

Correlation of Photosubstitution Quantum Efficiencies of $[\text{Cr L}_m \text{Cl}_n]^{(3-n)+}$ Complexes with Solvent Properties in Mixed Solvents by Statistical Relationships

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ABSTRACT

Objectives: This investigation focuses on the excited state aquation reactions of a series of $[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+}$ [$(\text{N})_x = (\text{en})_2, (\text{pn})_2, (\text{tn})_2, (\text{dien}), (\text{trien})$ and (tetren)] complexes in binary solvent(methanol/water) media. The main objective of this paper is to study the quantum yield (Φ) variation with respect to change of mole fraction (x_2)of solvents in aquation reactions of these Cr (III) complexes in mixed solvent media and to interpret the results in the light of statistical analysis to give meaningful qualitative and quantitative treatment.

Study design: The linear solvation energy relationship (LSER) is employed to correlate the Φ data with various empirical solvent parameters in single and multiple statistical equations.

Methodology: Visible light photolysis was carried out for the $[\text{Cr L}_m \text{Cl}_n]^{(3-n)+}$ complexes in water containing either methanol (MeOH) or 1,4-dioxane (Diox), x_2 ($x_{\text{MeOH}}/x_{\text{Diox}}$) 0, 0.029/0.0109 to 0.1602/0.0831, respectively.

Results: Photolysis of these complexes in these binary mixtures is good to excellent for few complexes and poor for the remaining cases. Solvent assisted photolysis in the binary solvent mixtures produced aquated products. In principle, the photoaquation takes place by associative mechanism and quantum yield for this reaction was found to exhibit linear x_2 dependence.

Conclusion: In summary, the available model analysis allows a definitive choice of the above two alternative pathways according an increase or decrease in Φ value at higher mole fractions of MeOH/Diox in the medium. This conclusion is more appealing and in

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order to gain more insight into the problem. This model analysis is extremely important because it can yield both qualitative (bulk solvent effect) and quantitative (short range solvation effect) information that may otherwise be difficult to arrive at.

Keywords: Cr (III) complexes; molecular dynamics; photo aquation reaction; solvation effect; statistical model; regression model;

1. INTRODUCTION

The photochemistry of chromium (III) complexes has been a central theme of inorganic photochemistry from the inception of the area in the early 1960s and interest continues to the present day (Anbalagan and Rajendran, 2006). Some of the problems identified at the outset, such as, the identity of the reaction excited states, are still actively being investigated and do not seem to have been completely resolved despite considerable research effort (Rajendran,2010). The effect of different solvents upon rates of chemical change was one of the earliest kinetic problems to be studied. Most of the substitution reactions, in solutions are strongly dependent on the medium (Shorter, 1982). Marcus and Hush have contributed significantly to the medium effect on various reactions using a continuum dielectric description. This description gives results that are in qualitative agreement with the experiment. However, classical dielectric models are an over simplification and, consequently, a quantitative agreement between the prediction of the models and experiments is rarely observed. The recent progress on the role of single component solvents concerns the role of both the static as well as dynamic solvent effects. The situation is more involved when dealing with the solvent mixtures in spite of some recent progress in this area (Reichardt, 1988). This is due to the fact that in mixtures, the reactivity may depend on preferential solvation phenomena, which are determined by the reactant (and product) interactions with the two kinds of solvent molecules as well as by different solvent-solvent interactions (Anbalagan and Rajendran, 2006). Relaxation phenomena, affecting the dynamic solvent effects, are also more complicated in mixtures than in pure solvents.

However, solvent mixtures are interesting in relation to many areas of chemistry and biology. In particular, using mixed solvents, it is possible to continuously change the macroscopic properties of the reaction media. In order to overcome the limitations of the continuum description several approaches have been used. Molecular descriptions of the solvent are, in principle, capable of overcoming some of the differences associated with a continuum treatment of the solvent (Shorter, 1982). A modern approach has been developed, which is based on the use of the non-local electrostatic theory of solute-solvent interactions. This is a convenient frame for incorporating both short-range solvent structure and long-range inter ionic interactions in the appropriate kinetic and equilibrium quantities (Amis and Hinton, 1973). In general, all these parameters constitute more comprehensive measures of solvent polarity than the relative permittivity or any other single physical characteristic, since they reflect more reliably and the complete picture of all intermolecular forces acting between solute and solvent molecules (Atkins, 1988). The solvent-dependent processes used to define solvent polarity parameters may be regarded as probes, which permit a purely empirical investigation of solvent effects. In the comparison of various empirical solvent scales, one finds surprisingly, that most of the existing empirical solvent scales agree with each other very well qualitatively and also quantitatively. We are interested to use simple

and multiple linear relationships in order to separate, quantify and rationalize various non-specific and specific solute-solvent-solvent interactions and structural effects on reactivities. Much information about reactivity could thereby be summarized in terms of a very simple mathematical equation that has dominated the development of the correlation analysis in chemistry. The application of the techniques of correlation analysis has proved strikingly successful and has greatly increased our understanding of the role of the solvent structure on reactivity (Anbalagan and Rajendran, 2006).

Medium controlled photosubstitution reactions of transition complexes are attractive and subsets of research for the following reasons solvent dependent photoreaction constitutes a potentially rich yet little explored field; a fair correlation between photoaquation yield and solvent empirical parameters could reveal important information regarding the complexity of solvation properties; photo induced substitutions are strongly linked with various energy dissipation process and hence catalyst reactions(Kosewer,1968). We have been particularly interested in the solvation dynamics on the photolabilisation of a series of $[Cr L_m Cl_n]^{(3-n)+}$ (L= en, tn, tetren, pn, trien and dien) in binary solvent mixtures (water-methanol/ 1,4-dioxane; compositions 0, 5, 10, 15, 20, 25, and 30 % (v/v) organic co solvent). Theoretical and solvent effect studies revealed that solvent medium interact with reactants/excited states via non specific and specific influences meanwhile, LF photolysis of chromium (III) complexes in solution causes ligand replacement via associative mechanism. Since, the formation and stability of excited state/intermediate determines the course of the reaction. Solvation effect is one of the key methods to elucidate the dynamics of the excited state species (Anbalagan and Rajendran, 2006).

