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Dipole Moment and FT-IR studies of Phenol with some substituted anilines

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ABSTRACT

The dipole moments of 1:1complexes formed between phenol and aniline, o-chloroaniline, and p-chloroaniline were measured in carbon tetrachloride at a temperature of 303 K. The dipole increments for these systems were calculated based on molecular orbital theory using bond angle data. The observed increase in dipole moment values provides evidence of hydrogen bonding between phenol and all three anilines. As the concentration of phenol increases, the FT-IR intensity decreases, and there is a slight increase in the half-width of the amine band. These observations suggest the formation of 1:1 complexes between phenol and anilines.

KEYWORDS: H-Bonding, Dipole moment, Dipolar increment, FT-IR.

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INTRODUCTION:

Aniline and its derivativesare extensively manufactured for diverse industrial and commercial applications such as dye production, pesticide formulation, and pharmaceutical manufacturing. Due to the inherent polarity of the amino group, derivatives of aniline tend to exhibit intermolecular or intramolecular hydrogen bonding when in the solid state or when dissolved in solvents. The presence of hydrogen bonding between the solute and solvent molecules can substantially enhance solubility, sometimes leading to exceptionally high or even unlimited solubility[1].

Dielectric studies are valuable tools for understanding the intra-intermolecular orientations of molecules. One of the physico-chemical methods used to investigate molecular complexes is the phenomenon of molecular orientation induced by a permanent electric field. The measurements carried out in the molecular interactions in binary and ternary solutions are used to identify the nature of complexes and to evaluate formation constants of the complex formed by AB and AB2 complexes[2].

Satheesh et al. performed dielectric permittivity measurements on binary mixtures of allyl alcohol with pyridine, 1,4-dioxane (associated-non-associated), and phenol (associated-associated) at 9.8 GHz and 1 kHz. The results indicated that the presence of the double bond in allyl alcohol did not significantly influence complex formation and relaxation mechanics in the complexes[3]. Additionally, several researchers have conducted dielectric measurements on acetophenone and its derivatives, contributing to the understanding of these compounds' properties and behaviour [4-7].

In recent years, numerous researchers have utilized dielectric methods to study the complexes formed between phenols and alcohols with ketones, esters, amides, aldehydes, and amines. These investigations have focused on the polarity of hydrogen-bonded complexes in non-polar solvents, represented by dipolar increments $\Delta\mu$, which exhibit a systematic dependence on the ΔpKa. The relationship between $\Delta\mu$ and ΔpKa generally follows a sigmoidal trend [8-10].More recently, another study by the authors [11] focused on rigid polar molecules and their mixtures, leading to the discovery of complex formation phenomena.

In the present work, the aim is to investigate the dipole moments of binary and complex systems using mixtures of aniline, o-chloroaniline, p-chloroaniline with phenol in CCl_4 at 303 K. The researchers will employ both polarization[12] and Huysken's method[13] to carry out these investigations.

2. EXPERIMENTAL STUDY:

2.1 Material

Aniline, o-chloroaniline, p-chloroaniline, phenol and CCl_4(AR grade) were purchased from precession scientific company in Coimbatore and used without any further and the physical parameters of all the chemicals used in this study were checked against their literature values.

2.2 Recording of FT-IR spectra

For the current study, a JASCO-460 series FT-Infrared spectrometer was employed, operating in a double beam configuration. Spectra of phenol in conjunction with various acceptor systems were recorded within the frequency range of 4000 to 400 cm^{-1}. For identifying the nature of the complexes, mixed solvent techniques were utilized to investigate the intensity variations of the characteristic bands of the interaction system .

2.3Determination of Dipole moment of 1:1 complex

The experimental procedure involved conducting dielectric measurements at a constant frequency of 300 kHz utilizing a Toshniwal RL09 dipole meter at room temperature 303K throughout the measurements, the cell was equipped with a glass jacket through which water was circulated. Additionally, the refractive indices of the substances under study were determined using Abbe's refractometer. For accurate and reliable results, all chemicals used in the experiments were purified following standard procedures and their properties were cross-validated against values reported in the existing literature.

