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Photophysical Behaviour of *p*-Dihydroxy Benzene in Different Solvents, pH and α-Cyclodextrin

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Spectral characteristics of *p*-dihydroxy benzene have been studied in different solvents, pH and α-cyclodextrin. Solvent study shows that the interaction of -OH group with the aromatic ring is less than that of $-NH_2$ group both in the ground and excited states. In absorption, the charge transfer interaction of -OH group in *p*-position is larger. pH studies reveals that *p*-dihydroxy benzene is more acidic than phenol. *p*-Dihydroxy benzene forms a 1:1 inclusion complex with α-cyclodextrin. In α-cyclodextrin medium, absorption spectra of *p*-dihydroxy benzene shows unusual blue shift, whereas in the excited state, the spectral characteristics of *p*-dihydroxy benzene follow the same trend in both aqueous and α-cyclodextrin medium. The inclusion complex of α-cyclodextrin with *p*-dihydroxy benzene is investigated by UV-visible and fluorimetry and scanning electron microscope.

Key Words: *p*-Dihydroxy benzene, Solvent effect, Proton transfer reactions, α-Cyclodextrin.

INTRODUCTION

Solvents play a significant role in chemical and biological processes. Works from a quite early period have witnessed the importance of solvents in chemistry[1]. Solvents have their own intrinsic characteristics due to which they can alter the reaction pathways by changing the energies of the reactants and contributing to the final states of a reaction[2]. This versatility of the solvents has drawn attention of many scientists to study the subject of salvation and salvation dynamics. The process of the rearrangement created charge or dipole is known as salvation dynamics[3]. Ultra short laser pulses have been developed to study the sub-pico second time scale phenomenon of salvation dynamics[4]. The polarity of the solvent is important in controlling the physico-chemical characteristics of process of the molecular level, compartmentalized water in cells, reverse micelles, micro emulsions, liposome's as well as the aqueous environment at the interfaces of normal micelles as known to be physicochemical different from the bulk water with regard to polarity structure[5-8] and pH.

The excited state proton transfer (ESPT) phenomena is well known from the works of Forster[9] and Weller[10]. Molecules like aromatic amines and phenols show

large enhancement in acidity due to migration of charge from electronegative atom center to the ring in the excited state compared to the ground state[11]. As a result, the ionization constant decreases by several units in the electronic excited state (pK_a*) relative to that in the ground state (pK_a). Hence, if the pH of the medium is intermediate between pK_a and pK_a*, the molecule, when excited in its neutral form readily deprotonates to produce the anion in the excited state, from which the stokes-shifted anion emission originates.

Among the known ESPT molecules, naphthols[12,13] stand out due to their extremely fast excited singlet state deprotonation rate. They are commonly called as excited state acids. However, addition of a solvent like methanol affects the proton transfer equilibrium in the excited state. Depending on the solvent composition, emission from both neutral and anion forms is observable. Since naphthols works remarkable in pH as well as a microenvironment, it is worthwhile to investigate some of the substituted phenols in different environments. In this record *p*-dihydroxy benzene was taken up for study. The electron donating resonance effect of *p*-dihydroxy benzene depending on the position of hydroxyl group in the phenol ring affects the proton transfer process. In this paper, we report photo physical behaviour of *p*-dihydroxy benzene in different solvents, pH and α-cyclodextrin medium.

EXPERIMENTAL

p-Dihydroxy benzene was obtained from Fluka Chemicals Ltd., α-cyclodextrin (Aldrich), spectrograde methanol, AR grade sulphuric acid and sodium hydroxide were used as such. Other solvents were further purified by the methods described in literature[14]. Triply distilled water was used for preparing aqueous solutions. A stock solution of *p*-dihydroxy benzene was prepared in methanol. A modified Hammett's acidity scale[15] (H_o) for solutions below pH 2 (using H_2SO_4-H_2O mixture) and Yagil's basicity scale[16] (H_) for solutions above pH 12 (using NaOH-H_2O mixture) were employed.

