N)_3]^{3+} + H_3O^+ \rightarrow [Cr^{III}(N–N)_3(H_2O)]^{3+} \quad (7)$$

$$[Cr^{III}(N–N)_3(H_2O)]^{3+} \rightarrow [Cr^{III}(N–N)_2(N–N)H(H_2O)]^{4+} \quad (8)$$

$$[Cr^{III}(N–N)_2(N–N)H(H_2O)]^{4+} + H_3O^+ \rightarrow [Cr^{III}(N–N)_2(H_2O)_2]^{3+} + (N–N)H_2{}^{2+} \quad (9)$$

The quantum yields for photoaquation at 303 K at pH 1.2 ($HClO_4$) upon LF excitation are given in Tables 1 and 2. From the quantum yield values, it is understood that it Φ changes remarkably with respect to the mole fraction of the organic cosolvent in the binary mixture. It shows vividly that the Φ is dependent on solvation characteristics. This is further substantiated by a Fig. 1, which is a typical plot of log Φ against x_2 (x_{MeOH}/x_{Diox}) of the mixed solvents. The striking feature is the Φ values decrease for $(N–N)_3$ and $(N–N)_2RCl$ complexes on increasing the mole fraction of the cosolvent methanol in the mixture. However, the photoefficiency is understood to increase with respect to x_{Diox} in the mixtures for $[Cr^{III}(N–N)_3]^{3+}$ but an exactly opposite trend is observed for the $[Cr^{III}(N–N)_2RCl]^{2+}$ series. A good correlation existing between log Φ and x_2 is obvious from Fig. 1. Certainly, the slopes of regression describe the sensitivity of photoaquation to added cosolvent. This change in Φ value is consistent with the linear relationship with x_2 of the medium, which results in meaningful and good relations, for example, $[Cr(en)_2(o\text{-}MeC_6H_4NH_2)Cl]^{2+}$, the results of correlation equations are; $\log \Phi = -0.241 - 1.100\,x_2$; (water–methanol; $r = 0.998$, S.D. = 0.004, Ψ = 0.05, $n = 6$, Temp. = 303 K) and $\log \Phi = -1.102 - 0.449\ x_2$; (water-1,4-dioxane; $r = 0.976$, S.D. = 0.014, Ψ = 0.17, $n = 6$, Temp. = 303 K).

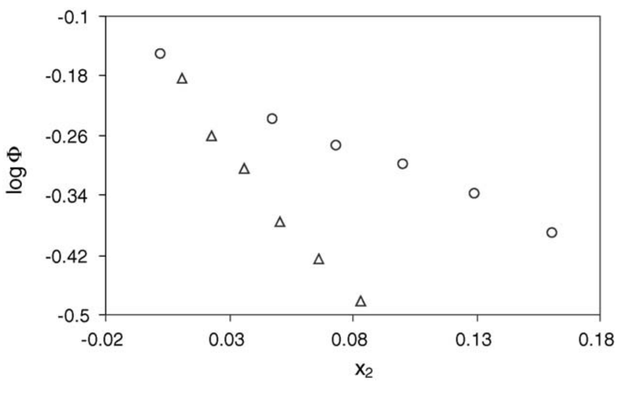


Fig. 1. Plot of log Φ versus mole fraction of cosolvent, x_2, for the aquation of $[Cr(en)_2(C_6H_5NH_2)Cl]Cl_2$ at 303 K in water–methanol (○) and water-1,4-dioxane (△).

The results from this part of the study have clearly established that all facets of the photosubstitution of chromium(III) complex ions are influenced by their environments albeit the extent of this depends upon the nature and composition of the media [30]. This means that the solvation on the second coordination sphere plays an important and significant role. The variation of the Φ value with mole fraction of organic cosolvent shows a minimum for en, pn, tn, $C_6H_4NH_2$, *o*-$MeC_6H_4NH_2$ and *p*-$MeC_6H_4NH_2$ complexes at the mole fraction of $x_{MeOH}/x_{Diox} = 0.1602/0.0831$ in the mixtures (a higher value is observed for $[Cr^{III}(N–N)_3]^{3+}$ at $x_{Diox} = 0.0831$). The dramic differences of Φ values, that is an increase/decrease with respect to x_2, illustrates a solvent cage effect. It means solvation mediated population of doublet $^*Cr^{III}$ (doublet) or quartet $^*Cr^{III}$ (quartet) is evident, the excited state is preferentially solvated in the sterically hindered "pocket" and is stabilized leading to reaction. The excited state species have been proposed to solvent caged doublet $^*Cr^{III}$ (doublet)/$^*Cr^{III}$ quartet capable of photoaquation on a time scale competitive with deactivation process [31].

