

Estimation of Ratio of Excited-State and Ground State Dipole Moments of 4-Methyl-7-Hydroxy-Chromen-2-One by Solvatochromic Method

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Abstract

In the present study the absorption and emission spectra of the synthesized compound 4-methyl-7-hydroxy-chromen-2-one was determined in organic solvents of different polarities. The effects of solvents on the compound were carried out by the determination of stoke's shifts. The bathochromic shift indicates the occurrence of $\pi \rightarrow \pi^*$ electronic transitions in the compound. Extinction coefficients were found vary in the range of 1.67×10^4 to 2.22×10^4 . Quantum yield was found to be 0.002 for less polar solvent cyclohexane and 0.97 for highly polar solvent water. The ratio of excited to ground state dipole moment was calculated by using solvatochromic shift methods viz. Lippert's, Bakhshiev's and Kawski-Chamma-Viallet's correlations. The estimated value was found to be 4.4 in this perspective.

Keywords: Fluorescence, Solvatochromic effects, Dipole moment, Quantum yield.

Introduction

Coumarin is important naturally occurring oxygen containing heterocyclic compound. These are δ -lactone of coumaric (o-hydroxycinnamic) acid. Coumarin and its derivatives are well known for its biological properties such as anticoagulant, antibacterial, antimicrobial, analgesic, anti-pyretic [1] antitumor, antimetastatic and fungicidal activity [2-3]. Coumarin derivatives also exhibited antimalarial activities

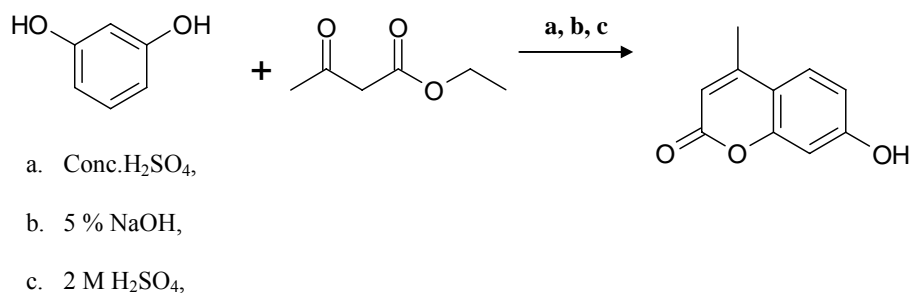
and good cytotoxicity against Col₂, KB, and LNCaP human cancer cell lines [4]. These compounds are used as rodenticides, fluorescent indicators [5-6], optical brighteners and laser dyes in the blue-green region [7].

To find out the ground and excited state dipole moments of organic compounds and dye molecules etc. is of great importance in determination of change in electronic distribution, geometrical structure, designing nonlinear materials and determination of the photochemical transformations. Several works has been carried out to find the ground and excited state dipole moments of different compounds theoretically and experimentally for last two decades [8-22]. The experimental method to find the single excited-state dipole moments by solvatochromism is based on the shift of absorption and fluorescence maxima in different solvents of varying polarity. Koutek obtained significant results by using solvatochromic method under suitable conditions.

The aim of present work is to determine the effect of different solvents of various polarities of the absorption and emission characteristics on the synthesized compound 4-methyl-7-hydroxy-chromen-2-one. The extinction coefficients, quantum yield and the ratio of excited to the ground-state dipole moment of the compound were experimentally determined. The ratio was evaluated by using Lippert's, Bakhshiev's and Kawski-Chamma-Viallet's solvatochromic correlations.

Experimental

The method of Pechmann and Duisberg was followed for the preparation of 7-hydroxy 4- methyl chromen-2-one, according to scheme 1. The solvents used in the present study were cyclohexane, carbontetrachloride, benzene, ethyl ether, dichloromethane, chloroform ethanol, ethyl-acetate, 1,4-dioxane, methanol, acetonitrile, dimethylsulfoxide, and N,N dimethylformamide are of A.R./G.R./spectroscopic grade. Double distilled water was taken for the experimental purpose. The required solutions were prepared at fixed solute concentration (3×10^{-5}) in all the solvents. The absorption spectra of the 4-methyl-7-hydroxy-chromen-2-one were recorded at room temperature with the help of Lambda-35 Perkin Elmer; UV-VIS spectrometer. The fluorescence spectra were recorded by using spectrofluorometer (Perkin-Elmer LS-55). The fluorescence quantum yield were determined using quinine sulfate as the standard ($\Phi_F = 0.54$ at $20 \pm 2^\circ\text{C}$).



