3.1 Introduction:

The effects of solvent environment on absorption and fluorescence spectra of highly fluorescent organic compounds has been the subject of several great motivating [1] investigations. Effects are complex, and are due to following several factors that affect the absorption and fluorescence emission spectra and quantum yields:

1. Solvent polarity
2. Rate of solvent relaxation
3. Probe conformational changes
4. Rigidity of the local environment
5. Internal charge transfer
6. Intermolecular charge transfer
7. Proton transfer and excited state reactions
8. Probe-probe interactions
9. Changes in radiative and non-radiative decay rates

These multiple effects provide many opportunities to investigate the effect of local environment on a fluorophore. However, it is difficult to know which effect is dominant in a particular experimental system, and predictably more than one effect will simultaneously affect the fluorophore. Excitation of a molecule by photon causes a redistribution of charges leading to conformational changes in the excited state. This can lead to an increase or decrease of dipole moment of the excited state as compared to the ground state.

A dipole moment represents a direct measure of electron distribution in a molecule of known geometry [2]. It is a physical constant which can be obtained by many experimental and theoretical techniques. A number of excellent texts,
monographs, and reviews devoted to dipole moments are available and contain a detailed discussion of the theory of dipole moments. Although most of these references are not recent [3-8], they provide an excellent source of information and a starting point for our research work. It seems worthwhile to point out here that, dipole moments convey most important sources of structural information about organic molecules in ground and excited state. Examples of the various practical applications of dipole moments include, but are not limited to: discrimination between isomers (cis and trans, o, m, and p, tautomers, etc.), conformational analysis, studies of molecular geometry, supporting evidence for resonance hybrids, information about the polar character of molecules (solubility in different solvents and permeability through membranes), information about electrical effects of substituent's (inductive, resonance), studies of hydrogen bonding and electron donor–acceptor interactions (e.g., charge transfer complexes) etc...

Experimental ground-state ($\mu_g$) dipole moments can be obtained in different ways. The first and most widely used approach is based on the measurement of dielectric constants. The second group [9–11] of methods make use of microwave spectroscopy and molecular beams (electric resonance, Raman spectroscopy, Stark effect etc.). Experimental techniques for the determination of excited state dipole moments are based on a change of the position of a spectral band (in an electronic spectrum) caused by an electric field which can be external (electrochromism) or internal (solvatochromism). Electro optical methods (electrochromism) are more accurate but are experimentally more difficult as they include electric polarization of fluorescence [12,13], electric dichroism [14], microwave conductivity [15] and stark splitting [16,17] are considered to be more accurate, but their use is limited to equipment sensitivity and the studies have been relatively restricted to very simple
molecules. The solvatochromic [18] method (solvent-shift) offers simplest method to

determine the dipole moments and is based on the shift of absorption and fluorescence

maxima used to estimate the excited state dipole moments of different molecules and

this method does not use any external field. It has long been known that

UV/VIS/near-IR absorption spectra of chemical compounds may be influenced by the

surrounding medium and solvents can bring about a change in the position, intensity,

and shape of absorption bands, this phenomenon is known as solvatochromism.

Knowledge of the dipole moment in the ground and excited state reflects the

charge distribution in the molecule and helps to assess the efficiencies of the quantum

chemical derivations, electronic and geometrical structure of the molecule in the

short-lived state, knowledge of the electronically excited molecule is quite useful in

deciphering the nature of the excited states, in determining the course of

photochemical transformation, electron correlation treatments and calculating the

electron density distribution in the singlet and triplet state. It has been useful in the

extraction of parameters like molecular polarizability in nonlinear optical materials

using electro optic methods [19]. An excellent overview of the solvatochromic

method by Koutek [18] has shown to facilitate satisfactory results. The statistical

analysis performed using various expressions in the process of identifying the best

parameters were based on the bulk solvent properties such as refractive index (n) and

dielectric constant (ε). The best expression identified by Koutek [18] was used earlier

by Kawski [13, 19], Bakshiev [20], Chamma-Viallet [21], Lippert [22] and Suppan

[23] several reports are available in the literature in which the above methods have

been used independently or with other methods to evaluate the excited state dipole

moments. Several organic compounds such as coumarin 6, coumarin7 and

coumarin30 have been widely studied by U.S.Raikar and co-workers [24- 26]. Apart
from the above mentioned methods there have been other authors who have used various other solvent parameters in order to relate the spectral shifts. One of the well used parameter is the $E_T$ (30) scale put forward by Reichardt [27]. Other parameters are also taken in to consideration by Katritzky et al [28].

From the extensive literature survey it is evident that there are several recent reports published on experimental and theoretical studies on the ground state ($\mu_g$) and excited state ($\mu_e$) dipole moments using the solvatochromic method applied to variety of organic fluorescent compounds. Our chosen laser dyes are ADS680HO, ADS740WS and Red Mega 480 whose dipole moments presented in this work is strongly fluorescent and their fluorescence properties are dependent on the surrounding environments. That is why; they are widely used as a laser dye [29-31], daylight fluorescent pigment [29], lithography [32], microlithography [33], imaging of biological tissues [34] and lipophilic fluorescent probe for biochemical and medicinal investigations [26, 27].

This chapter deals with the study of absorption and fluorescence spectra of ADS680HO, ADS740WS and Red Mega 480 at room temperature in various solvents, subsequently estimating the dipole moment of a chosen dye in ground and excited state with many methods.

### 3.2 Theory: Determination of dipole moments:

The independent Equations used for the estimation of ground and excited state dipole moments for three laser dyes are as follows

Lippert’s Equation [22, 35]

$$\bar{V}_a - \bar{V}_f = m_1 F(\varepsilon, n) + \text{const}$$

3.1
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Bakhshiev’s Equation [20, 36]

\[
\vec{V}_a - \vec{V}_f = m_z F_1(\epsilon, n) + \text{const}
\]

Kawski-Chamma-Viallet’s Equation [13, 19, 37]

\[
\frac{\vec{V}_a + \vec{V}_f}{2} = -m_z F_2(\epsilon, n) + \text{const}
\]

McRae’s Equation [38]

\[
\vec{V}_a = -m_z F_3(\epsilon) + \text{const}
\]

Suppan’s Equation [39]

\[
\vec{V}_a = -m_z F_4(\epsilon) + \text{const}
\]

The expression \( F(\epsilon, n) \) [Lippert’s polarity parameter], \( F_1(\epsilon, n) \) [Bakhshiev’s polarity parameter], \( F_2(\epsilon, n) \) [Kawski-Chamma-Viallet’s polarity parameter], \( F_3(\epsilon) \) [McRae’s polarity parameter] and \( F_4(\epsilon) \) [Suppan’s polarity parameter] are given below

\[
F(\epsilon, n) = \left[ \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right]
\]

\[
F_1(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right]
\]

\[
F_2(\epsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)} \left( \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \frac{3(n^4 - 1)}{2(n^2 - 1)^2}
\]

\[
F_3(\epsilon) = \left[ \frac{2(\epsilon - 1)}{\epsilon + 2} \right]
\]

\[
F_4(\epsilon) = \left[ \frac{2(\epsilon - 1)}{2\epsilon + 2} \right]
\]
and $\nu_f$ are absorption and fluorescence maxima are in wave numbers (cm$^{-1}$) respectively. $\varepsilon$ and $n$ are dielectric constant and refractive index of the solvents respectively. Plotting the graphs of Equation 3.1-3.5 it follows that $\left(\nu_a - \nu_f\right)$ versus $F(\varepsilon, n)$, $\left(\nu_a - \nu_f\right)$ versus $F_1(\varepsilon, n)$, $\frac{1}{2}\left(\nu_a + \nu_f\right)$ versus $F_2(\varepsilon, n)$, $\nu_a$ versus $F_3(\varepsilon)$ and $\nu_a$ versus $F_4(\varepsilon)$ should give linear graphs with slopes $m_1$, $m_2$, $m_3$, $m_4$, $m_5$ respectively and are given below

\[
m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad 3.11
\]

\[
m_2 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad 3.12
\]

\[
m_3 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad 3.13
\]

\[
m_4 = \frac{\mu_e(\mu_e - \mu_g)}{hca^3} \quad 3.14
\]

and

\[
m_5 = \frac{\mu_e(\mu_e - \mu_g)}{hca^3} \quad 3.15
\]

Where $\mu_g$ and $\mu_e$ are the ground and excited state dipole moments of the solute molecule respectively, $h$ and $c$ are plank’s constant and velocity of light in vacuum respectively and “a” is the Onsager cavity radius which is determined by Suppan's Equation [39] $a = (3 M/4\pi\delta N)^{1/3}$, where $M$ is the molecular weight, $\delta$ is the density of the solute molecule and $N$ is Avogadro’s number. The ratio $(M/\delta)$ molar volume is calculated based on the Bondi radii method [40] and this value is also
compared with atomic increment method by Edward JT [34,41] with assuming the fact that ground and excited state dipole moments are almost parallel to each other.

The following expressions are obtained on the basis of Equations 3.12 and Equation 3.13.

\[
\mu_g = \frac{m_3 - m_2}{2} \left( \frac{hca}{2m_2} \right)^{\frac{1}{2}}
\]

\[
\mu_e = \frac{m_3 + m_2}{2} \left( \frac{hca}{2m_2} \right)^{\frac{1}{2}}
\]

and

\[
\mu_e = \frac{m_2 + m_3}{m_3 - m_2} \mu_g
\]

The validity of above equations is based on the following certain assumptions [42]

1. \( \mu_g \) and \( \mu_e \) dipole moments are collinear.

2. The Onsager cavity radius is same in ground and excited state.

3. Polarizability of the molecule is ignored.

4. Hydrogen bonding effect is also ignored.

The above theoretical calculations correlate much better with microscopic solvent polarity \( E_T^N \) rather than bulk solvent polarity functions involving dielectric constant and refractive index (\( \varepsilon, n \)). The spectral shift with \( E_T^N \) parameter proposed by Reichardt [1, 27], and improved by Ravi et al. [43],

\[
\bar{V}_a - \bar{V}_f = 11307.6 \left[ \left( \frac{\delta\mu}{\delta\mu_B} \right)^2 \left( \frac{a_B}{a} \right)^3 \right] E_T^N + \text{const}
\]

Where \( \delta\mu_B = 9D \) and \( a_B = 6.2\text{Å} \) are dipole moment changes on excitation and Onsager cavity radius respectively of a betaine dye molecule (Reichardt et al.). \( \delta\mu \)
and \( a \) are corresponding quantities of ADS680HO, ADS740WS and Red Mega 480 laser dyes of our present interest. The change in dipole moment can be evaluated from the slope of Stokes shift versus \( E_T^N \) plot and is given by the equation.

\[
\Delta \mu = \mu_e - \mu_g = \sqrt{\frac{m_T^N \times 81}{\left(\frac{6.2}{a}\right)^3 \times 11307.6}} \tag{3.20}
\]

Where \( m_T^N \) is the slope between Stokes shift and \( E_T^N \) parameter.

Reichardt [27] proposed relationship between \( E_T^N \) and \( E_T^{(30)} \) for a solvent is given by

\[
E_T^N = (E_T^{(30)}(\text{solvent}) - 30.7) / 32 \tag{3.21}
\]

\( E_T^{(30)} \) values are based on the negatively solvatochromic pyridinium N-phenolate betaine dye. Value of \( E_T^{(30)} \) for a various solvent is given by [44]

\[
E_T^{(30)} (\text{kcal mol}^{-1}) = h \nu_m N_A
= (2.8591 \times 10^{-3}) \nu_m (\text{cm}^{-1})
= 28591/\lambda_m (\text{nm}).
\]

\( \lambda_m \) is the wavelength of the absorption maxima.