Absorption spectra were recorded with a Hitachi model U-2001 spectrophotometer while fluorescence measurements were made using a JASCO FP-550 recording spectrofluorimeter. pH values in the range 2-12 were measured by Elico pH meter model LI-10T. Experimental solutions were prepared by adding an aliquot of the stock solution to appropriate H_o/pH/H_ solutions just before taking measurements. The concentration of the resulting solution was above 10^{-5} M. The stock solution was prepared in methanol and the methanol content of the solution was about 2 %.

RESULTS AND DISCUSSION

Effect of solvents: Table-1 depicts the absorption maxima, log ε and fluorescence maxima of *p*-dihydroxy benzene and phenol in the solvents of different polarity and hydrogen bond forming tendency as well as at different proton concentrations. Due to very low solubility of *p*-dihydroxy benzene in cyclohexane, the spectrum

was obtained using 2 % ether solution of cyclohexane. This spectral maximum will be very near to the maximum if obtained in pure cyclohexane as the polarity of ether is very close to cyclohexane[17]. Furthermore, the trend observed in the maxima of the *p*-dihydroxy benzene in cyclohexane are similar to the trend in other solvents. Data in Table-1 clearly indicates that the absorption spectra of these isomers are red shifted in any one of the solvents compared to those of phenol. When compared to diamino benzenes (DAB)[18], blue shifts is observed in *p*-dihydroxy benzene for both polar and non-polar solvents. Comparision of absorption and fluorescence spectral shifts of diamino and dihydroxy benzenes reveals that the interactions of -OH group with the aromatic ring is less than that of $-NH_2$ group both in the ground and excited singlet states.

TABLE-1
ABSORPTION AND FLUORESCENCE SPECTRAL DATA (nm) OF *p*-DIHYDROXY BENZENE AND PHENOL IN DIFFERENT SOLVENTS

Solvents	*p*-Dihydroxy benzene			Phenol		
	λ_{abs}	log ε	λ_{flu}	λ_{abs}	log ε	λ_{flu}
Cyclohexane	293.0 290.0 224.0	3.47 3.46 3.68	320	278.5 271.7 265.5	3.57 3.60 3.43	300
Dioxane	294.4	4.10	330	279.0	3.66	302
Acetonitrile	294.7 225.0	4.10 4.80	330	279.3 273.5 211.0	3.69 3.80 4.29	302
Ethyl acetate	294.9	–	330	279.6 273.7	3.60 3.56	302
tert-Butyl alcohol	290.9 234.7	4.19 3.92	330	275.9	3.40	305
2-Butanol	287.0 331.5	4.11 3.93	330	275.7	3.53	305
Methanol	290.0 226.3	3.96 3.79	330	274.0	3.35	305
Water (neutral)	288.0 222.3	4.27 3.97	330	270.5 210.7	3.86 4.43	305
Monoanion	302.1 223.1	3.56 3.91	330	288.0 236.0	3.58 3.98	310
Dianion	318.0	3.62	Non fluores	– –	– –	– –

Absorption solvatochromic shifts of *p*-dihydroxy benzene in all solvents are found to be more than those of *o*- and *m*-isomers indicating that, in the ground state, the charge transfer interaction of hydroxy group in *p*-position is larger than *o*- and *m*-position. Compared to cyclohexane the absorption maxima of all isomers are red shifted in aprotic solvents and blue shifted in protic solvents. The spectral shifts observed in the absorption spectra of the *p*-dihydroxy benzene in aprotic and

protic solvents are consistent with the characteristic behaviour of -NH_2[19] and -OH group[20]. Like -NH_2 group the -OH group can also act like a bifunctional system, *i.e.*, it can interact with hydrogen donating solvents through its lone-pair or with hydrogen accepting solvents through the hydrogen atom of the hydroxyl group. Thus, with an increase in the hydrogen bonding capacity of the solvents, a blue shift on the latter case should be observed. In *p*-dihydroxy benzene the charge transfer interaction of the lone pair of the hydroxyl group with the phenyl ring is less, as it is clear from the absorption spectrum in all the solvents. The solute molecule will be acting preferentially as a hydrogen donor rather than a hydrogen acceptor due to the high polarity of the OH bond. This would explain the red shift observed in the absorption spectra in acetonitrile. When compared to methanol, a blue shift is observed in water indicating a hydrogen donor interaction due to its greater hydrogen donating capacity than that in methanol. But in the first excited singlet state the polarity of the OH bond is further increased due to the increased charge transfer interaction from the hydroxyl group to the aromatic ring and thus a continuous red shift is observed from cyclohexane to water.