4. Single solvent scale approach

Solvent scales have been proposed and used as potential empirical–solvent property indicators: the solvent relative permittivity, ε_r, Grunwald–Winstien, *Y* are important in the assignment of assignment of reaction course. Most of these scales

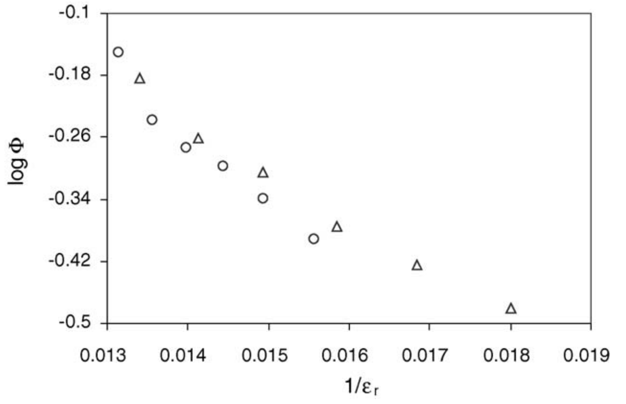


Fig. 2. Plot of log Φ versus $1/\varepsilon_r$, for the aquation of $[Cr(en)_2(C_6H_5NH_2)Cl]Cl_2$ at 303 K in water-methanol (○); correlation data: $m = -0.01$, $r = 0.976$, S.D. = 0.02 and Ψ = 0.17 and water-1,4-dioxane (△); correlation data: m = −0.016, $r = 0.991$, S.D. = 0.016 and Ψ = 0.1.

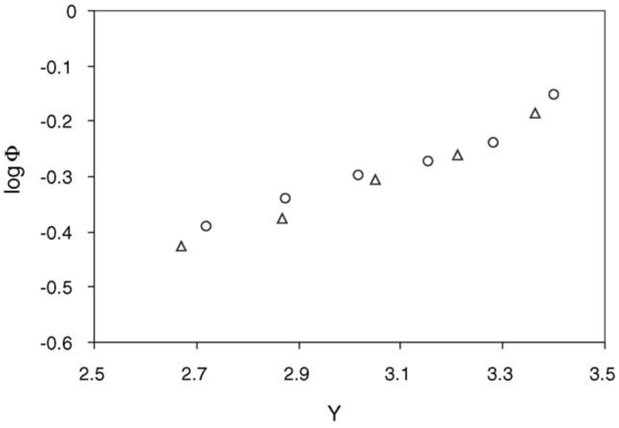


Fig. 3. Plot of log Φ versus Grunwald–Winstein parameter, *Y*, for the aquation of $[Cr(en)_2(C_6H_5NH_2)Cl]Cl_2$ at 303 K in water-methanol (○); correlation data: $m = 3.0$, $r = 0.977$, S.D. = 0.019 and Ψ = 0.17 and water-1,4-dioxane (△);correlation data: $m = 3.09$, $r = 0.993$, S.D. = 0.014 and Ψ = 0.09.

