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Solvatochromic Study of Organic Dyes: A Qualitative Approach using Semiempirical (ZINDO-IEFPCM) Method

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Abstract

The present investigation accounts for determining computationally the solvatochromic behavior of Coumarin dyes (C478, C519 and C523) in series of alcohols. Experimentally observed positive and negative solvatochromism are accounted for and their behavior is well explained by computational results. The semi empirical $E_T(30)$ *scale has been adopted to define the polarity dependent solvent-solute interaction. The ZINDO/PCM method follows the observed experimental trends for all the Coumarin dyes. The small discrepancies with experimental values are discussed in detail. Computational results suggest that ZINDO/PCM values lie in closer proximity to the experimental values depending on the polarity of Coumarin molecules. Switching between positive and negative solvatochromism in polarity scale referred as polarity switch is discussed.*

Keywords: Polarity scale, Positive and negative solvatochromism, ZINDO/PCM, Polarity switch.

1. Introduction

The information about electronic distribution of molecules in the ground and excited states can be obtained by the studies of solvatochromic effect on the absorption and fluorescence spectra of laser dyes. The predominant role of solute-solvent interaction on positive and negative solvatochromism, referred to as bathochromic and hypsochromic shift respectively, generally depends on their relative polarity, linear response to their electrostatic interaction, non-electrostatic interaction and hydrogen bonding strength, etc. The solute molecule finds itself in a cavity inside the solvent, resulting in a net stabilization of their ground state. Concept of modelling the cavity is different from spherical Onsager cavity to molecularly shaped cavities by various versions of polarizable continuum model (PCM) (Jacopo *et al.* 2005). If the dipole moment of solute increases through electronic transition, the excited state is formed inside the solvent cavity which is surrounded partly by oriented solvent dipoles. The net stabilization of the excited state as compared to the ground state with increasing solvent polarity results in bathochromic shift. Here the excited state is more dipolar than ground state ($\mu_{g}<\mu_{e}$). If there is a decrease in dipole moment of solute during the electronic transition, the excited state is formed in a strained solvent cavity of oriented dipoles not correctly disposed for its efficient stabilization. The energy of the ground state lowered more than that of the excited state with increasing solvent polarity results in a hypsochromic shift and in this case ground state is more dipolar than excited state ($\mu_{g}>\mu_{e}$). According to the valence-band theory, the extent and direction of sovatochromism depends on whether the zwitterionic mesomeric structure is more important in the ground or in the excited state (Reichardt, 2004). The solvent effect on absorption spectra is understood computationally by assuming the electronic states of the isolated and solvated molecule; and treating this effect only as a physical perturbation of the relevant molecular states.

Solvation capability defining the solvating power of dissolved a polar or dipolar, charged or neutral, species is commonly related to the solvent polarity function. The typical question of accuracy in defining the solvent polarity on solvent properties such as relative permittivity, dipole moment or refractive index remains in debate. The qualitative concept of grasping solvent polarity seems to be easy, but it is difficult to define precisely and even more difficult to express it quantitatively. Besides, many attempts to express it quantitatively by single macroscopic solvent properties are found to be inadequate. The empirical parameter has been introduced to provide a scale for polarity of solvents on highly selected solvent-sensitive reference process. Some particular approach of them like equilibrium, reaction rate and spectral absorption are assumed as suitable for large class of other solvent dependent process. Among many such ideas the most popular polarity scale $E_T(30)$ as proposed by Dimorth and Reichardt (Reichardt, 2004) is most commonly used. Here the solvent polarity scale was built on the basis of transition energy for the longest wavelength solvatochromic absorption band of the pyridinium N-phenolate betaine dye. The present study aims to understand the solvatochromism of Coumarin dyes on this polarity scale by comparing experimental results with computed values. The Zerner's Intermediate Neglect of Differential Overlap (ZINDO) method is used to compute absorption maxima of Coumarins in series of alcohols. The Polarizable Continuum Model (PCM) (Jacopo *et al.* 1994), (Miertus *et al.* 1981) using the integral equation formalism variant (IEFPCM) (Cances *et al*. 1997), (Caricato *et al*. 2006), which describes the solvent as structureless continuum medium defined by dielectric constant to account the bulk effect is combined with ZINDO calculations. ZINDO approach is successfully adopted with PCM for qualitative explanation of absorption maxima proved as less computational cost, than simulating absorption of molecule in different solvents with time dependent Hartree-Fock (TDHF) and time dependent density functional theory (TDDFT) methods. Coumarin dyes were selected for present study because they undergo very little nuclear reorganization and are solvatochromic owing to the change in electronic distribution resulting in an increase of dipole moments from ground to excited state (Mannekutla *et al.* 2008), (Patil *et al.* 2014). The large change in dipole moments of a molecule in the ground state and excited state is observed due to Coumarins are influenced by their immediate environment as energy in lowest singlet excited state relative to ground state is quite sensitive regardless of various substituent effects.

