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Solvatochromism and Prototropism of Some Alkyl Substituted Phenols

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The effects of solvents on absorption and fluresence of some dimethyl substituted phenols (DMPS) and trimethyl phenols (TMPS) show that hydrogen bonding interactions are predominant. The site of hydrogen donor interaction of water with DMPS and TMPS in the excited singlet state is found to be differnt from the site of interaction in the ground state. Acidity constants for neutral-monoanion equilibria in S_0 and S_1 states have been determined and discussed.

INTRODUCTION

Studies of photophysical properties are very useful in the elucidation of chemical behaviour and electronic orientation of organic and biomolecules.[1] Photophysical properties of aromatic carbo- and heterocyclic molecules with one functional group have been studied in great details.[2–4] It is well known that in the monofunctional molecules, electron-donating groups such as —OH and —NH_2 groups become stronger acids in the S_1 state and lead to a red shift or blue shift in the electronic spectra when these groups become deprotonated or protonated.[5–8] Fluorescence spectral studies at different temperatures were done for some xylenols[9], in nonpolar and hydrogen bond acceptor solvents. Recently excited state acidity of 1,3-napthalenediol[10] was reported. The present study was carried out to analyse both absorption and fluorescence spectral shifts of some dimethyl substituted phenols (DMPS) and trimethyl phenols (TMPS) in different solvents at different pH. Both DMPS and TMPS are having only deprotonation site and these phenols interact with hydrogen donor and acceptor solvents.

EXPERIMENTAL

The compounds such as 2,6-dimethyl phenol, 2,5-dimethylphenol, 3,4-dimethylphenol, 2,3,5-trimethylphenol, and 2,4,6-trimethylphenol were procured from Aldrich Chemical Company. All the above compounds were purified by recrystallisation using solvents reported in the literature[11] before use, and their purity was checked by similar fluorescence spectra when excited with different wavelengths. Triply-distilled water was used to prepare the aqueous solutions. BDH spectrograde methanol was used as such. Other solvents (AnalaR) were purified the methods described in the literature.[12] Absorption spectra were recorded with a JASCO UNIDEC-7800 spectrophotometer, while fluorescence measurements were made using a JASCO FB-550 recording spectrofluorimeter. pH values in the range 1–13 were measured on an ELICO pH-meter model LI-IOT. Experimental solutions were prepared by adding an aliquot of the stock solution to appropriate HO/pH/H-solutions, just before taking measurements. The concentration of the resulting solution was in the order of 10^{-4}–10^{-3} M.

RESULTS AND DISCSSION

Effect of solvents

The absorption and fluorescence spectra of DMPS and TMPS were observed in different solvents and the relevant data are compiled in Table-1. The fluorescence spectra of 2,5-DMP, 2,6-DMP and 2,4,6-TMP recorded in selected solvents are shown in Figs. 1, 2 and 3.

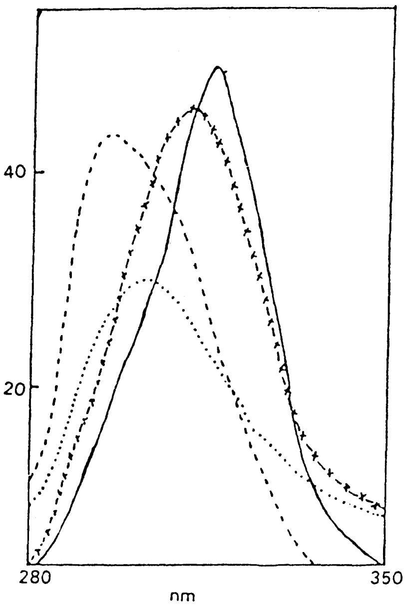

Fig. 1 Fluorescence spectra of 2,5-DMP in different solvents at 298 K
- - - cyclohexane, ... acetonitrile, -x-x- methanol, —— water

The interaction of solvents with the lone pair of —OH groups will lead to a blue shift and the solvent interaction with the hydrogen atom of the —OH group will lead to a red shift both in absorption and fluorescence spectra. In 3,4-DMP and 2,5-DMP the absorption maxima are red shifted from cyclohexane to methanol, but the absorption maxima in water is same as in cyclohexane. This may be due to the fact that in 2,5-DMP, the lone pair of electrons are involved in delocalisation and in 3,4-DMP, the electron-releasing alkyl group in the *para* position increases the electron density on oxygen atom and may lead to cancellation of solvent interactions. In 2,6-DMP, there is a significant blue shift

TABLE-1
ABSORPTION AND FLUORESCENCE SPECTRAL DATA (NM) OF VARIOUS DIMETHYL AND TRIMETHYLPHENOLS IN DIFFERENT SOLVENTS AND AT VARIOUS pH

