



## RESEARCH ARTICLE

# SOLVENT EFFECTS ON ELECTRONIC ABSORPTION AND FLUORESCENCE SPECTRA OF 2,4-QUINOLINEDIOL

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### ABSTRACT

The UV and fluorescence spectra of 2,4-quinolinediol (2,4-QDOL) were recorded in nine different solvents. Multiple regression analysis of 2,4-QDOL showed that the alcoholic solvent effect is best interpreted in terms of Taft's polar substituent constant ( $\sigma^*$ ), Kirkwood function of the dielectric constant ( $E_s$ ). The effects of solvent polarity and the extent of hydrogen bond on the absorption spectra of 2,4-QDOL were best interpreted by means of linear solvation energy relationships proposed by Kamlet and Taft. The Stoke's shift of fluorescence spectra correlated with theoretically derived solvent parameters  $E_T(30)$  and  $B_K$  values.

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## INTRODUCTION

A comprehensive account of the influence of molecular structure on the electronic and fluorescence spectra have been nicely discussed by various authors (Kamlet *et al.*, 1983; Suganya and Kabilan, 2004; Stalin and Rajendiran, 2005; Rahman and James Harman, 2006; Suresh Kumar *et al.*, 2006). The solvatochromic shift's can provide vial information regarding charge distribution in the solute molecule, geometry of the molecule, nature of the transition in the ground and excited states. Several authors (Aquino *et al.*, 2002; Hommud *et al.*, 2006; Rauf *et al.*, 2008; Nag and Goswami, 2009) reported the correlations between ultraviolet absorption frequencies and fluorescence

emission frequencies with the solvatochromic parameters  $\alpha$ ,  $\beta$  and  $\pi^*$  in order to predicting the effects of solvent polarity and the nature of hydrogen bond between solvent and solute molecules. In this work we report the UV and fluorescence spectra of 2,4-QDOL in nine different solvents and the  $\nu_{\max}$  values are subjected to correlation analysis and the results were discussed.

## MATERIALS AND METHODS

2,4-QDOL were obtained from Aldrich Chemical Company. The solvents used for recording the UV and fluorescence spectra were of UV spectral grade and used as such. Absorption measurements were made using SHIMADZU-UV-650 spectrophotometer while fluorescence measurements were made using an ELICO-SL- 174 spectro fluorimeter.

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## RESULTS AND DISCUSSION

The UV and fluorescence spectra of 2,4-QDOL is recorded in nine different solvents in the region 200-400 nm for the sake of studying the solvent effects. The UV absorption spectra of 2,4-QDOL is recorded in hexane and methanol-water mixtures of varying dielectric constants. The difference in absorption maxima between those in alcohol-water mixture and those in hexane is a direct measure of the excited state stabilization energy of the compound under investigation in various alcohol-water mixtures. The difference in the maximum absorption frequency  $\Delta v_{\max}$  ( $v_{\text{hexane}} - v_{\text{MeOH-water}}$ ) values and the dielectric parameters of the solvent mixtures are given in Table 1. To study the effect of polarity on the UV absorption data, the following plots  $\Delta v_{\max}$  versus  $\epsilon$  ( $r = 0.942$ );  $\Delta v_{\max}$  versus  $1/\epsilon$  ( $r = 0.892$ ) and  $\Delta v_{\max}$  versus  $f(\epsilon)$  ( $r = 0.887$ ) were drawn and a linear regression was also been carried out. These graphs showed a fair linearity between the stabilization energy and the dielectric constants of the methyl alcohol-water mixtures establishing the fact that the stabilization energy is increased by the solvation of the excited state.

As there is a perfect correlation between the stabilization energy of the excited state and dielectric constant of the medium, it was thought of great interest to see if any correlation exists between stabilization energy of the excited state and dielectric constant of the medium by varying the alcohols themselves. Hence the UV absorption spectra of 2,4-quinolinediol were recorded in hexane and in various alcoholic solvents. The absorption maximum  $v_{\max}$  and  $\Delta v_{\max}$  in various alcoholic solvents are presented in Table 2. Since the excited state of 2,4-quinolinediol involve charge separations hence it was attempted to see if any correlation existing between  $\Delta v_{\max}$  versus  $\epsilon$ ,  $1/\epsilon$  and  $f(\epsilon)$ . In all plots the correlation was extremely poor ( $r = 0.0071$ ,  $0.1742$  and  $0.1663$  respectively) and the correlation between  $\Delta v_{\max}$  versus  $\sigma^*$  (Taft's polar substituent constant) is also poor ( $r = 0.0668$ ). While trying to construct the better equation which can explain the anomalies in some alcohols the suitability of Taft's steric parameter ( $E_s$ ) was included and an attempt was made to involve the triparametric correlation

analysis with Kirkwood function  $f(\epsilon)$ , Taft's polar substituent constant  $\sigma^*$  and Taft's steric parameter  $E_s$  values. Comparison of the coefficient of multiple correlation ( $R$ ) shows that the solvent effect of 2,4-QDOL is best interpreted in terms of  $\sigma^*$ ,  $f(\epsilon)$  and  $E_s$  together and the corresponding multiparametric equation is given below.