2. Theory of ZINDO/PCM

The previous theoretical simulation work has been done on absorption of molecule in different solvents with time dependent Hartree-Fock (TDHF) and time dependent density functional theory (TDDFT) methods. Besides these, less computational costing ZINDO approach is adopted successfully with quantum mechanical treatment of solvents (PCM versions) for qualitative explanation of absorption maxima. Here the electronic spectra are interpreted by the Tamm-Dancoff approximation (TDA), with reference state as defined by Hartree-Fock. The detailed discussion and development of ZINDO and ZINDO/PCM theories are represented in (Caricato et al. 2004), (Caricato et al. 2006). We present in short the ZINDO/PCM theory with the idea to provide basic bench for further discussion. Actually, the PCM method represents solvent as a homogeneous continuum medium polarizable by the solute placed in a molecularly shaped cavity built in the bulk of the dielectric. It is now convenient to speak of solute-solvent interaction in terms of the solvent reaction potential $\hat{V}_{\text{int}}$. This potential term introduced as a perturbation to Hamiltonian of the isolated molecule, H^0: $H_{eff}\psi = [H^0 + V_{\text{int}}]\psi = E\psi$. The definition of potential is different as it depends on the method employed to set the electrostatic problem, which has to be solved within the framework of the QM equation $H_{eff}|\psi\rangle = E|\psi\rangle$. Generally, V_{int} is assumed as a summation of dispersion, repulsion and electrostatic forces between solute and solvent molecules. The IEFPCM assumes the solvent effect by the apparent surface charges on the cavity. These charges can be computed by matrix elements formed by linear equations which are related to dielectric constants and to the geometry of the boundaries.

3. Computational Details

The geometries of these molecules were first optimized in vacuum with semi-emphirical AM1 method and solvent effect is introduced by combining AM1/PCM, the molecules optimized in ground state in all alcohols. Subsequent geometries were assumed as initial guess for excited state calculation according to ZINDO/PCM in respective solvents vacuum using Gaussian 09 software package (Gaussian 09, Revision **E.01).**