The excited state reactivity of metal complexes is strongly affected by the nature of the solvent in binary solvent medium (Amis and Hinton, 1973). However little information is available on the relationship between the excited state and the solvation influence in terms of quantitative approach. In particular, it is possible by using mixed solvents to continuously change the macroscopic properties of reaction media. They have, therefore become a subject of both experimental and theoretical interest (Anbalagan and Rajendran, 2006). This kind of study has been chosen as probe reaction to study the influence of solvent mixtures on reactivity due to the existence of regression analysis using solvent empirical parameters. Transition metals and their related complexes serve many functions as catalysts, photo sensitizers and in biological systems (Rajendran, 2010). A number of striking observations during the past few years have resulted in speculation that ground and excited state reactions of metal complexes might be dramatically altered by solvent medium. A factor of great potential importance in modifying reactivities may be single or binary solvent medium. Their roles are very important in various biological systems such as electron transfer catalysts of heme-containing enzymes, active sites in heme proteins, which reversibly bind dioxygen and carbon monoxide and light harvesting systems in photosynthetic process (Wolfsburg, 2002). Among the transition metals, chromium has been observed to have a strong tendency to accumulate in the nuclear fraction of tissues. This important observation implies that chromium may play a role in the preservation of the structure of some nuclear substances, particularly RNA. Further, chromium was found to initiate enzyme activity (Rajendran, 2010).The toxicity of chromium to living organisms is well established and considerable interest exists for the determination and removal of this metal in environmental samples at trace levels. The use of Schiff base chromium (III) complexes as catalysts has been taken a step further in the design and synthesis of a novel supramolecular allosteric catalyst system (Rajendran, 2010).

The field of supramolecular photochemistry includes another important research line. The supramolecular photochemistry of transition metal complexes finds brilliant applications especially in the manufacture of photonic molecular devices (PMD) i.e., assemblies of molecular components capable of performing valuable light-induced functions such as charge separation, energy migration, and conformational changes (Balzani,1987). The applications of PMD span from solar energy conversion to signal processing, from spectral sensitization to photo controlled membrane permeability. Several attempts have been made to apply photo catalysis information regarding, solar-energy conversion, environmental decontamination and protection and synthesis of high-price organic compounds (Poonkodi and Anbalagan, 2001). Photon energy produced by photo catalysis is one of the most interesting energy sources of the future and will surely be used on a large scale in the chemical industry. The conversion of solar-energy into electricity has been a very active research field. Historically, chemically based systems such as photo galvanic and photo electrochemical cells comprising transition metals have been developed as an alternative for the solid-state silicon based cells. Spectral sensitization of nanocrystalline films of wide band-gap semiconductors by attached dyes of transition metal complexes has provided a successful solution to extending the range of activity of the cells to low-energy with effective results.

Some traditional topics of inorganic photochemistry, such as the ligand substitution reactions of Cr (III) complexes have continued to attract the attention of several research groups because investigations on suitable designed complexes have always revealed new interesting facets. The most noticeable trend in current years is a progressive displacement of interest from intra-and inter-molecular photochemical processes towards processes occurring in supramolecular systems (i.e., assemblies of two or more molecular components). This has been made possible by the extra ordinary progress of chemical synthesis and the extensive knowledge reached in the field of molecular photochemistry. A prominent research line in the field of supramolecular photochemistry is that concerning luminescent and / or redox active poly metallic complexes, where the various molecular components are assembled to obtain vectorial electron or energy migration. The most common "building blocks" to design such polynuclear systems are polypyridine complexes of Ru^{2+} , Os^{2+} , and Cr^{3+} , while the bridging ligands may range from simple anions like CN^- to multi chelating aromatic-type molecules(Balzani and Carrasitti,1970).

In several problems of practical interest, there is a need to modify the excited state behavior of a molecule. This can be done by perturbing the molecule via appropriate nuclear and / or electronic mechanisms. In most cases, such a perturbation can be performed by assembling the molecule with a perturber in appropriate supramolecular structures via ion-pairing second-sphere coordination and host-guest interaction Several other branches of inorganic photochemistry and photo physics continue to attract increasing interest (Balzani,1987). These include photochemistry of clusters, photochemistry on semiconductors, detailed luminescence problem photochemistry in liquid xenon pressure effects on photochemical reactions photochemistry in liquid membranes, Pico second time resolution, and application of enzymes in artificial photosynthetic systems. Particularly worth mentioning are the targeting and the selective photo cleavage of DNA by intercalation of luminescent and / or photo reactive complexes. Investigations on the excited state properties of simple coordination compounds will certainly continue to arrive at a better understanding of the factors that control the photochemical behavior. It is believed that most of the activity in the next few years will be concentrated on supramolecular species with the dual aim of making progress towards the elucidation of photo biological processes and the construction of artificial photochemical system capable of performing useful functions. Along these ways,

it is expected that much effort will be concentrated on the design, synthesis, and characterization of photonic molecular devices (PMDs), i.e. assemblies of molecular components capable of performing valuable light-induced functions such as charge separation, energy migration, and conformational changes. Some examples of PMDs have already begun to appear. Ranges of possible applications span from solar energy conversion to signal processing, from spectral sensitization to photo controlled membrane permeability, etc., The main objective of this work is to study the aquation reactions of a series of Cr (III) complexes in other mixed solvent media, which will definitely make a significant breakthrough in the field of complexes with special reference to substitution reactions of coordination complexes. This will help researchers to pursue novel *in vivo* and *in vitro* studies. From the extensive literature survey carried out, it is revealed that not much work has been done in this area especially using statistical and multiple regression models to interpret the mechanism of aquation reactions of Cr(III) complexes (in the excited state) in mixed solvent media.

2. EXPERIMENTAL DETAILS

2.1 Materials

[Cr(en)₂Cl₂]Cl, [Cr(tn)₂Cl₂]Cl, [Cr(tetren)Cl]Cl₂, [Cr(pn)₂Cl₂]Cl, [Cr(trine)Cl₂]Cl and [Cr(dien)Cl₃] were prepared by standard methods (Balzani and Carrasitti,1970). Analar grade methanol,1,4-dioxane and HClO₄ were used as received. Triply distilled water was used for the preparation of solutions.

