

Solvent Effects on the Solvatochromism of 7-Aminocoumarin Derivatives in Neat and Binary Solvent Mixtures: Correlation of the Electronic Transition Energies with the Solvent Polarity Parameters

Jin Yeong Choi, Eun Ju Park, Seung Hyun Chang, and Tai Jong Kang*

Department of Chemistry, Daegu University, Gvoungsan 712-714, Korea. *E-mail: tj kang@daegu.ac.kr

Received April 23, 2009, Accepted May 25, 2009

The change in the electronic absorption and emission energy of 7-aminocoumarin derivatives in binary solvent mixtures has been studied. The electronic transition energy along with the Stokes' shift is correlated with the orientation polarizability of the solvent as well as the empirical solvent polarity parameters $E_T(30)$. It is observed that the emission peak shift traces the change of $E_T(30)$ value very closely in binary solvent mixtures. The emission transition more strongly depends on the solvent polarity than the absorption, which indicates the dipole moment gets larger on excitation. From the dependence of the Stokes' shift of 7-aminocoumarins with the solvent polarity parameters and the ground state dipole moment obtained by the semi-empirical calculations, the excited state dipole moment was estimated. The fluorescence lifetime change of 7-aminocoumarins in binary solvent mixtures was measured and the results are explained in terms of molecular conformation and solvent polarity. The study indicates the empirical solvent polarity $E_T(30)$ is a good measure of microscopic solvent polarity and it probes in general the non-specific solvent interactions.

Key Words: Solvent effects, Solvatochromism, Stokes' shift, Solvent polarity parameters, $E_T(30)$

Introduction

Solvation plays a crucial role in various processes taking place in the liquid phase and thus studying the solvation process is important for understanding the solvent effects on chemical reactions.¹ Many biological processes including transportation, signaling, metabolism are also controlled by solvation.^{2,3}

Solvent parameters such as dielectric constant and refractive index are involved in representing various solvent properties. Polarity is an important solvent property for explaining solvent effects on many chemical processes. Different polarity parameters have been proposed over the years to account for solute-solvent interactions.¹ Due to the complexity of intermolecular interactions and the fluctuation of states, the development of a generally valid model for solutions is not an easy task. Thus, models with the non-specific solute-solvent interactions like van der Waals interactions are mainly dealt with. Several theoretical treatments have been developed to link quantitatively the solvent effects to the bulk properties of solvent. The simplest model among these treatments is given by Onsager⁴ and Kirkwood.⁵ In this model the solute molecule is assumed to be in a cavity of radius a with a point dipole μ and interacts with surrounding solvent molecules. Solvent molecules are considered as dielectric continuum and create the reaction field R through the dipolar interaction with the solute molecule. This reaction field is proportional to the magnitude of the dipole moment and the polarizability of the solvent, and is given as $R = 2\mu\Delta f(\epsilon, n)/a^3$. Sum of the interaction forces between the molecules of solvent and solute can be related to so-called polarity. Considering both the high- and low-frequency polarizability of solvent molecules, the orientation polarizability, $\Delta f(\epsilon, n)$ defined by the following equation would measure solvent polarity,

$$\Delta f(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (1)$$

where ϵ is a dielectric constant and n is a refractive index of the solvent medium. The polarizability of the solvent is a result of both the electron mobility and the dipole moment of solvent molecules.

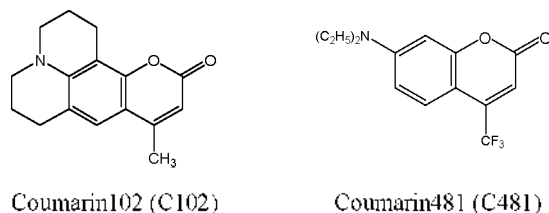
The concept of reaction field theory is useful in relating solvent effects with the change of electronic transition energy and frequency shifts in various spectroscopic applications. The electronic emission spectra as well as the absorption spectra of many chromophore containing organic molecules are commonly modified by the solvents. Spectral changes due to solvent properties may arise from either the physical intermolecular solute-solvent interactions such as dipolar interaction or the chemical processes such as electron (or proton) transfer, complexation, isomerization, etc. The solvent effects on the Stokes' shift of dye molecules were found to be correlated with this model. However, explaining solvent effects with the $\Delta f(\epsilon, n)$ parameter is not always satisfactory especially when there is a specific interaction between solute and solvent molecules and empirical polarity parameters are often employed. Such empirical polarity scales for studying solvent effects are mostly based on the use of dyes whose spectral profiles are significantly affected by polarity of the medium. Various solvatochromic models which allow the quantitative calculations of the solvent dependence of the electronic transition have been reported. The Kosower's Z value represents polarity in terms of the solvent influence on the transition of the longest wavelength charge transfer absorption of a salt, usually pyridinium iodide or the pyridinium zwitterion.^{6,7} The $E_T(30)$ measures solvent polarity with the charge transfer absorption maxima of propidium phenol betaine known as the Reichardt dye.^{8,9} The extreme sensitivity of absorption spectrum to

changes in the surrounding medium has made this molecule a useful probe in the study of micelle/solution interfaces,¹⁰ phospholipid bilayers,¹¹ and liquid chromatography.¹² Other empirical polarity parameters such as Y-scale and π^* -scale have been suggested, but it is important to recognize that there is no such thing as a single polarity parameter in explaining a multitude of solvent effects.