When considering components A (-OH group) and B ($-NH_2$ group) dissolved in an inert solvent, their dipole orientations are influenced by the movement of the liquid state. For a short period, the molecular orientations remain stable. In this context, the dipole moment can be expressed as follows:

$$D = \left[\frac{9KT\times10^{39}}{4\pi N_a}\right] \times \left[\frac{(\varepsilon-n^2)(2\varepsilon+n^2)}{\varepsilon(n^2+2)^2}\right] - \frac{C_S}{C_S^o}\left[\frac{(\varepsilon_S-n_S^2)(2\varepsilon+n_S^2)}{\varepsilon_S(n_S^2+2)^2}\right] \qquad (1)$$

where C_S and $C°_S$ is the actual concentration of the solvent in the solution and pure state respectively.

2.4 Dipolar Increment (Δμ)

The dipole increment may be written as:

$$\Delta\mu = \mu_{ab} - \mu_a - \mu_b \quad (2)$$

Above equation can be used to the dipolar increment. The calculated values reported in the Table-2. Thisindicates that polarization interaction occurs from the proton donor and acceptor. The redistribution of thecharges due to the dipole moment varies enormously.

2.5 Determination of enthalpy changes during bond formation

The relation between the enthalpy changes (ΔH_b) and dipolar increment ($\Delta\mu$) is given by:

$$\Delta\mu = \frac{A(-\Delta H_b)+[B+C(-\Delta H_b)]exp[A_1+B_1(-\Delta H_b)]}{1+[A_1+B_1(-\Delta H_b)]} \quad (3)$$

More than hundred OH..O complexes, including some OH..N complexes, were examined using the equation.The above equation may be modified for the purpose of calculatingof $-\Delta H_b$ from the known $\Delta\mu$. If it is written in Debye and $-\Delta H_b$ in $KJmol^{-1}$, the numerical values of the constants as follows:

For OH..O bond A=0.028, A1=-6.5, B=3.20, B1=0.085 , C=0.075

For OH..N bond A=0.0074, A1=-7.765, B=4.41, B1=0.172, C=0.045

RESULTS AND DISCUSSION

3.FT-IR Analysis

3.1 Binary System

The amine band spectra for different concentrations of aniline, o-chloroaniline, and p-chloroaniline dissolved in carbon tetrachloride are displayed in the figures (3.1, 3.2, and 3.3). Each compound shows a characteristic amine (-NH2) band at a concentration of about 0.03 moles/lit, with symmetry bands at 3395 cm-1 for aniline, 3399 cm-1 for o-chloroaniline, and 3397 cm-1 for p-chloroaniline, and corresponding asymmetry bands at 3479 cm-1, 3494 cm-1, and 3484 cm-1, respectively.