are based on kinetic and spectral data of a single standard probe molecule. They are able to represent the polarity, hydrogen bond acceptor–donor and other solute–solvent-interactions. Correlation analysis with solvent parameters based on a single probe molecule, the probe–solvent interactions of which are well understood and clearly defined, can lead to valuable and significant conclusions about the solvent-dependent process under study [32]. In continuum solvation models, the solvent molecules are not mediated explicitly but rather they are expressed as a homogeneous medium characterized by a bulk relative permittivity [33]. Laidler-Eyring, Fig. 2 clearly depicts a neat correlation between log Φ and $1/\varepsilon_r$ of the solvent media. The linearity reveals the effect of solvent structure on the solvation of excited state of the complexes. The following are the typical relationship for the complex $[Cr(pn)_3]Cl_3$ between logΦ and $1/\varepsilon_r$ of the media; log Φ = 0.008–0.010 $1/\varepsilon_r$; (water–methanol, $r = 0.992$, S.D. = 0.011, Ψ = 0.10, $n = 6$, Temp. = 303 K); and log Φ = 0.0128–0.013 $1/\varepsilon_r$; (water-1,4-dioxane, $r = 0.943$, S.D. = 0.047, Ψ = 0.047, $n = 6$, Temp. = 303 K). Similarly, all other systems are in good correlation with $1/\varepsilon_r$ of the medium, for instance; (water–methanol) $r = 0.944$–0.995, S.D. = 0.031–0.002, Ψ = 0.26–0.07, $n = 6$, Temp. = 303 K, (water-1,4-dioxane): $r = 0.943$–0.991, S.D. = 0.047–0.004, Ψ = 0.26–0.07, $n = 6$, Temp. = 303 K.

Macroscopic solvation of the reaction center may be understood using solvent parameters in linear free energy relations one such is the Grunwald–Winstein [34], scale. The correlation of log Φ with the Grunwald–Winstein solvent ionizing power, *Y* parameter in both the solvent mixtures studied showed satisfactory results. The generalized and suitable relationship is; $\log k = \log k_0 + \mathrm{m}Y$, in which, *k* and k_0 are replaced by Φ and Φ^0, respectively, these are nothing but solvent dependent and solvent specific variables. Fig. 3 is the representative plot obtained by plotting log Φ verses Grunwald–Winstein solvent ionizing power, *Y*. Examination of the statistical results for the chromium(III) complexes imply (slope $m = -3.25$–17.93, $r = 0.937$–0.997, Ψ = 0.05–0.27 and S.D. = 0.003–0.044) the magnitude of *m* values predict an associative pathway with a relatively tight excited state/intermediate, where bond formation is more progressed than bond cleavage [18]. Further, when log Φ of the complexes in the two binary mixtures of solvents studied are correlated, the phenomenon of dispersion is observed, i.e., lines of different slopes are observed in water–methanol (1,4-dioxane) solutions. This dispersion phenomenon is due to the fact that a different blend of non-specific and specific solvent influences interact with the solute by the solvent [35]. Furthermore, close similarity in *m* values suggests that a similar mechanism is operating in the series of chromium(III) complexes studied.

5. Discontinuum approach

Reichardt's solvatochromic parameter (E_T^N) provides an excellent and very sensitive characterization of the micropolarity of the solvation shell on the molecular microscopic level of solvents. Normalised E_T^N values are based on negative solvatochromic pyridinium *N*-phenolate betaine dye as probe molecule in extremely polar/nonpolar solvents [36] and high E_T^N values correspond to high solvent polarity. The use of this scale in correlations with energy-based solvent dependent processes in the photochemical reactions, has the advantage of giving immediate insight in the magnitude of solvent effects observed [32]. These scales measure solute/solvent interactions in a molecular microscopic level, considering solvents as a discontinuum of individual solvent molecules with their own solvent/solvent interactions. Moreover, the normalized E_T^N values are somewhat easier to handle [32], particularly in multiparameter equations. DN^N is the donor number (or donicity) proposed by Gutmann [37] which is an empirical semi quantitative measure of the nucleophilic properties of the electron pair donor (EPD) character of solvent. There is a very good relationship of log Φ with micropolarity parameter E_T^N and Gutmann donor number, DN^N in a biparametric Eq. (10) of the form

$$Q = Q_0 + \alpha\, E_T^N + \beta\, \mathrm{DN}^N \tag{10}$$

where Q and Q_0 represents log Φ and $\log \Phi^0$, respectively. The regression analysis for the complex $[Cr(tn)_3]Cl_3$ are; log Φ = −53.52 − 7.25 α + 70.9 β; (water–methanol,

Table 4
Statistical results coefficients and weighted contributions of solvent parameters in Krygowski–Fawcett equation for the photoaquation reaction of Cr(III) complexes in water–1,4-dioxane mixtures at 303 K