2.2 Apparatus

All photoreactions were carried out in water (MeOH(Diox) (20/0,19/1,18/2,17/3,16/4,15/5,14/6,v/v) mixed solvent. The reaction mixture was air-saturated, prepared instantaneously and transferred into a cylindrical cell of path length 3 cm, inner dia 2.5 cm and volume 15.5 ml made up of corning glass.^{2,3} Photo irradiation was carried out with ELH lamp, 120V, 300W, Kondo –Japan with a three compartment filter for 436 nm light source. The lamp intensity was in the range of 1.3731×10^{-8} – 5.6319×10^{-8} Einsteins⁻¹ as measured by ferrioxalate actinometry (Balzani and Carrasitti,1970). Efficiently stirred solutions of [Cr L_m L_n]⁽³⁻ⁿ⁾⁺, 1×10^{-2} M in 0.1M HClO₄ concentration of metal complex at pH 1.2 were irradiated in the cylindrical cell at 303K and the pH was monitored by systronics digital pH meter-335. To avoid problems with secondary photolysis, the solutions were photolysed to less than 5% conversion. The product was analyzed by estimating chloride, ammonia and absorption peaks detected UV-VIS absorption spectra using Shimadzu-240 uv-vis double beam spectrophotometer. Absorption at a wavelength of 529.5nm, (526.5, 488,544,557 and 482 nm) for en (tn, tetren, pn, trine and dien) complex was monitored for quantum yield measurement. The quantum yield values were averaged and recorded for further studies (Spectral data).

2.3 Regression Analysis

Linear solvation energy relationships (LSER) are useful in diagnosis of reaction mechanism. The influence of solvent effects on a single solute/excited state obeys the relationship:

$$Y_S = Y_o + \sum_{i=1}^n a_i x_i$$

Where Y_s represents the property to be correlated, Y_o is a property relating to a standard process.

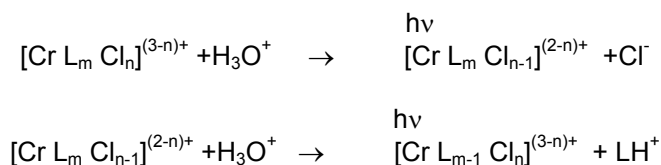
This LSER is suitable for experimental elucidation of manifold solvent effects because it simply allows the separation of solvent-solvent-solute interactions such as hydrogen bonding by a multiple correlation analysis. However, the parameters used feature different blends of fundamental intramolecular force (Reachardt, 1988). This makes the interpretation of individual parameters resulting to non-specific or specific interaction mechanism. Quantitative prediction of solvation effect is possible using LSER, the general form of the relationship is

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

The magnitude and sign of the coefficients (a_i) of the LSER provide insight into the important factors governing the modeled solvation influenced property.

3. RESULTS AND DISCUSSION

One of the most outstanding characteristics of the photochemistry of chromium (III) complexes is the efficiency of the photo substitution (Scheme 1). The reactive excited states are expected to be low-lying doublet 2E_g and quartet $^4A_{2g}$ states. Irradiation of the LF bands of $[\text{Cr L}_m \text{Cl}_n]^{(3-n)+}$ in binary mixed solvents (water-methanol/1,4-dioxane) brings about red shift of the vis spectral maxima. Product Analyses for Chloride and ammonia were done by gravimetric and colorimetric methods respectively. Analysis of free ligands reveals that ammonia aquation is predominant than that of chloride.



Scheme 1. Photoaquation of Cr (III) complex

The quantum yields for photoaquation in Water-MeOH and Water-1,4-Dioxane at 303K and pH 1.2 (HClO_4) upon LF excitation are collected in Table 1 and 2, respectively. It is observed that there is a regular gradation in Φ value with respect to the mole fraction of organic co solvent present in the binary mixture. Evidently, the quantum yield is solvent dependent, which is unusual in a complex of this type in the chosen medium. The solvent dependence of quantum yield is statistically significant; however, systematic errors could also be important (Karthikeyan et al., 2000).

The change in Φ , which is due to solute-solvent interaction, was expected to involve non-specific and specific solvation effect. Figure 1 is a typical plot of $\log \Phi$ against x_2 ($x_{\text{MeOH}}/x_{\text{Diox}}$) of mixed solvents, which correspond to the effect of change in mole fraction of organic co solvent in the binary mixtures.

Table 1. Variation of Quantum yields with respect to mole fraction of MeOH for the photo aquation of chromium (III) complexes in air-equilibrated water-methanol mixtures at 303 K

Complex	$\Phi_{\text{Cr(III)}} \times 10^{-2}$						
	X_{MeOH}						
	0	0.0229	0.0471	0.0728	0.1001	0.1292	0.1602
[Cr(en) ₂ Cl ₂]Cl	7.29	38.39	30.39	23.10	17.11	16.72	14.59
[Cr(pn) ₂ Cl ₂]Cl	36.39	30.74	26.98	24.15	20.08	18.19	14.74
[Cr(tn) ₂ Cl ₂]Cl	17.61	34.75	40.77	45.40	50.04	63.94	88.04
[Cr(dien)Cl ₃]	52.06	51.12	44.49	37.87	31.71	28.87	17.99
[Cr(trien)Cl ₂]Cl	16.15	46.84	43.17	36.74	33.98	30.34	27.56
[Cr(tetren)Cl]Cl	71.63	52.42	54.98	56.26	60.09	81.83	84.38

Table 2. Variation of Quantum yields with respect to mole fraction of MeOH for the photo aquation of chromium (III) complexes in air-equilibrated water-1,4-Dioxan mixtures at 303 K

Complex	$\Phi_{\text{Cr(III)}} \times 10^{-2}$						
	X_{MeOH}						
	0	0.0229	0.0471	0.0728	0.1001	0.1292	0.1602
[Cr(en) ₂ Cl ₂]Cl	7.29	5.17	4.23	3.38	3.33	3.04	3.03
[Cr(pn) ₂ Cl ₂]Cl	36.39	42.03	47.67	50.81	55.22	58.97	63.41
[Cr(tn) ₂ Cl ₂]Cl	17.61	14.36	13.22	12.97	11.11	7.41	5.56
[Cr(dien)Cl ₃]	52.06	57.28	61.53	67.21	76.21	83.78	90.86
[Cr(trien)Cl ₂]Cl	16.15	62.44	65.95	67.43	69.72	72.69	75.39
[Cr(tetren)Cl]Cl ₂	71.63	65.21	60.61	52.19	46.84	45.26	41.33