Generally the dipole moments \( \mu_g \) and \( \mu_e \) are not parallel to each other but are having a very small angle \( \phi \) between them and is given by [45]

\[
\cos \phi = \frac{1}{2\mu_g \mu_e} \left[ (\mu_g^2 + \mu_e^2) - \frac{m_g^2}{m_e^2} (\mu_e^2 - \mu_g^2) \right] \tag{3.22}
\]

3.3 Experimental:

ADS680HO, ADS740WS are purchased from American dye source, Inc. Canada and Red Mega 480 is from Sigma Aldrich were used as it is without further
purification. The Molecular structure for these highly fluorescent laser dyes are given in Figure 3.1 to Figure 3.3. All the solvents viz., methanol, ethanol, propanol, butanol, octanol, nonanol, decanol, DMSO, acetonitrile, ethyl acetate, benzene, toluene, glycerol, are of spectroscopic grade. Electronic absorption spectra are recorded on Ocean Optics spectrophotometer and Fluorescence spectra are recorded on Hitachi F-7000 spectrophotometer at room temperature.

3.4 Results and discussion:

Absorption and fluorescence spectra of ADS680HO, ADS740WS and Red Mega 480 in various solvent parameters like dielectric constant ($\varepsilon$) and refractive index (n) are recorded using spectrophotometer. Table 3.1 summarizes dielectric constant ($\varepsilon$), refractive index (n), $E_T^{N}$ values for various solvents. The calculated values of solvent polarity functions $F(\varepsilon, n)$, $F_1(\varepsilon, n)$, $F_2(\varepsilon, n)$, $F_3(\varepsilon)$, $F_4(\varepsilon)$ (Equation 3.1 to Equation 3.10) for various solvents employed in the present study is depicted in Table 3.2.

3.4.1 Dipole moment calculations of ADS680HO:

The absorption spectra of ADS680HO in different solvents show a maximum around 669.08 to 693.60nm (Table 3.3). Since, only the longest wavelength band (Figure 3.4) is sensitive to solvent polarity, the absorption shifts with solvent has been reported [17]. The fluorescence emission spectra are recorded by exciting the sample at its longest absorption maximum. The excitation maximum coinciding with the longest wavelength absorption band has been assigned the intramolecular charge transfer (ICT) [46]. Increase in solvent polarity shifts the absorption and emission maximum to the longer wavelength region.
The absorption and fluorescence maxima, Stokes shift values for all the solvents are given in Table 3.3. The fluorescence emission spectra show a maximum around 707.3 to 731.4nm in different solvents, shift of a maximum depending upon the solvent we used. The fluorescence emission spectra show little larger shift as compared with the absorption spectra. The absorption shift with solvent implies that the ground state energy distribution is affected to greater extent, possibly due to the polar nature of the dye in the ground state rather than the excited state.

The magnitude of the Stokes shift varies from 398cm$^{-1}$ to 885cm$^{-1}$. The values of the Stokes shift is also an indicative of the intramolecular charge transfer (ICT) [46]. The large magnitude of Stokes shift indicates the excited-state geometry could be different from that of the ground state. The general observation is an increase in the Stokes shift values with increasing solvent polarity which shows that there is an increase in the dipole moment on excitation.

The solvatochromic data can be used to identify the spectra, namely $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, etc. It is observed from Table 3.1 and Table 3.3., with increase in the polarity of the solvent, the fluorescence emission peak undergoes bathochromic (red) shift, confirming $\pi \rightarrow \pi^*$ transition [17]. The shift of the fluorescence wavelengths towards longer wavelengths could be caused, if the excited state charge distribution in the solute is markedly different from ground state charge distribution, and it gives rise to a stronger interaction with polar solvents in the excited state.

Table 3.6 summarizes the Stokes shift and arithmetic mean of Stokes values [47]. Figure 3.7 to Figure 3.12 shows the graphs of Stokes shift versus $F(\varepsilon,n)$ i.e. Lippert’s Polarity parameter, Stokes shift versus $F_1(\varepsilon,n)$ i.e. Bakshiev’s Polarity parameter, $\frac{1}{2}(\overline{v_e} + \overline{v_f})$ versus $F_2(\varepsilon,n)$ i.e. Kawski-Chamma-Viallet’s Polarity, $\overline{v_e}$
versus $F_3(\varepsilon)$ \ i.e. McRae’s Polarity parameter, $\vec{\nu}_a$ versus $F_4(\varepsilon)$ \ i.e. Suppan’s Polarity parameter, $\vec{\nu}_a$ versus $E_{\gamma}^N$ \ i.e. solvent Polarity parameter (Equation 3.19) and the slopes $m_1$, $m_2$, $m_3$, $m_4$, $m_5$ and $m_{\gamma}^N$ (Equation 3.11 to Equation 3.15 and Equation 3.20) are obtained from these graphs, respectively. A linear progression was done by employing Origin 6.0 software and the data was fit's to a straight line. The correlation coefficients, slopes, intercepts of the linearly fitted line data's are given in Table 3.9 and Table 3.12. Here in most of the cases, correlation coefficients are found to be larger than 0.82 it indicates a good linearity with selected number of Stokes shift data points. In few cases some of the solvents do not participate in the correlation. Generally this deviation from linearity may be due to specific solute–solvent interactions. The deviation from linearity for some solvents might probably be due to hydrogen bonding nature of the molecule and at the same time charge transfer in the excited state cannot be ruled out. For ADS680HO Onsager cavity radius is $a = 5.19\text{Å}$ is calculated by atomic increment method and various slopes are $m_1 = 1314.01$, $m_2 = 374.88$, $m_3 = 544.09$, $m_4 = 246.9$, $m_5 = 655.50$ and $m_{\gamma}^N = 311.18$ using Equations 3.11 to 3.15.& 3.19, we get the dipole moment $\mu_g = 0.53\text{D}$, $\mu_e = 2.86\text{D}$ (Solvatochromic method), $\mu_e = 4.96\text{D}$ (Lippert's method), $\mu_e = 14.16\text{D}$ (McRae method), $\mu_e = 36.72\text{D}$ (Suppan's method), $\mu_e = 1.67\text{D}$ ($E_{\gamma}^N$ solvent polarity method).

These differences between the values of $\mu_e$ may be in part, due to the various assumptions and simplifications made in the solvatochromic method, so the method is considered the right method to calculate the dipole moment of the molecule. The $\mu_e$ value obtained by Lippert's method is large, since it does not consider the polarizability [48-51]. The $\mu_e$ value obtained by suppan's method is large compared to
any other methods; also value of $\mu_e$ is calculated by Mc Rae it is also large. Both Suppan and Mc Rae assumptions made in the equations which do not involve the fluorescence maxima and refractive index of the solvents [23, 38, 39], without involvement of fluorescence maxima and refractive index of the solvent, it is insufficient to calculate the exact values of excited and ground state dipole moments, so the results are not reliable compared with that calculated from emission maxima and refractive index of the solvents. The value of $\mu_e$ calculated by $E^N_T$ almost agrees with solvatochromic method [43, 47].

The dipole moment of ADS680HO molecule in excited state is higher than the ground state. This is explained in terms of possible resonance structure as shown in Figure 3.25. The dipole moment of a probe molecule increases almost four times on excitation can be explained in terms of nature of emitted state of intramolecular charge transfer (ICT). Further a large change in the dipole moment on excitation suggests that, because of strong solvent polarity and hydrogen bonding effects due to the possibility of excited state is twisted intramolecular charge transfer (TICT) in nature [46]. Thus the presence of a large TICT and increase in planarity on excitation render the molecule more polar as compared to ground state giving rise to a large change in the dipole moment.

It is very interesting to note from the Table 3.12 that, variations are observed between the estimated values of $\mu_e$ obtained by different methods. Lippert method value is large due to not taken into account of polarizability. The $\mu_e$ values obtained by solvatochromic method (Equation 3.17 & Equation 3.18), almost agree with $E^N_T$ solvent polarity method compared to any other methods, because, other methods includes only absorption maxima and dielectric constant. In literature one may find
that large number of investigators has used solvatochromic shift method (Equation 3.17 & Equation 3.18) to estimate excited state dipole moment. We believe that the excited state dipole moments estimated from solvatochromic shift method are the most proper values.

The obtained values of $\mu_g$ and $\mu_e$ are positive and $\mu_e$ is very much larger than the $\mu_g$ it means the excited state is more polar than the ground state. It also indicates that the excited state electronic charge distribution should be substantially different from the ground state charge distribution. It also depicts that the observed transition is $\pi \rightarrow \pi^*$ [12, 45, 47].

The charge transfer band shows a shift of about 23.5nm in the absorption spectra on changing the solvent from methanol to benzene, while 24.1nm shift in fluorescence spectra from ethyl acetate to benzene. The pronounced absorption shift with solvent implies that the ground state energy distribution is lower to excited state because of polar nature of the dipole molecule ADS680HO [47, 53-55].

Assuming that the symmetry of the investigated solute molecule changes upon electronic transitions, the ground and excited state dipole moments are not exactly parallel [29-30, 45]. One more notable point is the large difference between the $\mu_e$ and $\mu_g$ values, clearly indicative of charge transfer in the molecular structure of a dye on excitation. Of course the large solvatochromic shifts in the present study are consistent with this observation. This indicates that on excitation, the orientation of the dipole moment has considerably changed. This change in the orientation in the dipole moment ($\Theta$) can be measured using the Equation 3.22 and it is 4.73°.
3.4.2 Dipole moment calculations of ADS740WS:

The absorption spectra of ADS740WS in different solvents show a maximum around 740.2 to 749.5nm (Table 3.4). Since only the longest wavelength band (Figure 3.5) is sensitive to solvent polarity and the absorption shifts with solvent has been reported [17]. The fluorescence emission spectra are recorded by exciting the sample at its longest absorption maximum. The excitation maximum coinciding with the longest wavelength absorption band has been assigned as the intermolecular charge transfer (ICT) [46]. Increase in solvent polarity shifts the absorption and emission maximum to the longer wavelength region.

The absorption and fluorescence maxima, Stokes shift values for all the solvents are given in Table 3.4. The fluorescence emission spectra show a maximum around 779.5 to 841.3nm in different solvents, shift of a maximum depending upon the solvent we used. The fluorescence emission spectra show little larger shift as compared with the absorption spectra. The absorption shift with solvent implies the ground state energy distribution is affected to greater extent, possibly due to the polar nature of the dye in the ground state rather than the excited state.

The magnitude of the Stokes shift varies from 614.7cm\(^{-1}\) to 1642.2cm\(^{-1}\). The values of the Stokes shift is also an indicative of the intramolecular charge transfer (ICT) [46]. The large magnitude of Stokes shift indicates the excited-state geometry could be different from that of the ground state. The general observation is that there is an increase in the Stokes shift values with increasing solvent polarity which shows that there is an increase in the dipole moment on excitation (Table 3.4).

The solvatochromic data can be used to identify the spectra, namely \(\pi \to \pi^*\), \(n \to \pi^*\), etc. It is observed from Table 3.1 and Table 3.4., with increase in the polarity
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of the solvent, the fluorescence emission peak undergoes bathochromic (red) shift, confirming \( \pi \rightarrow \pi^* \) transition [17]. The shift of the fluorescence wavelengths towards longer wavelengths could be caused, if the excited state charge distribution in the solute is markedly different from ground state charge distribution, and it gives rise to a stronger interaction with polar solvents in the excited state.

Table 3.7 summarize the Stokes shift and arithmetic mean of Stokes values [46]. Figure 3.13 to Figure 3.18 shows the graphs of Stokes shift versus \( \Phi(\varepsilon,n) \) i.e. Lippert’s Polarity parameter, Stokes shift versus \( \Phi_1(\varepsilon,n) \) i.e. Bakshiev’s Polarity parameter, \( \frac{1}{2}(\nu_a + \nu_f) \) versus \( \Phi_2(\varepsilon,n) \) i.e. Kawski-Chamma-Viallet’s Polarity, \( \nu_a \) versus \( \Phi_3(\varepsilon) \) i.e. McRae’s Polarity parameter, \( \nu_a \) versus \( \Phi_4(\varepsilon) \) i.e. Suppan’s Polarity parameter, \( \nu_a \) versus \( \Phi_5^N \) i.e. solvent Polarity parameter (Equation 3.19) and the slopes \( m_1, m_2, m_3, m_4, m_5 \) and \( m_5^N \) (Equation 3.11 to Equation 3.15 and Equation 3.19) are obtained from these graphs, respectively. A linear progression was done by employing Origin 6.0 software and the data was fit to a straight line. The correlation coefficients, slopes, intercepts of the linearly fitted line data’s are given in Table 3.10 and Table 3.12. Here in most of the cases, correlation coefficients are found to be larger than 0.85 it indicates a good linearity with selected number of Stokes shift data points. In few cases some of the solvents do not participate in the correlation. Generally this deviation from linearity may be due to specific solute–solvent interactions. The deviation from linearity for some solvents might probably be due to hydrogen bonding nature of the molecule and at the same time charge transfer in the excited state cannot be ruled out. For ADS740WS Onsager cavity radius \( a = 5.27 \text{Å} \) is calculated by atomic increment method and various slopes are \( m_1 = 10005.23, \)
m_2 = 307.01, m_3 = 758.7, m_4 = 370.25, m_5 = 1961.06 and \( m^N_N = 670.32 \) using the Equations 3.11 to 3.15., we get the dipole moment \( \mu_s = 1.60 \text{D}, \mu_e = 3.77 \text{D} \) (Solvatochromic method), \( \mu_e = 5.38 \text{D} \) (Lippert's method), \( \mu_e = 8.73 \text{D} \) (McRae method), \( \mu_e = 39.36 \text{D} \) (Suppan's method), \( \mu_e = 3.35 \text{D} \) (\( E^N_T \) solvent polarity method).