Solvents	2,6-DMP			2,5-DMP			3,4-DMP			2,3,5-TMP			2,4,6-TMP			E_T30	BK
	\ab (max)	log ε	\flu	\ab (max)	log ε	\flu	\ab (max)	log ε	\flu	\ab (max)	log ε	\flu	\ab (max)	log ε	\flu		
Cyclohexane	271.0	(4.58)	296	272.8	(4.68)	298	275.2	(4.58)	301	277.6	(4.59)	301	273.0	(4.53)	303	31.2	–0.001
Diethyl ether	272.2	(4.56)	298	274.5	(4.66)	303	276.4	(4.60)	303	278.2	(4.64)	302	277.0	(4.44)	305	34.6	0.317
Dioxane	272.4	(4.62)	299	275.2	(4.59)	304	276.4	(4.69)	304	278.4	(4.68)	303	277.2	(4.39)	306	36.0	0.043
Ethyl acetate	272.4	(4.59)	300	274.2	(4.62)	304	278.0	(4.32)	304	278.4	(4.56)	303	277.2	(4.38)	306	38.1	—
Dichloro methane	271.6	(4.69)	300	272.2	(4.64)	305	277.2	(4.52)	306	278.2	(4.38)	304	277.2	(4.56)	306	41.1	0.586
Acetonitrile	272.4	(4.53)	300	273.6	(4.20)	306	278.2	(4.52)	306	278.4	(4.63)	305	277.2	(4.37)	305	46.0	0.064
t-pentyl alcohol	272.2	(4.58)	301	273.4	(4.22)	306	278.0	(4.65)	307	278.4	(4.62)	305	277.4	(4.46)	305	41.9	—
t-Butyl alcohol	272.4	(4.56)	301	274.6	(4.40)	306	278.2	(4.65)	307	278.2	(4.60)	305	277.2	(4.42)	305	43.9	0.673
Ethyl alcohol	272.4	(4.99)	300	275.2	(4.78)	310	275.2	(4.25)	308	277.6	(4.86)	304	277.6	(4.56)	306	53.7	0.812
Methyl alcohol	272.4	(4.53)	300	275.2	(4.69)	312	277.2	(4.33)	308	277.6	(4.59)	305	277.6	(4.56)	306	55.5	0.858
Ethylene glycol	272.4	(4.50)	300	275.0	(4.65)	312	277.0	(4.35)	308	277.8	(4.56)	305	277.6	(4.56)	306	56.3	—
Water	269.4	(5.21)	305	272.8	(4.54)	315	275.2	(4.26)	310	276.0	(4.61)	307	272.8	(4.36)	308	63.1	0.913
Monoanion	286.4	(4.53)	309	289.5	(4.64)	316	292.8	(4.26)	316	288.8	(4.71)	313	294.4	(4.53)	317	—	—
Correlation coefficient $E_{(T)}^{(r)}30$	0.7227			0.9347			0.8860			0.9115			0.7265				
BK	0.6264			0.6735			0.7906			0.3711			0.7265				

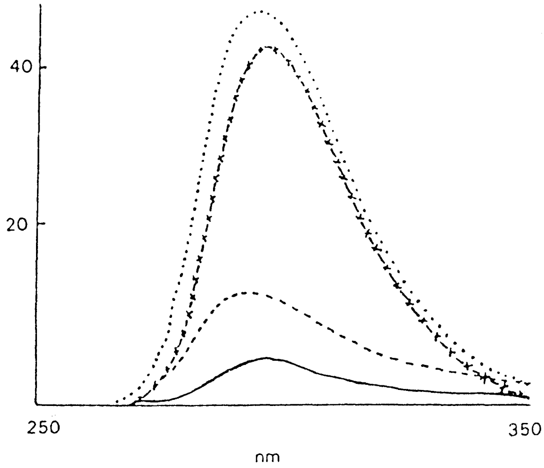

Fig. 2 Fluorescence spectra of 2,6-DMP in different solvents at 298 K
--- cyclohexane, ... acetonitrile, -x-x- methanol, —— water

in water. This is because of the presence of two methyl groups *ortho* to the hydroxyl group restricts the free rotation of the —OH group sterically and inhibit the resonance interaction of the —OH group with the ring and enhances the interaction with the hydrogen donor solvents. The same trend was observed in the absorption maxima of 2,3,5-TMP and 2,4,6-TMP. In 2,4,6-TMP the blue shift observed in water is more significant (4 nm) than in 2,3,5-TMP.