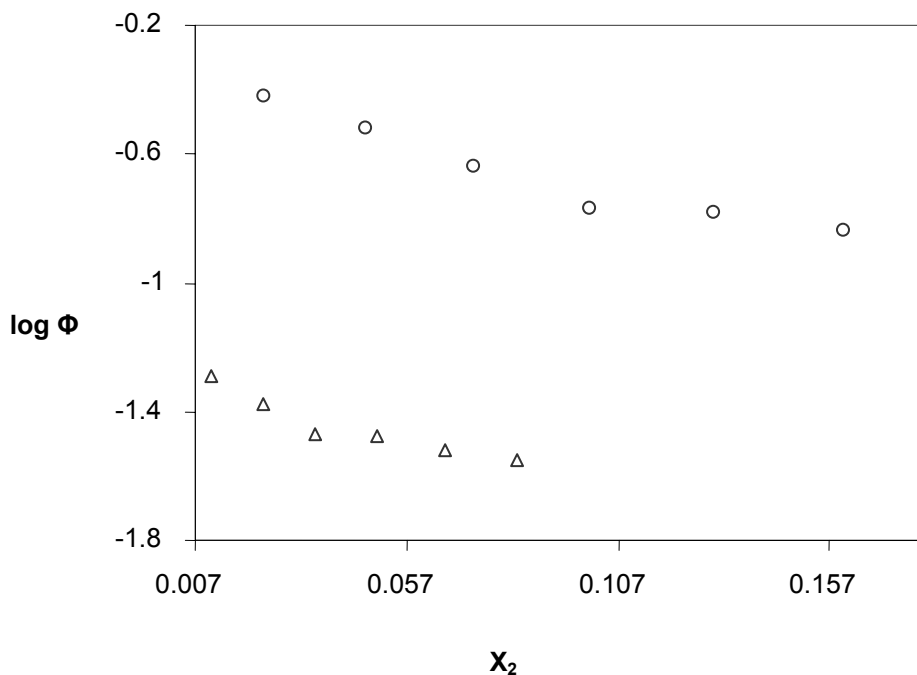


Fig. 1. Plot of $\log \Phi$ versus mole fraction of co solvent, x_2 , for the aquation of $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ at 303 K in water - methanol (o) and water-1,4-dioxane (Δ) mixtures

That is, the Φ values decrease for en, tn and tetren complexes, but increase for pn, trien and dien complexes, consistent with the linear relationship with x_2 of the medium. The relationship leads to the following eqs (1) and (2) for a typical complex $[\text{Cr}(\text{pn})_2\text{Cl}_2]\text{Cl}$

$$\log \Phi = -0.199 - 0.435x_2 \quad (1)$$

($r = 0.997$, $sd = 0.01$, $\Psi = 0.06$, $n = 6$, Temp = 303K; water-methanol)

$$\log \Phi = 0.159 + 0.411 x_2 \quad (2)$$

($r = 0.986$, $sd = 0.012$, $\Psi = 0.13$, $n = 6$, Temp = 303K; water-1,4-dioxane)

Similarly, photo reduction of Cr(VI) was found to be strongly dependent on the nature of alcohol present in the medium in an alcohol structure dependent study. 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 co solvent shows a maximum at the mole fraction of $x_2 = 0.1602$ in water-methanol and 0.081 in water-1, 4-dioxane. Other studies have established that when an organic co solvent is added to pure water, the structure of the latter is destroyed. Progressively, but the structure breaking must go through a maximum structure formation at first. The organic component of cosolvent packs the space including maximum structure formation within the structured water. Therefore, changes in solvent structure influenced substitution and are probably reproducible for the linearity.

It is observed that the quantum yield decreases in the case of en, pn, dien, and trien complexes as the concentration of methanol increases while an opposite trend is observed in the case of tn and tetren complexes. But in water - 1,4 - dioxane mixture, the quantum yield of photoaquation of en, pn, and tetren decreases as the concentration of 1,4 - dioxane increases while Φ of tn, dien and trien shows an opposite trend. This is a clear indication of participation of solvent in the photoaquation of chromium(III) - alkyl amine complexes.

3.1 Continuum Approach

There is a consistency in comparing different solvation models for solvent dependent Φ data. Solvation was modeled by a dielectric medium in ground /excited states of the complexes; $[\text{Cr L}_m \text{Cl}_n]^{(3-n)+} / ^*[\text{Cr L}_m \text{Cl}_n]^{(3-n)+}$. Figure 2 illustrates a clear correlation of $\log \Phi$ with $1/\epsilon_r$ of media. This is accordance with dielectric continuum model of reaction rate assuming the reacting species as charges (Anbalagan and Rajendran, 2006). The linearity in $\log \Phi$ value with $1/\epsilon_r$ reflects the effect of solvent structure on the solvation of excited state of the complexes. Therefore, $\log \Phi$ is correlated in the following manner for $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ as in eqs (3) and (4).

$$\log \Phi = 0.011 - 0.005 (1/\epsilon_r) \quad (3)$$

(Water-methanol, $r = 0.957$, $\text{sd} = 0.053$, $\Psi = 0.16$, $n = 6$, $\text{Temp.} = 303\text{K}$)

$$\log \Phi = 0.008 - 0.016 (1/\epsilon_r) \quad (4)$$

(Water-1, 4-dioxane, $r = 0.929$, $\text{sd} = 0.040$, $\Psi = 0.29$, $n = 6$, $\text{Temp.} = 303\text{K}$)

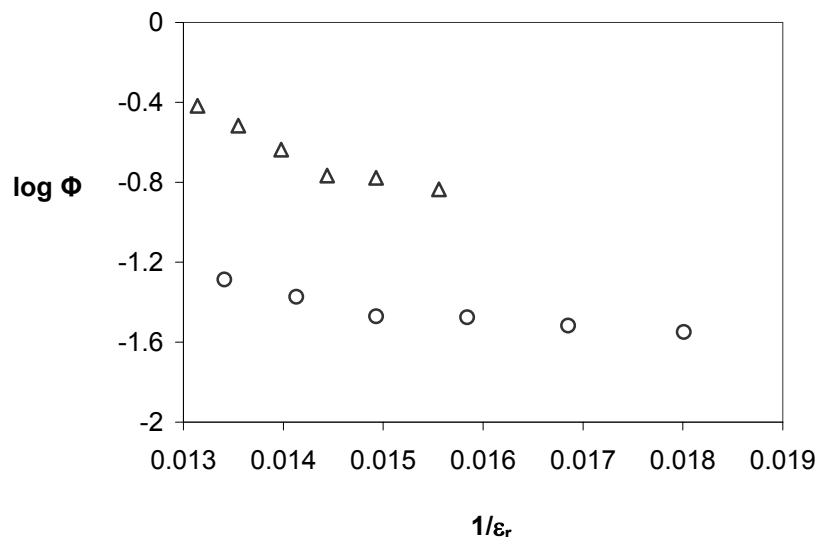


Fig. 2. Plot of $\log \Phi$ versus $1/\epsilon_r$ for the photoaquation of $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ at 303 K in water- methanol (o) and water-dioxane (Δ) mixtures

