Fluorescence spectroscopic studies on preferential solvation and bimolecular quenching reactions of Quinolin-8-ol in binary solvent mixtures

Kalpana Sharma[1], Raveendra Melavanki[1]∗, V T Muttannavar[2], P Bhavya[3], Meghana U[4] and Suma B[4]

[1]Department of Physics, M S Ramaiah Institute of Technology, Bengluru560054, Karnataka, India

[2]Department of Physics, JSS Science RSH PU College, Vidyagiri Dharwad-580003, Karnataka, India

[3]Department of Physics, New Horizon College of Engineering, Bengluru 560 103, India

[4]Department of Physics, Faculty of Mathematical and Physical Sciences, M S Ramaiah University of Applied Science, Bengaluru-560058, Karnataka, India

Corresponding author Email: melavanki73@gmail.com

Abstract. On account of the importance towards solvent mixtures in practical chemistry, binary solvent mixtures of acetonitrile (AN) and 1, 4-dioxane (DX) are used to study fluorescence behavior of this organic compound namely Quinolin-8-ol (QO). At the outset, preferential solvation is examined in AN-DX for this QO, in order to understand specific and nonspecific interactions. Further Suppan's dielectric enrichment model is implemented to identify the non-ideality and dielectric enrichment in AN-DX for preferential solvation. Bimolecular quenching reaction studies of Quinolin-8-ol have been carried out in mixtures of AN-DX to study the effect of dielectric constants and viscosity at room temperature. The quenching process is studied in all solvent mixtures by Steady state and Transient state method. Quenching is characterized by Stern-Volmer (S-V) plots having downward curvature. Interestingly, for moderate quenching concentration, downward curvature has been observed for the title molecule. The inter and intra molecular hydrogen bonding has profound role in the formation of different conformers in QO. Further, modified S-V equation is applied to analyze the fluorescence quenching reactions of QO molecule.

1. Introduction

Quinoline and its derivatives in particular 8-hydroxyquinoline is well known for clinical, industrial, biological and pharmacological usage. Out of which derivatives of 8-hydroxyquinoline are reported as potential antifungal and HIV-1 inhibitors. Fluorescence quenching is a bimolecular reaction in which the intensity of the fluorophore decreases with increase in quencher concentration.
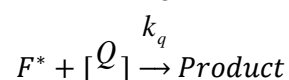
Quenching study helps to understand (i) the presence of multiple fluorescence emitting species (ii) accessibility of fluorophores to quenchers, (iii) protein in complex system etc. Recently fluorescence quenching study is used by the molecular biologist to discover gene using new techniques. Solvent mixtures have improved physical properties like intense solvation, viscosity, density, vapor pressure,

refractive index, relative permittivity, and freezing/boiling point. Studies have shown that, compared to individual solvents, bimolecular interactions show different results in the binary solvent mixtures1. In practical chemistry[2-6], mixed solvents are preferred for their reaction kinetics, chromatographic separations and hydrometallurgical application. In other cases, mixture medium helps enhance the physical characteristics of solvent medium such as polarity, density, viscosity etc. These mixture medium are specifically designed for discrete requirements so as to improve kinetic reactions[7]. Binary solvent mixtures facilitate to vary the solvent-solvent interaction and shed more light on understanding the solvation process[8]. Also, the mixed solvent system helps us to have more clarity on relative variation in solvent polarity as well as viscosity for fluorescence quenching experiments. Thus, our present work focuses on preferential solvation and bimolecular quenching reactions.

During the process of fluorescence quenching, whenever an external quenchers like CCL_4, C_6H_5Br, $C_3H_7KS_3$ metal ions, aliphatic amines, $CH3NO2$ are added to the fluorophore, there is a significant change in the environment[9-13]. Quenching reaction is illustrated by the equation

$$F^* + [Q] \xrightarrow{k_q} Product$$

where k_q is a bimolecular quenching rate constant. The study on fluorescence quenching plays a sensory role on various fields including biology, physical sciences, and medical sciences and also in chemical analysis. Type of quenching process is identified and analyzed by well-known Stern-Volmer (S-V) equation as given below