The fluorescence spectra are regularly red shifted as the polarity and proton donor capacities of the solvent increases. In a non-polar solvent cyclohexane, like absorption the fluorescence spectrum of *p*-dihydroxy benzene is red shifted than phenol. In *p*-dihydroxy benzene, both hydroxyl groups are placed asymmetrically. The symmetry of the OH groups are placed in opposite position may also leads to cancellation of solvent interaction. That is the reason, the fluorescence maxima of *p*-dihydroxy benzene is more red shifted in cyclohexane.

Corelation of solvatochromic shift with the solvent polarity: The variation of stoke's shift with the solvent polarity can be represented by the Lippert[21] equation

$$\bar{\nu}_{ss} = \frac{2(\mu_e - \mu_g)^2}{hca^2} f(D, n) + C$$

where $\bar{\nu}_{ss}$ is the Stoke's shift ($\bar{\nu}_{ss} = \bar{\nu}_{abs}\ max - \bar{\nu}_{flu}\ max$), μ_g and μ_e are, respectively the ground and excited state dipole moments of the solute molecule, 'C' is a constant, 'a' is the Onsagar cavity radius and f(D, n) is the Onsagar polarity function defined by the equation.

$$f(D, n) = \frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1}$$

where 'D' is the static dielectric constant and 'n' is the refractive index of the solvent. The other solvent polarity parameter used as an empirical parameter E_T (30); this is based on the spectral shifts of N-phenolbetain[22,23] in different solvents of varying polarity and hydrogen bonding.

In this study the stoke's shifts of *p*-dihydroxy benzene determined in solvents of varying polarity have been correlated with the *f*(D, n) (Fig.1) and E_T (30) (Fig. 2) parameters. Table-2 gives a list of solvents, corresponding polarity parameters and the stoke's shifts. A very good linearity found in the plot of stoke's shifts *versus* E_T

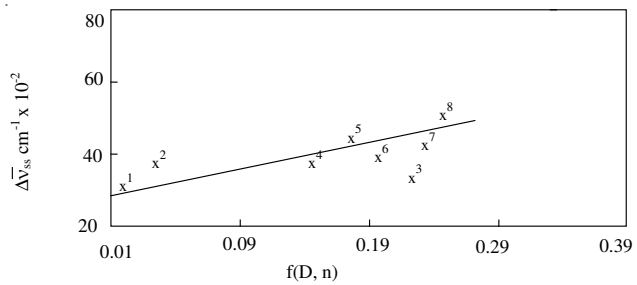

Fig. 1. Correlation of the Stoke's shifts (cm^{-1}) of *p*-dihydroxy benzene with the *f*(D, n) values of different solvents: (1) cyclohexane; (2) dioxane; (3) acetonitrile; (4) ethyl acetate; (5) 2-propanol; (6) *tert*-butyl alcohol; (7) methanol; (8) water

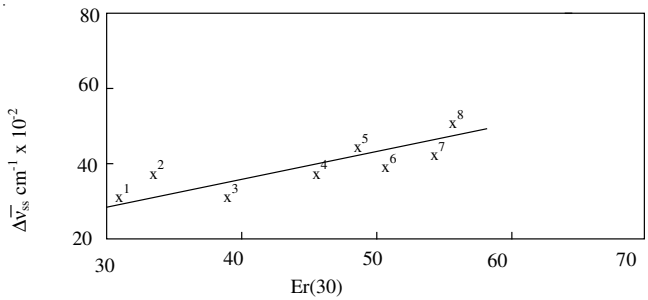

Fig. 2. Correlation of the Stoke's shifts (cm^{-1}) of *p*-dihydroxy benzene with the Er (30) values of different solvents: (1) cyclohexane; (2) dioxane; (3) acetonitrile; (4) ethyl acetate; (5) 2-propanol; (6) *tert*-butyl alcohol; (7) methanol; (8) water