Similarly, all other systems are in good correlation with reciprocal of relative permittivity of the medium (water-methanol: $r = 0.998$, $\text{sd} = 0.008$, $\Psi = 0.05$, $n = 6$, $\text{Temp.} = 303\text{K}$; water-

1,4-dioxane: $r = 0.983$, $sd = 0.013$, $\Psi = 0.14$, $n = 6$, Temp. = 303K). It is presumed that there should be some influence in addition to electrostatic contribution by non electrostatic component. Therefore, the Φ data is subjected to further analysis. Modified Grunwald-Winstien Equation of the form, $\log k = \log k_0 + mY$ has been successfully applied to several substitution and electron transfer reactions. In this analysis k and k_0 are replaced with Φ and Φ^0 which are solvent dependent and solvent specific variables. Fig 3 represents a linear relation between $\log \Phi$ and the solvent ionizing parameter Y .

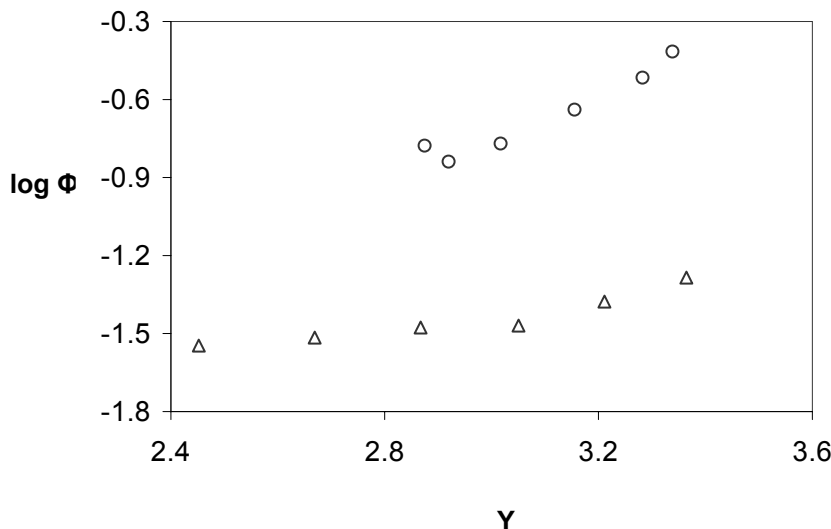


Fig. 3. Plot of $\log \Phi$ versus Grunwald - Winstein, Y for the photoaquation of $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ at 303 K in water- methanol (o) and Water - dioxane (Δ) mixtures

The slope m is the sensitivity towards changes in Y , a scale of solvent ionizing power based on the specific rates of solvolysis of 1-adamantyl chloride. Analysis of the data using the equation binds to a fair linear correlation with values of -1.724 to 4.356 for m ; and 1.487 to 4.504 for the intercept ($r = 0.994$, $\Psi = 0.06$ to 0.28 and $sd = 0.005$ to 0.055 for en , tn , tetren , pn , trien and dien complexes).

3.2 Supra Molecular Approach

In this approach, the solvent effects are modeled due to strong hydrogen bonding structure in the ligand phase. Indications of such a microstructure come from both neutron diffraction studies and molecular dynamics studies. Kaizaki et al. (1990) have successfully made a fair correlation between Guttmann's acceptor number of Cr (III) complexes in solvent - dependent deuteron nuclear magnetic resonance study.

Krygowski and Fawcett proposed two important solvent scales that can affect the reactivity of a solute. The interaction parallels the Lewis acidity and Lewis basicity character of solvents symbolized by E_T and DN respectively. In terms of these dual independent but complementary vectors, the linear free - energy relationship can be represented as per the equation $Q = Q_0 + \alpha E_T N + \beta D_N N$; where $E_T N$ is Reinhardt's solvatochromic parameter which provides an excellent and very sensitive characterization of the micro polarity of the

solvation shell on the molecular microscopic level of the solvents, whereas DN^N is the donor number (or donicity) proposed by Guttmann which is an empirical semi quantitative measure of the nucleophilic properties of the electron pair donor (EPD) solvent, Q_0 is the value of the solvent-dependent physicochemical property of the solute under investigation in the gas phase (or in an inert solvent) and α and β are the regression coefficients describing the relative sensitivity of the solute property Q to the Lewis acidic and Lewis basic solvent properties, respectively. For use in multiparameter correlation equations, the dimensionless normalized E_T^N and DN^N values seem to be more suitable and these values for the present study were calculated using regression analysis for $[Cr(en)_2Cl_2]Cl$ and are presented in eqs 5 and 6.

$$\log \Phi = 40.178 + 14.48 E_T^N - 64.59 DN^N \quad (5)$$

($R^2 = 0.984$, $sd = 0.027$, $\Psi = 0.14$, $n = 6$, Temp. = 303 K water-methanol)

$$\log \Phi = 9.610 + 6.21 E_T^N - 19.98 DN^N \quad (6)$$

$R^2 = 0.971$, $sd = 0.021$, $\Psi = 0.03$, $n = 6$, Temp. = 303 K water-1, 4-dioxane

The coefficients are converted into weighted contributions, $P(x_i)$ and are presented in Tables 3 and 4. A perusal of data shows that the percentage contribution values of Lewis basicity term $P(DN^N) \approx 83\%$ (52 - 92) is dominant over Lewis acidity $P(E_T^N) \approx 17\%$ (8 - 46) in methanolic solutions. Obviously the less polar transition state is stabilized at higher concentrations of organic co solvents which results in change in quantum yield values. Likewise, $p(DN^N) \approx 66\%$ contribution (34 - 85) is dominant over $p(E_T^N) \approx 34\%$ (15 - 66) in water - 1,4 - dioxane solutions.