In this work, we have studied the influence of solvent polarity on the frequencies of absorption and emission transition for two 7-aminocoumarin derivatives. The excited state dipole moments are estimated using the Lippert-Mataga model.^{13,14} Also the change of fluorescence lifetimes are investigated and related to the solvent polarity. Measurements on solvents effects are carried out both in neat and binary solvent systems covering wide range of solvent polarity. Solvent effects of nonspecific solute-solvent interactions are evaluated in terms of polarity parameters $\Delta f(\epsilon, n)$ and $E_T(30)$.

Experimental

Reichardt's dye (pentaphenyl pyridiniumphenilate) was purchased from the Sigma-Aldrich Chemical Co., and was used as a probe molecule to measure the $E_T(30)$ value of neat and binary solvents. 7-diethylamino-4-trifluoromethylcoumarin (Coumarin481) and 2,3,5,6-1*H*,4*H*-tetrahydro-8-methylquinolizino- $\langle 9,9a,1\text{-}gh \rangle$ coumarin (Coumarin102 or Coumarin480), whose molecular structure is shown as following were purchased from Exciton.



These 7-aminocoumarin dyes of laser grade were used without further purification. All the neat and binary solvents are the Sigma-Aldrich spectrograde reagents. Especially, benzene and acetonitrile were kept in molecular sieves for a day after purification in order to eliminate a trace of water content. Binary solvent system provides relatively easy way of changing solvent polarity without altering the physical and chemical properties of the medium greatly. Binary mixtures of benzene/acetonitrile, benzene/methanol, and 1,4-dioxane/water are used in this work. LUDOX[®] AS-30 colloidal silica solutions which is to scatter laser light for the fluorescence lifetime measurements was also purchased from the Sigma-Aldrich Chemical Co.

Absorption spectra were recorded on a Hewlett Packard UV-Vis HP8453 spectrophotometer which is equipped with photodiode array detectors. Fluorescence spectra were taken by using a Jasco FP-6300 Spectrofluorometer with a resolution of ~ 1 nm. Fluorescence decay was measured with a time-resolved spectrometer (PicoQuant FluoTime 200) by means of time-correlated single photon counting (TCSPC) method.

The excitation source is a pulsed diode laser (LDH400) of $\lambda_{\text{max}} = 395$ nm operated at 20 MHz. The FWHM of a laser pulse is typically 45 ps. The instrument response function of TCSPC system was ~ 190 ps using a Hamamatsu photomultiplier tube (PMT H5783-01). Dark counts were maintained below 100 cps. Fluorescence decay data were fitted to the appropriate exponential model after deconvolution of the instrument response function by an iterative deconvolution technique, using the Fluofit fluorescence decay analysis software, where reduced χ^2 and weighted residuals serve as parameters for goodness of fit.

Results and Discussion

Microscopic solvent polarity measured by $E_T(30)$. The solvent polarity parameter $E_T(30)$ was measured for various neat and binary solvent mixtures using the Reichardt's dye and compared to solvent polarization function $\Delta f(\epsilon, n)$. $E_T(30)$ is defined as the transition energy of the dissolved betaine dye in the appropriate solvent measured in kcal/mol according to the equation.

$$E_T(30) = hcN_A\nu \quad (2)$$

where h is the Plank's constant, c is the speed of light, N_A is Avogadro's number and ν is the electronic transition energy in wavenumber. It is often recommended to use the normalized E_T^N value for which water and tetramethylsilane(TMS) are used as reference solvents in each extreme polarity values.

$$E_T^N = \frac{E_T(30)_{\text{solvent}} - E_T(30)_{\text{TMS}}}{E_T(30)_{\text{water}} - E_T(30)_{\text{TMS}}} \quad (3)$$

The normalized E_T^N value is scaled approximately from 0 to 1 for most of solvents commonly used. The enormously large shift of charge transfer absorption band of the dye molecule makes E_T^N very sensitive parameter for characterizing the polarity of solvents. Fig. 1 shows the plot of E_T^N versus $\Delta f(\epsilon, n)$

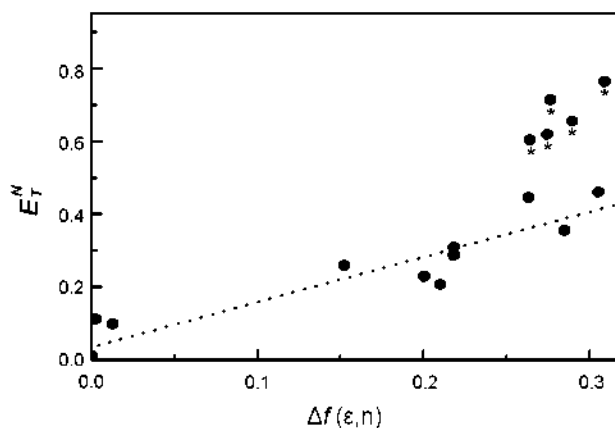


Figure 1. Plot of the empirical solvent polarity parameter, E_T^N vs. solvent orientation polarizability function, $\Delta f(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$ for various solvents. Data points with asterisk represent protic solvents.

for various aprotic as well as protic solvents. It is noted that there is a linear correlation between E_T^N and $\Delta f(\epsilon, n)$ for aprotic solvents, but large deviation is observed for protic solvents. This is probably due to the specific interactions like hydrogen bonding and thus $\Delta f(\epsilon, n)$ does not seem to explain microscopic solvent polarity very well for protic solvents.