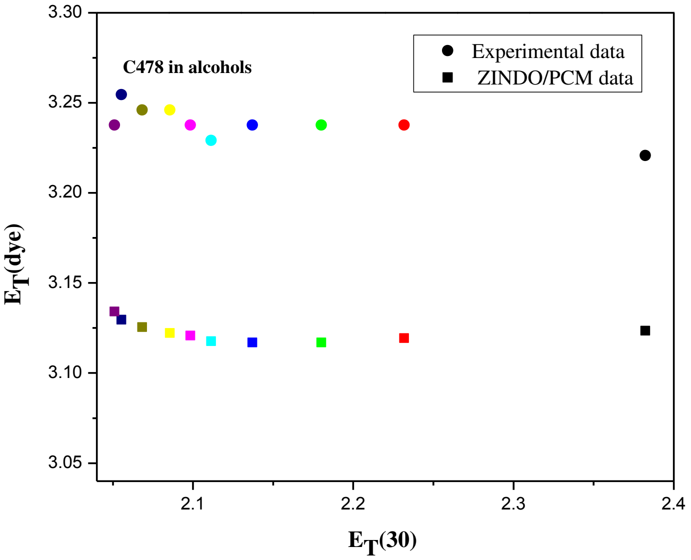
4. Results and Discussion

The solvent shifts can be accounted in terms of the overall effect of the interaction forces (which are mainly of van der Waals type) on the electron system of the molecule. A change of solvent is accompanied by changes in polarity, dielectric constant and polarizability of the surrounding medium, thus a number of solvents have been selected to study the solvatochromism. The experimentally observed absorption maxima $\lambda_{\max}(nm)$ is transformed into intermolecular charge transfer transition energy (eV) by using equation, $E_T(dye) = 28591.5/\lambda_{\max}(nm)$. The experimental absorption maxima data (methanol-decanol) of C478, C519 and C523 have been taken from our previous report (Patil *et al.* 2014). Electronic transition energies computed by ZINDO/PCM were compared with experimental results and summarized in Table 1. The fundamental aspect for comparing and evaluating both the theoretical and experimental results is to provide the physical insight on solute-solvent interaction. Plot of $E_T(dye)$ vs $E_T(30)$ polarity functions for C478 shows qualitative agreement between the transition energy predicted by ZINDO/PCM for $S_0 \rightarrow S_1$, and is in good agreement with the experimental values making it reliable calculation for excited state energies. The experimentally observed positive and negative solvatochromism trend is exactly followed by theoretically predicted values. Oscillating behaviour from positive to negative solvatochromism in polarity scale at particular stage, usually referred as polarity switch (Mallika *et al.* 2013), is observed. In case of C519 (Fig.1b), the computed values are very close to the experiment in most of the solvents. Comparing the results of C478 and C519 it clears the idea that excited energies of highly polar molecules are well characterized by ZINDO/PCM calculations. The resonance contributors which define the electron mobility in the aromatic ring are more in C519 than C478, making it more polar in nature (Patil *et al.* 2014). Small discrepancies in some of the solvents are attributed to discarding the hydrogen bonding at specific sites of solute because solvent structure is missing in PCM formulation. Fig.1(c) shows plot for C523 where behaviour of experimental results is followed by theoretical values. More polar nature of C523 than C478 enables ZINDO/PCM calculation to be in close proximity to the experimental results. Further detailed study necessitates explaining this result by considering the non electrostatic behaviour of solvents. The theoretical calculation has two advantages first, it provides effect of solvatochromism on solvated molecules and its behaviour on a polarity scale with less computational cost. The computational calculation thus estimates the properties of molecule in the solvent environment. Another advantage is that it helps to evaluate the energy distribution of molecule in ground and excited state in particular solvents. These results can be combined to see the change of energy in both states in subsequent solvents. Here looking more closely at the problem when there is change in solvent from pentanol to hexanol the positive solvatochromism switches to negative. Dipole moment which is form of energy is calculated for ground and excited state in all the individual solvents. The difference in these dipole moments remains almost unaltered (Fig. 2). The observation of subsequent difference in ground state and also the case of excited state dipole moments in solvents studied suffers abrupt change in value as crossing from pentanol to hexanol. This is the particular solvent where negative solvatochromism starts and this change in polarity scale is referred as polarity switch (Mallika *et al.* 2013).

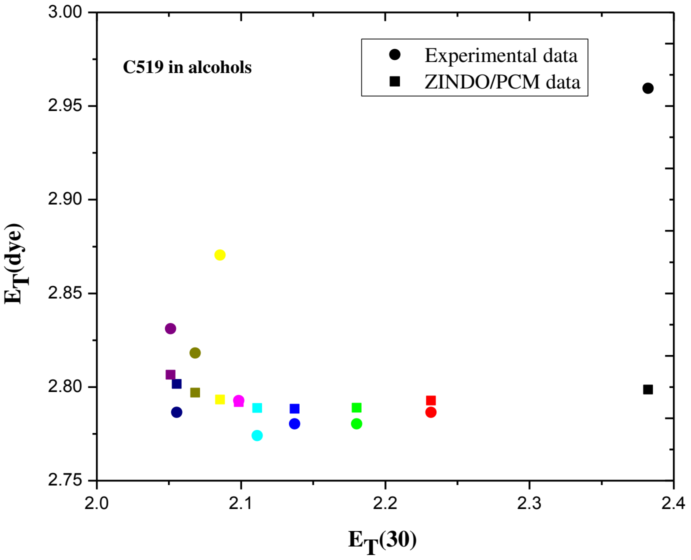
Table 1
Comparison of experimental and computed electronic transition energies (in eV).