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \qquad (1)$$

Where I_0 and I are the fluorescence intensity of QO molecule in the absence and presence of quencher (aniline) molecule respectively, K_{SV} is a S-V constant which is obtained by the slope of the linear S-V plot which is then used to calculate quenching constant kq through the equation $K_{SV} = K_q\tau_0$ where, τ_0 is the lifetime of the solute without quencher. However, S-V plot can also show upward[14] or downward[15-17] curvatures. Upward curvature is due to combined static and dynamic quenching, intersystem crossing and ground state complex formation etc. whereas, negative curvature is attributed to formation of hydrogen bandings and influence of the quencher molecules etc. Remarkably, quenching mechanisms are affected by quencher concentration, viscosity and polarity of the solvents.Suppan's model can be applied to understand the preferential solvation and dielectric enrichment. Effects of Solvent polarity and viscosity on QO molecule is analyzed bimolecular quenching reactions.

The selection of binary solvent mixtures of AN-DX provides a significant range of polarity (36-2.1) and viscosity (1.178-0.344cP) variation. Steady state techniques are used to study fluorescence quenching of QO with aniline as quencher in different binary solvent mixtures. Bimolecular quenching reactions data which are expected to arise from one of these reasons may be represented by modified 'Stern – Volmer' equation or Lehrer equation[18, 19].

2. Experimental details

Organic compound namely Quinolin-8-ol (QO) is synthesized using standard method[20-21]whose molecular structures is depicted in Fig**ure** 1. Solution of binary solvent mixtures is prepared in AN and DX. Double distilled aniline which is tested for purity is used as quencher. The solution concentration of QO is maintained as1 x 10^{-4}M/L. Quencher concentration is varied from 0M to 0.10M in different binary solvent mixtures. Absorption and emission measurements are recorded using UV-VIS Spectrophotometer (Model: Shimadzu UV-1800) and Hitachi fluorescence spectrophotometer F-2000 with perpendicular geometry is made use of for fluorescence measurement. Solute is excited with its excitation wavelength at room temperature by taking fresh samples every time in a rectangular quartz cuvette with slit width (5nm:5nm), operating voltage (400 V) are maintained constant throughout the measurements. Figure 2(a) and 2(b) represent the typical fluorescence spectrum of QO molecule in pure AN and DX solvent mixtures and Lifetime of QO is shown in figure, in 0 % AN + 100 % DX with

quencher concentration of 0.00M are recorded using TCSPC nanosecond fluorescence spectrometer (Model: HORIBA FLUOROLOG) K U Dharwad, Karnataka, India, with 5% experimental error.

3. Results and discussion

3.1. Preferential solvation studies

In preferential solvation studies, when solvent medium is added to solute, the solute –solvent interaction takes place in such a way that the microenvironment within the solvation sphere solute shows different bulk properties [22-23]. During solvation process, solvent and solute molecules establish intermolecular hydrogen bonds.
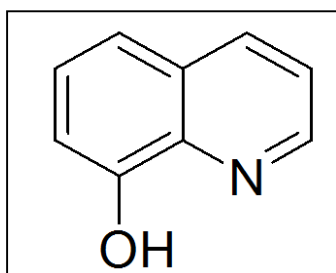

Figure 1. Molecular Structures of Quinolin-8-ol.

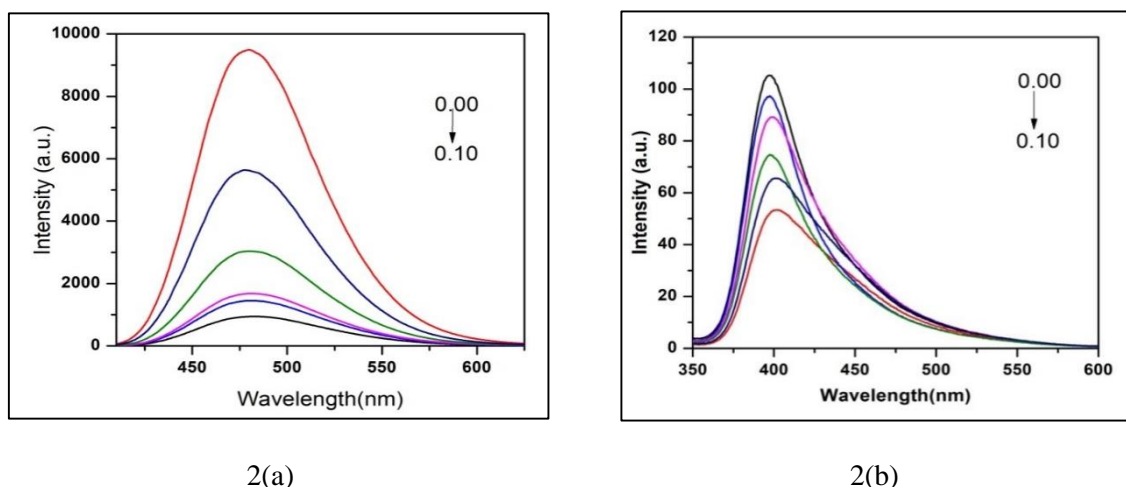2(a)   2(b)