These differences between the values of \( \mu_e \) may be in part, due to the various assumptions and simplifications made in the solvatochromic method, so the solvatochromic method is considered the right method to calculate the dipole moment of the molecule. The \( \mu_e \) values obtained by Lippert's method are large, since it does not consider the polarizability [48-51]. The \( \mu_e \) value obtained by suppan's method is large compared to any other method, value of \( \mu_e \) calculated by Mc Rae, it is also large. Both Suppan and Mc Rae assumptions made in the equations do not involve the fluorescence maxima and refractive index of the solvents [28, 38, 39], without involvement of fluorescence maxima and refractive index of the solvent, it is insufficient to calculate the exact value of excited and ground state dipole moments, so the results are not reliable compared with calculated from emission maxima and refractive index of the solvents. The value of \( \mu_e \) calculated by \( E^N_T \) almost agrees with solvatochromic method [43, 47].

The dipole moment of ADS740WS molecule in excited state is higher than the ground state. This is explained in terms of possible resonance structure as shown in Figure 3.26. The dipole moment of a probe molecule increases almost two times on excitation can be explained in terms of nature of emitted state of intramolecular charge transfer (ICT). Further a large change in the dipole moment on excitation suggests that, because of strong solvent polarity and hydrogen bonding effects it is possibility of excited state is twisted intramolecular charge transfer (TICT) in nature.
Thus the presence of a large TICT and increase in planarity on excitation render the molecule more polar as compared to ground state giving rise to a large change in the dipole moment.

It is very interesting to note from the Table 3.12 that, variations are observed between the estimated values of $\mu_e$ by Lippert method is large, since it does not taken into account of polarizability. The $\mu_e$ values obtained by solvatochromic method (Equation 3.17 & Equation 3.18), almost agree with $E_{T}^{W}$ solvent polarity method compared to any other methods, because, other methods includes only absorption maxima and dielectric constant. In literature one may find that a large number of investigators have used solvatochromic shift method (Equation 3.17 & Equation 3.18) to estimate excited state dipole moment. We believe that the excited state dipole moments estimated from solvatochromic shift method are the most proper values.

The obtained values of $\mu_g$ and $\mu_e$ are positive and $\mu_e$ is very much larger than $\mu_g$ which means that the excited state is more polar than the ground state. It also indicates that the excited state electronic charge distribution should be substantially different from the ground state charge distribution. It also depicts that the observed transition is $\pi \rightarrow \pi^*$ [12, 45, 47].

The charge transfer band shows a shift of about 9.3nm in the absorption spectra on changing the solvent from acetonitrile to DMSO, while 61.8nm shift in fluorescence spectra from butanol to propanol. The absorption shift with solvent implies that the ground state energy distribution is lower to excited state because of polar nature of the dipole molecule ADS740WS [47, 53-55].

Assuming that the symmetry of the investigated solute molecule changes upon electronic transitions, the ground and excited state dipole moments are not exactly
parallel [29, 30, and 45]. One more notable point is the large difference between $\mu_e$ and $\mu_g$ values, clearly indicative of charge transfer in the molecular structure of a dye on excitation. Of course the large solvatochromic shifts in the present study are consistent with this observation. This indicates that on excitation, orientation of dipole moment has considerably changed. This change in the orientation in the dipole moment ($\theta$) can be measured using an Equation 3.22 and it is $5.73^0$.

3.4.3 Dipole moment calculations of Red Mega 480:

The absorption spectra of Red Mega 480 in different solvents show a maximum around 490 to 507nm (Table 3.5). Since only the longest wavelength band (Figure 3.6) is sensitive to solvent polarity and the absorption shifts with solvent has been reported [17]. The fluorescence emission spectra are recorded by exciting the sample at its longest absorption maximum. The excitation maximum coincides with the longest wavelength absorption band has been assigned as the intramolecular charge transfer (ICT) [46]. Increase in solvent polarity shifts the absorption and emission maximum to the longer wavelength region.

The absorption and fluorescence maxima, Stokes shift values for all the solvents are given in Table 3.8. The fluorescence emission spectra show a maximum around 602 to 644nm in different solvents, with a shift of the maximum depending upon the solvent we used. The fluorescence emission spectra show little larger shift as compared with the absorption spectra. The pronounced absorption shift with solvent implies ground state energy distribution is affected to greater extent, possibly due to the polar nature of the dye in the ground state rather than the excited state.

The magnitude of the Stokes shift varies from $3458.43 \text{cm}^{-1}$ to $4392.37 \text{cm}^{-1}$. The values of the Stokes shift is also an indicative of the intramolecular charge
transfer (ICT) [46]. The large magnitude of Stokes shift indicates that the excited-state geometry could be different from that of the ground state. The general observation is that there is an increase in the Stokes shift values with increasing solvent polarity which shows there is an increase in the dipole moment on excitation.

The solvatochromic data can be used to identify the spectra, namely $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, etc. It can be noticed from Table 3.1 and Table 3.5. That, with increase in the polarity of the solvent, the fluorescence emission peak undergoes bathochromic (red) shift, confirming $\pi \rightarrow \pi^*$ transition [17]. The shift of the fluorescence wavelengths towards longer wavelengths could be caused, if the excited state charge distribution in the solute is markedly different from the ground state charge distribution, and it gives rise to a stronger interaction with polar solvents in the excited state.

Table 3.8 summarizes Stokes shift and arithmetic mean of Stokes values [46]. Figure 3.19 to Figure 3.24 shows the graphs of Stokes shift versus $F(\varepsilon,n)$ i.e. Lippert’s Polarity parameter, Stokes shift versus $F_1(\varepsilon,n)$ i.e. Bakshiev’s Polarity parameter, $\frac{1}{2}(\overline{\nu_a} + \overline{\nu_f})$ versus $F_2(\varepsilon,n)$ i.e. Kawski-Chamma-Viallet’s Polarity, $\overline{\nu_a}$ versus $F_3(\varepsilon)$ i.e. McRae’s Polarity parameter, $\overline{\nu_a}$ versus $F_4(\varepsilon)$ i.e. Suppan’s Polarity parameter, $\overline{\nu_a}$ versus $E_T^N$ i.e. solvent Polarity parameter (Equation 3.19) and the slopes $m_1$, $m_2$, $m_3$, $m_4$, $m_5$ and $m_7^N$ (Equation 3.11 to Equation 3.15 and Equation 3.19) are obtained from these graphs, respectively. A linear progression was done by employing Origin 6.0 software and the data was fit to a Straight line. The correlation coefficients, slopes, intercepts of the linearly fitted line datas are given in Table 3.11 and Table 3.12. Here in most of the cases, correlation coefficients are found to be larger than 0.85 it indicates a good linearity with selected number of Stokes shift data points. In few cases some of the solvents do not participate in the correlation. Generally this
deviation from linearity may be due to specific solute–solvent interactions. The deviation from linearity for some solvents might probably be due to hydrogen bonding nature of the molecule and at the same time charge transfer in the excited state cannot be ruled out. For Red Mega 480 laser dye Onsager cavity radius \( a = 4.53\text{Å} \) is calculated by atomic increment method and various slopes are \( m_1 = 5967.03, \ m_2 = 2138.13, \ m_3 = 3618.44, \ m_4 = 1321.5, \ m_5 = 4735.43 \) and \( m_N^G = 685.80 \) using the Equations 3.11 to 3.15., we get the dipole moment \( \mu_g = 1.54\text{D}, \mu_e = 5.99\text{D} \) (Solvatochromic method), \( \mu_e = 8.97\text{D} \) (Lippert's method), \( \mu_e = 17.42\text{D} \) (McRae method), \( \mu_e = 58.43\text{D} \) (Suppan's method), \( \mu_e = 2.95\text{D} \) (\( E_T^N \) solvent polarity method). These differences between the values of \( \mu_e \) may be in part, due to the various assumptions and simplifications made in the solvatochromic method, so the solvatochromic method is considered the right method to calculate the dipole moment of the molecule. The \( \mu_e \) value obtained by Lippert's method is large, since it does not considered the polarizability [48-51]. The \( \mu_e \) value obtained by suppan's method is large compared to any other methods; also value of \( \mu_e \) is calculated by McRae it is also large. Both Suppan and McRae assumptions made in the equations which do not involve the fluorescence maxima and refractive index of the solvents [28, 38, 39], without involvement of fluorescence maxima and refractive index of the solvent, it is insufficient to calculate the exact value of excited and ground state dipole moments, so the results are not reliable compared with that calculated from emission maxima and refractive index of the solvents. The value of \( \mu_e \) calculated by \( E_T^N \) almost agrees with solvatochromic method [43, 47].

The dipole moment of Red Mega 480 molecule in excited state is higher than the ground state. This is explained in terms of possible resonance structure as shown
in Figure 3.27. The dipole moment of a probe molecule increases almost four times on excitation can be explained in terms of nature of emitted state of intramolecular charge transfer (ICT). Further a large change in the dipole moment on excitation suggests that, because of strong solvent polarity and hydrogen bonding effects it is possibility of excited state is twisted intramolecular charge transfer (TICT) in nature[46]. Thus the presence of a large TICT and increase in planarity on excitation render the molecule more polar as compared to ground state giving rise to a large change in the dipole moment.

It is very interesting to note from the Table 3.12 that, small differences are observed between the estimated values of $\mu_e$ obtained by Lippert method are large compared to any other method, since it does not take into account of polarizability. The $\mu_e$ values obtained by solvatochromic method (Equation 3.17 & Equation 3.18), almost agree with $E^N_f$ solvent polarity method compared to any other methods, because, other methods includes only absorption maxima and dielectric constant only. In literature one may find that large numbers of investigators have used solvatochromic shift method (Equation 3.17 & Equation 3.18) to estimate excited state dipole moment. We believe that the excited state dipole moments estimated from solvatochromic shift method are the most proper values.

The obtained values of $\mu_g$ and $\mu_e$ are positive and $\mu_e$ is very much larger than the $\mu_g$ which means that the excited state is more polar than the ground state. It also indicates that the excited state electronic charge distribution should be substantially different from the ground state charge distribution. It also depicts that the observed is $\pi \rightarrow \pi^*$ transition [12, 45, 47].
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The charge transfer band shows a shift of about 17nm in the absorption spectra on changing the solvent from decanol to butanol, while 42nm shift in fluorescence spectra from decanol to methanol. The absorption shift with solvent implies that the ground state energy distribution is lower to excited state because of polar nature of the dipole molecule Red Mega 480 [47, 53-55].

Assuming that the symmetry of the investigated solute molecule changes upon electronic transitions, the ground and excited state dipole moments are not exactly parallel [29, 30, 45]. One more notable point is the large difference in the $\mu_e$ and $\mu_g$ values, clearly indicative of charge in the molecular structure of a dye on excitation. Of course the large solvatochromic shifts in the present study are consistent with this observation. This indicates that on excitation the orientation of the dipole moment has considerably changed. This change in the orientation in the dipole moment ($\theta$) can be measured using the Equation 3.22 and it is $1.82^0$.