The solvent polarity of binary solvent systems was measured and the change of E_T^N value of benzene/acetonitrile, benzene/methanol, and 1,4-dioxane/water mixture as a function of the mole fraction of more polar component is shown in Fig. 2 respectively. Langhals has proposed a trial equation in which polarity is related to the logarithm of the molar concentration of more polar solvent, and applied to various binary mixtures.¹⁵ The E_T^N values of binary solvent mixtures are not related to

their composition in a simple linear manner, but more intricate change is observed. The dotted line simply connects the E_T^N values of one solvent component to the value of the other solvent component of the mixture. The line would represent the change of E_T^N if the solvent mixture were an ideal solution. The fact that E_T^N values of binary solvent mixtures were not related to their composition in a simple manner suggests more or less non-ideal behavior of binary solvent mixtures. In both benzene/acetonitrile mixture and benzene/methanol mixture, addition of small amount of polar solvent to benzene causes a disproportionately large hypsochromic shift of betaine dye, which corresponds to an excessively large increase in E_T^N . This is occurring in the vicinity of mole fraction of 0.2. Above the mole fraction of 0.2, a rather linear increase of E_T^N is

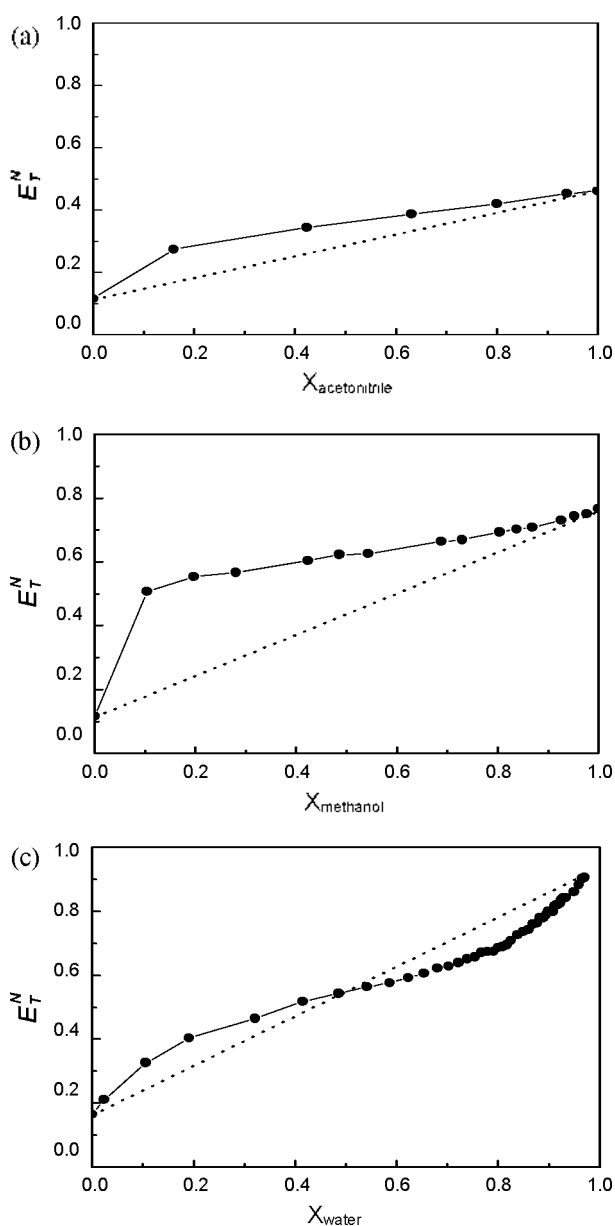


Figure 2. The empirical solvent polarity parameter, E_T^N is plotted as a function of X , the mole fraction of the more polar component of binary mixtures. (a) benzene/acetonitrile (b) benzene/methanol (c) 1,4-dioxane/water.