Figure 2. Emission spectra of Quinolin-8-ol in 2a) 100 % AN and 2(b) 100 % DX with varying quencher concentrations 0.00, 0.02, 0.04, 0.06, 0.08, 0.10
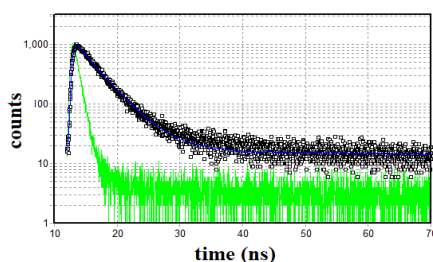

Figure 3. The fluorescence decay profile of Quinolin-8-ol in 0 % AN + 100 % DX with quencher concentration of 0.00M
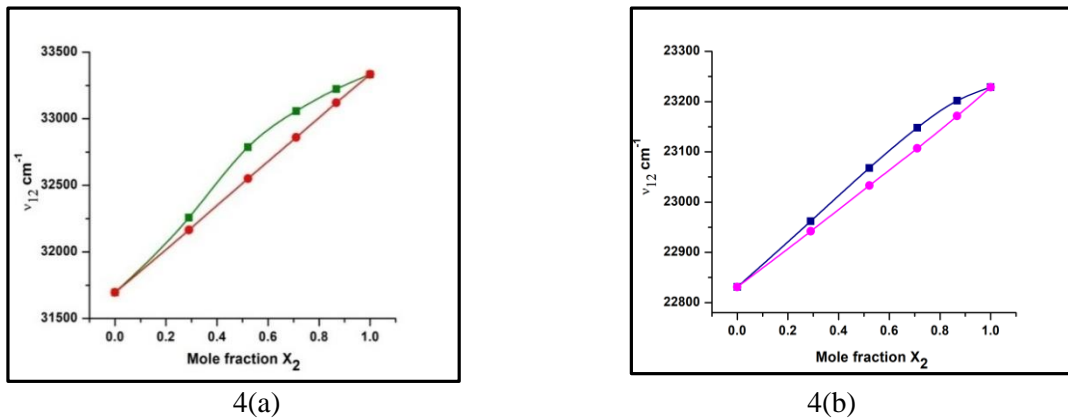
4(a)

4(b)

Figure 4. Plot of $\overline{\nu}_{12}$ vs. mole fraction of AN(X_2) in AN + DX mixture 4(a) absorption 4(b) emission of Quinolin-8-ol.
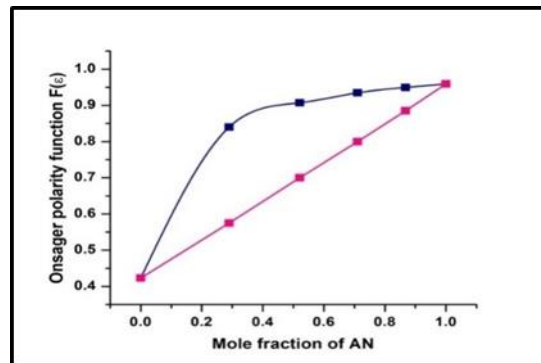

Figure 5. Plot of Onsager polarity function of vs. mole fraction of polar solvent (X_2) in AN+DX mixture.

