



FORMATION CONSTANT AND FREE ENERGY VALUES OF 1:1 COMPLEXES OF PARAFFIN WAX, CHOLESTROL, NAPHTHALENE WITH PHENOL

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ABSTRACT

Hydrogen bonding between paraffin wax, cholesterol, naphthalene with phenol is studied in carbon tetrachloride by using the FTIR spectroscopic method. Utilizing the Nash method, the formation constant (K) of the 1:1 complexes is calculated. Using the K value, the free energy change (ΔG) is also calculated. The calculated formation constant and free energy change values vary which suggests that the proton donating ability in the order: paraffin wax < cholesterol < naphthalene.

Key words:

FT-IR: formation constant; free energy;

Hydrogen bonding.

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INTRODUCTION

Intermolecular hydrogen bonding interaction plays an important role in determining the structures and activities of organic, organometallic and biological molecules [1-4] and also involved in the interaction of many substrates to the active site of enzymes [5]. Studies of the interaction between associated and non-associated liquids in inert media provide valuable information regarding molecular complex formation in solution. Infrared studies of methyl methacrylate and ethyl methacrylate in various solvents have been reported by Liu *et al.* (2004) and Zheng *et al.* (2004)[6]. Rosenberg and Smith (1963)[7] calculated the equilibrium constant of aliphatic esters-alcohol systems. Krueger and Hawkins (1973)[8] reported the OH stretching frequency of substituted benzyl alcohols (methoxy, methyl, chloro and nitro) in carbon tetrachloride using infrared technique. Dharmalingam *et al.* (2006a,b) [9,10] have reported the hydrogen bonding between acrylic esters with aliphatic alcohols in non-polar solvents through FTIR study. FTIR investigation of the properties of organic compounds is of great value in understanding the nature of molecular interaction between the molecules. Keeping both the industrial and scientific interests in mind, we report here the results of our investigation on the H-bonded complexes of paraffin wax, cholesterol and naphthalene with phenol in carbon tetrachloride using FTIR spectroscopic

measurement. This study is expected to provide better understanding of the nature of molecular orientation and particularly the role of specific solute-solute interactions on the stability of 1:1 complex formation between of paraffin wax, cholesterol and naphthalene with phenol in carbon tetrachloride.

Experimental section and method

MATERIALS

Paraffin wax, cholesterol, naphthalene, phenol and carbon tetrachloride with AR grade. paraffin wax pellets were boiled up to its boiling point 57°C. The liquid was collected and allowed to cool room temperature, purified paraffin wax was formed. cholesterol was heated up to its boiling point 148°C. Then liquid was allowed to cooling state, finally purified sample of cholesterol was formed. Naphthalene to purify the sample of naphthalene using the technique recrystallization methanol is the used the solvent for the recrystallization. The solvent is boiled and add to impure sample of naphthalene until its completely dissolved state. Allow the solution to room temperature. After the crystallization process complete using Buchner funnel to separate naphthalene crystals. carbon tetrachloride was treated with anhydrous calcium chloride, refluxed for eight hours and then distilled. The liquid was collected at its boiling point 76-77°C. Phenol was distilled under reduced pressure at boiling point 81°C (17mm of Hg), melting point 40.5-41°C. That was purified by vacuum sublimation melting point 93-93.5°C respectively. The

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physical parameters of all the chemicals used in this study were checked against their literature values

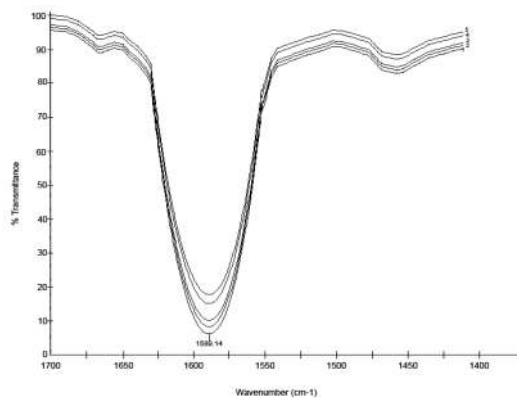
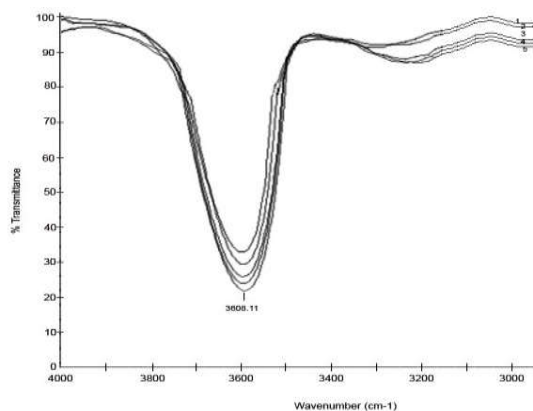