(N–N)/R	Statistical parameter							
	R^2	S.D.	Ψ	α	β	$P(E_T^N)$	$P(D_N^N)$	Intercept
	$[\mathrm{Cr^{III}(N{-}N)_3}]^{3+}$							
en	0.993	0.011	0.09	−4.55	11.46	28	72	−6.16
pn	0.985	0.016	0.13	1.55	-14.9	9	91	10.446
tn	0.999	0.004	0.03	−8.20	26.40	24	76	−14.77
	$[\mathrm{Cr^{III}(N{-}N)_2LCl}]^{2+}$							
$C_6H_5NH_2$	0.997	0.008	0.06	2.30	-1.53	60	40	−1.117
o-$MeC_6H_4NH_2$	0.994	0.006	0.08	−2.40	15.05	14	86	−10.67
p-$MeC_6H_4NH_2$	0.996	0.004	0.07	0.45	1.39	25	75	−2.02

R^2–Coefficient of multiple determination; S.D.–standard deviation; Ψ–Exner's statistical parameter; α and β–coefficients of E_T^N and D_N^N in equation 10; $P(E_T^N)$ and $P(D_N^N)$–weighted percentage contributions.

$R^2 = 0.986$, S.D. = 0.028, $\psi = 0.28$, $n = 6$, Temp. = 303 K) and $\log \Phi = -14.770 - 8.20\ \alpha + 26.40\ \beta$; (water-1,4-dioxane, $R^2 = 0.999$, S.D. = 0.004, $\psi = 0.03$, $n = 6$, Temp. = 303 K). The correlation equation yield a good collection data and presented in Tables 4 and 5. The $P(X_i)$ values were estimated and found to be $P(\mathrm{DN^N}) > P(E_T^N)$, that is, $P(DN^N) \approx (67–95)$; $P(E_T^N) \approx (5-33)$; (water–methanol) $P(DN^N) \approx (40–91)$; $P(E_T^N) = (9-60)$; (water–1,4-dioxane). Since methanol is a hydrogen bond acceptor (HBA) solvent as well as hydrogen bond donor (HBD) solvent, it stabilizes the reactant molecules rather than excited state through specific solvation, resulting in lowering of quantum yield. Since 1,4-dioxane, however, is a HBA solvent, the specific interaction between the excited state and the solvent through Lewis basicity interactions is more, and the excited state is solvated to a greater extent, resulting in fall/raise of quantum yields.

Considering the correlation between Lewis acidity and Lewis basicity with quantum yield data, the influence of specific solvation on reactivity is more pronounced. Therefore, it seems reasonable to use the polarizability of the mixture as an adequate solvent parameter to consider the influence of non-specific solvation on reactivity. Therefore, another solvatochromic comparison method developed by Kamlet and Taft to quantify and rationalize multiple interacting solvent effects on reactivity [38] is used. The quantum yield data was also subjected to correlation analysis with the solvatochromic parameters α, β and π^* in the form of linear solvation energy relationship (LSER) as given in Eq. (11).

$$\log \Phi = A_0 + s\pi * + a\alpha + b\beta \tag{11}$$

where π^* is an index of the solvent polarity/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 and describes the ability of the solvent to donate a proton in a solvent to solute hydrogen bond, β is the solvent HBA basicity which provides a measure of the solvent's ability to accept a proton (or 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. Combining the appropriate terms from the above equation, total solvatochromic equation can be obtained for complexes and for example, $[\mathrm{Cr(en)_2(}p\text{-}\mathrm{MeC_6H_4NH_2)Cl}]^{2+}$ the relationship yields; $\log \Phi = 20.649 + 51.9\alpha + 9.91\beta + 34.9\ \pi^*$; (water–methanol, $R^2 = 0.999$, S.D. = 0.001, $\psi = 0.03$, $n = 6$, Temp. = 303 K) and $\log\Phi = -33.435 + 1.67\alpha + 22.9\beta + 3.70\ \pi^*$; (water-1,4-dioxane, $R^2 = 0.999$, S.D. = 0.001, $\psi = 0.03$, $n = 6$, Temp. = 303 K). The $P(X_i)$ values have been recorded in Tables 5 and 6 and generally noted as $[P\pi^* < [P(\alpha) + P(\beta)]]$. The lower value of $P(\pi^*)$ may be attributed to the fact that the

Table 5
Statistical Results, the coefficients and weighted contributions of solvent parameters in Kamlet–Taft's equation for the photoaquation of chromium(III) complexes in water–methanol mixtures at 303 K