	C478		*C519*		*C523*	
Solvent	$E_{Exp}(eV)$	$E_{Theory}(eV)$	$E_{Exp}(eV)$	$E_{Theory}(eV)$	$E_{Exp}(eV)$	$E_{Theory}(eV)$
Methanol	3.220779	3.123504	2.959427	2.798655	2.792793	2.840714
Ethanol	3.237598	3.119340	2.786517	2.792730	2.805430	2.835128
Propanol	3.237598	3.116988	2.780269	2.788961	2.792793	2.831761

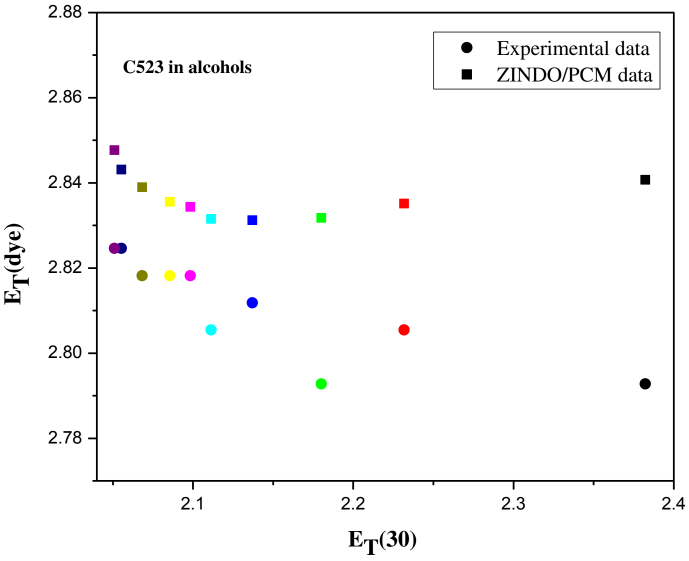
Butanol	3.237598	3.116988	2.780269	2.788334	2.811791	2.831244
Pentanol	3.229167	3.117615	2.774049	2.788710	2.805430	2.831503
Hexanol	3.237598	3.120832	2.792793	2.791975	2.818182	2.834350
Heptanol	3.246073	3.122167	2.870370	2.793296	2.818182	2.835517
Octanol	3.246073	3.125551	2.818182	2.797014	2.818182	2.838958
Nonanol	3.254593	3.129653	2.786517	2.801563	2.824601	2.843124
Decanol	3.237598	3.134083	2.831050	2.806573	2.824601	2.847694



(a)



(b)



(c)

Figure.1 *Comparison of experimental transition energies of (a)C478, (b)C519 and (c)C523 with calculated ZINDO-PCM on* $E_T(30)$ *scale in alcohols (methanol-decanol).*

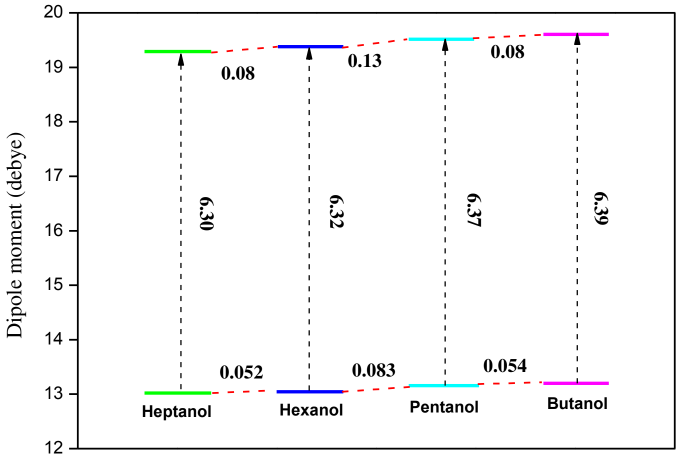


Figure.2 *Schematic diagram for the polarity switch in case of C523.*

5. Conclusion

In the present study solvatochromism of Coumarin dyes are compared with ZINDO/PCM results. The ZINDO/PCM calculation explains the observed positive and negative solvatochromism. Depending on polarity of molecule the ZINDO/PCM values are nearer to measured ones as it can be seen in cases of C519 and C523compared to C478. The study also provides strong evidence about the accuracy and shortfalls of ZINDO/PCM method by considering three different Coumarin molecules with variation in their polarity.

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