Fig 1 FT-IR Spectra of phenol with naphthalene in CCl₄ system

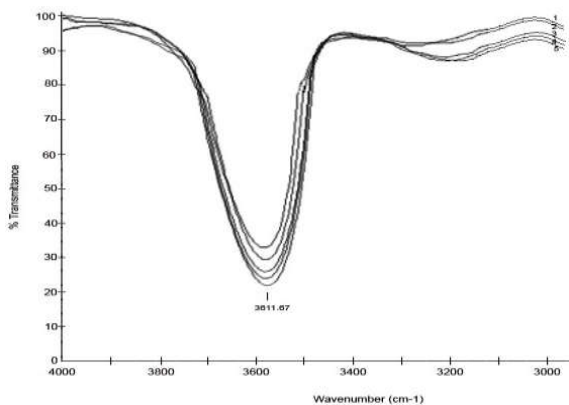
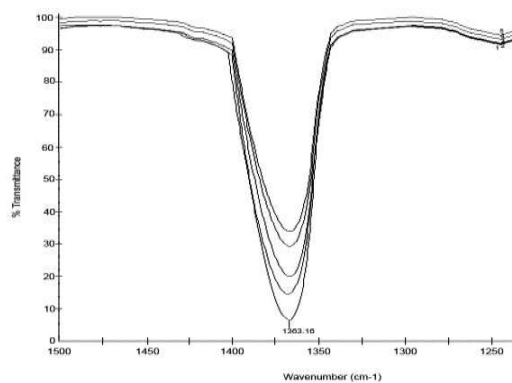


Fig 2. FT-IR Spectra of phenol with cholesterol in CCl₄ system

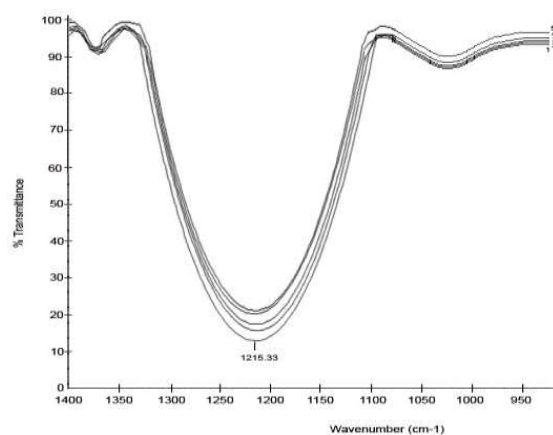
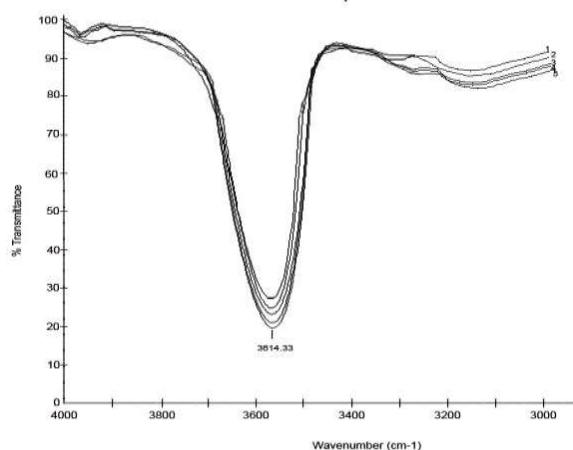


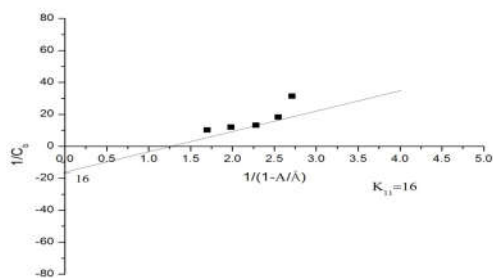
Fig 3 FT-IR Spectra of phenol with paraffin wax in CCl₄ system

Table 1 Naphthalene with phenol in Carbon tetrachloride system of C=C Stretching vibration and hydroxyl absorbance.

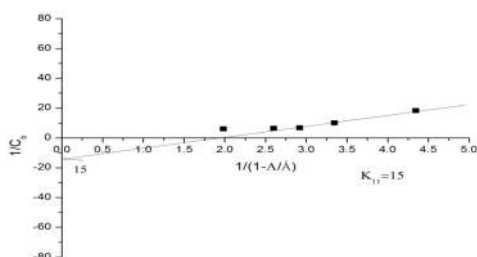
Concentration (moles lit ⁻¹)	Free hydroxyl Band Absorbance	Inverse of the Observed concentration	Carbonyl Band Absorbance	$X = \frac{1}{1 - \frac{A}{A^0}}$
0.03	0.1144	31.2500	0.1739	2.7121
0.05	0.1264	18.1818	0.1674	2.5506
0.07	0.1452	13.1313	0.1549	2.2844
0.09	0.1648	11.9047	0.1249	1.9844
0.11	0.1853	10.2040	0.1135	1.7006

Table 3 Paraffin Wax with phenol in Carbon tetrachloride system of C-C Stretching vibration and hydroxyl absorbance.