This means that the solvation on the second coordination sphere plays an important role in elevating the quantum yield. In another attempt the quantum yield data were subjected to biparametric equation consisting of two solvent scales such as, E_T^N and β . A modified LFER eq of the form, $Q = Q_0 + \alpha E_T^N + \beta DN^N$ was applied to understand the solvational contributions on the photoaquation of $[Cr(N)_xCl_y]^{(3-y)+}$ ions. The model expressions for $[Cr(en)_2Cl_2]^+$ are shown in eqs. 7 and 8.

$$\log \Phi = -16.569 + 14.3 E_T^N + 11.4 \beta \quad (7)$$

$R^2 = 0.984$, $sd = 0.014$, $\Psi = 0.14$, $n = 6$, Temp. = 303 K water-methanol

$$\log \Phi = -15.659 + 5.99 E_T^N + 47.22 \beta \quad (8)$$

$R^2 = 0.971$, $sd = 0.022$, $\Psi = 0.18$, $n = 6$, Temp. = 303 K water - 1,4 -dioxane

Tables 5 and 6 show the physical effects of the solvent composition due to solvating ability $P(\beta) \approx 60\%$ (24 - 90) on excited state is more dominant than Lewis acidity $P(E_T^N) \approx 40\%$ (10 - 76). A similar trend is observed in 1,4-dioxane mixture also. $P(\beta) \approx 88\%$ (59 - 96) and $P(E_T^N) \approx 12\%$ (4 - 41). The results obtained show that organic co solvent contents of the irradiated solution bring about an evidence of change of quantum yield due to effective solvation.

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

Complex	Statistical parameter							
	R ²	Sd	Ψ	α	β	P(E _T ^N)	P(D _N ^N)	Intercept
[Cr(en) ₂ Cl ₂]Cl	0.984	0.027	0.14	14.48	-64.59	18	82	40.178
[Cr(pn) ₂ Cl ₂]Cl	0.904	0.396	0.34	110.9	-932.3	11	89	681.46
[Cr(tn) ₂ Cl ₂]Cl	0.988	0.020	0.11	8.59	-96.1	8	92	72.62
[Cr(dien)Cl ₃]	0.971	0.035	0.17	-8.85	101	8	92	-77.56
[Cr(trien)Cl ₂]Cl	0.993	0.009	0.09	2.57	3.04	48	52	52.16
[Cr(tetren)Cl]Cl ₂	0.917	0.340	0.32	6.86	-69.8	9	91	-5.42

R² – Coefficient of multiple determination; sd – standard deviation; Ψ- Exner's statistical parameter; α and β – coefficients of ETN and DNN in equation 7; P(ETN) and P(DNN) – weighted percentage contributions

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

Complex	Statistical parameter							
	R ²	Sd	Ψ	α	β	P(E _T ^N)	P(D _N ^N)	Intercept
[Cr(en) ₂ Cl ₂]Cl	0.971	0.021	0.03	6.21	-19.98	24	76	9.61
[Cr(pn) ₂ Cl ₂]Cl	0.995	0.006	0.08	-1.97	3.58	35	65	-1.50
[Cr(tn) ₂ Cl ₂]Cl	0.938	0.027	0.27	-4.48	25.77	15	85	-17.50
[Cr(dien)Cl ₃]	0.995	0.007	0.08	-0.80	-2.61	23	77	2.74
[Cr(trien)Cl ₂]Cl	0.986	0.006	0.12	-0.74	0.38	66	34	0.17
[Cr(tetren)Cl]Cl ₂	0.983	0.013	0.14	2.07	-3.07	40	60	0.43

R² – Coefficient of multiple determination; sd – standard deviation; Ψ- Exner's statistical parameter; α and β – coefficients of ETN and DNN in equation 7; P(ETN) and P(DNN) – weighted percentage contributions

Considering the correlation between Lewis acidity and Lewis basicity with quantum yield data, the influence of specific solvation effect 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. Hence, the photoaquation quantum yield values were also fitted to another expression, namely a solvatochromic comparison method developed by Kamlet and Taft to quantify and rationalize multiple interacting solvent effects on reactivity.

The quantum yield data were subjected to correlation analysis with the solvatochromic parameters α , β and π^* in the form of the linear solvation energy relationship (LSER) as per the eq.

$$\log k = A_0 + s \pi^* + a \alpha + b \beta.$$

In all the cases of $[\text{Cr}(\text{N})_x(\text{Cl})_y]^{(3-y)+}$ ion the photoaquation quantum yields show an excellent correlation in which the specific solvation effects (Tables 7 and 8) play major role. The relationships for $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ are shown in eqs 9 and 10.

$$\log \Phi = 39.774 + 14.5 \pi^* - 63 \alpha + 0.8 \beta \quad (9)$$

$$R^2 = 0.984, \text{sd} = 0.016, \Psi = 0.14, n = 6, \text{Temp.} = 303 \text{ K water-methanol}$$

$$\log \Phi = -198.955 + 24.5 \pi^* + 10.5 \alpha + 564 \beta \quad (10)$$

$$R^2 = 0.991, \text{sd} = 0.015, \Psi = 0.10, n = 6, \text{Temp.} = 303 \text{ K, water - 1,4 -Dioxane}$$

Majority of the total number of values are in general agreement with higher participation influence of solvational components than general medium effect, namely specific effect is $P(\alpha) \approx 49\%$ (1 - 80), $P(\beta) \approx 27\%$ (1 - 59) while non - specific effect is able to account only for minor role $P(\pi^*) \approx 23\%$ (1 - 41) in water-methanol mixture. A similar argument is valid for all the complexes in water - 1, 4 - dioxane also. $P(\alpha) \approx 16\%$ (14 - 19), $P(\beta) \approx 81\%$ (68 - 84) and $P(\pi^*) \approx 4\%$ (1 - 13).