(30) Fig. 2 than stoke's shift *versus f*(D, n) Fig. 1. A good correlation of stoke's shift with the E_T (30) scale indicates hydrogen bonding interactions are predominant.

TABLE-2
STOKE'S SHIFT (cm^{-1}) OBSERVED FOR *p*-DIHYDROXY BENZENE AND PHENOL IN DIFFERENT SOLVENTS WITH E_T (30) AND *f*(D, n) SOLVENT POLARITY PARAMETERS

Solvents	Stoke's shift (cm^{-1})		E_T (30)	f(D, n)
	p-Dihydroxy benzene	Phenol		
Cyclohexane	2997	2717	31.0	-0.001
Dioxane	3793	2860	36.1	0.020
Acetonitrile	3758	2834	46.1	0.305
Ethyl acetate	3723	2795	38.2	0.201
tert-Butyl alcohol	4205	3604	44.0	0.245
2-Butanol	4663	3631	47.2	–
Methanol	4300	3844	55.6	0.309
Water	4541	4334	63.2	0.320
Correlation coefficient				
E_T (30)	0.8926	0.8932	–	–
f(D, n)	0.7796	0.6723	–	–

Effect of proton concentration: The absorption and fluorescence spectra of *p*-dihydroxy benzene have been studied in the H_o/pH/H_ range of -10-16. The absorption and fluorescence maxima of various prototropic species are given in Table-1. The absorption spectra of the prototropic species of *p*-dihydroxy benzene is shown in Fig. 3. With the decrease in pH from 5 the absorption spectra is unaffected up to Ho -10. With increase in pH from 5-7, the absorption maxima move to longer wavelength. This is due to the formation of monoanions obtained by deprotonation of one of the hydroxyl group. Further increase in basicity of the solution the maxima are red shifted continuously. The red shifted spectrum is due to the formation of a dianion obtained by the deprotonation of the second hydroxyl group. No further change in absorption spectrum is noticed even at H_ 16. The above behaviour resembles to that of the aromatic compounds containing the hydroxyl group[24].

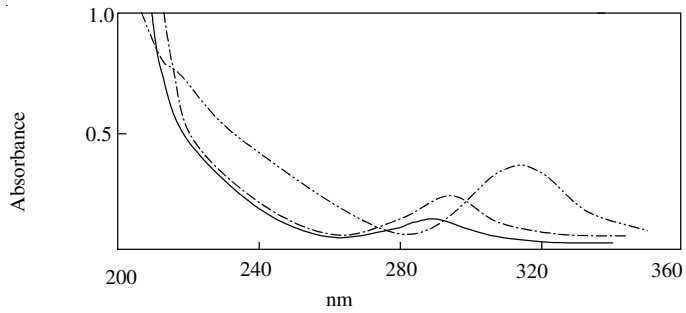

Fig. 3. Absorption spectra of prototopic species of *p*-dihydroxy benzene at 300 K concentration 2×10^{-5} mol dm^{-3} (–) neutral, (–·–) monoanion, (–··–) dianion

The fluorescence spectra of neutral and monoanions of *p*-dihydroxy benzene is shown in Fig. 4. The neutral species is very weak fluorescent. When the acidity is decreased, the emission intensity of the weakly fluorescent band increases considerably as a consequence of monoanion formation. The formation of monoanion is complete in the pH range 1-7. When the pH is increased from 7, the monoanion fluorescence is quenched from pH 7.5. This is due to the formation of dianions.