Typically, solvation studies have been carried out by the assumption of a continuum solvent shell model[24]. From the literature survey it is found that, functional groups of the solvent usually make strong interaction with large dipole moment[25,26] experimentally preferential solvation is determined by the equation (2) as given below

$$X_2^L = \frac{\vartheta_{12} - \vartheta_1}{\vartheta_2 - \vartheta_1} \qquad (2)$$

Whereϑ_1, ϑ_2 and ϑ_{12} are the wave number of the solvent 1, solvent 2 and binary solvent mixture respectively. X_2^L is bulk mole fraction in the cybotaticregion. Preferential solvation index can be calculated by the equation (3)

$$\delta_{s2} = X_2^L - X_2 \qquad (3)$$

The second method[27] incorporates proportionality coefficient of the ratio of the molecules of solvent 2 in reference to solvent 1 in the cybotactic region of the solute given by parameter f_2/f_1. It is the ratio of molecules of the same solvent in reference to the other in the bulk of the solution, where

$$\frac{f_2}{f_1} = \left(\frac{X_1}{X_2}\right)\left(\frac{\vartheta_{12} - \vartheta_1}{\vartheta_2 - \vartheta_1}\right) \qquad (4)$$

This parameter is equivalent to the exchange constant K_{ps}[28] for the description of E_T[30]variation with composition in binary mixtures, where $K_{ps} = \frac{X_2^L X_1}{X_1^L X_2}$

Figure 4 (a) and 4(b) shows ground and excited state mole fraction with increasing for both absorption and emission maxima's in QO respectively. It is observed that, the experimental curve is deviated from the theoretical curve. Which indicates that solute under study is preferentially solvated

by AN and DX solvents. We have calculated different preferential solvation parameters and they are given in Table 1 and 2. From Tables 1 and 2 it is observed that δ_{s2} values are found to be positive. Also $\frac{f_2}{f_1}$ is >1for both absorption and emission maxima's. By above observations both in ZPE state and excited energy state of QO, solute is preferentially solvated by more polar solvent AN[29]. It determines non-specific interactions in the studied solvent mixtures.

In additionSuppan's equation[24] (5) is used to determine the non-linearity ratio of binary solvent mixtures with polarity of the solvent mixtures and mole fractions.

$$\rho_{exp} = \frac{2\int_0^1 (\gamma_{exp} - \gamma_{lin,bulk}) dx_p}{\Delta\gamma_{p-n}} \qquad (5)$$

where, ρ_{exp} is ratio of experimental nonlinearity, γ_{exp} is energy of the absorption or emission peak for a binary solvent mixture with a polar mole fraction of x_p and $\gamma_{lin,bulk}$ same for an ideal solvent mixture given by $\gamma_{lin,bulk} = x_p\gamma_p + x_n\gamma_n$. $\Delta\gamma_{p-n}$ represents the Stokes shift between AN and DX solvents.

Kauffmanand co-workers[30, 33] have shown that there can be a well approximated relation between ρ_{ps} and Zps given by $\rho_{ps} = 0.31Z_{ps}$ when ρ_{ps} is less than 1. Figure 5 shows the ideal and non-ideal behavior of QO in different binary solvent mixtures. The non-linearity ratio calculated from equation (5) is observed to be ρ_{dn}=0.533. And for QO ρ_{exp}= 0.150 for absorption band and for emission band ρ_{exp}=0.101 is observed. It is observed that, Non-linearity ratio calculated of the binary solvent mixtures is more than QO. This indicates that, preferential solvation of QO is not due to dielectric enrichment. This is also ascertained by negative preferential solvation index Zps which is obtained as -1.237for absorption and -1.394 for emission band for QO in its excited state.

3.2 Evaluation of Fluorescence Quenching Reactions

S-V plots with downward curvature are studied by many researchers[34-40]. It may be attributed due to the dark complex formation, hydrogen bond formation, charge transfer between acceptor –donor etc. Quenching data of the fluorescent probes is evaluated by tern-Volmer equation (6)[18, 19]given below.

$$I = (1-f)I_0 + \frac{fI_0}{1+K_{SV}[Q]} \qquad (6)$$

where *I* and *I₀* are the fluorescent intensities of QO molecule with and without quencher, *f* is the accessible fluorophores fraction, [*Q*] is the quencher concentration, K_{SV} is the S-V constant.

