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# Effect of Solvent on Spectroscopic Characteristics and Energy Transfer Processes of Some Laser Dyes

This article summarizes recent progress and the authors work in the field of solvation effects on spectroscopic properties of some organic compound. For many aromatic molecules the position and the structure of the fluorescence spectrum are strongly dependent on the solvent. The wavelength displacement can often be correlated with changes in solvent dielectric constant and the solvent index of refraction. A general review for the effect of the solvent is presented including studying the relationship between energy transfer processes and quantum efficiency with different solvent types.

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## 1. Introduction

The spectral properties of organic molecules are usually modified in solvation processes, Solvation refers to the reorientation of solvent molecules around a solute molecule, an effect which does not take place in rigid medium [1]. For many aromatic molecules the position and the structure of the absorption and fluorescence spectrum are strongly dependent on the used solvent properties. The wavelength displacement can often be correlated with changes in solvent dielectric constant and the solvent index of refraction. Usually prepared organic molecules solutions contain very small quantities of dye. Typical dye concentrations are 10-2 to 10-6 M. For this reason, the solvent in which the dye is dissolved plays an important role when defining physical properties. In moderate to higher polarity solvents the properties like Stokes' shifts, fluorescence quantum yields fluorescence lifetimes, radiative and non-radiative rate constants follow more or less linear correlation with the solvent polarity [2,3]. To determine if a molecule is polar it must be known two things, the polarity of the bonds in a molecule and how these bonds are arranged. So the molecule is considered polar if its center of negative and positive charge do not coincide this polar molecule have a dipole but if these dipoles are equally and in opposite to each other the dipoles cancel-out and the molecule considered nonpolar. Therefore, solvent polarity plays an important role in shifting the lasing wavelength of fluorescence and absorption spectrum of lasing compounds. In a majority of circumstances, increasing solvent polarity will shift the gain curve toward longer wavelength. In the case of more polar dyes, the shift can be as high as 20-60 nm [3]. Thus for many dyes which where use in optical, chemical, biomedical and technological field we must choose a suitable solvent coincide with the molecule properties and take on a count amount of a shift(increasing or decreasing the frequency) that including reaching to the required goals.

## 2. Materials and Methods

The existent theories on the intermolecular interaction in liquid express the supply of some type of interaction by different function of solvent parameters. Hence there are four types of interactions. The first one concerned the interaction between permanent dipoles of the solute and solvent. This contributes to the shift only if both molecules are polar. If the usual approximation is made, that the chromophore is a spherical particle of radius d, the following expression is obtained [1].

$$\Delta v_1 = v_1 - v_0 = D\left\{\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right\} \qquad (1)$$

Here ε is the dielectric constant, n is the refractive index of the solvent, and

$$\frac{-2}{d^3}\{(\mu^0_{solute})\,(\mu^1_{solute}\cos B - \mu^0_{solute})\} \qquad (2)$$

Here $\mu^1_{solute}$ and $\mu^0_{solute}$ are magnitude of the permanent dipole moments of the excited and ground states of the chromophore, respectively, and B is the angle between them in the molecule coordinate system.

Secondly, interaction between the permanent solute dipole and induced solvent dipole: This term arises in second-order perturbation- theory treatment. Its value is zero if the chromophore is nonpolar. Otherwise, the shift is given by the following expression [1]

$$\Delta v_2 = c\left\{\frac{n^2-1}{2n^2+1}\right\} \qquad (3)$$

Here

$$c = \frac{1}{d^3}\{(\mu^1_{solut})^2 - (\mu^0_{solut})^2\} \qquad (4)$$

The third interaction is between induced solute dipole and permanent solvent dipole: Here, the solute in a particular electronic state is represented by a spherical volume of radius d and of electronic polarizability $\alpha$ that is imbedded in continuum of dielectric constant $\epsilon$ and of refractive index n. In the limit that the solute is approximately isotropic, the shift due to this interaction is given by the following expression [1, 4].

$$\Delta v_3 = B\left\{\frac{(\varepsilon-n^2)\,(2\varepsilon+n^2)}{\varepsilon(n+2)^2}\right\} \qquad (5)$$

Here

$$B = -\left\{\frac{108ln^2\left(\frac{R}{d}\right)}{R^3}\,k_B T\,(\alpha_1-\alpha_0)\right\} \qquad (6)$$