Analysis of fluorescence solvatochromic shifts reveals that there is a regular red shift for all DMPS and TMPS and increasing polarity and hydrogen bonding capacity of solvents. But the red shifts are more for DMPS compared to TMPS. The above observations indicate that the behaviour of TMPS is different from DMPS in the excited state. The presence of three methyl groups may reduce the polarity of —O—H bond. This may lead to reduced hydrogen donor interaction when compared to DMPS. Generally in the study of solvent effects the Stokes shifts for the solvents are compared with the theoretical derived solvent parameters $E_T(30)^{*13,14}$ and BK^{15} values. The Stokes shifts in various solvents along with $E_T(30)$ and BK values are given in Table-1. Among these two parameters the $E_T(30)$ incorporates both hydrogen bonding and solvent polarity effects, whereas BK value incorporates only the solvent polarity effect. A plot of Stokes shifts with $E_T(30)$ gives a good correlation and a poor correlation with BK values. This shows that the hydrogen bonding interactions are predominant over the solvent polarity.

Specific hydrogen bonding in 2,6-DMP

A comparative study of solvatochromic effect of 2,6-DMP (POH) and 2,6-dimethylphenylether (POE) have also been carried out to explain the specific hydrogen bonding in 2, 6-DMP. The absorption and fluorescence maxima of POH and POE in selected solvents are compiled in Table-2.

TABLE-2
ABSORPTION AND FLUORESCENCE SPECTRAL DATA FOR 2,6-DMP (POH) AND 2,6-DIMETHYLPHENYLETHER (POE) IN DIFFERENT SOLVENTS

S. No.	Compound	Cyclohexane	Acetonitrile	Methanol	Water
1.	POH \ ab (max) \ flu (max)	271.0 296.0	272.4 298.0	272.4 300.0	269.6 305.0
2.	POE \ ab (max) \ flu (max)	268.9 298.0	270.0 298.0	269.0 297.0	263.2 293.0

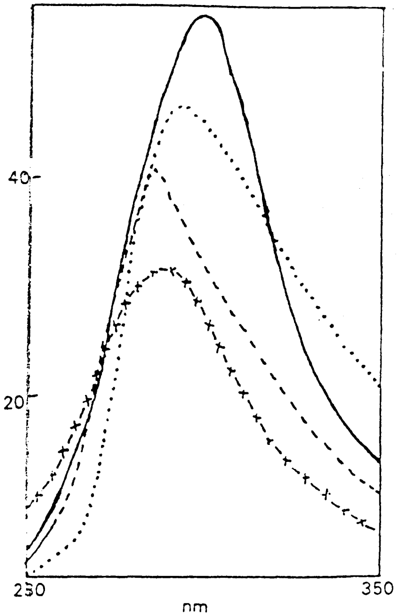

Fig. 3 Fluorescence spectra of 2,4,6-TMP in different solvents at 298 K
--- cyclohexane, ... acetonitrile, -x-x- methanol, —— water

The observed solvatochromic shifts in POH indicate that the dispersive and hydrogen acceptor solvent interactions with the solute are predominant in acetonitrile and methanol, whereas the hydrogen donor solvent interaction is more operative in water.

On ethylation of POH, the hydrogen donor capacity is absent, and there is a slight red shift in acetonitrile and methanol. In water, there is a significant blue shift. In POE, the resonance interaction of $—OC_2H_5$ group with the ring is sterically inhibited by the two *ortho*-alkyl substituents and the lone pair of electron interactions are more with the solvent and the hydrogen acceptor capacity increases. Fluoresence maxima of POE in all solvents are also in accordance with the absorption maxima.

Acidity constants

The ground state pKa values for the equilibrium between neutral form and monoanion were determined spectrophotometrically. The pKa* values in the S_1

state (pK*) for the equilibrium are determined with the help of Foster cycle method.[16] The data are compiled in Table-3.

TABLE-3
GROUND AND EXCITED SINGLET STATE ACIDITY CONSTANTS OF DMPS AND TMPS FOR THE EQUILIBRIUM NEUTRAL FORM $\rightleftharpoons$ ANION

No.	Compound	pKa	Foster cycle		
			pK_{ab}^*	pK_{flue}^*	pK_a^* (ave)
1.	2,6-DMP	10.50	5.87	9.61	7.74
2.	2,5-DMP	10.49	6.05	10.28	8.17
3.	3,4-DMP	11.06	6.47	9.77	8.12
4.	2,3,5-TMP	11.58	8.21	10.27	9.24
5.	2 4,6-TMP	10.23	4.58	8.29	6.44

The pK* values indicate that all the five compounds are more acidic in the S_1 state than in the ground state.

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