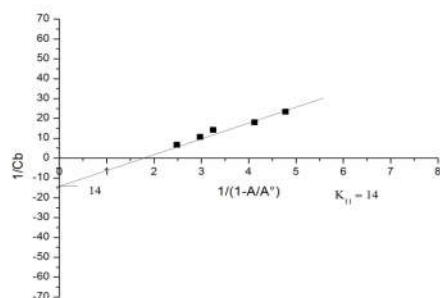
Concentration (moles lit ⁻¹)	Free hydroxyl Band Absorbance	Inverse of the Observed concentration	Carbonyl Band Absorbance	$X = \frac{1}{1 - \frac{A}{A^0}}$
0.03	0.09913	18.1818	0.2596	4.3470
0.05	0.01219	10.0000	0.2365	3.3508
0.07	0.01338	6.6666	0.2218	2.9230
0.09	0.15237	6.3694	0.1739	2.6018
0.11	0.17831	5.8823	0.1366	1.9869



Plot 1 Naphthalene with phenol in Carbon tetrachloride system of C=C Stretching vibration and hydroxyl absorbance.



Plot 2 Cholesterol with phenol in Carbon tetrachloride system of C-O Stretching vibration and hydroxyl absorbance.



Plot 3 Paraffin Wax with phenol in Carbon tetrachloride system of C-C Stretching vibration and hydroxyl absorbance.

Table 3 Paraffin Wax with phenol in Carbon tetrachloride system of C-C Stretching vibration and hydroxyl absorbance.

Concentration (moles lit ⁻¹)	Free hydroxyl Band Absorbance	Inverse of the Observed concentration	Carbonyl Band Absorbance	$x = \frac{1}{1 - A/A^\circ}$
0.03	0.0887	23.2558	0.1426	4.7800
0.05	0.1186	17.8571	0.1366	4.1253
0.07	0.1312	14.0285	0.1249	3.2522
0.09	0.1442	10.6382	0.1191	2.9759
0.11	0.1644	6.6666	0.1079	2.4882

Recording of FT-IR spectra

SHIMADZU series FTIR spectrometer with resolution of $\pm 0.01 \text{ cm}^{-1}$ was used. Spectra were recorded at 298K in the range of $4000 - 400 \text{ cm}^{-1}$, and NaCl cell of path length 0.05 cm^{-1} was

Table 4 Formation constant and Free energy values of 1:1 complexes

System	Nash method	Free energy
	$K_{11} \text{ lit mol}^{-1}$	$-\Delta G_{11}$
Phenol+		
Naphthalene	16	6.8696
Cholesterol	15	6.7097
Paraffin wax	14	6.5388

used. The spectrometer possesses auto align energy optimization and dynamically aligned interferometer. It is fitted with aKBr beam splitter incorporation of a high-energy ceramic light source, a temperature-controlled, high-sensitivity DLATGS detector. A baseline correlation was made for the spectra recorded.

RESULT AND DISCUSSION

The observed spectral data of paraffin wax, cholesterol, naphthalene with phenol in carbon tetrachloride are reported in figures. The hydroxyl absorption bands in the range is (3604-3614), and carbonyl absorption bands in the range is (1215-1589). For ternary mixtures, the proton acceptor concentration is fixed at 0.03 mol l^{-1} varying the proton donor concentrations 0.03 mol l^{-1} to 0.11 mol l^{-1} by changing the concentrations, the free O-H band intensity increases with increasing. But at the same time the revise trend is noticed for the carbonyl absorption band. From the observation, it indicates that the existence of 1:1 complex formation between the free hydroxyl group and carbonyl group. This type of 1:1 complex formation between methacrylates and phenol in carbon tetrachloride system was reported by Khan and Sivagurunathan(2008)[11]. The association between donor A and donor B complex AB can be represented by the equilibrium $A+B \leftrightarrow AB$, if only 1:1 complexes are present. The formation constant (K) for the 1:1 complex is calculated with the help of Nash(1960)[12] method.

CALCULATION

Formation constant and free energy of the 1:1 complex

NASH METHOD

In this method at lower concentration of alcohol the influence of the higher order complexes on the absorption spectrum of the base is neglected. The concentration A, B and AB involved in the interaction are assumed to be obeying Beer's law at a given frequency characteristic of the 1:1 complex[13]. Here one assumes that the existence of a chemical equilibrium of the from.