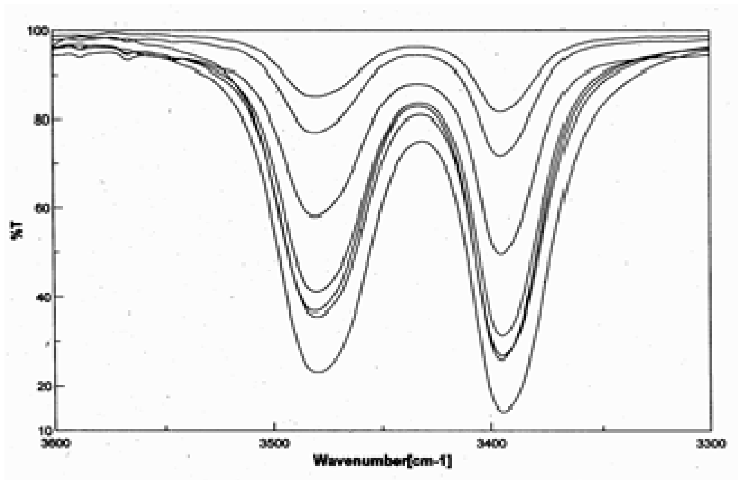

Fig. 3.1 Aniline in carbon tetrachloride system

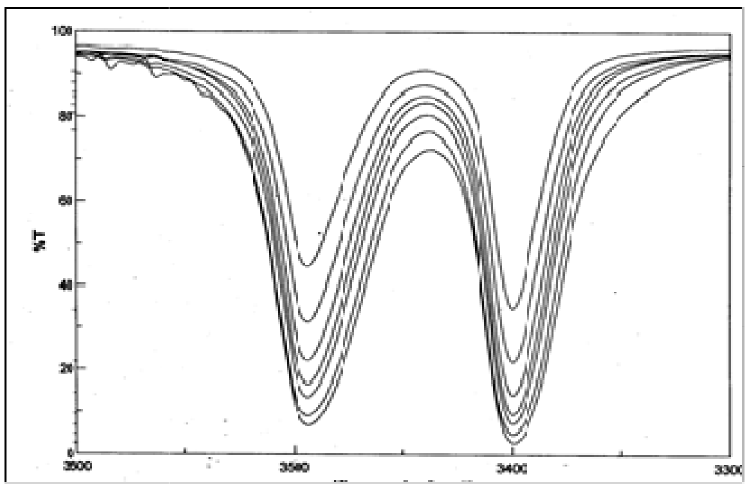

Fig. 3.2 *o*-chloroaniline in carbon tetrachloride system

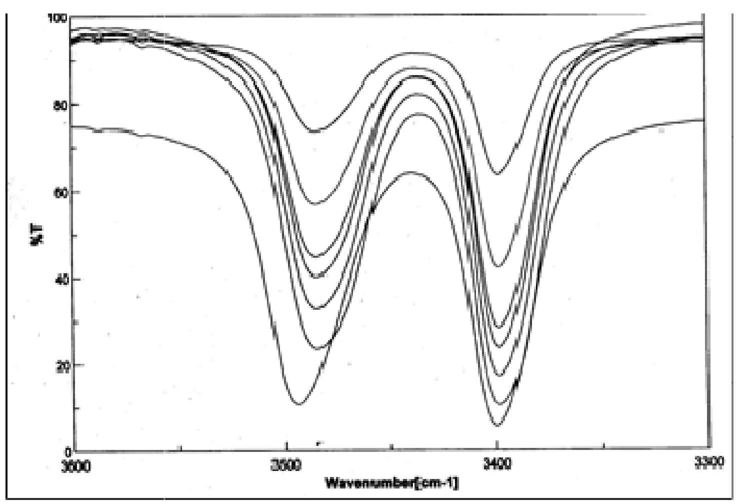

Fig. 3.3 *p*-chloroaniline in carbon tetrachloride system

When the concentration of aniline, o-chloroaniline and p-chloroanilinerises, the intensity of the bands also increase, but no frequency shift is observed in all the three cases. This behaviour indicates that there is no solute – solvent interaction. The intensity of the symmetry band is more when compared to the asymmetry band.

3.1.1*FT-IR studies of Hydrogen bonded complexes*

The amine (NH_2) absorption band spectra of 0.05 mole/lit solutions of aniline, o-chloroaniline, and p-chloroaniline in carbon tetrachloride with varying phenol concentrations is shown in fig. 3.4,3.5,3.6. In this system, the free amine stretching band of aniline in carbon tetrachloride is observed at3396 cm^{-1} (symmetry) and 3578 cm^{-1} (asymmetry). These bands were identified at 3399 cm^{-1} (symmetry) and 3592 cm^{-1} (asymmetry) for o-chloroaniline in CCl_4, and at 3398 cm^{-1} (symmetry) and 3580 cm^{-1} (asymmetry) for p-chloroaniline in CCl_4.