Here kB is the Boltzmann constant, T the absolute temperature of the solution, R the radius of the spherical shell containing the molecule, and $\alpha_0$ and $\alpha_1$ are the electronic polarizabilities of the solute in the ground and excited electronic state, respectively

Finally, the interaction between naturally induced dipoles of solute and solvent: This interaction is present whether solvent and solute molecules are polar or non- polar. McRae found that the shift takes the following form [5,6]:

$$\Delta v_4 = A\left\{\frac{n^2-1}{2n^2+1}\right\} \qquad (7)$$

where A is taken to be a solute, transition-dependent, parameter which is assumed to be solvent independent. It has the form [1]:

$$A = -\left(\frac{1}{d^3}\right)\left[\left\{\sum_{i\neq 1} A_{1i}\left(\mu^{1i}_{solute}\right)^2\right\} - \left\{\sum_{i\neq 0} A_{0i}\left(\mu^{0i}_{solute}\right)^2\right\}\right] \qquad (8)$$

Here $\mu's$ are to represent the transition dipoles and A's some weighing factors. In the two cases, when the solvent and solute are such that one is polar and one is nonpolar, or if both are nonpolar, the frequency shifts in absorption and emission are predicted to be [7,8].

## 3. Experimental Work

Coumarin 334 dye (denoted as C334) ($C_{17}H_{17}NO_3$) with molecular weight of 283.33 g/cm$^3$, Rhodamine 590 dye (denoted as R590) ($C_{28}H_{31}N_2O_3Cl$) with molar mass of 479.02 g/mol supplied by Lambda Physic were used in this work. Also, ethyl alcohol ($C_2H_5OH$), DMSO ($C_2H_8OS$ $C_2H_8OS$) with molar mass of 78.13 g/mol and Chloroform ($CHCl_3$) with molecular weight of 119.38 g/mol, were used as solvents.

The dye solutions were prepared by dissolving the required amount of the dye in the solvent. The required weight of the dye was measured using a Matter balance of 0.1mg sensitivity. This weight W (in g) was calculated using the following equation:

$$W = M_w V\,C/1000 \qquad (9)$$

where $M_w$ is the molecular weight of the dye (g/mol), V is the volume of the solvent (mL), and C is the dye concentration

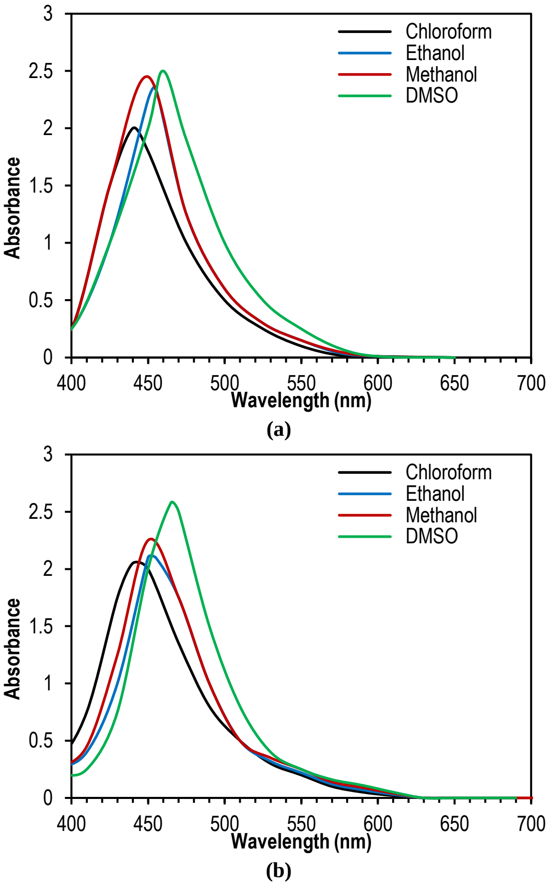
To prepare a dilute solution, the following equation was used:

$$C_1\,V_1 = C_2\,V_2 \qquad (10)$$

where $C_1$ is the high concentration ,$V_1$ is the volume before dilution (L), $C_2$ is the low concentration, and $V_2$ is the total volume after dilution [l]

## 4. Results and Discussion

Laser dyes have shown a significant influence throughout using solvent. The normalized absorption spectra of C334 and R590 dye solutions are shown in Fig. (1). A reasonable shift occurs in absorption spectrum as a result of mutual interaction between solute and solvent. This shift depends on the nature of this interaction, the solvent type, and the concentration of the dye. This figure clarifies the influence of the solvent on the position of absorption peaks. The spectra are shifted towards longer wavelength as the polarity of the solvent increases.



