Self-Absorption Effect on the Spectral Properties of 2-Methylnaphthalene in Different Solvent

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Abstract

The fluorescence spectra for 2-Methylnaphthalene solution which dissolved in hexane, ethanol and paraffin as a function of concentration at excitation wavelength (λex= 270nm) was measured and investigated the quantum efficiency (qFM), the radiative fluorescence lifetime (τFM), rate parameter of radiative (KFM) and non-radiative (KIM) processes were calculated. Where the quantum efficiency is equal to (qFM=0.20) and (qFM=0.15) for 2-methylnaphthalene solution dissolved in hexane and ethanol at concentration [10^{-4}M], respectively. But the quantum efficiency of 2-methylnaphthalene in paraffin is equal to (qFM=0.24) at same concentration. This different in the values of quantum efficiency refers to different in polar solvent and viscosity of solutions. It's found that the increase in molar concentration led to decrease the intensity of spectrum, quantum efficiency and rate parameter of radiative process.
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(K_FM) because of the effect of self-absorption phenomena. In additional, the quantum efficiency measurement was calculated relative to standard compound of naphthalene with quantum efficiency (q_FM=0.14) at same excitation wavelength. All measurement were carried at room-temperature.

Theory

Luminescence is the emission of light from any substance and occurs from electronically excited states. Luminescence formally divided into two categories: fluorescence and phosphorescence depending on the nature of the excited state(1). Fluorescence is a radiative process when molecules transition between states of the same multiplicity (S_1 → S_0). But when molecules transition between states of different multiplicity is described as phosphorescence (T_1 → S_0). Symbols (S- Singlet, T- Triplet) refers to singlet and triplet electronic states respectively. While non-radiative processes occur when molecules transition between isoenergetic vibrational levels of different electronic states. Such transitions are normally preceded by radiationless thermal activation of the initial electronic state and followed by radiationless de-activation of the final electronic state. A radiationless transition between states of the same multiplicity is described as internal conversion(2). One between states of different multiplicity is described as intersystem crossing as shown in figure[1].

![Jablonski diagram](image)

*Fig.-1: Jablonski diagram the Symbols (ISC and IC) refers to intersystem crossing and internal conversation(3).*
That each processes a rate constant determines probability occurrence that process. The molecular fluorescence quantum efficiency ($q_{FM}$) which is defined the ratio of the number of fluorescence photons emitted by a system of molecules in dilute solution to the number of molecules excited into $S_1$ (the number of absorbed photons) is equal to:

$$q_{FM} = \frac{K_{FM}}{K_{FM} + K_{IM}} = \frac{\tau_M}{\tau_{FM}} \quad \text{............. (1)}$$

Where $K_{FM}$ and $K_{IM}$ the rate constant of radiative emission (fluorescence) and radiationless processes by internal quenching.

$\tau_M$: the molecular fluorescence lifetime of the excited state which is defined the average time that molecule spends in the excited state prior to return to the ground state and is equal to:

$$\tau_M = \frac{1}{K_{FM} + K_{IM}} \quad \text{............. (2)}$$

The lifetime of the fluorescence in the absence of non-radiative processes is called the intrinsic or natural lifetime, which is defined as the reciprocal of the radiative transition probability $K_{FM}$ (in Sec$^{-1}$), is given by (3):

$$\tau_{FM} = \frac{1}{K_{FM}} \quad \text{............. (3)}$$

The intensity of fluorescence can be described by a wide verity of processes such decreases in intensity are called quenching. Quenching can occur by different mechanisms. Collision quenching occurs when the excited state of fluorophore is deactivated upon contact with some other molecule in solutions, other type of quenching is radiative migration (4). There is commonly an overlap of the 0-0 bands of the fluorescence and absorption spectra, the spectral overlap may be considerable and lead to self-absorption of the fluorescence emission. If ($a$) is the probability of self-absorption of an emitted photon, so that ($1- a$) is the photon escape probability. Photons which are absorbed are re-emitted with quantum efficiency ($q_{FM}$) and lifetime ($\tau_M$). The phenomena of self- absorption is reduced through the use of solutions with a low concentration or by the correction to the value of quantum yield ($\Phi_{FM}$) and molecular lifetime ($\tau$) were equal to the following:

$$\Phi_{FM} = \frac{q_{FM}(1-a)}{1-aq_{FM}} \quad \text{............. (4)}$$
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\[ \tau = \frac{1}{(1-a)K_{FM} + K_{IM}} \]

Practically, the probability of self-absorption (a) is calculated from the following equation:
\[ a = 1 - \frac{A_m^T}{A_m} \]
Where \( A_m^T \) and \( A_m \) represent the area under the fluorescence spectrum of the concentrated and diluted solution, respectively. Normalized in the low-energy region.