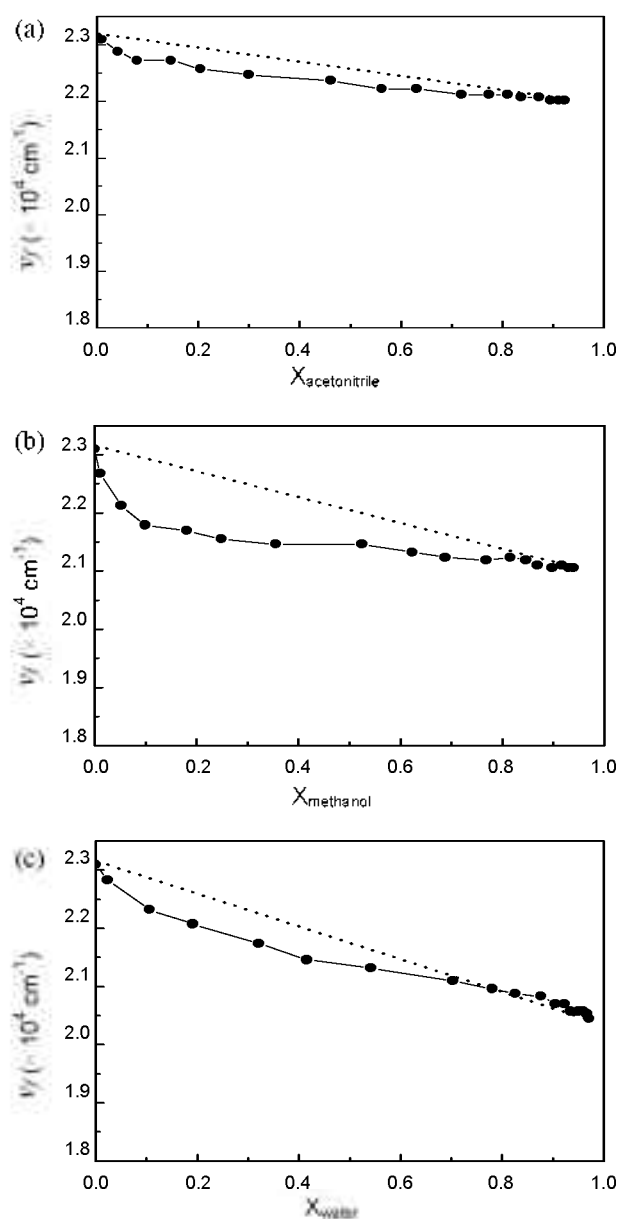


Figure 3. Dependence of the wavenumbers of fluorescence peak maximum of Coumarin102 on X , the mole fraction of more polar solvent of binary mixture (a) benzene/acetonitrile (b) benzene/methanol (c) 1,4-dioxane/water.

observed. This phenomenon can be understood by preferential or selective solvation of a probe molecule by the more polar component of binary solvent mixture. When preferential solvation is favored, the E_T^N values measure the microscopic polarity of the solvation shell on molecular level and thus may not be well correlated with the bulk properties of solvent mixture. In 1,4-dioxane/water mixture, change of E_T^N shows sigmoidal variation as the mole fraction of water increases. This can be explained by supposing that betaine dyes are preferentially solvated by water in 1,4-dioxane-rich region and by 1,4-dioxane in water-rich region respectively. There will be self-association between water molecules through hydrogen bonding in water-rich region. The increase of 1,4-dioxane mole fraction breaks the network of self-associated water molecules, which leads to the increased chance of water interaction with a probe. Competition between solute-solvent and solvent-solvent interaction might determine the microscopic polarity of solvation shell and E_T^N value shows positive or negative deviation from the ideal mixture. In 1,4-dioxane/water binary solvent, probe/water interaction is favored at low water concentration and probe/1,4-dioxane interaction is favored at high water concentration.

Solvatochromic shifts and the estimation of the excited state dipole moment. Absorption and fluorescence spectra of coumarin dyes were measured in binary solvent mixtures. In Fig. 3, the wavenumbers of the emission peaks for coumarin 102 dissolved in three binary solvent mixtures are plotted as a function of mole fraction of more polar solvent. Similar change was observed for the absorption peaks as well. It is interesting to note that the pattern of peak shift in both absorption and fluorescence follows exactly the change of E_T^N values. In other words, the downward deviation from the linear relationship in acetonitrile/benzene and methanol/benzene binary mixtures matches the upward deviation of E_T^N values that is shown in Fig. 2. This is attributed to the fact that preferential solvation is taking place in binary solvent mixtures. The sigmoidal change of E_T^N (30) value is also manifest in the peak shift of coumarin102 in dioxane/water binary solvent systems. It is suggested that the microscopic solvent polarity is probed very well by an empirical polarity measure of E_T^N . The plot of the Stokes' shift of coumarin102 in benzene/methanol binary solvent as a function of $\Delta f(\epsilon, n)$ is compared to the plot of the Stokes' shift as a function of E_T^N in Fig. 4. The latter ($R = 0.9535$) seems to give better correlation than the former ($R = 0.9011$). The absorption and fluorescence peak shift for coumarin481 as a function of E_T^N were also measured and observed to be in better correlation with the E_T^N value.

