

FT-IR studies on interactions between Indole and Coumarin

^[1] C V Madhusudhana Rao, ^[2] V. Vasantha Kumar, ^[3] L N Sivakumar Konathala

^[1] Department of Physics, CMR Institute of Technology, Hyderabad-501401, India.

^[2] Department of Physics, Vignan Institute of Technology and Science, Hyderabad-508284, India.

^[3] Analytical Science Division, CSIR-Indian Institute of Petroleum, Dehradun, India.

Abstract: - The hydrogen-bonded complexes formed by indole and coumarin were investigated by varying concentrations. The association constant was calculated from Benesi-Hildebrand equation. Our results show that a 1:1 complex was formed between N-H group of indole and the carbonyl group of coumarin. Free energy change of the 1:1 complex was also determined.

Index Terms: Indole; Coumarin; Hydrogen bond; Association constants; Free energy change.

INTRODUCTION

The study of hydrogen-bonding properties of indole ring is an interesting topic because of the presence of indole ring in many biologically active and naturally occurring compounds [1]. Hydrogen bonds constitute a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. Spectroscopic [2,3] studies have suggested that hydrogen bonds can occur in many systems. The hydrogen bonding motif is a powerful tool to know the donor properties of its pyrrolic NH group. However, in recent years, experimental and theoretical studies have stressed the hydrogen-bonding acceptor properties of the indole p-cloud [4,5].

These hydrogen-bonding acceptor properties, apart from playing an important role in the stabilization processes of indoles in their natural environments, are also fundamental for understanding the spectral and excited state dynamical properties of indole derivatives. IR and Raman spectroscopy are the vital tools for the investigation of hydrogen bonding between donors and acceptors.

Indole is the nucleus of the amino acid tryptophan, its intermolecular interactions with biochemical receptors play an interesting role in biologically significant processes as the structural stabilization and functioning of the proteins. Since indole ring possesses potential donor and acceptor hydrogen-bonding sites, as well as electron donor centers, indole derivatives are enabled to interact with their biochemical receptors through a variety of binding forces. In this sense, hydrogen bonding and stacking interactions can participate competitively or cooperatively to yield different types of intermolecular indole-acceptor complexes or even hybrid structures.

Although most of the experimental and theoretical investigations on this field have been focused on the conventional hydrogen bonds involving the acidic NH group of indole, the ability of indole to form hydrogen-bonded-complexes is also well recognized. In fact, indole can act as an H-donor interacting with bases [6,7] and also as a base against itself or other H-donors [8].

Carbonyl groups are common in biological systems and have an electron rich oxygen atom, which can act as a proton acceptor site. Furthermore, hydrogen-bonded interactions involving the carbonyl group are of fundamental interest for modeling the behavior in real biosystems [9]. Coumarin and its derivatives which have carbonyl groups are known to exhibit photosensitizing properties and find that the application as fragrances, pharmaceuticals and agrochemicals [10].

Electronic structure and spectral properties are prominent properties to evaluate the relationship between biological activity and molecular structure. The aim of this study is to determine the existence of hydrogen bonding in indole:coumarin system. In this work, we have investigated the spectra of indole and coumarin by analyzing the FTIR absorption of the complexes in the region 4000–500 cm⁻¹, at room temperature, it is evaluated that, how hydrogen bonding is influencing the molecular vibrations of the complexes.

II. EXPERIMENTAL SECTION

Indole and coumarin (Aldrich) were used without further purification. Carbon tetrachloride are of Spectrochem grade and purified by standard method [11]. A Perkin Elmer FTIR spectrometer with a resolution of $\pm 1\text{cm}^{-1}$ was used for this study. FTIR spectra were obtained at room temperature (25 °C) in the region of 4000-400 cm⁻¹.

III. RESULTS AND DISCUSSION

In the present investigation, the IR spectra were recorded by fixing the concentration of proton donor (indole) at 0.01 mol L⁻¹ and concentration of proton acceptor (coumarin) varies from 0.01 mol L⁻¹ to 0.13 mol L⁻¹ in steps of 0.01 mol L⁻¹. It is observed from the spectra of titrations of indole and coumarin that a constant decrease in N-H band of indole and a constant increase in carbonyl band of coumarin with increasing coumarin concentration. This observation clearly indicates the formation of 1:1 hydrogen bonded complex between N-H group of indole and carbonyl group of coumarin as shown in Figure 1.