Because of the many problems associated with absolute quantum yield measurements, several simple relative methods have been devised which substitute a compound of "known" quantum yield in place of standard scatter as a reference. Relative measurement full conveniently into two classes: optically dense and optically dilute methods (5).

The determination of quantum yields using optically dilute solutions is the most common method currently employed. The optically dilute measurement rests on Beer's law:

\[ I_a = I_0 B = I_0 (1 - 10^{-Ad}) \]

Where
B: is the fraction of light absorbed by the sample.
\( I_0 \): is the intensity of the incident light (quanta/sec).
\( I_a \): is the intensity of the absorbed light (quanta/sec).
A: is the absorbance/cm.
d: is the path length (cm).

If the luminescence intensity for each compound is proportional to \( I_0 B \), then the expression for the quantum yield becomes (6):

\[ \Phi_{FM} = \Phi_{FR} \left( \frac{B_x}{B_x} \right) \left( \frac{I(\lambda x)}{I(\lambda r)} \right) \left( \frac{n_x^2}{n_r^2} \right) \left( \frac{D_x}{D_r} \right) \]

Where
\( I(\lambda) \): is the relative intensity of the exciting light at wavelength \( \lambda \).
n: is the average refractive index of the solution to the luminescence.
D: is the integrated area under the corrected emission spectrum.
Subscripts x and r refer to the unknown and reference solution.
A more commonly used relation is obtained by expanding the exponential of eq. (7) in a power series of \((Ad)\) and truncating the result:

\[
B = (1 - 10^{-Ad}) = 1 - [1 - 2.303Ad + (2.303Ad)^2/2 + \ldots]\ldots (9)
\]

At low concentration or in optically dilute solution

\[
B = 2.303Ad \ldots (10)
\]

Substitution of the approximate expression for \(B\) in eq. (8) yield the working equation commonly employed by investigators using calibrated spectrometers

\[
\Phi_{FM} = \Phi_{FR} \left( \frac{A_r}{A_x} \right) \left( \frac{I(\lambda_r)}{I(\lambda_x)} \right) \left( \frac{n_r^2}{n_x^2} \right) \left( \frac{D_x}{D_r} \right) \ldots (11)
\]

Many assumptions are inherent in eq. (8) and (11). For both unknown and reference it is assumed that:

1- The integrated luminescence intensity is proportional to the fraction of light absorbed.
2- All geometrical factors are identical.
3- The excitation beams are monochromatic.
4- Reflection losses are the same internal reflection effects are equal.
5- Re-absorption and reemission are negligible.
6- All light emanating from the cuvette is isotropic.

If any one of these conditions does not hold, serious error can be introduced into the final value. The approximate eq. (9) introduces \(\approx 5\%\) systematic error for \(Ad = 0.043\) if the detector views either symmetrically around the centre or the entire cuvette. If this error is unacceptable, the exact form of the equation or lower optical densities must be used(7).

Alternatively, both the standard and the unknown solution can be made up to have equal absorbencies at their respective exciting wavelengths and the need for any correction factor is eliminated. Even if the two experimental optical densities are not exactly the same, eq. (11) may be used for relatively high optical densities if the two absorbencies are comparable. Equations (8) and (11) do not correct for re-absorption and re-emission. Fortunately, the real beauty of the optically dilute method is that these corrections are rarely necessary unless the material happens to
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be excited in an absorption minimum and there is substantial overlap between the absorption & the emission.

Many of researchers used this method such as J.B. Birks and J.B.Aladekoman(8), to determination of quantum efficiency for aromatic compound like naphthalene and its derivatives such as (2-methylnaphthalene),(2,6-dimethylnaphthalene) and (2-ethylnaphthalene). In 1972, A.W. Jackson(9), calculate quantum yield and lifetime of (2,3-pentanedione) at various temperature. In 1984 (10) study the fluorescence quantum yield and free rotor effect and found the fluorescence quantum yield ($\Phi_{FM}$) for dyestuff(1) approaches unity in ethanol-ether (1:1) glass at 98˚.

Fluorescence and phosphorescence properties of naphthalene in aqueous D-Glucose solutions containing (6-Deoxy-6-iodo-β-cyclodextrin) at room temperature has been observed by Sanyo Hamai in 1997(11), the fluorescence quantum yield of naphthalene in aqueous solution was evaluated to be ($q_{FM} = 0.086$). T.S. Ahn(12) andet al. in 2007, study self-absorption correction for solid-state photoluminescence quantum yield obtained from integrating sphere measurements. In 2008(13) study the measurement of the fluorescence quantum yield using a spectrometer with an integrating sphere detector. Ryszard Misiak(14) and et al., in 2011 study self-absorption correction and efficiency calibration for radioactivity measurement of environmental samples by gamma-ray spectrometry.