3.5 Conclusions on dipole moment calculations:

The following conclusions has been drawn from the dipole moment measurements using Lippert’s, Solvatochromic, McRae’s, Suppan’s Polarity parameter and solvent polarity $E_T^N$ methods.

1. The polarity of a molecule depends on electron density. With supply of additional energy there will be transition of electron from ground state to excited state. Which leads to the delocalization of the excited state, it may be solute-solvent interactions or intramolecular hydrogen bonding via solvents. Because of the movement of electron from ground state orbital to excited state orbital, there will be increase of dipole moment with reference to ground state dipole moment.
2. The ground state and excited state dipole moments of structurally similar laser
dyes were evaluated using solvatochromic, Lippert, Backshiev, Kawski-
Chamma-Viallet, McRae, Suppan, Solvent Polarity methods. The dipole
moments of molecules in the excited state have been measured. It is observed
that corresponding solvents exhibited red shift (bathochromic) both for
absorption and fluorescence maxima indicating a $\pi \to \pi^*$ transition.

3. The spectral shift indicates the presence of general and specific type of solvent
solute interaction.

4. The linear $E_T (30)$ dependence of Stokes shift indicates the existence of
general type of solute-solvent interaction.

5. It is observed that there is bathochromic shift in absorption maximum in most
of the solvents provides the strong evidence of excited state dipole moment is
larger than the ground state dipole moment. The calculated dipole moments
indicate that, for all chosen laser dyes, the excited-state dipole moment ($\mu_e$) is
larger than the ground-state ($\mu_g$). Increase in the singlet excited state dipole
moments is about $\Delta \mu = 2.33$ D (ADS680HO), 2.17 D (ADS740WS) and 4.45
D (Red Mega 480) that demonstrates, the dyes are more polar in excited state
as compared with ground state. Additionally, large change in dipole moments
on excitation suggests that excited states are twisted intramolecular charge
transfer (TICT) in the solvent environment. TICT process increases planarity
of dyes molecular structure on excitation and increases the change in dipole
moment.

6. In addition the observed bathochromic shift absorption spectra with solvent
implies that, the excited state energy distribution is affected to a greater extent,
possibly due to the greater polar nature of the ADS680HO, ADS740WS and Red Mega 480 dye molecules in the excited state than the ground state.

7. The observed smaller slope values ($m_1$ and $m_2$) indicate a rather small variation of the dipole moment values between the ground state and excited state. This suggests that the emission of dye molecule originates from a state, which although more polar than the ground state, is probably due to excited intramolecular charge transfer (ICT) state. Charge transfer accompanying excitation to the lowest excited state usually results in the excited state molecule having a larger dipole moment than the ground state.

8. It may be noted that all estimated values of $\mu_g$ and $\mu_e$ for all dyes tested are different. This can be attributed to the structural differences between these molecules. The higher dipole moments in the first electronically excited state indicates that the observed absorption band for these molecules attributed to $\pi \rightarrow \pi^*$ transition. This observation in very good agreement with literature. Also plotted the possible resonance structures for dye molecules.

9. It is very interesting to observe that, values of small differences are observed between the estimated values of $\mu_e$ obtained by Lippert method is large, since it does not taken into account of polarizability. The $\mu_e$ values obtained by solvatochromic method, almost agree with $E_T^N$ solvent polarity method compared to any other methods, because, other methods (Suppan's and Mc Rae) includes only absorption maxima and dielectric constant but not considered the fluorescence maxima and refractive index of the solvents. In literature one may find that large numbers of investigators have used solvatochromic shift method to estimate excited state dipole moment. Now we
strongly recommend that the excited state dipole moments estimated from solvatochromic shift method is the most proper values than the other any methods.

10. Assuming the symmetry of the investigated solute molecule changes upon electronic transitions, the ground and excited state dipole moments are not exactly parallel. One more noticeable point is the large difference between $\mu_e$ and $\mu_g$ values, clearly indicative of charge in the molecular structure of a dye on excitation. Of course the large solvatochromic shifts in the present study are consistent with this observation. This indicates that on excitation, the orientation of the dipole moment has considerably changed. This change in the orientation in the dipole moment ($\theta$) measured for ADS680HO, ADS740WS and Red Mega is $4.73^0$, $5.73^0$ and $1.82^0$ respectively.

11. The Lippert, Mc Rae and Suppan equations partially explains the effect of solvent polarity, but does not account for other effects such as hydrogen bonding to the fluorophore or intramolecular charge transfer (ICT) that depends on solvent polarity.

12. Emission from fluorophores generally occurs at wavelengths longer than those at which absorption occurs. This loss of energy due to variety of dynamic processes that follows the light absorption. The fluorophore is typically excited to the first singlet state ($S_1$). The excess vibrational energy is rapidly lost to the solvent. If the fluorophore is excited to the second singlet state ($S_2$) it rapidly decays to the $S_1$ state in $10^{-12}$ s due to internal conversion. Solvent effect shift explains the emission to still lower energy due to stabilization of
the excited state by the polar solvent molecules. Typically, the fluorophore has larger dipole moment in the excited state than in the ground state.

3.6 Correlation with multiparameter solvent polarity scale:

Chemists and Physicists have tried to understand solvent effects on chemical reactions in terms of the so called solvent polarity [56]. Since many years, which is not easy to define and to express quantitatively, but what does solvent polarity really mean? In simple idealized electrostatic models for the description of solvation of ions and dipolar molecules, considering solvents as nonstructured continuum, has led to the use of physical constants, such as dielectric constant ($\varepsilon$), permanent dipole moment ($\mu$), refractive index ($n$), or functions thereof, as macroscopic solvent parameters for the evaluation of medium effects. However, solute/solvent interactions take place on a molecular microscopic level within a structured discontinuum consisting of individual solvent molecules, capable of mutual solvent interactions. For this reason, and because of neglecting specific solute interactions, the electrostatic approach to medium effects often failed in correlating observed solvent effects with physical solvent parameters. In reality, satisfactory quantitative descriptions of medium effects have to take into account all specific and nonspecific solute/solvent interactions i.e., at higher concentrations. Therefore, from a more pragmatic point of view, it seems to be more favourable to define “solvent polarity” simply as [56] the "overall solvation capability (or solvation power) of solvents", which in turn depends on the action of all possible, specific and nonspecific, intramolecular interactions between solute ions or molecules and solvent molecules, excluding, however, those interactions leading to definite chemical alterations of the ions or molecules of the solute (such as protonation, oxidation, reduction, chemical complex
formation, etc.). This definition of solvent polarity becomes more and more accepted by the scientific community. Apparently, solvent polarity thus defined cannot be described quantitatively by single physical solvent parameters such as dielectric constant, dipole moments, etc. The lack of comprehensive theoretical expressions for the calculation or prediction of solvent effects on chemical reactivity, and the inadequacy of defining solvent polarity in terms of simple physical solvent characteristics, have led to the introduction of so-called empirical parameters of solvent polarity. On the basis of the assumption that in particular, carefully selected, well-understood and strongly solvent-dependent chemical reactions or spectral absorptions may serve as suitable model processes for recording medium effects; various empirical solvent polarity scales have been developed this way.

Reichardt [56] defined "solvent polarity" $E_T$ (30) as the overall solvation capability for reactants as well as molecules in the ground state and excited state, which in turn depends upon on the action of all possible, specific and nonspecific, intramolecular forces between solute and solvent molecules, including coulomb interactions between ions, directional interactions between dipoles, and inductive, dispersion, hydrogen bonding, and charge transfer forces, solvophobic interactions, oxidation, reduction, complex formations. $E_T^N$ is a dimensionless "normalized scale" defined by the Equation 3.21.

One of the most ambitious, and very successful, quantitative treatments of solvent effects by means of a multiparameter equation introduced by Kamlet and Taft [57] in 1976 and is called Linear Solvation Energy Relationship (LSER). Using the UV/VIS/ near IR spectroscopically derived solvatochromic parameters. The solvent dependent spectral shifts originate from [58-63]:
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a. Specific solute–solvent interactions (e.g. hydrogen-bonding, Intramolecular charge transfer (ICT), proton transfer).

b. Non-specific interactions (dielectric enrichment) of the solvent.

In fact, there is a strong competition between the solute-solute, solute-solvent and solvent-solute interactions that determines the nature of solvatochromic behaviour of the solute molecules. The solvent effect can be further evaluated by means of solvent polarity scale and solvatochromic parameters [56, 64-66]. However, to explain multi-parameter solvent polarity scale for quantitative and qualitative assessment of the solvent/solute interactions, the spectroscopic shifts can be used. Effect of solvent polarity on the spectral features of the solute can be interpreted by means of linear solvation energy relationship (LSER) concept that can be formulated as Kamlet–Abboud–Taft (KAT) (Equation 3.23) and Katritzky (KTZ) (Equation 3.24).

\[
\left( \bar{v}_a - \bar{v}_f \right) = \left( \bar{v}_a - \bar{v}_f \right)_0 + a.\alpha + b.\beta + s.\pi^* \tag{3.23}
\]

\[
\left( \bar{v}_a - \bar{v}_f \right) = \left( \bar{v}_a - \bar{v}_f \right)_0 + a.\alpha + b.\beta + \frac{n^2 - 1}{2n^2 + 1} \left( \frac{\varepsilon - 1}{2\varepsilon + 1} \right) + s.E_T(30) \tag{3.24}
\]

Where \(\pi^*\) is a measure of the solvent dipolarity/polarizability [62], \(\beta\) is the scale of the solvent hydrogen bond acceptor (HBA) basicities [57], \(\alpha\) is the scale of the solvent hydrogen bond donor (HBD) acidities [65]. \(\varepsilon, n\) and \(E_T(30)\) [56, 59] are relative permittivity, refractive index and empirical polarity parameter of the solvent, respectively. \(\left( \bar{v}_a - \bar{v}_f \right)_0\) is the regression value of the solute property in the reference solvent. The Katritzky equation estimates independent contributions of solvent dipolarity, polarizability, and other specific interactions (e.g. hydrogen bonding, extra
π-π interaction). In order to have a comparable a, b and s values for Katritzky equation, all the parameters should be re-normalized and rescaled. The regression coefficients a, b and s in these equations measure the relative susceptibilities of the solute property (such as absorption, fluorescence and other spectroscopic parameters) to the indicated solvent parameters.

Scales of dipolarity/polarizability concept is the solute-solvent interactions can be dissected into general, which have electrostatic and dispersive origins and can be related conceptually to reaction field theories and specific interactions which include hydrogen bonding donor/acceptor interactions. π* defined by Kammlet-Abboud-Taft (KAT) is intended to provide the information about the non specific part of van der Waals interactions between solute and solvents. The scale was based on the treatment of the solvatochromic shifts undergone by selected absorption bands of a variety of aromatic molecules.

KAT (Kamlet-Abboud-Taft) equation comprises spectroscopic polarity scales including hydrogen bonding donor ability (α), hydrogen bonding accepting ability (β) and dipolarity/polarizability (π*) is a multiparameter scale. The KAT equation originally evaluates specific hydrogen bonding interactions between solute and solvent, while the KTZ (Katritzky) equation basically evaluates dipolarity/polarizability interactions.

The results for both KAT and KTZ scales were calculated using the multi-linear regression analysis in Microsoft Excel by means of Data Analysis tool pack.