$$\Delta v_{\max} = -1203381 + 2517617 f(\epsilon) - 165744\sigma^* - 26882 E_s \quad \dots\dots\dots (1)$$

( $R = 0.9850$ ;  $SE = 210$ ,  $n = 5$ )

The UV and fluorescence spectra of 2,4-QDOL were recorded in nine different solvents (Table 3) in order to study the solvent polarity and the nature of hydrogen bond existing between the solvent and solute molecules. These effects are interpreted by means of the linear solvation energy relationship (LSER), a concept proposed by Kamlet and Taft (1980) using the general solvation equation of the form

$$v = v_0 + S\pi^* + a\alpha + b\beta \quad \dots (2)$$

where  $\alpha$ ,  $\beta$  and  $\pi^*$  are solvatochromic parameters and  $a$ ,  $b$  and  $S$  are the solvatochromic coefficients. In eqn. (2),  $\pi^*$  is an index of the solvent dipolarity/polarizability, which is a measure of the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. The variable  $\alpha$  is a measure of the solvent hydrogen-bond donor (HBD) acidity and describes the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The variable  $\beta$  is a measure of the solvent hydrogen-bond acceptor (HBA) basicity and describes the ability of a solvent to accept a proton in a solute-to-solvent hydrogen bond. The correlation of the spectroscopic data were carried out by means of multiple linear regression analysis. It was found that  $v_{\max}$  for 2,4-QDOL in nine different solvents for which the solvatochromic constants are known, showed a good correlation with  $\pi^*$ ,  $\alpha$  and  $\beta$  values (Kamlet *et al.*, 1983). The results of the multiple linear regression analysis is

$$v_{\max} (\pi-\pi^*) = 4.26 \times 10^4 - 6973.5 \pi^* - 2642.8 \beta + 8628.6 \alpha \quad \dots\dots\dots (3)$$

( $R = 0.993$ ,  $n = 9$ ,  $SE = 427.04$ )

For fluorescence spectra, the results of multiple linear regression analysis is

**Table 1.  $\nu$  and  $\Delta\nu_{\max}$  values of 2,4-quinolinediol in various percentage of methanol-water mixtures**

Methyl alcohol % in MeOH-H <sub>2</sub> O	$\nu_{\max}$ (cm <sup>-1</sup> )	$\Delta\nu_{\max}$ (cm <sup>-1</sup> )	$\epsilon$	1/ $\epsilon$	f( $\epsilon$ )
100	44209	1509	33	0.0303	0.4776
90	44131	1431	40.41	0.0248	0.5061
80	44091	1391	46.72	0.0214	0.5053
70	43975	1275	52.45	0.0191	0.5047
60	43975	1275	57.45	0.0174	0.5043
50	43764	1064	61.98	0.0161	0.5040

 $\nu_{\max}$  hexane = 42700 cm<sup>-1</sup>**Table 2.  $\nu$  and  $\Delta\nu_{\max}$  values of 2,4-quinolinediol in various alcohols**

Solvent	$\nu_{\max}$ (cm <sup>-1</sup> )	$\Delta\nu_{\max}$ (cm <sup>-1</sup> )
Methanol	44209	-1501
Ethanol	44843	-2135
1-Propanol	43403	-695
2-Propanol	43750	-1042
2-Methyl-2-propanol	44691	-1983

 $\nu_{\max}$  hexane = 42708 cm<sup>-1</sup>**Table 3. Absorption and fluorescence spectral data for 2,4-quinolinediol**

Solvent	Absorption spectra		Fluorescence spectra	Stoke's shift
	$\nu_{\max}$ (cm <sup>-1</sup> )	$\pi-\pi^*$	$\nu_{\max}$ (cm <sup>-1</sup> )	
Hexane	42708		42212	496
Methanol	44209		27624	16585
1-Propanol	43403		27855	15548
2-Propanol	43750		27855	15895
Water	44723		27894	16829
Cyclohexane	43066		33059	10007
Ethylacetate	37313		29138	8175
Chloroform	42408		25907	16501
Tetrahydrofuron	37119		32206	4913

$$\nu_{\max} = 3.62 \times 10^4 - 8410.2 \pi^* - 2991.9 \beta - 1347.8 \alpha \quad (4)$$