**MATERIALS AND METHODS**

The solution of 2-Methylnaphthalene in hexane, ethanol, paraffin prepared at room temperature with concentration [10⁻⁴, 10⁻³, 10⁻², 5×10⁻² M]. 2-Methylnaphthalene purchased from Uma Company imported from India. Fluorescence spectra were recorded on a (JASCO- model-FP-770) spectrofluorometer; samples were mounted in cubic cell of quartz dimensions (1×1×5) cm³ at right angle 90˚ with incident beam. This optical geometry was chosen to eliminate the effect of scattered incident radiation and reduce the phenomenon of self-absorption. The fluorometry has dedicated computer which control instrumental operating (excitation and emission wavelength, monochromator slit width, detector parameter).
In this research we use exciting wavelength ($\lambda_{ex} = 270 nm$) in the measurements. When measured the concentration [$10^{-4}$, $10^{-3}$ M] we used slit width of excitation ($S_{ex} = 1.5 nm$) and same value to slit width of emission ($S_{em} = 1.5 nm$), but in concentration [$10^{-2}$, $5 \times 10^{-2}$ M] the slit width of excitation ($S_{ex} = 3 nm$) and slit width of emission ($S_{em} = 5 nm$), the measurements were made in the same sensitivity of photomultiplier where the oxygen was expelled by evacuation prior to sealing the specimen cell. Naphthalene use as a standard compound dissolved in hexane, ethanol and paraffin with concentration [$10^{-4}$ M] and quantum efficiency equal to ($q_{FM} = 0.14$), at room temperature.

**RESULTS AND DISCUSSION**

In this research, we study fluorescence spectra of naphthalene solution dissolved in hexane, ethanol and paraffin with concentration [$10^{-4}$ M] and then study the solutions of (2MN) is one of the naphthalene derivatives, is naphthalene molecule with added methyl group ($CH_3$) as shown in figure [2], with concentration [$10^{-4}$, $10^{-3}$, $10^{-2}$ & $5 \times 10^{-2}$ M] and observation the effect of increasing concentration in the form of the fluorescence spectrum as well as calculation of quantum efficiency.

![Naphthalene and Methylene](image)

**Chemical formula of compounds**

Figure [3-a] shows the fluorescence spectrum of naphthalene dissolved in hexane at concentration [$10^{-4}$ M] at exciting wavelength ($\lambda_{ex} = 270$ nm), where it appears in the shape of spectrum is structure consists of two peaks located at wave numbers ($29.673 \times 10^3 cm^{-1}$) ($28.409 \times 10^3 cm^{-1}$) which are found the same values of fluorescence spectrum of naphthalene solutions in ethanol and paraffin as in figure [3-b, c]:
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Fig.-3: fluorescence spectrum of naphthalene in hexane, ethanol and paraffin at concentration $[10^{-4}]$ M, $\lambda_{ex}=270$ nm.

The fluorescence spectrum of 2-Methylnaphthalene solutions has been measured at different concentrations are $[10^{-4}, 10^{-3}, 10^{-2}, 5\times10^{-2}$ M] in the solvents mentioned previously, at exciting wavelength ($\lambda_{ex}=270$ nm). We have found that the fluorescence spectrum of 2-Methylnaphthalene in hexane at concentration $[10^{-4}$M] be structure into three peaks located at wave numbers $(31.4 \times 10^3$ cm$^{-1}$), $(30.66 \times 10^3$ cm$^{-1}$) and $(29.93\times10^3$ cm$^{-1}$) as in figure [4]. We found the value of quantum efficiency is equal to($q_{FM} = 0.20$), notes the increase in the value of quantum efficiency comparison with the quantum efficiency of naphthalene, the reason is due to the influence of methyl group substitutes to increase the rate of radiative processes.
Fig. -4: fluorescence spectra of 2MN in hexan at concentration $=10^{-4}$ M, $\lambda_{ex}$ = 270 nm

At concentration $[10^{-3} \text{ M}]$ noted decrease in the relative fluorescence intensity and disappear the first peak, where the spectrum shows two peaks located at wave number $(30 \times 10^{3} \text{ cm}^{-1})$ and $(29.26 \times 10^{3} \text{ cm}^{-1})$, figure-5.