3.7 Results and discussion:

In order to understand solvent effects on chemical reactions and physical absorptions in a more quantitative way, a magnitude of empirical solvent polarity
scales, derived from various physicochemical processes, have been proposed during the last few decades. The most comprehensive and easiest way to determine is based on the solvatochromic method. Some of these have been used to introduce comprehensive solvent scales; others are possible and promising candidates for this purpose. $E_T (30)$ scale as one of the more comprehensive solvent scale has been exhaustively discussed at some length. The popular solvatochromic comparison method, introduced by Kamlet and Taft and further developed by Abboud, has been used to demonstrate the advantages of a multiparameter treatment of solvent effects. This was followed by a comparison of some of the solvatochromic solvent scales, which shows that many of the empirical parameters are linearly related to each other, thus demonstrating the similarity of the intramolecular solute and solvent interactions in many cases. Taking into account the wide variation in chemical structure of the probe molecules used for construction of a solvent scale, the question arises which of them are the most representative compounds in modelling solute/solvent interactions, leading to a more or less universal solvent polarity scale. Because solute/solvent interactions do not depend on the solvent structure alone, but always also on the chemical structure of the probe solute, the establishment of a universal, generally valid solvent polarity scale seems to be attainable. From a more puristic physical-organic chemist’s point of view, the application of empirical parameters of solvent polarity has certainly its inherent weaknesses and limitations. In using such parameters, one should always be aware of the fact that one simply compares the solvent effect under study with another solvent-dependent model process. So, the solvent effect under study can be understood qualitatively and quantitatively in that way and to the extent as the solvent influence on the model process is known. However, this kind of procedure is very common in chemistry.
In order to estimate the comparable coefficient values a, b & s for ADS680HO, ADS740WS and Red Mega 480 laser dye solute molecules, we have re-normalized and rescaled the parameters for all the used solvents (Table 3.13, Table 3.16 and Table 3.19), this scale can provide information about the excitation process, the results for both KAT and KTZ scales, we calculated using multi-linear regression analysis and results are listed in Table 3.14, Table 3.17 & Table 3.20. The obtained results were transformed into percentage contributions and summarized in Table 3.15, Table 3.18 & Table 3.21.

Choice of appropriate set of solvents is very important in reliable solvatochromic analysis, Therefore according to statistical factors (larger coefficient of correlation and smaller values of significance F-test) and visual inspection we have removed the inappropriate data and selected the maximum number of data that satisfy the statistical data (Table 3.14, Table 3.17 and Table 3.20).

Analysis of Stokes shift data, using KAT and KTZ multiparameter polarity scales [67]; confirm the same contribution on the way to solvent reorientation process. It means, solvent molecules reorient in such a way that: it supports in changing the molecular interactions, and therefore parameter contributions, from ground state toward excited state. However, it should be noted that such correlation have made with fewer number of data and therefore this conclusion should be made generally.

We have employed Kamlet-Abboud-Taft and Katritzky multilinear analyses for characterizing the solvent contribution into specific features of the ADS680HO, ADS740WS and Red Mega 480 laser dyes. Correlation analysis of spectroscopic data with multiple polarity parameters was carried out by multiple linear regression analysis. It was found that Stokes shift data for chosen dyes shows satisfactory
correlations with different parameters. The results of the multiple regressions are presented in Table 3.15, Table 3.18 and Table 3.21.

3.7.1 Multiparameter analysis of ADS680HO dye:

- The sign of "s" coefficient, for Kamlet-Abboud-Taft parameter and Katritzky is positive, it indicates, overall contribution of dipolarity and polarizability increases the stabilization of excited state of ADS680HO dye in all solvents.

- However, the coefficients "a" is positive(KAT), hydrogen bond donor from solvent to ADS680HO dye will establish ( $\alpha$ is the scale of the solvent hydrogen bond donor (HBD) acidities), because of alcohol group from the solvent donates the proton to two -OH groups of the dye, makes the excited state to be more stable than the ground state.

- "b" is negative (KAT) and its contribution is minute compare to contribution by "a" this suggests the stabilization of excited state with inactive chain is prohibits, so $\beta$ is the scale of the solvent hydrogen bond acceptor (HBA) basicities its contributions is very minute.

- Two –OH groups in the dye helps to increase in the HBD and HBA, on the contrary, ClO$_4^-$ and N in the dye makes the "a" and "b" negative in Katritzky parameter.

- The KAT percentage contribution of solvatochromic parameters for ADS680HO dye with different solvents is $P_{\pi^*}$ = 39.6%, $P_{\alpha}$=12.3%, $P_{\beta}$=48.1%. Even though "b" is negative, because of presence of two –OH groups, hydrogen bond acceptor $P_{\beta}$ (HBA) contribution is maximum.

- The KTZ percentage contribution of solvatochromic parameters for ADS680HO dye with different solvents is $P_{ET (30)}$ = 45.2% , while $P_{\varepsilon} +P_{\eta}$ =
54.8%. It witnesses, major contribution is due to solvent basicity and dipolarity/polarizability than $E_T$ (30) parameter.

- In case of ADS680HO the nonbonding electrons on tertiary amino group contribute towards the mobility of electrons on the aromatic ring. The nitrogen atom of tertiary amino group being $sp^3$ hybridized has more electron donating tendency. Upon excitation, the tertiary amino group becomes strong electron donor. These observed variations in the dipole moments of the laser dyes which can be explained by the resonance structures (or hybrid) (Figure 3.25). Generally it predicts the location of positive and negative electrostatic potentials in the molecule.

3.7.2 Multiparameter analysis of ADS740WS dye:

- The sign of "s" coefficient, for Kamlet-Abboud-Taft parameter and Katritzky is negative, it indicates, overall contribution of dipolarity and polarizability decreases the stabilization of excited state of ADS740WS dye in all solvents.

- Coefficient of "a" is positive (KAT), hydrogen bond donor from solvent to ADS740WS dye will establish bonding with ($\alpha$ is the scale of the solvent hydrogen bond donor (HBD) acidities) alcohol group transfers the proton to trivalent N.

- "b" is positive (KAT) and this contribution is small compare to "a" this suggests the stabilization of excited state with inactive chain, so $\beta$ is the scale of the solvent hydrogen bond acceptor (HBA) basicities it contribution is much higher.
• However, the coefficients "a" is negative (KTZ), there is no hydrogen bond established between the solvent and dye molecules (α is the scale of the solvent hydrogen bond donor (HBD) acidities).

• Two SO\(^-\) and SO\(_3\)Na groups in the dye makes the sign of "s" Kamlet-Abboud-Taft parameter as negative.

• The KAT percentage contribution of solvatochromic parameters for ADS740WS dye with different solvents is \( P_{\pi^*} = 36.8\% \), \( P_{\alpha^*} = 36.8\% \), \( P_{\beta^*} = 26.4\% \). because of presence of –OH group, \( P_{\alpha^*} \) is maximum. It makes the hydrogen bond donor (HBD) contribution maximum with trivalent N.

• The KTZ percentage contribution of solvatochromic parameters for ADS740WS dye with different solvents is \( P_{E_T(30)} = 34.1\% \), while \( P_{\varepsilon^*} + P_{\pi^*} = 65.9\% \). It witnesses, major contribution due to solvent basicity and dipolarity/polarizability than \( E_T \) (30) parameter.

• In case of ADS680HO and ADS740WS the nonbonding electrons on tertiary amino group contribute towards the mobility of electrons on the aromatic ring. The nitrogen atom of tertiary amino group being sp\(^3\) hybridized has more electron donating tendency. Upon excitation, the tertiary amino group becomes strong electron donor. These observed variations in the dipole moments of the laser dyes which can be explained by the resonance structures (or hybrid) (Figure 3.26), generally predicts the location of positive and negative electrostatic potentials in the molecule.
3.7.3 Multiparameter analysis of Red Mega 480 dye:

- The sign of "s" coefficient, for Kamlet-Abboud-Taft parameter and Katritzky is positive, it indicates, overall contribution of dipolarity and polarizability increases stabilization of excited state of Red Mega 480 dye in all solvents.

- However, the coefficients "a" is positive (KAT), hydrogen bond establishes between the dye and solvent molecules (α is the scale of the solvent hydrogen bond donor (HBD) acidities) because of two =O groups, one –OH group makes the excited state to be more stable than the ground state.

- "b" is positive (KAT) and this contribution, suggests the stabilization of excited state with inactive chain SO\textsuperscript{3}−, so, β is the scale of the solvent hydrogen bond acceptor (HBA) basicities.

- Two =O groups, one –OH group in the dye helps to increase in the HBD and HBA, the dye makes the "a" and "b" positive in Katritzky parameter (KTZ).

- The KAT percentage contribution of solvatochromic parameters for Red Mega 480 dye with different solvents is $P_{\pi^*} = 13.6\%$, $P_{\alpha} = 31.2\%$, $P_{\beta} = 55.2\%$, because of presence of two =O groups, one –OH group makes the hydrogen bond acceptor $P_{\beta}$ (HBA) contribution is maximum.

- The KTZ percentage contribution of solvatochromic parameters for Red Mega 480 dye with different solvents is $P_{E_T(30)} = 48.2\%$, while $P_e + P_n = 51.8\%$. It witnesses, major contribution due to solvent basicity and dipolarity/polarizability than $E_T(30)$ parameter.

- In case of Red Mega 480 dye the nonbonding electrons on carbonyl group, tertiary amino group and ring oxygen contribute towards the mobility of electrons on the aromatic ring. The nitrogen atom of tertiary amino group
being sp\(^3\) hybridized has more electron donating tendency. Upon excitation, the carbonyl group becomes highly electrophilic and tertiary amino group becomes strong electron donor. Also there is possibility of electron mobility between ring oxygen and carbonyl group. These observed variations in the dipole moments of the three dipolar laser dyes which can be explained by the resonance structures (or hybrid); generally it predicts the location of positive and negative electrostatic potentials in the molecule. Resonance (Figure 3.27) structure predicts the electron contributors are more in Red Mega 480, and hence the charge separation is larger.

3.8 Conclusions on multiparameter polarity calculations:

The following conclusions are made from the multiparameter polarity calculations,

1. Solvent effect on absorption and emission spectra of investigated ADS680HO, ADS740WS and Red Mega 480 laser dyes are complex and strongly depend on the nature of solvents and the substituent groups. Investigated solute-solvent interactions are generally controlled by dipolarity/polarizability and basicity of the solvents.

2. The obtained excited-state dipole moment by Lippert, Bakhashiev, Kawski-Chamma-Viallet, Mc-Rae, Suppan and Solvent polarity methods. We found that dye possesses higher dipole moment in excited state than the ground state. This demonstrates that laser dyes are more polar in excited state than the ground state. The change in the dipole moment between the excited state and ground state is due to intramolecular charge transfer (ICT); a large change in dipole moment on excitation suggests that excited state is twisted intramolecular charge transfer (TICT).
3. The obtained values of dipole moments in the ground and excited states with percentage contributions of solvatochromic parameters for investigated dyes demonstrates relative resonance structures and quantify the interactions between solvent and the dyes molecules. In resonance structures, non bonding electrons on the nitrogen atom, terminal thiol group, alcohol group entirely participate towards the mobility of \( \pi \) electrons into the aromatic ring, upon excitation, dye interacts with the solvent causing rising planarity of structures in excited states and then increase in molecular polarity.

4. In case of ADS680HO and ADS740WS the nonbonding electrons on tertiary amino group. The nitrogen atom of tertiary amino group being \( \text{sp}^3 \) hybridized has more electron donating tendency. Upon excitation, the tertiary amino group becomes strong electron donor. These observed variations in the dipole moments of the laser dyes which can be explained by the resonance structures (or hybrid); generally it predicts the location of positive and negative electrostatic potentials in the molecule.