The solvent sensitivity of the Stokes' shift is commonly explained by the following Lippert-Mataga equation which is based on the Onsager's reaction field theory.^{13,14}

$$v_a - v_f = \frac{2(\mu_e - \mu_g)^2}{4\pi\epsilon_0 h c a_0^3} \Delta f(\epsilon, n) \quad (4)$$

where v_a and v_f are the wavenumbers of absorption and fluorescence transition, respectively. h is the Planck's constant, c the speed of light, μ_e and μ_g are the excited state and ground state dipole moments of a solute molecule. a_0 is the cavity

radius, and $\Delta f(\epsilon, n)$ is the solvent polarity function. This equation is only an approximation and contains assumptions such that the fluorophore is considered to be spherical and no specific interaction with the solvent is assumed. A further limitation results from the difficulty of estimating the cavity radius for molecules with nonspherical shape. Based on quantum mechanical perturbation theory of absorption and fluorescence band shift, Kawski *et al.* suggested similar equations with a different form of solvent terms.¹⁶

$$v_a - v_f = m_1 f_1 + C_1 \quad (5)$$

$$v_a + v_f = -m_2 \left(f_1 + \frac{3(n^4 - 1)}{(n^2 + 2)^2} \right) + C_2 \quad (6)$$

where C_1 , C_2 are constants and

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{4\pi\epsilon_0 h c a_0^3}, \quad m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{4\pi\epsilon_0 h c a_0^3},$$

$$f_1 = \left[\frac{\epsilon - 1}{\epsilon + 2} \frac{n^2 - 1}{n^2 + 2} \right] \left[\frac{2n^2 + 1}{n^2 + 2} \right]$$

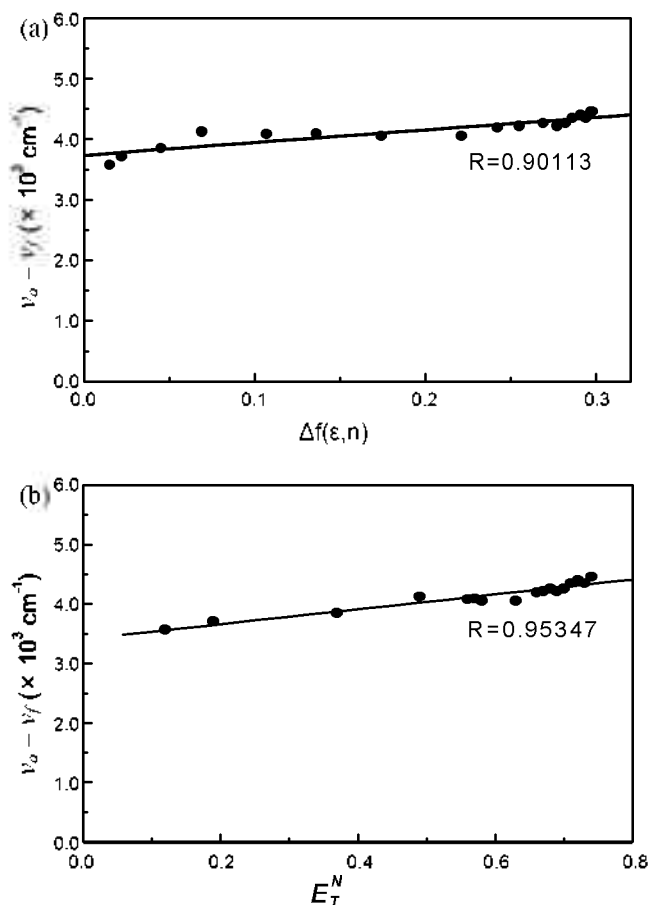


Figure 4. Dependence of the Stokes' shift of coumarin102 in benzene/methanol binary solvent mixture on (a) the solvent orientation polarizability function, $\Delta f(\epsilon, n)$ (b) the empirical solvent polarity parameter, E_T^N .

The m_1 and m_2 values are determined from the slope of $(\nu_a - \nu_f)$ and $(\nu_a + \nu_f)$ vs. respective solvent polarity functions. From the above equations, the ratio of excited to ground state dipole moment is simply given by

$$\frac{\mu_e}{\mu_g} = \left| \frac{m_1 + m_2}{m_1 - m_2} \right| \quad (7)$$

Without knowing the cavity radius, the dipole moment ratio of the excited to the ground state can be evaluated. If one has information on the cavity radius, the ground and the excited state dipole moments can be determined independently.

From the slope of the Fig. 5(a) in which peak shifts are related with bulk solvent parameters, it is estimated that $\mu_e/\mu_g = 2.3$ for coumarin102 and $\mu_e/\mu_g = 2.1$ for coumarin481. The excited state dipole moments are about twice larger than the ground state. The result is already presumed from the Stokes' shift measurement since the Stokes' shift gets larger with the solvent polarity. The ground and excited state dipole moment for coumarin102 and coumarin481 are summarized in Table 1 along with the slopes m_1 and m_2 . The ground state dipole moment calculated from the semi-empirical AM1 calculation is estimated to be ~ 6.4 D for Coumarin102 and ~ 6.2 D for coumarin481. From Eq.(7), the excited state dipole moments for coumarin102 and coumarin481 are about 13.1 D and 13.6 D respectively. Thus the excited state dipole moments increase by about ~ 7 D upon excitation.