S-V equation can also be written in linear form as given in the below equation (7). Here graph of $I_0 /\Delta I$ versus 1/[Q] gives intercept 1/f and slope of the straight line K_{SV}.

$$\frac{I_0}{\Delta I} = \frac{1}{f} + \frac{1}{fK_{SV}[Q]} \qquad (7)$$

In our case, QO molecule shows downward curvature in different binary solvent mixtures of AN-DX. Using the above equation (6-7) quenching reactions are analyzed. Figure 6 shows the S-V plot constructed using equation (1). It is observed that S-V plot shows linear curvature at lower quencher concentration and downward curvature at higher quencher concentration. Linear S-V plot is attributed to dynamic quenching reactions and downward S-V plot may be due to inter and intra molecular hydrogen bond formation within the solution[37].

Identification of the quenching mechanism is done by proper interpretation of the K_{SV} data and spectral analysis. Figure7 shows the modified S-V plot which is constructed by using equation (7). It is observed that, there is no new or additional peaks appear in the absorption as well as in emission spectra of QO in different solvent mixture. This is attributed to the formation of non-fluorescent complex between the aniline and Quinolin-8-ol during the time of excitation. Table 3 represents the calculated values of K_{SV} and quenching rate parameters. It is observed that, f value is almost equal to unity (*f≤1*) and the variation of K_{SV} is observed between143.119 M⁻¹ for 100% DX + 0% AN to 27.875M⁻¹ for 0% DX + 100% AN respectively. The corresponding bimolecular quenching rate parameters are found to be more which suggests that quenching mechanism is efficient in binary solvent mixtures of AN-DX. Whereas, diffusion limited quenching reactions are verified by using the equation (8) and (9) as given below
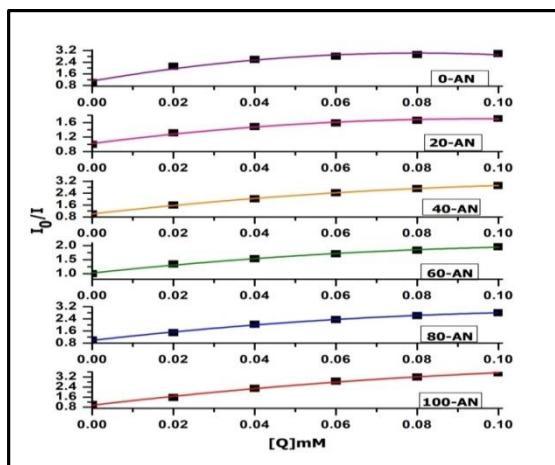
Figure 6. Stern-Volmer (S-V) plots of I0/I versus [Q] exhibiting negative deviation for Quinolin-8-ol +aniline system in different mixtures of AN+DX solvents.
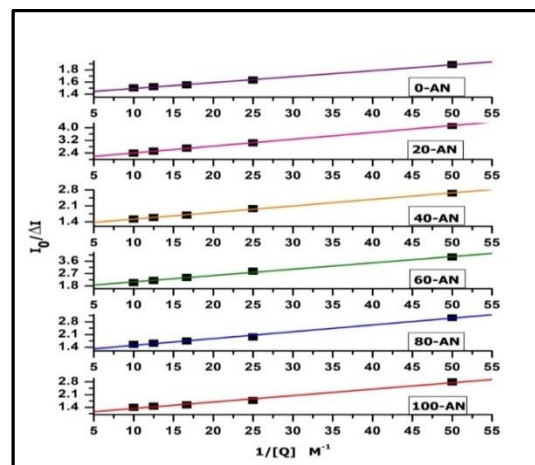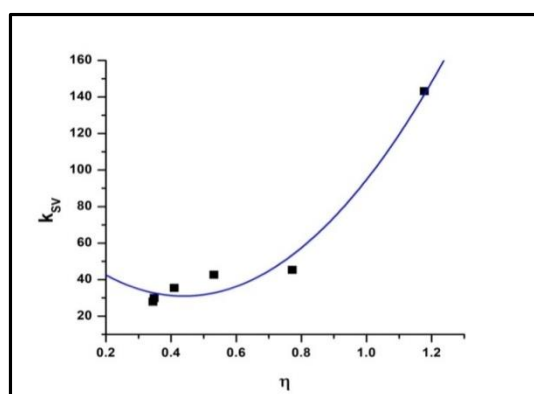