Fig.-5: fluorescence spectra of 2MN in hexan at concentration $=10^{-3}$ M, $\lambda_{ex}$ = 270 nm

But when the concentration equal to $[10^{-2}, 5 \times 10^{-2} \text{ M}]$ the second peak disappear because of self-absorption was increase and the fluorescence spectra is structureless as shown in figure [6]:
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Fig.-6: fluorescence spectra of 2MN in Hexan at concentration (a) \([10^{-2}] \) M, (b) \([5\times10^{-2}] \) M, \(\lambda_{ex}=270 \) nm

In addition, for the fluorescence spectrum of 2-Methylnaphthalene in ethanol and paraffin at same concentrations shown in figure (7), (8). The quantum efficiency of 2-Methylnaphthalene in ethanol is equal to \(q_{FM}=0.16\), this difference in the value of a quantum efficiency due to the different type of solvent. The decrease in the intensity of the peaks with increased of concentration is caused by the phenomenon of self-absorption where re-absorption of emitted photons before leaving the solution by the molecules in the ground state leading to decrease of quantum efficiency by (2%) or (3%), respectively, for the value at the concentration \([10^{-4}] \) M]and using the necessary correction, according to the relation (4), (6) was reached approached value.
Fig.-7: fluorescence spectra 2MN in Ethanol, $\lambda_{ex}=270$ nm, (a) $[10^{-4} \text{ M}]$, (b) $[10^{-3} \text{ M}]$, (c) $[10^{-2} \text{ M}]$ (d) $[5 \times 10^{-2} \text{ M}]$

That decrease in the value of quantum yield will be accompanied by an increase in the fluorescence lifetime ($\tau_{FM}$) and thus a decrease in the rate parameter of radiation processes and increase the rate parameter of radiationless processes.
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Fig. 8: Fluorescence spectra 2MN in Paraffin, λ<sub>ex</sub>=270 nm, (a) [10<sup>-4</sup> M], (b) [10<sup>-3</sup> M], (c) [10<sup>-2</sup> M], (d) [5× 10<sup>-2</sup> M]

Where increasing rate of non-radiative transition (internal conversion).

The tables [1], [2] and [3] describe the values of quantum efficiency, rate parameter of radiative and non-radiative processes depending on previous relationships.
Table -1: the quantum efficiency, rate of radiative and non-radiative processes of 2MN solutions in Hexane.

<table>
<thead>
<tr>
<th>[M] mol</th>
<th>$\Phi_{FM}$</th>
<th>$\tau_{MNsec}$</th>
<th>$\tau_{FMsec}$</th>
<th>$K_{FM} \times 10^{6} \text{ sec}^{-1}$</th>
<th>$K_{IM} \times 10^{6} \text{ sec}^{-1}$</th>
<th>$(K_{FM})_0 \times 10^{6} \text{ sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>0.20</td>
<td>59</td>
<td>295</td>
<td>3.4</td>
<td>13.2</td>
<td>1.7</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.17</td>
<td>60</td>
<td>352</td>
<td>2.8</td>
<td>13.7</td>
<td>1.5</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0.14</td>
<td>60.8</td>
<td>434</td>
<td>2.3</td>
<td>14</td>
<td>1.2</td>
</tr>
<tr>
<td>$5 \times 10^{-2}$</td>
<td>0.12</td>
<td>61</td>
<td>469</td>
<td>2.1</td>
<td>14.13</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Table -2: the quantum efficiency, rate of radiative and non-radiative processes of 2MN solutions in Ethanol.

<table>
<thead>
<tr>
<th>[M] mol</th>
<th>$\Phi_{FM}$</th>
<th>$\tau_{MNsec}$</th>
<th>$\tau_{FMsec}$</th>
<th>$K_{FM} \times 10^{6} \text{ sec}^{-1}$</th>
<th>$K_{IM} \times 10^{6} \text{ sec}^{-1}$</th>
<th>$(K_{FM})_0 \times 10^{6} \text{ sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>0.15</td>
<td>47</td>
<td>313</td>
<td>3.15</td>
<td>18.1</td>
<td>1.7</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.13</td>
<td>47.5</td>
<td>365</td>
<td>2.7</td>
<td>18.5</td>
<td>0.97</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0.12</td>
<td>47.8</td>
<td>398</td>
<td>2.5</td>
<td>19.1</td>
<td>0.9</td>
</tr>
<tr>
<td>$5 \times 10^{-2}$</td>
<td>0.11</td>
<td>48</td>
<td>436</td>
<td>2.3</td>
<td>19.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table-3: the quantum yields of 2-MN solutions in Paraffin

<table>
<thead>
<tr>
<th>[M] mol</th>
<th>$\Phi_{FM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>0.24</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.19</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0.17</td>
</tr>
<tr>
<td>$5 \times 10^{-2}$</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Reduced intensity of fluorescence spectrum and the quantum efficiency with increased an molar concentration for 2-Methylnaphthalene because of the phenomenon of self-absorption of emitted photons before leaving the solution by the molecules as a result that increase in radiationless processes and decrease radiation processes. So effect methyl group (CH$_3$) substation in naphthalene molecule, an increase the rate of radiative transition and quantum efficiency compared with naphthalene compound.
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REFERENCES