According to Ravi *et al.*, a correlation of the Stokes' shift with E_T^N is given by the following equation.¹⁷

$$\nu_a - \nu_f = 11308 \left[\left(\frac{\Delta\mu}{\Delta\mu_B} \right)^2 \left(\frac{a_B}{a} \right)^3 \right] E_T^N + const \quad (8)$$

where $\Delta\mu$'s and a 's are the dipole moment change on excitation and the cavity radius respectively. B denotes the betaine dye used for polarity measurement. From the slope of Fig. 5(b) and by using $\Delta\mu_B = 9$ D and $a_B = 6.2$ Å, it is estimated that the dipole moment of coumarin102 increases by about 2.1 D upon excitation when the literature value of 3.5 \sim 4.0 Å for the cavity radius is applied.^{13,19} This number is much smaller than the one obtained using Eq.(7). Given the m_1 and m_2 values and the ground state dipole moment, the cavity radius should be about 6 \sim 7 Å to yield the estimated value of the excited state dipole moments of 13 \sim 14 D. When 6.8 Å for the cavity radius is used in Eq.(8), the excited state dipole moment of coumarin102 agrees well with the value predicted from Eq.(7). It should be noted that this cavity radius is much larger than the

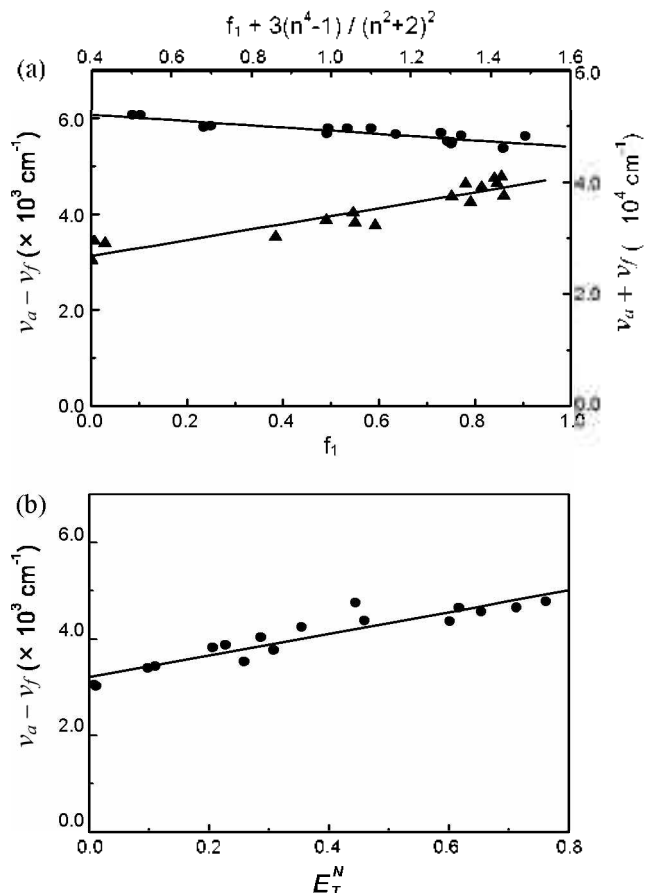


Figure 5. (a) Plot of the Stokes's shift $(\nu_a - \nu_f)$ vs. f_1 , and $(\nu_a + \nu_f)$ vs. $\left[f_1 + \frac{3(n^4 - 1)}{(n^2 + 2)^2} \right]$ for coumarin102 in neat solvents. (b) Plot of the Stokes's shift $(\nu_a - \nu_f)$ vs. E_T^N for coumarin102 in neat solvents. The slope is used to estimate the change of dipole moment upon excitation in Table 1.

values of 3.5 \sim 4.0 Å generally considered for 7-amino-coumarins of similar size in the literature. The discrepancy is attributed primarily to a shape of the cavity that 7-amino-coumarins and solvents are forming. It may suggest that the cavity shape is very much distorted from a spherical shape and is more like elliptical. Thus whenever the cavity radius is applied for calculations, it should be taken very carefully. It is also possible that the direction of the ground and excited state dipole moment is not parallel to each other.

Solvent polarity and fluorescence lifetime change. The excited state solute/solvent interactions are often reflected in the lifetimes of the excited electronic state as well as in the spectral position and shape of the emission bands. Fluorescence

Table 1. Estimation of the excited state dipole moments

	compounds	m_1 (cm^{-1})	m_2 (cm^{-1})	m_0 (cm^{-1})	a (Å)	$\Delta\mu$ (D)	μ_g (D)	μ_e/μ_g	μ_e (D)
$f(\epsilon, n)$	C102	1656	4802				6.38	2.05	13.10
	C481	1924	5169				6.24	2.19	13.64
E_T^N	C102			2249	3.98	2.06			8.44
	C481			2552	4.00	2.22			8.46

[†]Slope estimated from Eq.(8). ^{**}Cavity radius estimated from the molecular volume assuming a spherical shape. ^{***}Ground state dipole moment estimated from the semi-empirical AM1 calculations