The quantum yield of aquation reaction at 303 K increases from 17.61×10^{-2} at $x_2 = 0$ to 88.04×10^{-2} at $x_2 = 0.1602$ in methanolic solution for tn and increases from 71.63×10^{-2} at $x_2 = 0$ to 84.38×10^{-2} at $x_2 = 0.1602$ in methanolic solution for tetren complex. This enhancement of quantum yield may be interpreted in terms of solvent cage or atmosphere effect in mixed solvents; such ion atmosphere effect is currently discussed as a suitable model for solvation effect. The proposed models and dielectric continuum models are recently discussed in charge transfer transition in methylene bridged metallocene salt and deuterium NMR studies on bimolecular electron transfer in ruthenium amine complexes (Karthikeyan et al., 2000). The quantum yield of Cr(III) complexes significantly changes with respect to inverse relative permittivity, this suggests the solvent polarity can be used to provide a reasonable explanation of the behavior of chromium(III) - alkyl amine complexes in water - methanol / 1,4 - dioxane mixtures.

Table 5. Statistical results, the coefficients and weighted contributions of solvent parameters in the photoaquation reaction of Cr(III) complexes in water – methanol mixtures at 303 K

Complex	Statistical parameter							
	R ²	Sd	Ψ	α	β	P(E _T ^N)	P(β)	Intercept
[Cr(en) ₂ Cl ₂]Cl	0.984	0.014	0.14	14.3	11.4	56	44	-16.57
[Cr(pn) ₂ Cl ₂]Cl	0.995	0.011	0.08	-0.71	-6.11	10	90	1.34
[Cr(tn) ₂ Cl ₂]Cl	0.986	0.022	0.13	8.07	16.8	32	68	-11.54
[Cr(dien)Cl ₃]	0.968	0.037	0.20	-8.11	-17.4	32	68	10.97
[Cr(trien)Cl ₂]Cl	0.993	0.009	0.09	2.42	-0.74	76	24	-9.50
[Cr(tetren) Cl] Cl ₂	0.921	0.033	0.31	6.92	12.7	35	65	-2.6

R² – Coefficient of multiple determination; sd – standard deviation; Ψ- Exner's statistical parameter; α and β – coefficients of ETN and DNN in equation 7; P(ETN) and P(DNN) – weighted percentage contributions

Table 6. Statistical results, the coefficients and weighted contributions of solvent parameters in the photoaquation reaction of Cr(III) complexes in water – 1,4-Dioxane mixtures at 303 K

Complex	Statistical parameter							
	R ²	Sd	Ψ	α	β	P(E _T ^N)	P(β)	Intercept
[Cr(en) ₂ Cl ₂]Cl	0.971	0.022	0.18	5.99	47.22	11	89	-15.66
[Cr(pn) ₂ Cl ₂]Cl	0.995	0.006	0.08	-1.90	-8.15	19	81	2.94
[Cr(tn) ₂ Cl ₂]Cl	0.985	0.026	0.13	-8.59	-124	6	94	30.01
[Cr(dien)Cl ₃]	0.996	0.007	0.07	-0.85	6.02	12	88	-0.528
[Cr(trien)Cl ₂]Cl	0.994	0.005	0.08	-0.20	5.1	4	96	-0.95
[Cr(tetren) Cl] Cl ₂	0.983	0.013	0.14	2.06	7.56	21	79	-3.54

R² – Coefficient of multiple determination; sd – standard deviation; Ψ- Exner's statistical parameter; α and β – coefficients of ETN and DNN in equation 7; P (ETN) and P(DNN) – weighted percentage contributions

Table 7. 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

Complex	R ²	sd	Ψ	S	a	B	P(π*)	P(α)	P(β)	Intercept
[Cr(en) ₂ Cl ₂]Cl	0.984	0.016	0.14	14.5	-63	0.08	19	80	1	39.77
[Cr(pn) ₂ Cl ₂]Cl	0.997	0.010	0.06	96.4	-85.4	55.6	41	26	23	-15.68
[Cr(tn) ₂ Cl ₂]Cl	0.999	0.007	0.03	8	497	277.4	1	64	35	-631.87
[Cr(dien)Cl ₃]	0.994	0.019	0.08	312	681	-30.8	30	66	4	462.23
[Cr(trien)Cl ₂]Cl	0.993	0.011	0.09	9.84	104.8	64.2	5	58	37	-145.24
[Cr(tetren)Cl]Cl ₂	0.988	0.016	0.012	465	-11.9	514.4	40	1	59	-585.31

R² – correlation coefficient of multiple regression; sd – standard deviation; Ψ- Exner's statistical parameter; s, a and b – coefficients of equation 10; P(π), P(α) and P(β) – weighted percentage contributions*

Table 8. 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

Complex	R ²	sd	Ψ	s	a	b	P(π*)	P(α)	P(β)	Intercept
[Cr(en) ₂ Cl ₂]Cl	0.991	0.015	0.10	-240	105	564	3	15	82	-199
[Cr(pn) ₂ Cl ₂]Cl	0.998	0.004	0.04	9.98	-14	-49.6	13	19	68	14.57
[Cr(tn) ₂ Cl ₂]Cl	0.988	0.028	0.12	24.8	-176	-1050	2	14	84	367.6
[Cr(dien)Cl ₃]	0.995	0.009	0.98	-1.39	-23	-129	1	15	84	50.45
[Cr(trien)Cl ₂]Cl	0.994	0.006	0.07	0.338	-7.5	-38.4	1	16	83	15.14
[Cr(tetren)Cl]Cl ₂	0.985	0.015	0.13	-2.4	51.8	298	1	15	84	-112

R² – correlation coefficient of multiple regression; sd – standard deviation; Ψ- Exner's statistical parameter; s, a and b – coefficients of equation 10 ; P(π), P(α) and P(β) – weighted percentage contributions*

From the extensive study made it shows that the solvation contributions of complexes as a function of weight percentage values. The general observation is that $[P(\alpha) + P(\beta)] > P\pi^*$. It is expected that the solvent mixtures are good hydrogen bond acceptor / donor. The lower value of $P(\pi^*)$ indicates that the immediate solute ; $[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+} / *[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+}$ environment influence substantially than that of long - range interactions outside of the first solvation sphere. Several plausible explanations of this behavior are either the solvatochromic probe which may be influenced by the solvent shells beyond the first solvation sphere, or a solvent reorganization occurs to allow more solvent molecules to interact with; $[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+} / *[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+}$ species. This promises the concept of well-caged complex ions of both reactant / excited states. Kamlet-Taft's solvatochromic parameters establish specific and non - specific solvent contribution in the formation and stabilization.