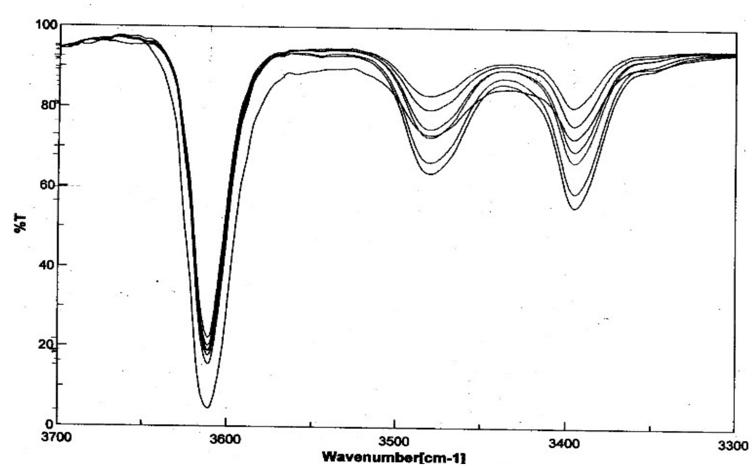

Fig. 3.4 Phenol with aniline in carbon tetrachloride system

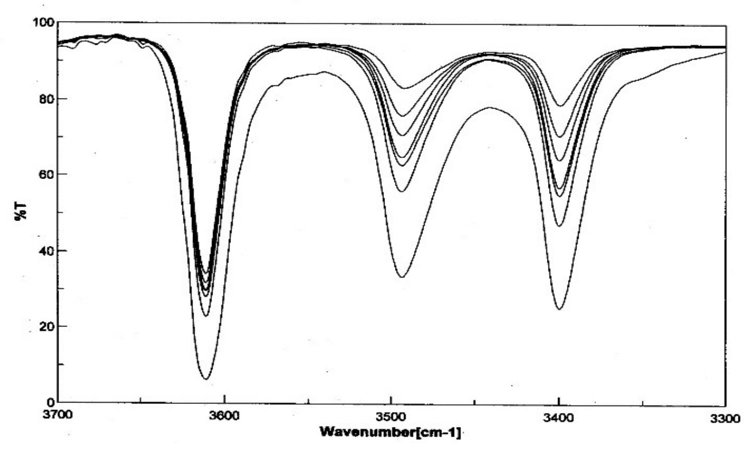

Fig. 3.5 Phenol with *o*-chloroaniline in carbon tetrachloride system

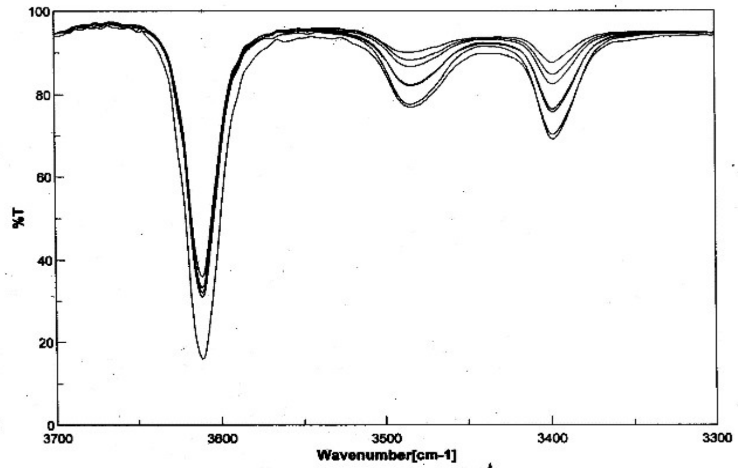

Fig. 3.6 Phenol with *p*-chloroaniline in carbon tetrachloride system

In all the three cases as the concentration of phenol increases, the intensity of amine band decreases while the half width slightly increases, this behaviour indicate that the existence of 1: 1 complex. When the concentration of phenol increases, the intensity of the free OH band also increases.

3.2 Dipole moment

The dipole moment of the donor and acceptor were calculated by Huyskens method, which builds on Onsager theory using carbon tetrachloride as solvent. These are closely agreed with the results from solution data. The values of dielectric constant, density and refractive indices measured with different concentration of the proton donor C_b are recorded in table1.For the range of concentration studied, the plot of C_a/C_bversusΩ_b is a straight line and is shown in fig 1. This inhibits for the formation of higher order complexes. Hence, it may be taken as an indication for the 1:1 complex. The $\Delta\mu$ values in the present investigation are less than <6D. Our results may be on the basis that complex formation arise due to the polarization interaction caused by charge transfer and that higher order complex may be AB_2, A_2B, A_3B etc. are not sustainable. This also supports the fact that the curve C_a/C_bversusΩ_b is linear in all the cases and is independent of the ratio of the concentration C_a/C_b in the range of concentrations that indicate the absence of co-operative effects in H-bond chains. In complexes with phenol, only AB complexation must prevail. As observed from the table 2 the dipole moment of the complexed species are higher than the vector sum of their individual components. The increase in the dipole moment could be interpreted as due to the formation of H-bond producing the displacement of electrons and nuclei. Some authors[14,15]shown that is the dipolar increment $\Delta\mu < 3$. This is found to be so whether the H-bond is purely ionic, the other 50% should arise from the electronic displacement. The reported values of Δμ is very low and does not support the deprotonation. In the presently investigated all systems, has been found to be the ranging from 1.58 to 5 .42D. It may be concluded that the complexation may polarization effects. Similar results also have drawn by Malathiet. el.[9],Thennappan and sabesan[16] for alcohol mixtures.Balamuralikrishnan[17]for the mixtures of alcohol with aniline's. The molar polarization of the solution and solute were calculated by Huysken's method and displayed in table 3. The plot of polarization versus mole fraction for all the systems shown in fig 2.C_a=0.05 mol/lit

Table-1: Variation of dielectric constant (ε), refractive index (n) of the solution and Experimentalquantity Ω_b withC_b