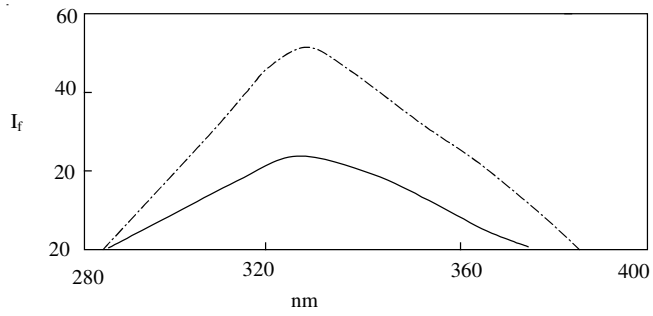

Fig. 4. Fluorescence spectra of prototopic species of *p*-dihydroxy benzene at 300 K concentration 2×10^{-5} mol dm^{-3} (–) neutral, (–·–) monoanion

Spectral characteristics of *p*-dihydroxy benzene in different concentration of α-cyclodextrin: Table-3 and Fig. 5 and 6 show the absorption and fluorescence maxima of *p*-dihydroxy benzene in different α-cyclodextrin concentrations. The

TABLE-3
ABSORPTION AND FLUORESCENCE MAXIMA (nm) OF *p*-DIHYDROXY BENZENE AT DIFFERENT CONCENTRATION OF α-CYCLODEXTRIN

Concentration of α-cyclodextrin	*p*-Dihydroxy benzene		
	λ_{abs}	log ε	λ_{flu}
Water (without α-cyclodextrin)	288.0 222.0	4.17	330
0.0010 M	290.0 223.0	4.17	330
0.0015 M	290.0 223.0	4.15	330
0.0020 M	290.5 223.5	4.13	330
0.0025 M	290.5 223.5	4.11	330
0.0030 M	291.0 224.0	4.11	330
0.0035 M	291.0 224.0	4.11	330
0.0040	296.0 224.0	4.11	330
Excitation wavelength (nm)	277	–	–
Binding constant K_B (M^{-1})	202.47	–	–

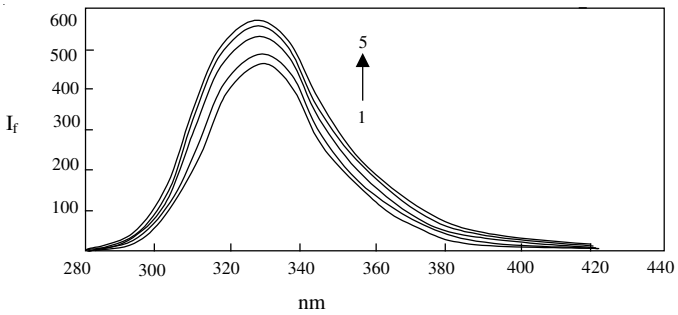

Fig. 5. Fluoresence spectra of *p*-dihydroxy benzene at various concentration of α-cyclodextrin (in mol dm^{-3}); (1) without α-cyclodextrin, (2) 1×10^{-3}, (3) 2×10^{-3} (4) 3×10^{-3} (5) 4×10^{-3}

absorption maximum is slightly red shifted by the addition of α-cyclodextrin. This may be due to the formation of an inclusion complex between *p*-dihydroxy benzene and α-cyclodextrin[25]. No clear isosbestic point is observed in absorption spectrum. The complexation is completed at 4×10^{-3} mol dm^{-3} α-cyclodextrin concentrations. Above 4×10^{-3} mol dm^{-3}, α-cyclodextrin concentractions, the absorption band