(a)

(b)

**Fig. (1) Absorption spectra of (a) Coumarin 334 and (b) Rhodamine 590 in different solvents**

Fluorescence spectra of these dyes had also been affected by solvent polarity, as can be seen in Fig. (2) and the peak positions are listed in table (1). The peaks of fluorescence bands are largely red-shifted when the solvent polarity increases as compared to absorption bands under the same conditions. This fact indicates an increase in dipole moment of excited state compared to ground state [9]. It can be stated that the peak at lower wavelength of these spectra is corresponding to non-aggregated molecules and the peak at longer wavelength is caused by excimer emission of aggregated molecules.

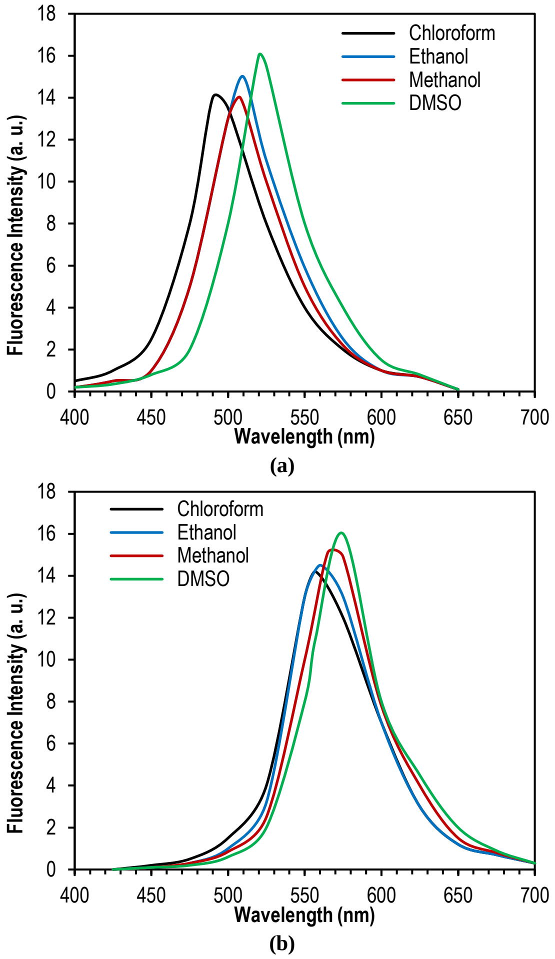


**Fig. (2) Fluorescence spectra of (a) Coumarin 334 and (b) Rhodamine 590 in different solvents**

**Table (1) Peak wavelengths of absorption and fluorescence spectra of both dyes in different solvents**

| Solvent | Molecules | $\lambda_{abs}$ (nm) | $\lambda_{fluo}$ (nm) |
|---|---|---|---|
| DMSO | Coumarin | 462 | 520 |
| | Rhodamine | 542 | 574 |
| Methanol | Coumarin | 453 | 508 |
| | Rhodamine | 534 | 570 |
| Ethanol | Coumarin | 451 | 506 |
| | Rhodamine | 530 | 563 |
| Chloroform | Coumarin | 442 | 494 |
| | Rhodamine | 523 | 558 |

Because the transfer of excitation energy between molecules be an effective and important phenomenon in extensive application [10], and particularly in the development of dye laser, the transfer of excitation energy between C334 and R590 was investigated to clarify the effect of solvent on this process. Figure (3) shows the effect of solvent on the efficiency of energy transfer process.