5. In case of Red Mega 480 dye the nonbonding electrons on carbonyl group, tertiary amino group and ring oxygen contribute towards the mobility of electrons on the aromatic ring. The nitrogen atom of tertiary amino group being \( \text{sp}^3 \) hybridized has more electron donating tendency. Upon excitation, the carbonyl group becomes highly electrophilic and tertiary amino group becomes strong electron donor. Also there is possibility of electron mobility between ring oxygen and carbonyl group. These observed variations in the dipole moments of the three dipolar laser dyes which can be explained by the resonance structures (or hybrid), generally predicts the location of positive and negative electrostatic potentials in the molecule. Resonance structure predicts
the electron contributors are more in Red Mega 480, and hence the charge separation is larger, therefore the dipole moment is higher than that of the other two molecules. Whereas for ADS680HO and ADS740WS there are fewer resonance contributors, it would imply a lesser degree of charge separation and hence the dipole moment is smaller compared to other two molecules. Red Mega 480 has a moderate value of dipole moment. It can be visualized by the possible two resonating structures.
3.9 References:

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### Table 3.1 Solvent Parameters.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant $\varepsilon$</th>
<th>Refractive index $n$</th>
<th>$E_T(30)$ $[68]$</th>
<th>$E_T^N$ $[68]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>33.7</td>
<td>1.329</td>
<td>55.4</td>
<td>0.762</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
<td>1.361</td>
<td>51.9</td>
<td>0.654</td>
</tr>
<tr>
<td>Propanol</td>
<td>20.2</td>
<td>1.377</td>
<td>48.4</td>
<td>0.546</td>
</tr>
<tr>
<td>Butanol</td>
<td>17.4</td>
<td>1.399</td>
<td>49.7</td>
<td>0.593</td>
</tr>
<tr>
<td>Octanol</td>
<td>10.30</td>
<td>1.429</td>
<td>48.1</td>
<td>0.537</td>
</tr>
<tr>
<td>Nonanol</td>
<td>8.83</td>
<td>1.427</td>
<td>47.8</td>
<td>0.528</td>
</tr>
<tr>
<td>Decanol</td>
<td>8.00</td>
<td>1.437</td>
<td>47.7</td>
<td>0.525</td>
</tr>
<tr>
<td>DMSO</td>
<td>47.2</td>
<td>1.479</td>
<td>45.1</td>
<td>0.444</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>38.8</td>
<td>1.344</td>
<td>45.6</td>
<td>0.466</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>6.02</td>
<td>1.372</td>
<td>38.1</td>
<td>0.228</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.28</td>
<td>1.499</td>
<td>34.3</td>
<td>0.111</td>
</tr>
<tr>
<td>Tolune</td>
<td>2.38</td>
<td>1.497</td>
<td>33.9</td>
<td>0.099</td>
</tr>
<tr>
<td>Glycerol</td>
<td>46.53</td>
<td>1.472</td>
<td>57.2</td>
<td>0.818</td>
</tr>
</tbody>
</table>

### Table 3.2 Calculated values of $F(\varepsilon,n), F_1(\varepsilon,n), F_2(\varepsilon,n), F_3(\varepsilon), F_4(\varepsilon)$ for various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$F(\varepsilon,n)$</th>
<th>$F_1(\varepsilon,n)$</th>
<th>$F_2(\varepsilon,n)$</th>
<th>$F_3(\varepsilon)$</th>
<th>$F_4(\varepsilon)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.309</td>
<td>0.857</td>
<td>0.653</td>
<td>1.832</td>
<td>0.956</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.289</td>
<td>0.812</td>
<td>0.652</td>
<td>1.772</td>
<td>0.940</td>
</tr>
<tr>
<td>Propanol</td>
<td>0.277</td>
<td>0.781</td>
<td>0.647</td>
<td>1.730</td>
<td>0.928</td>
</tr>
<tr>
<td>Octanol</td>
<td>0.263</td>
<td>0.749</td>
<td>0.646</td>
<td>1.691</td>
<td>0.916</td>
</tr>
<tr>
<td>Nonanol</td>
<td>0.23</td>
<td>0.63</td>
<td>0.6</td>
<td>1.51</td>
<td>0.86</td>
</tr>
<tr>
<td>Decanol</td>
<td>0.215</td>
<td>0.586</td>
<td>0.583</td>
<td>1.446</td>
<td>0.839</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.203</td>
<td>0.55</td>
<td>0.571</td>
<td>1.396</td>
<td>0.822</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.263</td>
<td>0.841</td>
<td>0.744</td>
<td>1.878</td>
<td>0.969</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>0.2</td>
<td>0.49</td>
<td>0.5</td>
<td>1.250</td>
<td>0.77</td>
</tr>
<tr>
<td>Benzene</td>
<td>$3.24 \times 10^{-3}$</td>
<td>$7.04 \times 10^{-3}$</td>
<td>0.34</td>
<td>0.600</td>
<td>0.46</td>
</tr>
<tr>
<td>Tolune</td>
<td>0.013</td>
<td>0.029</td>
<td>0.35</td>
<td>0.630</td>
<td>0.48</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.26</td>
<td>0.84</td>
<td>0.74</td>
<td>1.880</td>
<td>0.97</td>
</tr>
</tbody>
</table>
Table 3.3 Absorption maxima, Fluorescence maxima and Stokes Shift for ADS680HO.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption Maximum (nm)</th>
<th>Fluorescence Maximum (nm)</th>
<th>Stokes Shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>669.08</td>
<td>711.2</td>
<td>885.15</td>
</tr>
<tr>
<td>Ethanol</td>
<td>671.88</td>
<td>710.8</td>
<td>814.95</td>
</tr>
<tr>
<td>Propanol</td>
<td>670.10</td>
<td>707.8</td>
<td>794.86</td>
</tr>
<tr>
<td>Butanol</td>
<td>677.75</td>
<td>710.6</td>
<td>682.09</td>
</tr>
<tr>
<td>Octanol</td>
<td>679.02</td>
<td>711.6</td>
<td>674.27</td>
</tr>
<tr>
<td>Nonanol</td>
<td>680.50</td>
<td>708.2</td>
<td>574.77</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>679.20</td>
<td>707.3</td>
<td>584.93</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>678.00</td>
<td>714.4</td>
<td>751.50</td>
</tr>
<tr>
<td>DMSO</td>
<td>674.70</td>
<td>713.6</td>
<td>807.95</td>
</tr>
<tr>
<td>Benzene</td>
<td>693.60</td>
<td>731.4</td>
<td>745.12</td>
</tr>
<tr>
<td>Toluene</td>
<td>692.00</td>
<td>711.6</td>
<td>398.03</td>
</tr>
<tr>
<td>Glycerol</td>
<td>690.40</td>
<td>724.3</td>
<td>677.92</td>
</tr>
</tbody>
</table>

Table 3.4 Absorption maxima, Fluorescence maxima and Stokes Shifts for ADS740WS.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption Maximum (nm)</th>
<th>Fluorescence Maximum (nm)</th>
<th>Stokes Shift (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>741.1</td>
<td>806.3</td>
<td>1092.16</td>
</tr>
<tr>
<td>Ethanol</td>
<td>742.1</td>
<td>796.6</td>
<td>921.04</td>
</tr>
<tr>
<td>Propanol</td>
<td>739.2</td>
<td>841.3</td>
<td>1642.22</td>
</tr>
<tr>
<td>Butanol</td>
<td>743.8</td>
<td>779.5</td>
<td>614.69</td>
</tr>
<tr>
<td>DMSO</td>
<td>749.5</td>
<td>805.3</td>
<td>924.45</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>740.2</td>
<td>780.2</td>
<td>693.75</td>
</tr>
</tbody>
</table>
Table 3.5 Absorption maxima, Fluorescence maxima and Stokes Shifts for Red Mega 480.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorption Maximum (nm)</th>
<th>Fluorescence Maximum (nm)</th>
<th>Stokes Shift (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>502</td>
<td>644</td>
<td>4392.37</td>
</tr>
<tr>
<td>Ethanol</td>
<td>503</td>
<td>630</td>
<td>4007.70</td>
</tr>
<tr>
<td>Propanol</td>
<td>503</td>
<td>622</td>
<td>3803.55</td>
</tr>
<tr>
<td>Butanol</td>
<td>507</td>
<td>621</td>
<td>3620.81</td>
</tr>
<tr>
<td>Nonanol</td>
<td>501</td>
<td>606</td>
<td>3458.43</td>
</tr>
<tr>
<td>Decanol</td>
<td>490</td>
<td>602</td>
<td>3796.87</td>
</tr>
<tr>
<td>DMSO</td>
<td>499</td>
<td>637</td>
<td>4341.49</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>501</td>
<td>635</td>
<td>4212.05</td>
</tr>
</tbody>
</table>

Table 3.6 Stokes Shift, arithmetic mean of Stokes values of ADS680HO.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\overline{\nu}_a) cm(^{-1})</th>
<th>(\overline{\nu}_f) cm(^{-1})</th>
<th>(\overline{\nu}_a - \overline{\nu}_f) cm(^{-1})</th>
<th>(\overline{\nu}_a + \overline{\nu}_f)/2 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>14945.9</td>
<td>14060.74</td>
<td>885.15</td>
<td>14503.32</td>
</tr>
<tr>
<td>Ethanol</td>
<td>14883.61</td>
<td>14068.66</td>
<td>814.95</td>
<td>14476.13</td>
</tr>
<tr>
<td>Propanol</td>
<td>14923.15</td>
<td>14128.28</td>
<td>794.87</td>
<td>14525.72</td>
</tr>
<tr>
<td>Octanol</td>
<td>14754.7</td>
<td>14072.61</td>
<td>682.09</td>
<td>14413.66</td>
</tr>
<tr>
<td>Butanol</td>
<td>14727.11</td>
<td>14052.84</td>
<td>674.27</td>
<td>14389.97</td>
</tr>
<tr>
<td>Nonanol</td>
<td>14695.08</td>
<td>14120.3</td>
<td>574.77</td>
<td>14407.69</td>
</tr>
<tr>
<td>DMSO</td>
<td>14723.2</td>
<td>14138.27</td>
<td>584.93</td>
<td>14430.74</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>14749.26</td>
<td>13997.76</td>
<td>751.50</td>
<td>14373.51</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>14821.4</td>
<td>14013.45</td>
<td>807.95</td>
<td>14417.43</td>
</tr>
<tr>
<td>Benzene</td>
<td>14417.53</td>
<td>13672.41</td>
<td>745.12</td>
<td>14044.97</td>
</tr>
<tr>
<td>Toluene</td>
<td>14450.87</td>
<td>14052.84</td>
<td>398.03</td>
<td>14251.85</td>
</tr>
<tr>
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<td>14484.36</td>
<td>13806.43</td>
<td>677.92</td>
<td>14145.4</td>
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</table>
Table 3.7 Stokes Shift, arithmetic mean of Stokes values of ADS740WS.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\bar{v}_a$ cm$^{-1}$</th>
<th>$\bar{v}_f$ cm$^{-1}$</th>
<th>$\bar{v}_a - \bar{v}_f$ cm$^{-1}$</th>
<th>$(\bar{v}_a + \bar{v}_f)/2$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>13493.46</td>
<td>12402.33</td>
<td>1092.16</td>
<td>12948.10</td>
</tr>
<tr>
<td>Ethanol</td>
<td>13475.27</td>
<td>12553.35</td>
<td>921.04</td>
<td>13014.66</td>
</tr>
<tr>
<td>Propanol</td>
<td>13528.14</td>
<td>11886.37</td>
<td>1642.22</td>
<td>12707.76</td>
</tr>
<tr>
<td>Butanol</td>
<td>13444.47</td>
<td>12828.74</td>
<td>614.69</td>
<td>13136.41</td>
</tr>
<tr>
<td>DMSO</td>
<td>13342.23</td>
<td>12417.73</td>
<td>924.45</td>
<td>12879.65</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>13509.86</td>
<td>12817.23</td>
<td>693.75</td>
<td>13163.44</td>
</tr>
</tbody>
</table>

Table 3.8 Stokes Shift, arithmetic mean of Stokes values of Red Meg 480.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\bar{v}_a$ cm$^{-1}$</th>
<th>$\bar{v}_f$ cm$^{-1}$</th>
<th>$\bar{v}_a - \bar{v}_f$ cm$^{-1}$</th>
<th>$(\bar{v}_a + \bar{v}_f)/2$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>19920.32</td>
<td>15527.95</td>
<td>4392.37</td>
<td>17724.13</td>
</tr>
<tr>
<td>Ethanol</td>
<td>19880.72</td>
<td>15873.02</td>
<td>4007.70</td>
<td>17876.87</td>
</tr>
<tr>
<td>Propanol</td>
<td>19880.72</td>
<td>16077.17</td>
<td>3803.55</td>
<td>17978.94</td>
</tr>
<tr>
<td>Butanol</td>
<td>19723.87</td>
<td>16103.06</td>
<td>3620.81</td>
<td>17913.46</td>
</tr>
<tr>
<td>Nonanol</td>
<td>19960.08</td>
<td>16501.65</td>
<td>3458.43</td>
<td>18230.87</td>
</tr>
<tr>
<td>Decanol</td>
<td>20408.16</td>
<td>16611.3</td>
<td>3796.87</td>
<td>18509.73</td>
</tr>
<tr>
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<td>20040.08</td>
<td>15698.59</td>
<td>4341.49</td>
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</tr>
<tr>
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<td>15748.03</td>
<td>4212.05</td>
<td>17854.06</td>
</tr>
</tbody>
</table>
Table 3.9 Slope, Intercept and correlation coefficient data’s of ADS680HO.