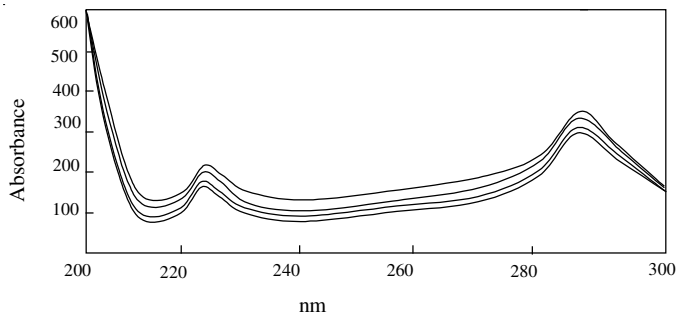

Fig. 6. Absorption spectra of *p*-dihydroxy benzene at various concentration of α-cyclodextrin (in mol dm^{-3}); (1) without α-cyclodextrin, (2) 1×10^{-3}, (3) 2×10^{-3} (4) 3×10^{-3} (5) 4×10^{-3}

maxima and the absorption remain unchanged. These finding indicates the formation of inclusion complex between α-cyclodextrin and *p*-dihydroxy benzene.

The fluorescence spectra of *p*-dihydroxy benzene at different α-cyclodextrin concentrations are displayed in Fig. 5. The fluorescence intensity of *p*-dihydroxy benzene in water gradually increases upon addition of α-cyclodextrin. The enhancement of the fluorescence intensity suggest the formation of an inclusion complex between *p*-dihydroxy benzene and α-cyclodextrin. An increase in the fluorescence intensity for the formation of an inclusion complex was observed earlier. The complexation is complete at 4×10^{-3} mol dm^{-3} α-cyclodextrin concentration and there is no change in the fluorescence by further addition of α-cyclodextrin (Fig. 5).

The α-cyclodextrin dependence of *p*-dihydroxy benzene fluorescence can be analyzed by the Benesi-Hildebrand plot as given by equation

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K_B(I' - I_0)[\alpha\text{-cyclodextrin}]}$$

where [α-cyclodextrin] represents the concentrations of α-cyclodextrin and I_0, I are the fluorescence intensities in the absence and the presence of α-cyclodextrin, respectively, K_B is the binding constant. A linear relation is observed when $1/(I-I_0)$ is plotted against 1/[α-cyclodextrin] (Fig. 7), which suggesting 1:1 stoichiometry in the *p*-dihydroxy benzene and α-cyclodextrin complex. The binding constants are so small compared with other guest α-cyclodextrin complex. This is probably due to inter (or) intra molecular hydrogen bond present in the complex. The internal diameter of the α-cyclodextrin is approximately 4.9 Å and its height is 7.9 Å. The length of *p*-dihydroxy benzene is lower than that of the upper rim of α-cyclodextrin cavity. Thus the *p*-dihydroxy benzene molecules completely included in the α-cyclodextrin cavity.

Microscopic morphological observation: The powered form of *p*-dihydroxy benzene and α-cyclodextrin was observed by scanning electron microscope. We we also observed powered form of inclusion complex (Fig. 8). These pictures clearly elucidated the difference of *p*-dihydroxy benzene and inclusion complex. As seen

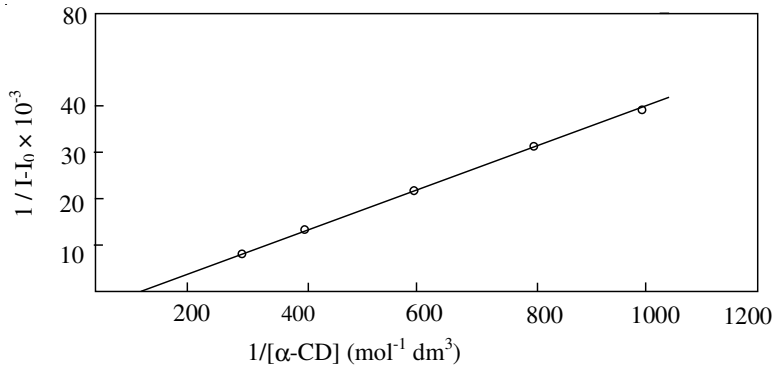

Fig. 7. Benesi-Hildebrand plot for the complexation of *p*-dihydroxy benzene with α-cyclodextrin

Fig. 8. Scanning electron microscope (a) α-cyclodextrin (b) *p*-dihydroxy benzene (c) *p*-dihydroxy benzene:α-cyclodextrin

from the SEM figures α-cyclodextrin shows sheeted structure, *p*-dihydroxy benzene shows stick structure and the complex structure is different from α-cyclodextrin and *p*-dihydroxy benzene. Modification of crystals and powder can be assumed as a proof of the formation of new inclusion complex.