Chromium (III) complexes show two component photochemistry with prompt and slow components. That is, photochemistry of Cr(III) complexes in general occur from quartet and doublet states(Anbalagan and Rajendra,2006). There are two basic assumptions: (i) prompt ISC and prompt reaction of the excited quartet states are unimportant reaction and (ii) reaction occurs via relaxed quartet state. Two types of reaction mechanisms are considered possible in this photoaquation as shown in Scheme 2; the photoexcited $*[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+}$ solvated to form solvent caged $*[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+}$ followed by excited state relaxation to $*[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+}$ (Q_1) quartet and $*[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+}$ (D_1) doublet states. The fast and slow components of photoaquation originate from quartet and doublet states respectively. The preferential solvation stabilizes either $*\text{Cr}^{\text{III}}(Q_1)$ or $*\text{Cr}^{\text{III}}(D_1)$ or both under visible irradiation ($\lambda = 436 \text{ nm}$) in the binary mixed solvent media. If the photoaquation takes place through the fast component $*\text{Cr}^{\text{III}}(Q_1)$, which is in higher concentration, the Φ values linearly increase with an increase in x_2 of the medium. However, the concentration of $*\text{Cr}^{\text{III}}(D_1)$ is reasonably considered to be lower than that of quartet states. On the other hand if the photoaquation originates from $*\text{Cr}^{\text{III}}(D_1)$ state, which is presumed to be accumulated in higher concentration than that of $*\text{Cr}^{\text{III}}(Q_1)$, the Φ values diminishes in value when x_2 increases in the medium. This suggests that either $*\text{Cr}^{\text{III}}(Q_1)$ or $*\text{Cr}^{\text{III}}(D_1)$ is reasonably stabilized by the solvent environment due to macroscopic solvent-solute interactions and microscopic effective solvation thorough Lewis acid-base interactions. That is $P(DN^N) > P(E_T^N)$ in water- methanol (Dioxane) solutions. The model equations 11 and 12 for quantum efficiency from quartet (Φ_{Q_1}) and (Φ_{D_1}) are:

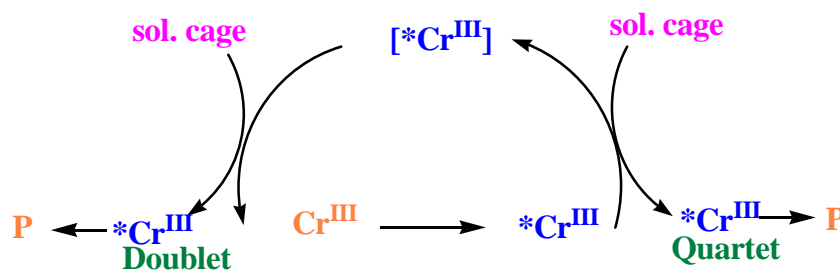
$$\Phi_{Q_1} = \eta_Q + \eta_{\text{ISC}} \eta_{\text{BISC}} \eta_Q / (1 - \eta_{\text{ISC}} \eta_{\text{BISC}}) \quad (11)$$

$$\Phi_{D_1} = \eta_D \eta_Q / (1 - \eta_{\text{ISC}} \eta_{\text{BISC}}) \quad (12)$$

Where η is the efficiency of a process, ISC = Intersystem crossing, BISC = back- ISC, Φ_Q = reaction from quartet excited state and Φ_D = reaction from doublet state.

Therefore, there is a rapid non - radiative decay process influencing the doublet lifetime of chromium (III) complexes in binary solvents. It competes with photo conversion of quartet state, which itself is in competition with intersystem crossing and non- radiative decay. Chromium (III) complexes undergo photo substitution as suggested previously through pentagonal bipyramidal transition state structure. The occurrence of long-lived seven coordinated intermediate is well solvated in the solvent cage both by long range and short range solvent-solvent interactions. Therefore, the regression analysis indicates that some local structure is understood in terms of consecutive solvation shells. As a first

approximation, it seems reasonable to represent a strong specific or hydrogen bond donor / acceptor interactions in binary mixture with the nearest neighbor configuration. The continuum model is realized to understand the long range solvation effects of the medium on $^*[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+}$ / $^*[\text{Cr}(\text{en})_2\text{RCl}]^{2+}$ reflecting in the stabilization of excited state. This is due to strong hydrogen-bond effect and non-electrostatic component, the hydrophobic effect due to -CH₃ group of CH₃OH and C₄H₈O₂ of 1,4 - dioxane leading to stabilization of the excited state species (Anbalagan and Rajendran, 2006).



Scheme 2. Communication between doublet and quartet excited states in solvent cage

There is a good agreement in solvent dependent Φ data with respect to fast (quartet) and slow (doublet) photo conversion paths. Both are in competition with one another and also with intersystem crossing / non-radiative decay. The matter is complexed due to the fact that excited state $^*[\text{Cr}(\text{N})_x\text{Cl}_y]^{(3-y)+}$ / $^*[\text{Cr}(\text{en})_2\text{RCl}]^{2+}$ is well solvent caged and stabilized. One aspect at this stage is that the molecules of solvation sphere rotate during the decay of reacting state so as to enable the formation of seven-coordinated system on return to the ground state. Hence, ligand replacement is either enhanced or inhibited remarkably by the mixed solvent media. In summary, the available model analysis allows a definitive choice of the above two alternative pathways according an increase or decrease in Φ value at higher mole fractions of methanol / dioxane in the medium. This conclusion is more appealing and enables one to gain better insight into the problem.

4. CONCLUSION

- Visible light photolysis was carried out for the $[\text{Cr} \text{I}_m \text{Cl}_n]^{(3-n)+}$ complexes in water containing either methanol (MeOH) or 1,4-dioxane (Diox), x_2 (x_{MeOH} / x_{Diox}) 0, 0.029/0.0109 to 0.1602/0.0831 respectively.
- Photolysis of these complexes in these binary mixtures is good to excellent for few complexes and poor for the remaining cases.
- Solvent assisted photolysis in the binary solvent mixtures produced aquated products.
- In principle, the photoaquation takes place by associative mechanism and quantum yield for this reaction was found to exhibit linear x_2 dependence.
- In summary, the available model analysis allows a definitive choice of the above two alternative pathways according an increase or decrease in ϕ value at higher mole fractions of MeOH/Diox in the medium. This conclusion is more appealing in order to gain more insight into the problem.

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