(R = 0.776, n = 9, SE = 387.2)

The negative sign of the S and b coefficients in the solvatochromic equation (3) and (4), indicates that a bathochromic shift with both increasing solvent polarity and solvent hydrogen-bond acceptor basicity. This suggests that most of the solvatochromism is due to solvent polarity and basicity rather than solvent acidity in the present system under investigation. Generally in the study of solvent effect the Stoke's shift for the solvents are compared with the theoretically derived solvent parameters  $E_T(30)$  and  $B_K$  values. These solvent parameters to correlate molecular spectroscopic

properties. Among these two parameters the  $E_T(30)$  incorporates both hydrogen bonding and solvent polarity effects whereas the  $B_K$  parameter represents only solvent polarity effects. The Stoke's shift in various solvents along with  $E_T(30)$  and  $B_K$  values are given in Table 3. The Stoke's shifts in all the solvents are correlated with  $B_K$  parameters and  $E_T(30)$  values. The results of correlation indicate a betterment in  $B_K$  parameter ( $r = 0.935$ ) than  $E_T(30)$  parameter ( $r = 0.502$ ). This clearly indicates that in the present system, solvent polarity effect influences the Stoke's shift more than hydrogen-bonding effects.

### Conclusion

The absorption spectra of 2,4-quinolinediol in various percentage of methanol-water mixtures and

its interpretation shows that the stabilization energy increased by the solvation of the excited state. The UV spectral studies of the various alcoholic solvents shows that the  $\Delta v_{\max}$  values are well correlated with the triparametric equations involving  $\sigma^*$ ,  $f(\epsilon)$  and  $E_s$  parameters. UV and fluorescence spectral studies of various solvents and the Kamlet and Taft multiparametric equation (eqn. 2) showed a better correlation with  $\pi^*$ ,  $\alpha$  and  $\beta$  values and their coefficient indicates that most of the solvatochromism is due to solvent polarity and solvent hydrogen bond acceptor basicity rather than solvent hydrogen bond donor acidity.

## REFERENCES

- Aquino, A.J.A., Tunega, D., Haberbauer, G., Gerzabek, M.H. and Lischka, H. 2002. Solvent effects on hydrogen bonds – A theoretical study. *J. Phys. Chem.*, 106: 1862.
- Hommud, H., Ghannoum, A. and Mosoud, M. S. 2006. Spectral regression and correlation coefficients of some benzaldimines and salicylaldimines in different solvents. *Spectrochim. Acta A*, 63: 255.
- Kamlet, M.J., Abboud, J.M., Abraham, M.H. and Taft, R.W. 1983. A comprehensive collection of the solvatochromic parameters  $\pi^*$ ,  $\alpha$  and  $\beta$  and some methods for simplifying the generalized solvatochromic equation. *J. Org. Chem.*, 48: 2877.
- Kamlet, M.J., Abboud, J.M. and Taft, R.W. 1980. Linear solvation energy relationships. *Prog. Phys. Org. Chem.*, 13: 485.
- Nag, A. and Goswami, D. 2009. Solvent effect on two photon absorption and fluorescence of rhodamine dyes. *J. Photochem. Photobiol. A*, 206: 188.
- Rahman, M. and James Harman, H. 2006. Absorbance change and static quenching of fluorescence of mesotetra (4-sulfonatophenyl) porphyrin (TPPS) by trinitrotoluene (TNT). *Spectrochim. Acta A*, 65: 901.
- Rauf, M.A., Soliman, A.A. and Khattab, M. 2008. Solvent effect on spectral properties of Neutral Red. *Chem. Cent. J.*, 2: 19.
- Stalin, T. and Rajendiran, N. 2005. Effects of solvent, pH and  $\beta$ -cyclodextrin on the photophysical properties of 4-hydroxy-3,5-dimethoxybenzaldehyde: Intramolecular charge transfer associated with hydrogen bonding effect. *Spectrochim. Acta A*, 61: 3087.
- Suganya, K. and Kabilan, S. 2004. Substituent and solvent effects on electronic absorption spectra of some N-(substituted phenyl) benzene sulphonamides. *Spectrochim. Acta A*, 60: 1225.
- Suresh Kumar, H.M., Kunabenchi, R.S., Biradar, J.S., Math, N.N., Kadadevarmath, J.S. and Inamdar, S.R. 2006. Analysis of fluorescence quenching of new indole derivative by aniline using Stern-Volmer plots. *J. Luminescence.*, 116: 35.

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