Where B is a donor molecule and A is an acceptor. For purposes of orientation, one assumes that only A and AB absorb in the wavelength region of interest and for temporary mathematical convenience, it is taken that the concentration of A is to be very small relative to that of B. the equilibrium constant appropriate to reaction (1) is given in concentration units by

$$K_c = \frac{C_{ab}}{C_a C_b} \quad (2)$$

Where C_{ab} is the formation constant of the complex AB and C_a and C_b are the formal concentrations of A and B per centimeter of path (A) is given by

$$A = \varepsilon_a C_a + \varepsilon_{ab} C_{ab} \quad (3)$$

Where ε_a and ε_{ab} are the molar absorptivities of species A and AB respectively. In the absence of complexing agent B, the total absorbance per centimeter is given by

$$A^0 = \varepsilon_a C_a^0 \quad (4)$$

Where C_a^0 is the initial concentration of A. If one divides equation (3) by equation (4) and substitutes for C_{ab} from equation (2).

$$\frac{A}{A^0} = \frac{C_a}{C_a^0} \left[1 + \frac{\varepsilon_{ab}}{\varepsilon_a} k C_b \right] \quad (5)$$

By introducing conservation of species A

$$C_a^0 = C_a + C_{ab} \quad (6)$$

And invoking equation (2) on second time one finds

$$\frac{C_a}{C_a^0} = (k C_b + 1)^{-1} \quad (7)$$

When equation (7) is substituted into equation (5) which results

$$\frac{A}{A^0} = \left[1 + \frac{\varepsilon_{ab}}{\varepsilon_a} k C_b \right] / (1 + k C_b) \quad (8)$$

For convenience, let one defines

$$\frac{A}{A^0} = Z \quad (9)$$

$$\frac{k \varepsilon_{ab} C_b}{\varepsilon_a} = \alpha \quad (10)$$

$$\text{and } C_b = \frac{1}{Y} \quad (11)$$

Then the equation (8) becomes

$$Z = \frac{(1 + \alpha/Y)}{(1 + k/Y)} \quad (12)$$

Equation (12) may be solved explicit for obtain

$$Y = \frac{(kz - \alpha)}{(1 - Z)} \quad (13)$$

When now one defines

$$X = \frac{1}{(1 - Z)} \quad (14)$$

And substitutes equation (14) into equation (13) a linear equation results

$$Y = X(k - \alpha) - k \quad (15)$$

The physical significance of the equation (15) is quite clear. When the reciprocal of the donor concentration is plotted against the reciprocal of one minus the absorbance ratio value and a straight line should result if 1:1 complex formation occurs. The intercept of this line is the negative of the formation constant and the slope is related to the molar absorptivity of the complex.

Free energy

The free energy [14,15] function provided the measure of chemical affinity under conditions of constant temperature and pressure energy changes in a chemical reaction can be defined as,

$$\Delta G = G_{(\text{product})} - G_{(\text{Reaction})} \quad (1)$$

Where $\Delta G = 0$, there is no network obtainable, the system is in a stable of equilibrium. When ΔG is positive, network must be put in to the system to effect the reaction can proceed spontaneously with accomplishment of the network. The larger amount of this work that can be accomplished the further removed is the reaction from equilibrium. For this reason $-\Delta G$ as often been called the driving force of the reaction.

Using the formation constant, obtained in the present investigation, the free energy (ΔG) were calculated for the systems under consideration with the relation.

$$\Delta G = -RT \ln K_{11} \quad (2)$$

Where R is gas constant.

The absolute temperature 298K and K_{11} is formation constant. The free energy of the bond formation obtained at 25°C for the system and values are given in table 4. It has been found that two opposing effects are possibly operative in these mixtures; namely, specific interactions between the carbonyl group and O-H group, and non-specific interactions (i.e., the breaking of intermolecular hydrogen bonds)

The formation constant (K) and free energy (ΔG) values for between paraffin wax, cholesterol, naphthalene with phenol in carbon tetrachloride solution are increasing in the order: paraffin wax < cholesterol < naphthalene. This change in K and ΔG values indicate that the proton donating ability of the proton donor varies of paraffin wax, cholesterol and naphthalene. The calculated K and ΔG values for proton acceptors are found with acceptors are found with paraffin wax, cholesterol and naphthalene, which reveal that the proton donating ability of phenol. Our result that is in close agreement with the formation constant value was reported by Vanderheyden and zeegers-Huyskens (1983)[16] in phenol derivatives with acceptor.

CONCLUSION

From the study, it may be concluded that proton donating ability of phenol and proton accepting ability of paraffin wax, cholesterol and naphthalene are linearly.

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