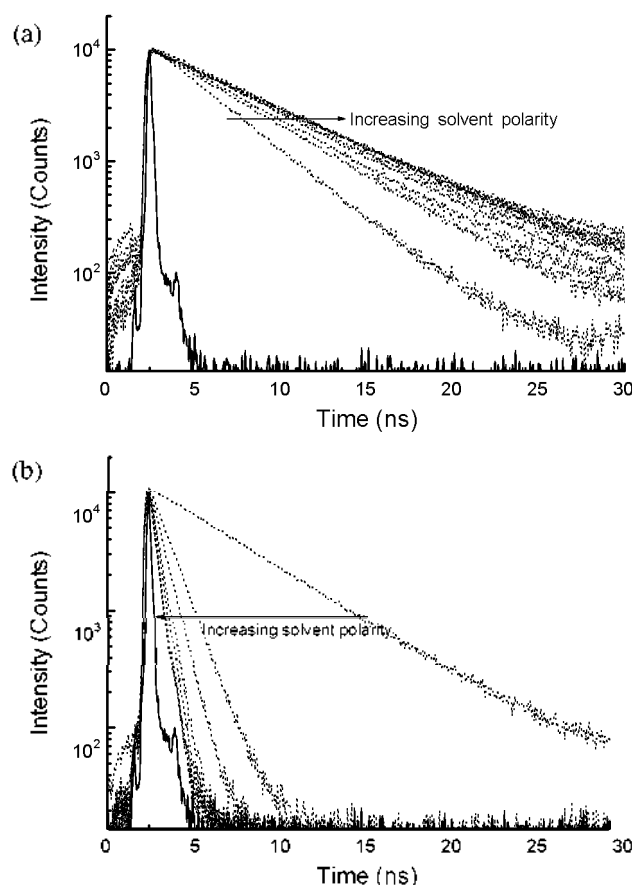


Figure 6. Typical fluorescence decay curves for (a) coumarin102, and (b) coumarin481 in 1,4-dioxane/water. The mole fraction of water is varied from 0 to 0.97. The instrument response function is shown in early time.

lifetimes have been measured for coumarin102 and coumarin481 in binary solvent systems. Fig. 6 shows typical fluorescence decay curves for coumarin102 and coumarin481 in 1,4-dioxane/water. The fluorescence lifetimes of two coumarin probes change with solvent polarity in the opposite direction. The lifetime of coumarin102 gradually increases with increasing solvent polarity, but the fluorescence lifetime of coumarin481 rapidly decreases as the solvent polarity increases. The fluorescence decays are found to be non-single exponential and properly represented by the sum of two exponential functions

in all the binary solvent mixtures. The average fluorescence lifetime, $\langle \tau \rangle$ defined by the following equation is summarized in Table 2.

$$\langle \tau \rangle = \sum f_i \tau_i, \quad f_i = \frac{A_i \tau_i}{\sum_n A_n \tau_n} \quad (9)$$

where A 's and τ 's are the amplitude and the decay time constant of each exponential function.

Solvatochromic shift of 7-aminocoumarins is mainly due to the dipole moment change upon excitation, whereas fluorescence lifetime change is attributed to conformational stability of the excited state molecule. For coumarin102, the fluorescence lifetime changes linearly and appears to be slightly increasing with the solvent polarity in all the binary solvent mixtures studied. The rotation of the amine moiety in 7-position is inhibited for coumarin102 and the conformational rigidity is maintained. It is asserted that no other states than S_1 is involved for emission, which makes this molecule a good solvation probe.²⁰ The excited state is stabilized, and the increase of fluorescence lifetime is observed. Meanwhile the fluorescence lifetime of coumarin481 decreases rapidly as the solvent polarity increases. The sharp reduction of fluorescence lifetime is observed in all three binary solvent mixtures—benzene/acetonitrile, benzene/methanol and dioxane/water. The change takes place over the narrower range of E_T^N values in aprotic solvents than in protic solvents. It seems that a specific solute-solvent interaction is not the dominant feature for the nonradiative decay pathways even though its contribution to the deactivation process is not completely ruled out. Several factors such as molecular structure, solvent polarity and viscosity, temperature might affect the nonradiative decay pathways. It has been reported that substituents and solvent polarity are more important for the TICT state formation of the 7-aminocoumarins.²¹⁻²³ The dielectric threshold above which solvent dependence of fluorescence lifetime is markedly reduced was also reported.²⁴ The sharp decrease of the fluorescence lifetime in coumarin481 with increasing solvent polarity is reminiscent of the earlier work,²¹ and is related to the nonradiative decay process which involves the intramolecular charge transfer accompanied by twisting of 7-amino group. The formation of the twisted intramolecular charge transfer (TICT) state is responsible for the nonradiative decay