Scheme 1: General method of synthesis of 4-Methyl-7-hydroxy- chromen-2-one (1).

Results and discussion

Absorption and fluorescence characteristics

Fig. 1 shows the shifts of absorption spectra of 4-methyl-7-hydroxy-chromen-2-one in carbon- tetrachloride and water. The band positions of absorption and emission maxima, stoke's shift and quantum yield for the compound with chosen solvents of different polarities are given in table 1. In the present table the solvents are arranged in order of increasing polarity. The absorption spectra of the compound were found varying from less polar solvent (cyclohexane) to high polar solvent (water). Less polar solvent, cyclohexane showed the absorption peak (λ_{max}) at 327.2nm with the value of molar extinction coefficient (ϵ) 1.67×10^4 . The peak corresponds to the vibrational structure of first electronically excited state. However, in water the peak position was found to be 321.0 with the value of extinction coefficient 2.22×10^4 . The high oscillator strength is indicative of highly absorbing molecule which is a characteristic property of compound. Fig 2 shows the emission spectra in carbontetrachloride and water. The 0-0 band for emission in cyclohexane lies at 359 nm showing a Stoke's shift of 2707 cm^{-1} . However, the difference of Stoke's shift of 6018 cm^{-1} was found by taking the low polar solvent cyclohexane to high polar solvent water. This is indicative of different charge distribution in the ground and excited state. The values of measured fluorescence quantum yields (ϕ_F) in different solvents with increasing polarity were found to vary in the range 0.002 to 0.97. However, the maximum value of quantum yield was found to be 0.98 for ethanol.

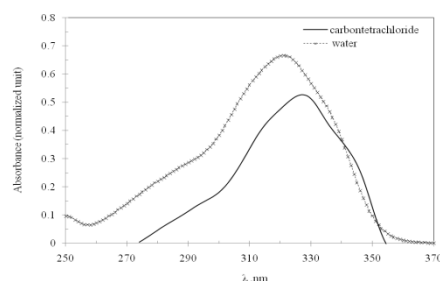


Figure 1: Solvent effect on the absorption spectra of 4-methyl-7 hydroxy chromen-2-one, (3×10^{-5} M) in CCl_4 and water.

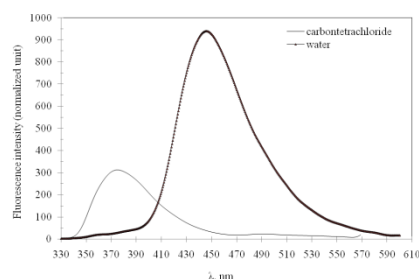


Figure 2: Solvent effect on the fluorescence emission spectra of 4-methyl-7 hydroxy chromen-2-one, 3×10^{-5} M in CCl_4 and water.

Table 1: Electronic absorption and fluorescence and quantum yield of 4-methyl-7-hydroxy- chromen-2-one in different solvents.

solvent	Absorpton Maxima	Photophysical properties		
	$\lambda_{\text{abs, nm}}$ ($\epsilon_1 \times 10^4$)	$\lambda_{\text{emm, nm}}$	Stoke's shift Δ, cm^{-1}	Quantum Yield (ϕ_F)
Cyclohexane	327.2 (1.67)	359.0	2710	0.002
Carbontetracholoride	344.3 (1.76)	374.9	2370	0.46
Benzene	324.8 (1.93)	373.1	3982	0.20
Ethyl ether	320.8 (2.10)	347.2	2377	0.14
Dichloromethane	322.4 (2.11)	374.6	4321	0.51
Chloroform	323.8 (1.99)	375.0	4211	0.58
Ethanol	323.5 (1.93)	378.1	4466	0.98
Ethyl acetate	319.2 (1.80)	369.3	4245	0.05
1-4 dioxane	319.5 (1.85)	368.7	4183	0.04
Methanol	322.4 (2.31)	379.8	4689	0.74
Acetonitrile	318.5 (1.88)	370.5	4402	0.08
DMSO	323.4 (2.04)	379.8	4586	0.37
N,N-dimethylformamide	322.9 (1.77)	378.5	4552	0.52
Water	321.0 (2.22)	445.8	8728	0.97