N–N/R	R^2	S.D.	Ψ	s	a	b	$P(\pi^*)$	$P(\alpha)$	$P(\beta)$	Intercept
	$[\mathrm{Cr^{III}(N{-}N)_3}]^{3+}$									
en	0.990	0.020	0.11	112	−530	−170	14	65	21	528.5
pn	0.996	0.008	0.07	147	−113	98	41	32	27	−45.31
tn	0.975	0.021	0.17	−80	−425	−324	10	51	39	641.8
	$[\mathrm{Cr^{III}(N{-}N)_2LCl}]^{2+}$									
$C_6H_5NH_2$	0.975	0.021	0.30	190	−42.3	185	45	10	45	−190.9
o-$MeC_6H_4NH_2$	0.996	0.004	0.20	−9.6	31.2	4.2	22	69	9	−26.9
p-$MeC_6H_4NH_2$	0.999	0.001	0.03	34.9	51.9	9.91	36	54	10	20.64

R^2–correlation coefficient of multiple regression; S.D.–standard deviation; Ψ–Exner's statistical parameter; s, a and b–coefficients of Eq. (11); $P(\pi^*)$, $P(\alpha)$ and $P(\beta)$–weighted percentage contributions.

Table 6
Statistical Results, the coefficients and weighted contributions of solvent parameters in Kamlet–Taft's equation for the photoaquation of chromium(III) complexes in water–1,4-dioxane mixtures at 303 K

(N–N)/R	R^2	S.D.	Ψ	*s*	*a*	*b*	$P(\pi^*)$	$P(\alpha)$	$P(\beta)$	Intercept
	$[Cr^{III}(N–N)_3]^{3+}$									
en	0.992	0.016	0.10	19.6	−44	−196	7	17	76	64.1
pn	0.991	0.015	0.10	2.83	53.3	356	1	13	86	−130
tn	0.995	0.013	0.08	27.35	−131	−714	3	15	82	252.3
	$[Cr^{III}(N–N)_2LCl]^{2+}$									
$C_6H_5NH_2$	0.997	0.010	0.06	−10.4	18.8	66.9	11	20	79	−22.9
o-$MeC_6H_4NH_2$	0.996	0.006	0.06	4.88	−52	−319	1	14	85	112.6
p-$MeC_6H_4NH_2$	0.999	0.001	0.03	3.70	1.67	22.9	13	6	81	−33.4

R^2–correlation coefficient of multiple regression; S.D.–standard deviation; Ψ–Exner's statistical parameter; s, a and b–coefficients of Eq. (11); $P(\pi^*)$, $P(\alpha)$ and $P(\beta)$–weighted percentage contributions.

immediate solute environment influences substantially than that of long range interactions outside of the first solvation sphere. The study of solvent effects on photosubstitution reactions of Cr(III) complexes is more complex. The total quantum yield for (N–N) loss was remarkably complex and medium dependent. There is an inclination to interpret this in terms of entering ligand as an indication and formation/stabilization of excited state/intermediate in favour of a primary dissociative event.

The solvent dependence of Φ values is in favour of seven coordinated structure with degree bond weakening of the leaving ligand in the transition state [39] as shown in the Tables 1 and 2 for $[Cr^{III}(N–N)_3]^{3+}$ and $[Cr^{III}(N–N)_2RCl]^{2+}$ complexes. The Φ increases/decreases with an increase in x_2 of the medium, these results suggest that the photodissociation of the ligand may occur from both the doublet and quartet excited states, the latter lives shorter than the former. The overall quantum yield can be expressed as

$$\Phi_{\text{tot}} = \Phi(^4T) + \Phi(^2E) = \Phi(^4T) + \Phi(^2E)\, k_{\text{isc}}(k_{\text{D}} + k_{\text{S}}[x_2])^{-1}$$