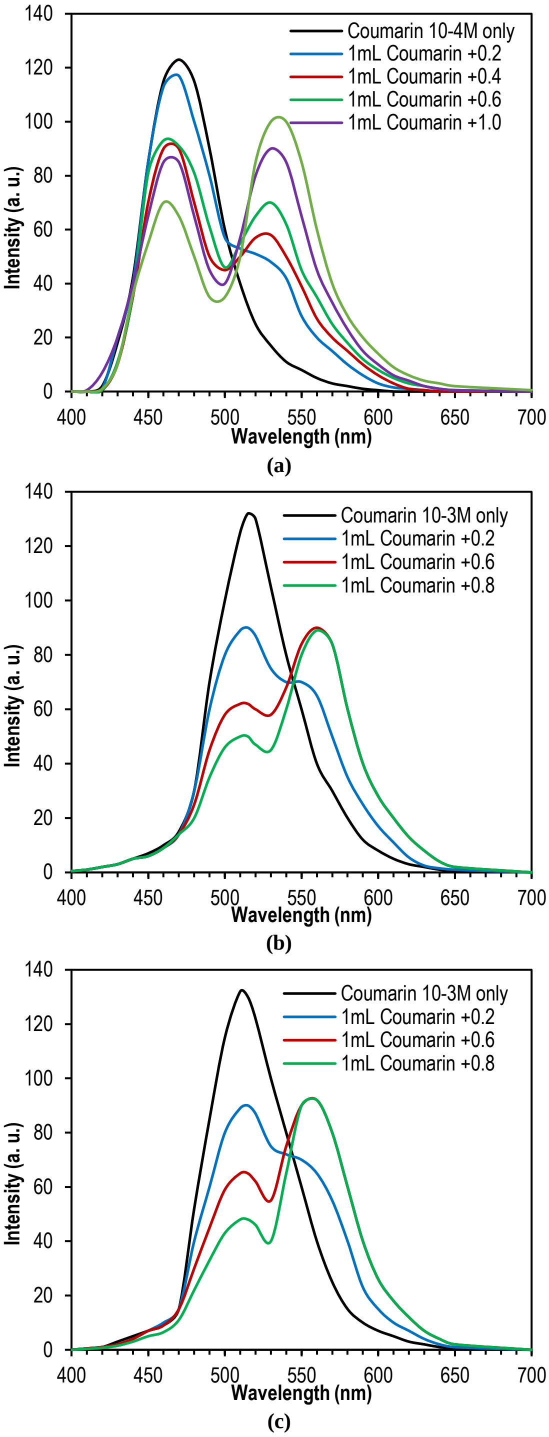


**Fig. (3) Energy transfer process between Coumarin 334 and Rhodamine 590 (a) in DMSO, (b) in ethanol, and (c) in chloroform**

There is a clear relation between the solvent polarity and quantum efficiency [11] and the quantum efficiency of energy transfer process had been calculated by the following relation to determine the optimal solvent for these processes:

$$E = 1 - \frac{\phi_D}{\phi_D^{\circ}} \qquad (11)$$

Here $\phi_D$ and $\phi_D^{o}$ are the quantum yield of donor fluorescence in the presence and absence of acceptor, respectively. The value of E can thus be determined by experiment. The results were listed in table (2)

Throughout the calculation of quantum yield for dye solutions in different solvents and different concentrations, it was found that its value decreases with increasing the solvent polarity. In DMSO, for example, the quantum efficiency decreases due to the high polarity of the solvent, while in ethanol, it was found that the value of quantum efficiency reaches to its maximum value. This indicates that the efficiency of this processes can be improved by using a particular solvent.

## 5. Conclusion

The polarity of solvent plays an important role in shifting lasing wavelength in laser dyes as increasing the polarity of solvent causes a shift in gain curve toward longer wavelengths. It is clearly observed that using ethanol, which has refractive index of about 1.361 (lower than that of DMSO and chloroform), a homogeneous lasing spectrum is obtained at a low threshold pump beam intensity. So, this property makes ethanol one of the best solvents for laser dyes. Although, using DMSO as a solvent produces lasing spectrum with higher intensity.

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**Table (2) Quantum efficiency of energy transfer processes in different solvents**

| Donor Concentration [M] | Acceptor Concentration [M] | Q (Ethanol) | Q (DMSO) | Q (Chloroform) |
|---|---|---|---|---|
| $0.5 \times 10^{-4}$ | 0.16 | 68.52 | 35.61 | 35.57 |
| | 0.28 | 69.16 | 34.14 | 34.10 |
| | 0.37 | 72.76 | 35.08 | 35.04 |
| | 0.44 | 78.58 | 33.52 | 33.48 |
| | 0.5 | 83.10 | 38.08 | 38.04 |
| | 0.54 | 87.51 | 49.63 | 49.57 |
| | 0.58 | 87.99 | 52.78 | 52.72 |
| | 0.61 | 88.55 | 63.32 | 63.25 |
| | 0.64 | 90.75 | 73.02 | 72.93 |