From the absorption spectra (λ_{abs}), it is observed that the band positions showed hyperchromic shift of about 6nm on changing solvent polarity (cyclohexane to water). The fluorescence emission spectra are also characterized by one peak (λ_{emm}). On going from cyclohexane to water the observed peaks λ_{emm} , are found red-shifted (app. 87nm) from 359-446 nm. This bathochromic shift reflects the occurrence of $\pi \rightarrow \pi^*$ electronic transitions in the 4-methyl-7-hydroxy-chromen-2-one singlet excited state. The fluorescence wavelength shift to a great extent is indicative of stronger interaction of the solute with polar solvents in the excited state.

Determination of excited to ground stated dipole moment ratio

The solvato-chromic method is used to determine the excited singlet-state dipole moment of 4-methyl-7-hydroxy-chromen-2-one by using Lippert's, Bakhshiev's and Kawski-Chamma-Viallet's formula respectively [23-24]:

$$\bar{\nu}_a - \bar{\nu}_f = SF(\epsilon, n) + const \quad (1)$$

$$\bar{\nu}_a - \bar{\nu}_f = S_1 F_1(\epsilon, n) + const \quad (2)$$

$$(\bar{\nu}_a - \bar{\nu}_f) / 2 = S_2 F_2(\epsilon, n) + const \quad (3)$$

The expression for Lippert's polarity function, $F(\epsilon, n)$, Bakhshiev's polarity function, $F_1(\epsilon, n)$ and Kawski-Chamma-Viallet's polarity function $F_2(\epsilon, n)$ were evaluated by following expressions:

$$F(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] \quad (4)$$

$$F_1(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (5)$$

$$F_2(\varepsilon, n) = \left[\frac{2n^2 + 1}{2(n^2 + 2)} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \right] \quad (6)$$

Where, $\bar{\nu}_a$ and $\bar{\nu}_f$ indicate the wave numbers (cm^{-1}) of electronic absorption and fluorescence emission maxima, n and ε represent the refractive index and the dielectric constant of the solvents.

From the above equations the graphs were plotted and the slopes S , S_1 and S_2 were determined and are given as follows:

$$S = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \quad (7)$$

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \quad (8)$$

$$S_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca_0^3} \quad (9)$$

where, μ_e and μ_g represent the permanent dipole moments in the ground and in the excited singlet state, respectively, h represents Planck's constant and c , the velocity of light in vacuum, a_0 , the Onsager cavity radius of the solute molecule.

The graphs in between $(\bar{\nu}_a - \bar{\nu}_f)$ versus F , $(\bar{\nu}_a - \bar{\nu}_f)$ versus F_1 , and $(\bar{\nu}_a + \bar{\nu}_f)/2$ against the solvent polarity functions F_2 were plotted and are given in figs 3, 4 and 5 respectively. The slopes S , S_1 and S_2 were determined respectively from these graphs. The satisfactory results were obtained from the statistical treatment of Lipert's, Bakhshiev's and Kawski-Chamma-Viallet's correlations. The slope of 7220 cm^{-1} is found for Lipert's with intercept of 2664 cm^{-1} . The slope of 2375 cm^{-1} is found for Bakhshiev's with intercept of 2656 cm^{-1} . However, for Kawski-Chamma-Viallet's, the slope and intercept are found to be -1488 cm^{-1} and 29637 cm^{-1} , respectively. Figs 3, 4 and 5 show that the solvents, cyclohexane, 1-4 dioxane, Acetonitril, nn-dimethylformeldhide, ethyl-ether, dichloromethane and water did not obey the Lipert's correlation, while the solvents cyclohexane, 1-4 dioxane, chloroform, nn-dimethylformeldhide, ethyl ether, dicholoromethane and water did not obey Bakhshiev's correlation and carbontetra-chloride, methanol, acetonitrile, ethyl acetate, nn-dimethylformeldhide, ethyl-ether and water did not obey Kawski-Chamma-Viallet's correlation. The correlation coefficients value was found to be approximately 0.90 showing the good linearity against the majority of solvents.