Quantum yield for the photoaquation of the (N–N) ligand is influenced/controlled by the solvation sphere of the excited state. These findings indicate that conversion of the ^2E state having aquation character more than that of ^4T, which is in competition with all other relaxation processes. If the quantum yield is markedly increasing then the doublet excited state is preferably solvent caged stabilized and allowance is admitted for aquation. This solvation effect is considered to originate from the nature of the bond between the excited state and close range solvent molecules. The increase in doublet reactivity is due to the hydrophobic stabilization by effective solvation of the doublet state, otherwise, concerted communication between ^2D and ^4Q leads to population of the latter. The hydrophobic stabilization is attributed due to added methanol/dioxane, which are definitely increased in the solvation shell of the complex ion as x_2 increases. In addition, if the quartet and doublet states are energetically sufficiently close, thermal repopulation of the quartet state can take place. Then the photoaquation will predominantly originate from quartet in competition with all other decay processes, this virtually decreases the yield. That is, an enhancement in yield with respect to x_2 of the medium indicates solvent stabilized population of ^2D state on the contrary, population of ^4Q state leads to retardation in yield with increase in mole fraction of the co-solvent in the medium.

The solvation mechanism could explain the change in Φ values during the photochemical reactions of $[Cr^{III}(N–N)_3]^{3+}$ and $[Cr^{III}(N–N)_2RCl]^{2+}$ provided non-specific and specific solvent effects play vital role. In Scheme 1, a solvent molecule enters in to the coordination sphere of the complex in the trans position with respect to the ligand undergoing labilization; regardless of which edges is attacked. Photoaquation of chromium(III) complexes occur from both $^4Q^*$ and $^2D^*$ states, which are represented by;

$$[Cr^{III}(N–N)_3]^{3+} + h\nu \rightarrow {}^4Q_1{}^*$$

$$^4Q_1{}^* \rightarrow [Cr^{III}(N–N)_3]^{3+}$$

$$^4Q_1{}^* \rightarrow [Cr^{III}(N–N)_2(H_2O)_2]^{3+} + (N–N)H_2{}^{2+}$$

$$^2D_1{}^* \rightarrow [Cr^{III}(N–N)_3]^{3+}$$

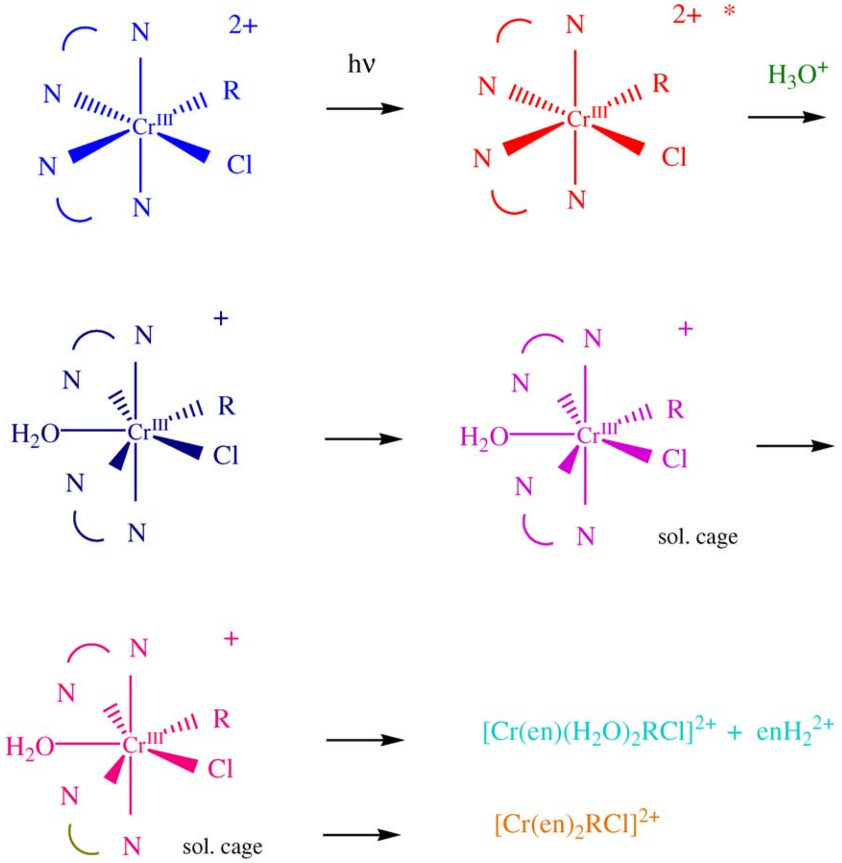
$$^2D_1{}^* \rightarrow [Cr^{III}(N–N)_2(H_2O)_2]^{3+} + (N–N)H_2{}^{2+}$$