Table 2. Variation of the average fluorescence lifetimes with the empirical solvent polarity parameter, E_T^N

benzene / acetonitrile				benzene / methanol				1,4-dioxane / water			
$\chi_{\text{acetonitrile}}$	E_T^N	$\langle \tau \rangle$, ns		χ_{methanol}	E_T^N	$\langle \tau \rangle$, ns		χ_{water}	E_T^N	$\langle \tau \rangle$, ns	
		C102	C481			C102	C481			C102	C481
0.000	0.116	3.0	4.1	0.000	0.116	2.9	4.1	0.000	0.165	3.4	4.8
0.300	0.316	3.1	4.5	0.356	0.576	3.8	2.6	0.542	0.564	3.5	1.2
0.461	0.353	3.3	3.7	0.525	0.630	4.1	2.0	0.703	0.628	4.5	0.8
0.631	0.387	3.4	2.4	0.688	0.666	4.2	1.4	0.826	0.708	5.3	0.6
0.774	0.415	3.5	1.6	0.815	0.689	4.4	1.1	0.904	0.800	5.6	0.5
0.837	0.429	3.6	1.4	0.869	0.708	4.5	0.9	0.934	0.842	5.7	0.4
0.873	0.438	3.6	1.3	0.898	0.721	4.5	0.9	0.950	0.861	5.8	0.4
0.895	0.443	3.6	1.3	0.917	0.730	4.5	0.8	0.959	0.883	5.9	0.4
0.923	0.450	3.6	1.1	0.939	0.740	4.5	0.8	0.971	0.906	5.9	0.4

of the excited states. The high sensitivity of fluorescence lifetime can be utilized in probing the solvent polarity especially when the solvatochromic shift is poor. Near-infrared fluorescent dyes for biological imaging were reported and a fluorescence lifetime-based polarity index was suggested.²⁵

Conclusion

The solvatochromic shift of electronic absorption and emission spectra are studied for 7-aminocoumarins in neat and binary solvent systems. The solvent effect on the solvatochromism is correlated to the empirical polarity parameter E_T^N as well as the bulk solvent parameter function. Preferential solvation is taking place in binary solvent mixtures since the change of peak shift seems to reflect the change of E_T^N very closely. The E_T^N value measures microscopic solvent polarity and it seems to probe more or less non-specific solvent interactions. The excited state dipole moment of 7-aminocoumarins was estimated from the dependence of Stokes' shift on the solvent parameters. The dipole moments of 7-aminocoumarins increase by about twice upon excitation. The cavity shape is assumed to be very much elliptical and the cavity radius is predicted to be much larger than the generally considered value for these 7-aminocoumarins.

Acknowledgments. This work is supported in part by the Daegu University Research Grant.

References

1. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; VCH: 2004.
2. Gordon, D. J.; Balbach, J. J.; Tycko, R.; Meredith, S. C. *Biophys. J.* **2004**, *86*, 428.
3. Prusiner, S. B. *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 13363.
4. Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
5. Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.
6. Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253.
7. Kosower, E. M.; Mohannad, M. *J. Phys. Chem.* **1970**, *74*, 1153.
8. Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1.
9. Reichardt, C. *Liebigs Ann. Chem.* **1971**, *752*, 64.
10. Pliening, P.; Baumgartel, H. *Ber. Bunsenges. Phys. Chem.* **1982**, *96*, 161.
11. Zachariasse, K. A.; Van Phuc, N.; Kozankiewicz, B. *J. Phys. Chem.* **1981**, *85*, 2676.
12. Johnson, B. P.; Khaledi, M. G.; Dorsey, J. G. *J. Chromatogr.* **1987**, *384*, 221.
13. Von Lippert, E. *Z. Electrochem.* **1957**, *61*, 962.
14. Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem., Soc. Jpn.* **1956**, *29*, 465.
15. Langhals, H. *Angew. Chem. Int. Engl.* **1982**, *21*, 724.
16. Kawski, A. *Progress in Photochemistry and Photophysics Vol. 1*; Rabek, J. F., Ed.; CRC press: 1992, and references therein.
17. Ravi, M.; Soujanya, T.; Samanta, A.; Radhakrishnan, T. P. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 2739.
18. Mannekutla, J. R.; Mulimani, B. G.; Inamdar, S. R. *Spectrochim. Acta Part A* **2008**, *69*, 419.
19. Raikar, U. S.; Renuka, C. G.; Nadaf, Y. F.; Mulimani, B. G.; Karguppikar, A. M.; Soudagar, M. K. *Spectrochim. Acta Part A* **2006**, *65*, 673.
20. Lewis, J. E.; Maroncelli, M. *Chem. Phys. Lett.* **1998**, *282*, 197.
21. Jones II, G.; Jackson, W. R.; Choi, C. Y.; Bergmark, W. R. *J. Phys. Chem.* **1985**, *89*, 294.
22. Barik, A.; Kumbhakar, M.; Nath, S.; Pal, H. *Chem. Phys.* **2005**, *315*, 277.
23. Dahiya, P.; Kumbhakar, M.; Mukherjee, T.; Pal, H. *Chem. Phys. Lett.* **2005**, *414*, 148.
24. Chu, G.; Yangbo, F. *J. Chem. Soc., Faraday Trans. I* **1987**, *83*, 2533.
25. Berezin, M. Y.; Lee, H.; Akers, W.; Achilefu, S. *Biophys. J.* **2007**, *93*, 2892.