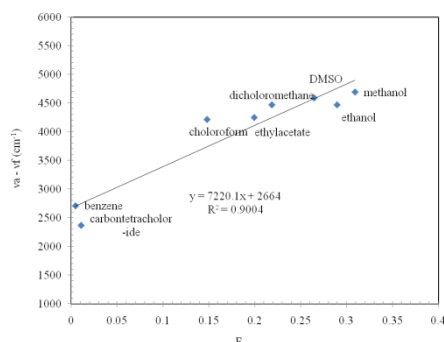


Figure 3: The variation of Stokes shift with F by using Lippert's equation in different solvents.

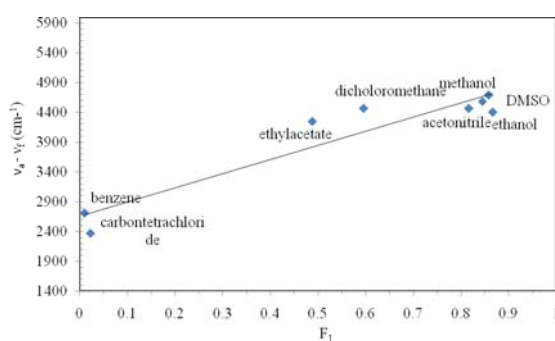


Figure 4: Bakshiev correlation between the solvent spectral shifts and the F_1 solvent polarity function.

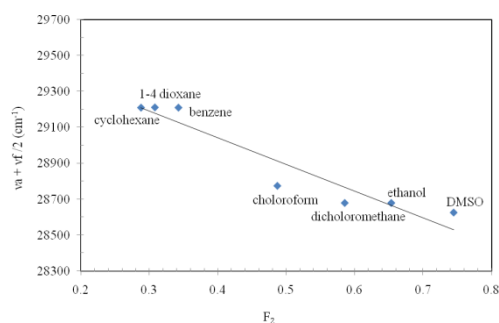


Figure 5: Kawski-Chamma-Viallet correlation between the solvent spectral shifts and the F_2 solvent polarity function.

The ratio of the first excited singlet state and the ground state dipole moments is calculated by using the relation [20-21]:

$$\frac{\mu\theta}{\mu g} = \left| \frac{S_1 + S_2}{S_2 + S_2} \right|$$

The experimentally obtained value 4.4 shows that the dipole moment of 4-methyl-7-hydroxy-chromen-2-one is moderately high in the first excited singlet state than in the ground state. The comparatively higher value of μ_e than μ_g shows the existence of difference in the electronic charge distribution in the excited singlet state relative to the ground state. This result confirms that an extended π electronic delocalized system is present in the organic compound, with important charged resonance structures in the excited singlet state. The $\pi \rightarrow \pi^*$ may increase the magnitude of charges leading to increase in the dipole moment of 4-methyl-7-hydroxy-chromen-2-one in excited state.

Conclusion

We have successfully synthesized 4-methyl-7-hydroxy-chromen-2-one, characterized by spectral and fluorescence studies. The absorption and fluorescence spectra were measured in various solvents of different polarities. A ratio of excited state and ground dipole moment was found to be 4.4 indicates the existence of difference in the electronic charge distribution in the excited singlet state relative to the ground state. The values of extinction coefficients were found in the range 1.67×10^4 to 2.22×10^4 . The quantum yield in different solvents were evaluated and found to be 0.002 for low polar solvent cyclohexane and 0.97 for high polar solvent water.

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