Figure 7. Modified linear Stern-Volmer (S-V) plots of I0/(I0–I) versus 1/[Q] in different mixtures of AN+DX solvents for Quinolin-8-ol +aniline system.
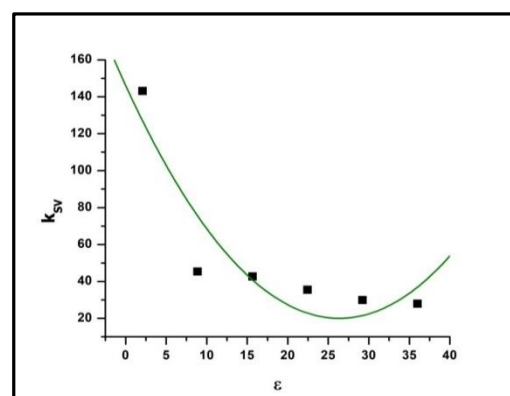
$$k_d = 4\pi N'DR \qquad (8)$$

where, k_d is diffusion rate constant, D is diffusion coefficient which is the sum of $D_S + D_Q$ in cm^2s^{-1}, N' is Avogadro number in per mill mole and R molecular radii which is the sum of $R_S + R_Q$ in $Å$[20]. Here the diffusion coefficients are calculated using Stokes-Einstein equation [40]

$$D = \frac{kT}{a\pi\eta R} \qquad (9)$$

where T is the absolute temperature, k is Boltzmann constant, , η is viscosity of the solvent (in cP), R is the radius of solute molecule and 'a' is Stoke – Einstein number. In our case 'a' value is taken 6 for QO molecule and 3 for aniline. From Table 3 it is observed that, as the polarity of the binary solvent mixtures increases K_{SV} and k_q values decreases. Figure 8(a) shows the increase in $^{LH}K_{SV}$ values with increase in viscosity of solvents and Figure 8(b) shows the increase of $^{LH}K_{SV}$ with ε, suggests that, the reacting species are of opposite charge. Further, the downward curvature is attributed to the stable inter and intra molecular hydrogen bonding in the ground state which is represented structures shown in Figure 9 and Figure 10.

8(a)

8(b)

Figure 8. Variation of S-V constant Ksv as a function of 8(a) viscosity (η) and 8(b) dielectric constant (ε) for Quinolin-8-ol.
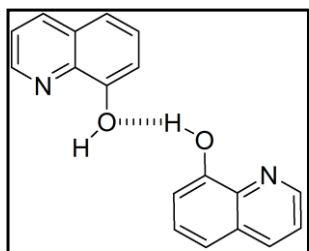
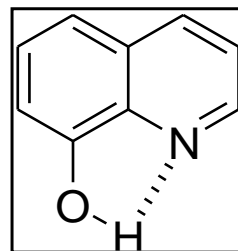**Figure 9.** Inter molecular hydrogen bonding between the two QO molecules

Figure 10. Intra molecular hydrogen bonding within the molecule.

Table 1: The values $\bar{\nu}_{12}$ cm^{-1}, bulk mole fraction (X2) of Acetonitrile (AN) in Dioxane (DX), local mole fractions (X_1^L of DX, X_2^L of AN), preferential solvation index δ_{s2} and preferential solvation constant $\left(\frac{f_1}{f_2}\right)$ for absorption maxima of Quinolin-8-ol.

Mixture Ratio	X_2	$\bar{\nu}_{12}$	X_1^L	X_2^L	δ_{s2}	$\frac{f_2}{f_1}$
DX$_{100}$	0	31695.72	-	-	-	-
DX$_{80}$/AN$_{20}$	0.2899	32258.06	0.6566	0.3434	0.0535	1.2810
DX$_{60}$/AN$_{40}$	0.5212	32786.89	0.3337	0.6663	0.1451	1.8344
DX$_{40}$/AN$_{60}$	0.7101	33057.85	0.1682	0.8318	0.1217	2.0186
DX$_{20}$/AN$_{80}$	0.8673	33222.59	0.0676	0.9324	0.0651	2.1096
AN$_{100}$	1	33333.33	-	-	-	-

Table 2: The values $\bar{}$ cm^{-1}, bulk mole fraction (X2) of Acetonitrile (AN) in Dioxane (DX), local mole fractions (X_1^L of DX, X_2^{Lb} of AN), preferential solvation index δ_{s2} and preferential solvation constant $\left(\frac{f_1}{f_2}\right)$ for emission maxima of Quinolin-8-ol.