The quantum yield measured in the air-equilibrated aqueous solution is; $\Phi_{\text{tot}} = \Phi\,(^4Q_1{}^*) + \Phi\,(^2D_1{}^*)$ where $\Phi\,(^4Q_1{}^*)$ and $\Phi\,(^2D_1{}^*)$ are the quantum yields from the photoaquation at the excited quartet and doublet state respectively. The efficiency of intersystem crossing [40] which populates $^2D_1$ state is η^1_{isc}. A linear dependence of Φ on η^{-1} (medium viscosity) was reported for the photoaquation of $Cr(NH_3)_2(NCS)^{4-}$ in glycerol/water mixtures. Tables 1 and 2 illustrate that the quantum yield parallels the composition of the medium [39] and reaches a limiting value at higher x_2 which is in agreement with the earlier findings. These trends emphasized the significant role played by cage effects even if their detailed understanding remains uncertain, which are presented in the following steps:

$$MX_6 \xrightarrow{h\nu} {}^*MX_6, \qquad {}^*MX_6 \rightarrow MX_6,$$

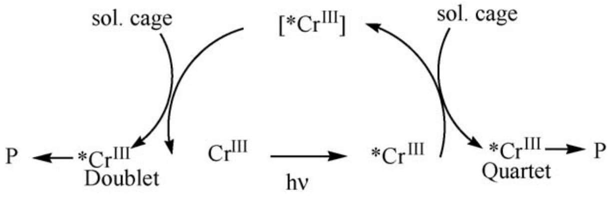
$$^*MX_6 + S \rightarrow MX_6(S), \qquad MX_6(S) \rightarrow MX_6(S)_{\text{sol. cage}},$$

$$MX_6(S)_{\text{sol. cage}} \rightarrow MX_6(S), \qquad MX_6(S)_{\text{sol. cage}} \rightarrow MX_5 + X$$



Scheme 1. Photoaquation of chromium(III) complex; solvation influence leading to favourable and unfavourable cage for product formation.

where S represents a solvent (water) molecule, which competes with × for the sixth coordination site on M within the solvent cage. The formed binary mole, $MX_6(S)_{\text{sol. cage}}$, in turn, is undergoing solvent mediated population of quartet Φ (^{4}T) or doublet Φ (^{2}E), this accounts the increase/decrease in Φ as the concentration organic co-solvent in the medium increases. The proposed mechanism involving two distinct excited states is depicted in Scheme 2. The photoefficiency is promoted if the doublet state is more populated than that of quartet due to effective solvation mediated processes. Our empirical model analysis based on simple and multiple regression equations establish better donor characteristics of mixed solvents $P(\mathrm{DN}^{\mathrm{N}}) > P(E_{\mathrm{T}}^{\mathrm{N}})$ in water-methanol (1,4-dioxane) solutions. Scheme 2 proposed solvent mediated cycle for the photoaquation of chromium(III) complexes involving both quartet and doublet reactivity that arise from non-specific and specific solvent–solute interactions.



Scheme 2. Population of excited state due to concerted solvent cage perturbation of the excited state of chromium(III) complex.

6. Conclusion

Prediction of solvation contributions on Φ data emerges due to the following; (1) the photoefficiency of $[Cr^{III}(N–N)_3]^{3+}$ and $[Cr^{III}(N–N)_2RCl]^{2+}$ is enhanced or retarded in binary mixed solvents (water/methanol or 1,4-dioxane) because of solvent asymmetric influence; (2) there is a concerted solvent cage perturbation on excited doublet (^{2}E)/quartet (^{4}T) leading to population control thereby, responding change in Φ; (3) hydrogen bonding of solvent on excited states (measured as a function of $P(\alpha)$, $P(\beta)$ values) influence preferential solvation, which in turn, alters degree of participation of water and organic cosolvent; (4) the amines are generally rigid (sterically reinforced and cyclic ligands) leading to a steeper strain therefore to an increasing importance of strain energy effects. Hence, various effects determine the population of ^{4}A/^{2}E states leading to product distribution. Thus, the model analysis being standard will substantially contribute for a quantum approach on solvation effect.

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