Conclusion

Based on the above discussion the following conclusions can be drawn. Solvent study shows that the interaction of OH group with the aromatic ring is less than that of amino group both in the ground and excited states. The charge transfer interaction of OH group in *p*-position is larger in absorption. pH studies reveals that *p*-dihydroxy benzene is more acidic than phenol. In α-cyclodextrin medium, absorption spectra of *p*-dihydroxy benzene, mono and dianions shows unusual blue shifts, whereas in the excited state, the spectral characteristics of *p*-dihydroxy benzene follow the same trend in both aqueous and α-cyclodextrin medium. SEM study support the formation of 1:1 inclusion complex.

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REFERENCES

1. C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, VCH, Weinheim (1990).
2. F. Cichos and C.V. Borczyskawski, *J. Phys. Chem*., **101**, 8179 (1997).
3. R.M. Stratt and M. Moroncelli, *J. Phys. Chem*., **100**, 12981 (1996).
4. D.M. Willard, R.E. Ritter and N.E. Levinger, *J. Am. Chem. Soc*., **120**, 4151 (1998).
5. G. Klose and F. Stelzmer, *Biochem. Biophys. Acta*, **1**, 363 (1999).
6. A. Goto, S. Harada, J. Fujita, Y. Miwa, H. Yashioka and H. Kishimoto, *Langmuir*, **9**, 86 (1993).
7. N. Sarkar, K. Das, A. Datta and K. Bhattacharya, *J. Phys. Chem*., **100**, 10523 (1996).
8. A. Datta, M.S. Pal and K. Bhattacharya, *Anal. Sci*., **14**, 199 (1998).
9. T. Forster, *Z. Electrochem*., **54**, 531 (1950).
10. A. Weller, *Progr. React. Kint*., **1**, 187 (1961).
11. K. Sivakumar, T. Stalin and N. Rajendiran, *Spectrochim. Acta A*, **62**, 993 (2005).
12. S.P. Webb, L.A. Philips, S.W. Yeh, L.M. Tolbert and J.H. Clark, *J. Phys. Chem*., **90**, 5154 (1986).
13. J.G. Lee, G.W. Robinson, S.P. Webb, L.A. Philips and J.H. Clark, *J. Am. Chem. Soc*., **108**, 6538 (1986).
14. J.A. Reddick and N.B. Bunger, in ed.: A. Weissberger, Techniques of Chemistry Organic Solvents, vol. 8, Wiley Interscience, New York (1970).
15. M.J. Jorgenson and D.R. Harter, *J. Am. Chem. Soc*., **85**, 878 (1963).
16. G. Yagil, *J. Phys. Chem*., **71**, 1034 (1967).
17. J.C. Dearden and W.F. Fobes, *Can. J. Chem*., **37**, 1294 (1959).
18. R. Manoharan and S.K. Dogra, *Bull. Chem. Soc. (Japan*), **60**, 4409 (1987).
19. N. Rajendiran and M. Swaminathan, *Spectrochim. Acta*, **52A**, 1785 (1996).
20. N. Rajendiran and M. Swaminathan, *Indian J. Chem*., **40A**, 331 (2001).
21. E. Lippert, *Z. Naturforsch*., **10A**, 541 (1955).
22. E.M. Kosower and M. Mohammed, *J. Am. Chem. Soc*., **90**, 3271 (1968).
23. C. Reichardtand K. Dimorth, *Liebigs Am. Chem*., **661**, 1 (1983).
24. T. Stalin, P.V. Rani, B. Shanthi and A. Sekar, *Indian J. Chem*., **45A**, 3 (2006).
25. S. Santra and S.K. Dogra, *J. Photochem. Photobiol. A Chem*., **101**, 221 (1996).

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