Mixture Ratio	X_2	$\bar{\nu}_{12}$	X_1^L	X_2^L	δ_{s2}	$\frac{f_2}{f_1}$
DX$_{100}$	0	22831.05	-	-	-	-
DX$_{80}$/AN$_{20}$	0.2899	22962.11	0.6705	0.3295	0.0396	1.2038
DX$_{60}$/AN$_{40}$	0.5212	23068.05	0.4042	0.5958	0.0746	1.3544
DX$_{40}$/AN$_{60}$	0.7101	23148.15	0.2028	0.7972	0.0871	1.6050
DX20/AN80	0.8673	23201.86	0.0677	0.9323	0.0650	2.1054
AN100	1	23228.8	-	-	-	-

Table 3: Viscosity (η), dielectric constant (ε), the fraction of accessible flourophores (f), S-V constant (K_{SV}), biomolecular quenching rate parameter (k_q) and diffusion rate constant (k_d)

R_Y=3.157 Å, R_Q=2.840 Å, τ_0=3.51 ns

Solvents	η(cP)	Dielectric constant(ε)	f	$^{LH}K_{SV}$ (M^{-1})	$^{LSV}K_{SV}$	k_q x10^9 ($M^{-1}s^{-1}$)	k_d x10^9 ($M^{-1}s^{-1}$)
DX$_{100}$	1.1780	2.10	0.717	143.119	23.009	40.77	8.64
DX$_{80}$/AN$_{20}$	0.7720	8.88	0.508	45.359	8.539	12.92	13.18
DX$_{60}$/AN$_{40}$	0.5315	15.66	0.813	42.647	21.048	12.15	19.14
DX$_{40}$/AN$_{60}$	0.4099	22.44	0.612	35.456	9.546	10.10	24.82
DX$_{20}$/AN$_{80}$	0.3482	29.22	0.889	29.903	27.457	8.52	29.22
AN$_{100}$	0.3443	36.00	1.015	27.875	36.319	7.94	29.55

4. Conclusion

From the above discussion we can conclude that,

  (i)   QO is preferential solvated by more polar solvent acetonitrile.
  (ii)   As per Suppan's theory, non-linearity ratio calculated for the title molecule which is found to be smaller than the AN-DX binary solvent mixtures in the absence of the solute dipole.
  (iii)   Efficient fluorescence quenching is observed through S-V plots with negative deviation which is attributed to intermolecular hydrogen bond formations.
  (iv)   Quenching reactions are found to be diffusion limited in binary solvent mixtures of QO molecule.
  (v)   With these findings, QO molecule can be used for sensing applications