<table>
<thead>
<tr>
<th>Method</th>
<th>Slope</th>
<th>Intercept</th>
<th>Correlation coefficient</th>
<th>No of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lippert’s</td>
<td>1314.01</td>
<td>381.79</td>
<td>0.88</td>
<td>12</td>
</tr>
<tr>
<td>Bakhshiev’s</td>
<td>374.88</td>
<td>440.25</td>
<td>0.82</td>
<td>12</td>
</tr>
<tr>
<td>Kawski Chamma Viallet’s</td>
<td>544.09</td>
<td>14042.66</td>
<td>0.89</td>
<td>12</td>
</tr>
<tr>
<td>McRae’s</td>
<td>246.9</td>
<td>14342.48</td>
<td>0.86</td>
<td>12</td>
</tr>
<tr>
<td>Suppan’s</td>
<td>655.50</td>
<td>14165.70</td>
<td>0.87</td>
<td>12</td>
</tr>
<tr>
<td>$E^N_T$</td>
<td>311.18</td>
<td>549.589</td>
<td>0.89</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 3.10 Slope, Intercept and correlation coefficient data’s of ADS740WS by different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Slope</th>
<th>Intercept</th>
<th>Correlation coefficient</th>
<th>No of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lippert’s</td>
<td>10005.23</td>
<td>694.89</td>
<td>0.86</td>
<td>6</td>
</tr>
<tr>
<td>Bakhshiev’s</td>
<td>307.01</td>
<td>730.35</td>
<td>0.91</td>
<td>6</td>
</tr>
<tr>
<td>Kawski Chamma Viallet’s</td>
<td>758.7</td>
<td>12468.44</td>
<td>0.87</td>
<td>6</td>
</tr>
<tr>
<td>McRae’s</td>
<td>370.25</td>
<td>12801.84</td>
<td>0.85</td>
<td>6</td>
</tr>
<tr>
<td>Suppan’s</td>
<td>1961.06</td>
<td>11612.01</td>
<td>0.91</td>
<td>6</td>
</tr>
<tr>
<td>$E^N_T$</td>
<td>670.32</td>
<td>600.53</td>
<td>0.89</td>
<td>6</td>
</tr>
</tbody>
</table>
Table 3.11 Slope, Intercept and correlation coefficient data of Red Mega 480 laser dye by different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Slope</th>
<th>Intercept</th>
<th>Correlation coefficient</th>
<th>No of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lippert’s</td>
<td>5967.03</td>
<td>2477.71</td>
<td>0.95</td>
<td>8</td>
</tr>
<tr>
<td>Bakhshiev’s</td>
<td>2138.13</td>
<td>2496.65</td>
<td>0.92</td>
<td>8</td>
</tr>
<tr>
<td>Kawski Chamma Viallet’s</td>
<td>3618.44</td>
<td>20501.13</td>
<td>0.91</td>
<td>8</td>
</tr>
<tr>
<td>McRae’s</td>
<td>1321.5</td>
<td>21014.42</td>
<td>0.89</td>
<td>8</td>
</tr>
<tr>
<td>Suppan’s</td>
<td>4735.43</td>
<td>21727.91</td>
<td>0.85</td>
<td>8</td>
</tr>
<tr>
<td>$E^N_T$</td>
<td>685.80</td>
<td>4347.19</td>
<td>0.91</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 3.12 Ground-state, Excited state Dipole moment of ADS680HO, ADS740WS and Red Mega 480 dyes.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Cavity radius ‘a’ (Å)</th>
<th>$\mu_g$ (D)</th>
<th>$\mu_e$ (D)</th>
<th>$\mu_e$ (D)</th>
<th>$\mu_e$ (D)</th>
<th>$\mu_e$ (D)</th>
<th>$\mu_e$ (D)</th>
<th>$\mu_e$ (D)</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADS680HO</td>
<td>5.19</td>
<td>0.53</td>
<td>2.86</td>
<td>4.90</td>
<td>14.16</td>
<td>36.72</td>
<td>1.67</td>
<td>5.39</td>
<td>4.73</td>
</tr>
<tr>
<td>ADS740WS</td>
<td>5.27</td>
<td>1.60</td>
<td>3.77</td>
<td>5.38</td>
<td>8.73</td>
<td>39.36</td>
<td>3.35</td>
<td>2.36</td>
<td>5.73</td>
</tr>
<tr>
<td>Red Mega 480</td>
<td>4.53</td>
<td>1.54</td>
<td>5.99</td>
<td>8.97</td>
<td>17.42</td>
<td>58.43</td>
<td>2.95</td>
<td>3.89</td>
<td>1.82</td>
</tr>
</tbody>
</table>

1 Debye = $3.33564 \times 10^{-30}$ Cm=$10^{-18}$ esu cm.

a Ground state dipole moment calculated from Equation 3.16

b Excited state dipole moment calculated from Equation 3.17 Solvotochromic method
c Excited state dipole moment calculated from Lippert’s Equation 3.11
d Excited state dipole moment calculated from Mc Rae’s Equation 3.14
f Excited state dipole moment calculated from Suppan’s Equation 3.15
h Excited state dipole moment calculated from microscopic solvent polarity function $E^N_T$
i Ratio of excited to ground state dipole moments calculated from Equation 3.18
j Angle between excited state to ground state dipole moment with solvotochromic data
Table 3.13 Spectroscopic polarity parameters [68] and polarity functions are used in multiparameter analysis of ADS680HO laser dye.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε</th>
<th>n</th>
<th>$E_T(30)$</th>
<th>α</th>
<th>β</th>
<th>$\pi^*$</th>
<th>$E_T^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>33.7</td>
<td>1.329</td>
<td>55.4</td>
<td>0.98</td>
<td>0.66</td>
<td>0.60</td>
<td>0.762</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
<td>1.361</td>
<td>51.9</td>
<td>0.86</td>
<td>0.75</td>
<td>0.54</td>
<td>0.654</td>
</tr>
<tr>
<td>Propanol</td>
<td>20.2</td>
<td>1.377</td>
<td>48.4</td>
<td>0.76</td>
<td>0.84</td>
<td>0.48</td>
<td>0.546</td>
</tr>
<tr>
<td>Butanol</td>
<td>17.4</td>
<td>1.399</td>
<td>49.7</td>
<td>0.84</td>
<td>0.84</td>
<td>0.47</td>
<td>0.593</td>
</tr>
<tr>
<td>Nonanol</td>
<td>8.83</td>
<td>1.427</td>
<td>47.8</td>
<td>0.13</td>
<td>0.73</td>
<td>0.528</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>38.8</td>
<td>1.344</td>
<td>45.6</td>
<td>0.19</td>
<td>0.4</td>
<td>0.66</td>
<td>0.466</td>
</tr>
<tr>
<td>DMSO</td>
<td>47.2</td>
<td>1.479</td>
<td>45.1</td>
<td>0.00</td>
<td>0.76</td>
<td>1.00</td>
<td>0.444</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.28</td>
<td>1.5</td>
<td>34.3</td>
<td>0.00</td>
<td>0.55</td>
<td>0.111</td>
<td></td>
</tr>
<tr>
<td>Tolune</td>
<td>2.38</td>
<td>1.497</td>
<td>33.9</td>
<td>0</td>
<td>0.11</td>
<td>0.49</td>
<td>0.099</td>
</tr>
</tbody>
</table>

Table 3.14 Regression fits to solvatochromic polarity scales for Stokes shift of ADS680HO laser dye.

<table>
<thead>
<tr>
<th>Multiparameter scale</th>
<th>$(\nu_a - \nu_f)_0$ ($10^3$ cm$^{-1}$)</th>
<th>a ($10^3$ cm$^{-1}$)</th>
<th>b ($10^3$ cm$^{-1}$)</th>
<th>S ($10^3$ cm$^{-1}$)</th>
<th>R$^a$</th>
<th>SD$^b$</th>
<th>F$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Katritzky</td>
<td>1.559 ($\pm 0.011$)</td>
<td>-0.472 ($\pm 0.009$)</td>
<td>-4.871 ($\pm 0.035$)</td>
<td>0.00643 ($\pm 0.00001$)</td>
<td>0.97</td>
<td>123</td>
<td>2</td>
</tr>
<tr>
<td>Kamlet-Abboud-Taft</td>
<td>0.465 ($\pm 0.002$)</td>
<td>0.334 ($\pm 0.002$)</td>
<td>-0.088 ($\pm 0.002$)</td>
<td>0.215 ($\pm 0.004$)</td>
<td>0.92</td>
<td>132</td>
<td>2</td>
</tr>
</tbody>
</table>

Number of the solvents: 9  
R$^a$ – square, SD$^b$ - standard error, F$^c$ - statistic

Table 3.15 Percentage contribution of solvatochromic parameters of ADS680HO laser dye.

<table>
<thead>
<tr>
<th>Multiparameter scale</th>
<th>$P_\varepsilon$ (%)+$P_n$ (%)</th>
<th>$P_{E_T(30)}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{\pi^*}$ (%)</td>
<td>$P_\alpha$ (%)</td>
</tr>
<tr>
<td>Katritzky</td>
<td>54.8</td>
<td>45.2</td>
</tr>
<tr>
<td>Kamlet-Abboud-Taft</td>
<td>39.6</td>
<td>12.3</td>
</tr>
</tbody>
</table>
Table 3.16 Spectroscopic polarity parameters [68] and polarity functions are used in multiparameter analysis of ADS740WS laser dye.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\varepsilon$</th>
<th>n</th>
<th>$E_T(30)$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\pi^*$</th>
<th>$E^N_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>33.7</td>
<td>1.329</td>
<td>55.4</td>
<td>0.98</td>
<td>0.66</td>
<td>0.60</td>
<td>0.762</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
<td>1.361</td>
<td>51.9</td>
<td>0.86</td>
<td>0.75</td>
<td>0.54</td>
<td>0.654</td>
</tr>
<tr>
<td>Propanol</td>
<td>20.2</td>
<td>1.377</td>
<td>48.4</td>
<td>0.76</td>
<td>0.84</td>
<td>0.48</td>
<td>0.546</td>
</tr>
<tr>
<td>Butanol</td>
<td>17.4</td>
<td>1.399</td>
<td>49.7</td>
<td>0.84</td>
<td>0.84</td>
<td>0.47</td>
<td>0.593</td>
</tr>
<tr>
<td>DMSO</td>
<td>47.2</td>
<td>1.479</td>
<td>45.1</td>
<td>0.00</td>
<td>0.76</td>
<td>1.00</td>
<td>0.444</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>38.8</td>
<td>1.344</td>
<td>45.6</td>
<td>0.19</td>
<td>0.4</td>
<td>0.66</td>
<td>0.466</td>
</tr>
</tbody>
</table>

Table 3.17 Regression fits to solvatochromic polarity scales for Stokes shift of ADS740WS laser dye.

<table>
<thead>
<tr>
<th>Multiparameter scale</th>
<th>$(\bar{\nu}_a - \bar{\nu}_f)_0$</th>
<th>$a$</th>
<th>$b$</th>
<th>$s$</th>
<th>$R^a$</th>
<th>SD$^b$</th>
<th>F$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10$^3$ cm$^{-1}$)</td>
<td>(10$^3$ cm$^{-1}$)</td>
<td>(10$^3$ cm$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Katritzky</td>
<td>0.621(±0.067)</td>
<td>-5.958 (±0.23)</td>
<td>5.927 (±1.73)</td>
<td>0.858 (±0.08)</td>
<td>0.95</td>
<td>164</td>
<td>1.3</td>
</tr>
<tr>
<td>Kamlet-Abboud-Taft</td>
<td>0.473(±0.019)</td>
<td>0.635 (±0.12)</td>
<td>7.618 (±1.65)</td>
<td>-1.112 (±0.22)</td>
<td>0.91</td>
<td>131</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Number of the solvents: 6. $R^a$ – square, SD$^b$ - standard error, F$^c$ - statistic

Table 3.18 Percentage contribution of solvatochromic parameters of ADS740WS laser dye.