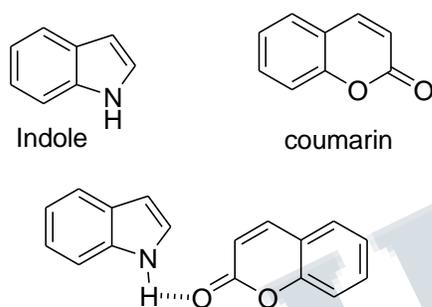


Figure 1. 1:1 complex formation of indole and coumarin

To explain the stability of the complexes, formation constants were calculated (Table 1) from the variation of the absorbance by using *Benesi-Hildebrand* equation [12,13]. For a 1:1 [Indole]:[Coumarin] complex, the formation constant K can be defined as follows:



$$K = \frac{[\text{Indole: Coumarin}]}{[\text{Indole}][\text{Coumarin}]}$$

The numerical value of K can be obtained from observed absorbance decrease I₀-I as a function of coumarin concentration.

$$1/(I_0 - I) = 1/(I_0 - I_{inf}) [C] K + 1/(I_0 - I_{inf})$$

Where I₀ is the initial absorbance of indole (N-H band), I is the absorbance of indole (N-H band) at various concentrations of coumarin, I_{inf} is the absorbance when all of the coumarin molecules have been complexed with the indole molecules and C is the concentration of coumarin. This

equation assumes that only a 1:1 complex is formed. This assumption can be readily tested using a reciprocal plot (*Benesi- Hildebrand plot*) of 1/ΔI Vs 1/[C]. This plot will be linear if only a 1:1 complex is formed, but will show curvature if complexes of other stoichiometry are being formed. In Fig. 2, *Benesi- Hildebrand plot* of indole:coumarin complex is shown. For this plot regression coefficient (R) is 0.997 indicating that a 1:1 complex is formed.

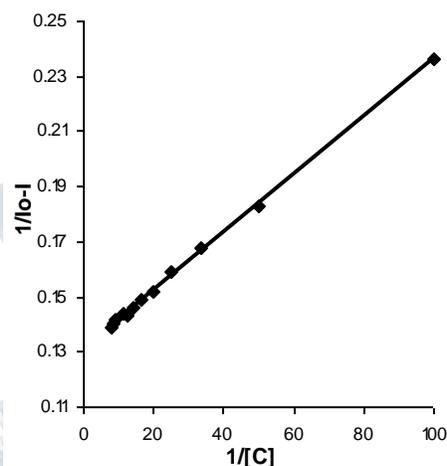


Figure.2: *Benesi-Hildebrand plot of indole:coumarin complex. The plot is based on the absorbance changes of N-H band of indole at 3491cm⁻¹ with a 1:1 model: 1/ΔI vs. 1/[C].*

The free energy change (ΔG) of formation can be calculated from the obtained formation constant value by

$$\Delta G = -RT \ln K$$

where R is the universal gas constant, T is the absolute temperature and K is the formation constant. The free energy change (ΔG) and formation constant values are shown in table 1.

Table 1. Spectral data, formation constant and free energy change (ΔG) of indole with coumarin

v _{NH} (cm ⁻¹)	v _{c=O} (cm ⁻¹)	K (L mol ⁻¹)	-ΔG (Kcal mol ⁻¹)
3491	1741	131.6	2.889

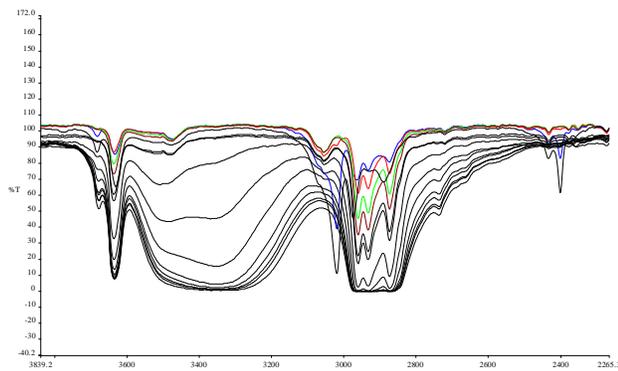


Fig 3: FTIR spectra of Indole-Coumarine with different concentrations. Wavenumber on X-axis and Transmittance on Y-axis.

4. CONCLUSIONS

In conclusion, an experiment for the formation of hydrogen bonding between indole and coumarin was done. It is explained that the donor indole can form hydrogen bond with acceptor coumarin leading to the formation of a 1:1 complex. The formation constant and free energy change of the 1:1 complexes of indole:coumarin were evaluated.

5. REFERENCES

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