References

[1]   C. Reichardt, T. Welton 2011 *Solvents and solvent effects in organic chemistry* 4th edition (Germany: John Wiley & Sons)
[2]   S. S. Murthy 1998 Cryobiology, **36 (2)** 84.
[3]   L. R. Snyder 1974 Review. Analytical Chemistry **46 (11)**1384.
[4]   S. Roy, B. Bagchi 2013 The Journal of chemical physics **139 (3)** 034308.
[5]   Y. Marcus 2017 Pharm Anal Acta. **8 (1)** 537.
[6]   S. Wu, L. Wang, P. Zhang, H. El-Shall, B. Moudgil, X. Huang, L. Zhao, L. Zhang and Z. Feng 2018 Hydrometallurgy **175** 109.
[7]   V. V. Koppal, R. M. Melavanki, R. A. Kusanur and N. R. Patil 2018 Lumin. **33(6)** 1019.
[8]   A. Maitra A and S. Bagchi 2008 Journal of Molecular Liquids **137** 131.
[9]   H. S. Geethanjali, D. Nagaraja, R. M. Melavankiand R. A. Kusanur 2015 Journal of Luminescence **167** 216.
[10] H. S. Geethanjali, D. Nagaraja and R. M. Melavanki 2015Journal of Molecular Liquids **209** 669.
[11] C. TanielianC, L.Golder and C. Wolff 1984 Journal of Photochemistry **25** 117.
[12] R. M. Melavanki, R. A.Kusanur, J. S. Kadadevaramath and M. V. Kulkarni 2010 Journal of fluorescence. **20 (6)** 1175.
[13] L. Ding, H. Liu, L. Zhang, L. Li and J. Yu 2018 Sensors and Actuators B: Chemical **254** 370.
[14] J. K. Chen, S. M. Yang, B. H. Li, Lin C H and S. Lee 2018 Langmuir. **34 (4)** 1441.
[15] T. Htun 2004 Journal of fluorescence **14 (2)** 217.
[16] P. Bhavya, R. M. Melavanki, R. A. Kusanur, K. Sharma, V. T. Muttannavar and L. R. Naik 2018 Luminescence **33** 933.
[17] S. L. Bhattar, G. B. Kolekar and S. R. Patil 2009 Indian Journal of Chemistry Section A **48A** 1383.
[18] ChaofengDai, Yunfeng Cheng, Jianmei Cui and Binghe Wang 2010 Molecules **15** 5768.
[19] Gary AMolander, SarahL. J Trice and Spencer D. Dreher 2010 J. Am. Chem. Soc. **132** 17701.
[20] R. A. Kusanur, M. Ghate, M. V. Kulkarni 2004 Journal of Chemical Sciences **116 (5)** 265.
[21] R. A. Kusanur and M. V. Kulkarni 2014 Asian Journal of Chemistry **26 (4)** 1077.

[22] V. V. Koppal, R. M. Melavanki, R. A. Kusanur, P. Bhavya and N. R. Patil 2018 J. Mol. Liq. **260** 221.

[23] Y. Marcus Y 1983Australian journal of chemistry **36 (9)** 1719.

[24]   P. Suppan 1987 Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, **83 (2)** 495.

[25] C. Lerf and P. Suppan 1992 Journal of the Chemical Society Faraday Transactions **88 (7)** 963.

[26] A. KumaráLaha 1992 Journal of the Chemical Society, Faraday Transactions **88 (12)** 1675.

[27] M. Roses, J. Ortega and E. Bosch 1995 Journal of solution chemistry **24 (1)** 51.

[28] D. Skwierczynski and K. A. Connors 1994 J. Chem. Soc., Perkin Trans. **20** 467.

[29] G. Suganthi, C. Meenakshi and V. Ramakrishnan 2010 Journal of fluorescence. **20 (1)** 95.

[30] M. Khajehpour, C. M. Welch, K.A. Kleiner and J.F. Kauffman 2001 The Journal of Physical Chemistry A.**105 (22)** 5372.

[31] H. Kaur, S. Koley and S. Ghosh 2014 The Journal of Physical Chemistry B **118 (27)** 7577.

[32] S. Koley, H. Kaur and S. Ghosh 2014 Physical Chemistry Chemical Physics. **16 (40)** 22352.

[33] M. Khajehpour and J.F. Kauffman 2000 The Journal of Physical Chemistry A **104 (30)** 7151.

[34] J. R. Lackowicz 1983 *Principle of Fluorescence Spectroscopy* (New York: Plenum Press).

[35] K. K. Rohatgi-Mukherjee 1992 *Fundamental of Photochemistry* (New Delhi: Wiley Eastern Ltd).

[36] T. Htun 2004 J. Fluoresc. **14** 217.

[37] Vishwas D. Suryawanshi, Anil H. Gore, Laxman S.Walekar, Prashant V. Anbhule, Shivajirao R. Patil and Govind B. Kolekar 2013 Journal of Molecular Liquids **184** 4.

[38] Vivek Polshettiwar, Audrey Decottignies, Christophe Len and Aziz Fihri 2010 Chem Sus Chem. **5** 502.

[39] Cao Z, Nandhikonda P and Heagy MD 2009J. Org. Chem. **74** 3544.

[40] A. Einstein 1956 *Investigation on the Theory of Brownian movement* (USA: Courier Corporation).