<table>
<thead>
<tr>
<th>Multiparameter scale</th>
<th>$P_{\varepsilon_f}$ (%)+$P_n$ (%)</th>
<th>$P_{E_T (30)}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{\pi^*}$ (%)</td>
<td>$P_a$ (%)</td>
</tr>
<tr>
<td>Katritzky</td>
<td>66</td>
<td>34</td>
</tr>
<tr>
<td>Kamlet-Abboud-Taft</td>
<td>37</td>
<td>37</td>
</tr>
</tbody>
</table>
Table 3.19 Spectroscopic polarity parameters [68] and polarity functions are used in multiparameter analysis of Red Mega 480 laser dye.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε</th>
<th>n</th>
<th>$\varepsilon_T(30)$</th>
<th>A</th>
<th>b</th>
<th>$\pi^*$</th>
<th>$E_T^\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>33.7</td>
<td>1.329</td>
<td>55.4</td>
<td>0.98</td>
<td>0.66</td>
<td>0.60</td>
<td>0.762</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
<td>1.361</td>
<td>51.9</td>
<td>0.86</td>
<td>0.75</td>
<td>0.54</td>
<td>0.654</td>
</tr>
<tr>
<td>Propanol</td>
<td>20.2</td>
<td>1.377</td>
<td>48.4</td>
<td>0.76</td>
<td>0.84</td>
<td>0.48</td>
<td>0.546</td>
</tr>
<tr>
<td>Butanol</td>
<td>17.4</td>
<td>1.399</td>
<td>49.7</td>
<td>0.84</td>
<td>0.84</td>
<td>0.47</td>
<td>0.593</td>
</tr>
<tr>
<td>Nonanol</td>
<td>8.83</td>
<td>1.427</td>
<td>47.8</td>
<td>0.13</td>
<td>0.1</td>
<td>0.73</td>
<td>0.528</td>
</tr>
<tr>
<td>Decanol</td>
<td>8.0</td>
<td>1.437</td>
<td>47.7</td>
<td>0.70</td>
<td>0.82</td>
<td>0.45</td>
<td>0.525</td>
</tr>
<tr>
<td>DMSO</td>
<td>47.2</td>
<td>1.479</td>
<td>45.1</td>
<td>0.00</td>
<td>0.76</td>
<td>1.00</td>
<td>0.444</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>38.8</td>
<td>1.344</td>
<td>45.6</td>
<td>0.19</td>
<td>0.4</td>
<td>0.66</td>
<td>0.460</td>
</tr>
</tbody>
</table>

Table 3.20 Regression fits to solvatochromic polarity scales for Stokes shift of Red Mega 480 laser dye.

<table>
<thead>
<tr>
<th>Multiparameter scale</th>
<th>$\bar{V}_a - \bar{V}_f$</th>
<th>a (10$^3$ cm$^{-1}$)</th>
<th>b (10$^3$ cm$^{-1}$)</th>
<th>s (10$^3$ cm$^{-1}$)</th>
<th>$R^a$</th>
<th>SD$^b$</th>
<th>F$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Katritzky</td>
<td>-1.543 (±0.045)</td>
<td>9.813 (±0.044)</td>
<td>2.150 (±0.087)</td>
<td>0.0119 (±0.0004)</td>
<td>0.89</td>
<td>186</td>
<td>1.9</td>
</tr>
<tr>
<td>Kamlet-Abboud-Taft</td>
<td>2.223 (±0.009)</td>
<td>0.621 (±0.007)</td>
<td>0.251 (±0.006)</td>
<td>1.981 (±0.012)</td>
<td>0.97</td>
<td>129</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Number of the solvents: 8, $R^a$-square, SD$^b$-standard error, F$^c$-statistic

Table 3.21 Percentage contribution of solvatochromic parameters of Red Mega 480 laser dye.

<table>
<thead>
<tr>
<th>Multiparameter scale</th>
<th>$P_{\varepsilon_T}(%) + P_{n}(%)$</th>
<th>$P_{\varepsilon_T(30)}(%)$</th>
<th>$P_{\pi^*}(%)$</th>
<th>$P_{\pi}(%)$</th>
<th>$P_{\beta}(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Katritzky</td>
<td>51.8</td>
<td>48.2</td>
<td>13.6</td>
<td>31.2</td>
<td>55.2</td>
</tr>
<tr>
<td>Kamlet-Abboud-Taft</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter III : Dipole Moment Measurements

Molecular formula : \( \text{C}_{37} \text{H}_{39} \text{N}_2 \text{O}_6 \text{Cl} \) (ADS680HO)

IUPAC Name : 2-[5-(1,3-Dihydro-3,3-dimethyl-(2-hydroxyethyl)-2H-benz[e]indol-2-ylidene)-1,3-pentadienyl]-3,3-dimethyl-1-(2-hydroxyethyl)-3Hbenz[e]indolium perchlorate

![Molecular Structure and IUPAC name of ADS680HO](image1)

Figure 3.1 Molecular Structure and IUPAC name of ADS680HO

Molecular formula : \( \text{C}_{35} \text{H}_{43} \text{N}_2 \text{O}_6 \text{S}_2 \text{Na} \) (ADS740WS)

IUPAC Name : 2-[7-(1,3-Dihydro-3,3-dimethyl-1-(4-sulfobutyl)-2H-indol-2-ylidene)-1,3,5-heptatrienyl] -3,3-dimethyl-1-(4-sulfobutyl)-3H-indolium

![Molecular Structure and IUPAC name of ADS740WS](image2)

Figure 3.2 Molecular Structure and IUPAC name of ADS740WS.
Molecular formula : C$_{28}$H$_{30}$N$_2$O$_5$S (Red Mega 480)

IUPAC Name : 1-(5-carboxypentyl)-6-{2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]ethenyl}pyridinium-3-sulfonate

Figure 3.3 Molecular Structure and IUPAC name of Red Mega 480.

Figure 3.4 Absorption and emission spectra of ADS680HO in decanol.
Chapter III: Dipole Moment Measurements

Figure 3.5 Absorption and emission spectra of ADS740WS in Ethanol.

Figure 3.6 Absorption and emission spectra of Red mega480 in Ethanol.
Figure 3.7 Plot of Stokes shift versus $F(\varepsilon, n)$ i.e. Lippert’s Polarity parameter of ADS680HO in different solvents, (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-octanol, 6-Nonanol, 7-ethyl acetate, 8-acetonitrile, 9-DMSO, 10-benzene, 11-tolune, 12-glycerol) (---Linear fit).

Figure 3.8 Plot of Stokes shift versus $F_1(\varepsilon, n)$ i.e. Bakshiev’s Polarity parameter of ADS680HO in different solvents, (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-octanol, 6-Nonanol, 7-ethyl acetate, 8-acetonitrile, 9-DMSO, 10-benzene, 11-tolune, 12-glycerol) (-----Linear fit).
Figure 3.9 Plot of $\frac{1}{2}(\vec{v}_a^+ + \vec{v}_f)$ versus $F_2(\epsilon, n)$ i.e. Kawski-Chamma-Viallet’s Polarity parameter of ADS680HO in different solvents (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-octanol, 6-Nonanol, 7-ethyl acetate, 8-acetonitrile, 9-DMSO, 10-benzene, 11-tolune, 12-glycerol) (---Linear fit).

Figure 3.10 Plot of $v_a^+$ versus $F_3(\epsilon)$ i.e. McRae’s Polarity parameter of ADS680HO in different solvents (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-octanol, 6-Nonanol, 7-ethyl acetate, 8-acetonitrile, 9-DMSO, 10-benzene, 11-tolune, 12-glycerol) (---Linear fit).
Figure 3.11 Plot of $\nu_a$ versus $F_4(\varepsilon)$ i.e. Suppan’s Polarity parameter of ADS680HO in different solvents (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-octanol, 6-Nonanol, 7-ethyl acetate, 8-acetonitrile, 9-DMSO, 10-benzene, 11-tolune, 12-glycerol). (Linear fit).

Figure 3.12 Plot of $\nu_a - \nu_f$ versus $E_T^N$ i.e. solvent Polarity parameter of ADS680HO in different solvents (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-octanol, 6-Nonanol, 7-ethyl acetate, 8-acetonitrile, 9-DMSO, 10-benzene, 11-tolune, 12-glycerol) (Linear fit).
Figure 3.13 Plot of Stokes shift versus $F(\varepsilon, n)$ i.e. Lippert’s Polarity parameter of ADS740WS in different solvents. (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-DMSO, 6-acetonitrile. (---Linear fit).

Figure 3.14 Plot of Stokes shift versus $F_1(\varepsilon, n)$ i.e. Bakshiev’s Polarity parameter of ADS740WS in different solvents. (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-DMSO, 6-acetonitrile. (---Linear fit).
Figure 3.15 Plot of $\frac{1}{2}(\nu_a + \nu_f)$ versus $F_2(\varepsilon, n)$ i.e. Kawski-Chamma-Viallet’s Polarity parameter of ADS740WS in different solvents. (1- methanol, 2- ethanol, 3-propanol, 4-butanol, 5- DMSO, 6- acetonitrile. (--- Linear fit).

Figure 3.16 Plot of $\nu_a$ versus $F_3(\varepsilon)$ i.e. McRae’s Polarity parameter of ADS740WS in different solvents. (1) methanol, 2-ethanol, 3-propanol, 4-butanol, 5-DMSO, 6- acetonitrile. (--- Linear fit).
Chapter III : Dipole Moment Measurements

Figure 3.17 Plot of $\bar{\nu}_a$ versus $F_4(\varepsilon)$ i.e. Suppan’s Polarity parameter of ADS740WS in different solvents. (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-DMSO, 6-acetonitrile. (---Linear fit).

Figure 3.18 Plot of $\bar{\nu}_a - \nu_f$ versus $E_N^{T}$ i.e. solvent Polarity parameter of ADS740WS in different solvents. (1-methanol, 2-ethanol, 3-propanol, 4-butanol, 5-DMSO, 6-acetonitrile. (---Linear fit).
Figure 3.19 Plot of Stokes shift versus $F(\varepsilon, n)$ i.e. Lippert’s Polarity parameter of Red Mega 480 in different solvents. (1-methanol, 2-ethanol, 3-isopropanol, 4-butanol, 5-nonanol, 6-decanol, 7-DMSO, 8-acetonitrile) (--- linear fit).

Figure 3.20 Plot of Stokes shift versus $F_1(\varepsilon,n)$ i.e. Bakshiev’s Polarity parameter of Red Mega 480 in different solvents. (1-methanol, 2-ethanol, 3-isopropanol, 4-butanol, 5-nonanol, 6-decanol, 7-DMSO, 8-acetonitrile) (--- linear fit).
Figure 3.21 Plot of $\frac{1}{2}(\overline{\nu_a} + \overline{\nu_f})$ versus $F_2(\varepsilon, n)$ i.e. Kawski-Chamma-Viallet’s Polarity parameter of Red Mega 480 in different solvents. (1-methanol, 2-ethanol, 3-isopropanol, 4-butanol, 5-nonanol, 6-decanol, 7-DMSO, 8-acetonitrile) (linear fit).

Figure 3.22 Plot of $\overline{\nu_a}$ versus $F_3(\varepsilon)$ i.e. McRae’s Polarity parameter of Red Mega 480 in different solvents. (1-methanol, 2-ethanol, 3-isopropanol, 4-butanol, 5-nonanol, 6-decanol, 7-DMSO, 8-acetonitrile) (linear fit).
Figure 3.23 Plot of $\nu_a$ versus $F_d(\varepsilon)$ i.e. Suppan’s Polarity parameter of Red Mega 480 in different solvents.(1-methanol, 2-ethanol, 3-isopropanol, 4-butanol, 5-nonanol, 6-decanol, 7-DMSO, 8-acetonitrile) (------- linear fit).

Figure 3.24 Plot of $\nu_a$ versus $N_T$ i.e. solvent Polarity parameter of Red Mega 480 in different solvents.(1-methanol, 2-ethanol, 3-isopropanol, 4-butanol, 5-nonanol, 6-decanol, 7-DMSO, 8-acetonitrile) (------- linear fit).
Figure 3.25 Possible resonance structure of ADS680HO laser dye.

Figure 3.26 Possible resonance structure of ADS740WS laser dye.

Figure 3.27 Possible resonance structures of Red Mega 480 laser dye.