Phenol with aniline in CCl_4 system				
C_b	ε	n	C_a/C_b	Ω_b
0.03	2.228	1.453	0.6666	9.0955
0.05	2.230	1.454	0.4000	5.2926
0.07	2.243	1.456	0.2857	4.6869
0.09	2.253	1.457	0.2222	4.2819
0.11	2.268	1.459	0.1818	4.2037
0.13	2.273	1.460	0.1538	3.6655
0.15	2.283	1.462	0.1333	3.3855

C_a=0.05 mol/lit

Phenol with O- chloroaniline in CCl_4 system				
C_b	ε	n	C_a/C_b	Ω_b
0.03	2.238	1.452	0.6666	12.8388
0.05	2.253	1.452	0.4000	10.4013
0.07	2.263	1.455	0.2857	7.4701
0.09	2.273	1.457	0.2222	6.163
0.11	2.283	1.459	0.1818	5.3368
0.13	2.293	1.46	0.1538	4.9581
0.15	2.303	1.462	0.1333	4.5028

C_a=0.05 mol/lit

Phenol with p-chloroaniline in CCl_4 system				
C_b	ε	n	C_a/C_b	Ω_b
0.03	2.253	1.454	0.6666	15.3030
0.05	2.278	1.455	0.4000	13.1805
0.07	2.293	1.456	0.2857	10.7678
0.09	2.303	1.457	0.2222	8.975
0.11	2.313	1.458	0.1818	7.8618
0.13	2.328	1.459	0.1538	7.4272
0.15	2.343	1.461	0.1333	6.9206

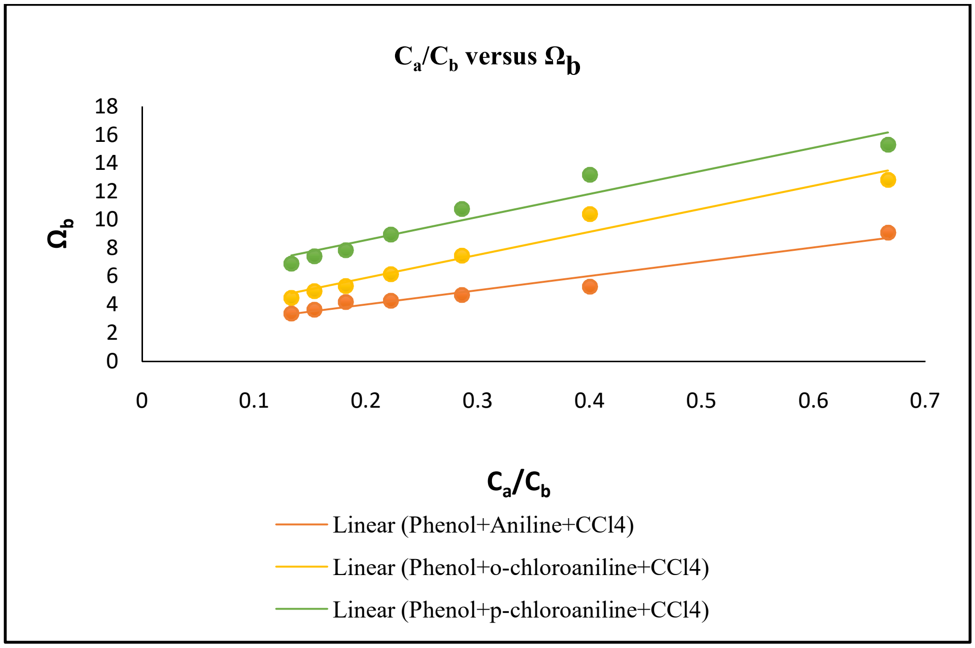

Fig 1. C_a/C_b **versus** Ω_b

Table-2 Dipole moments of the compounds, and their complexes

Donar	Acceptor	μ_{ab}cis	μ_{ab}trans	Pka	Δμ	-ΔHb	μ_{ab}	μ_b
Phenol	**Aniline**	2.34	2.91	4.60	4.32	49.01	3.35	1.41
	o-chloroaniline	2.35	2.91	2.62	5.34	56.51	4.29	1.58
	P-chloroaniline	3.12	3.79	3.81	6.31	67.98	4.99	2.12

Table 3: Molar polarization

Mole fraction of the solute	Molar polarization of aniline + CCl_4	Molar polarization of o-chloroaniline + CCl_4	Molar polarization of p-chloroaniline+ CCl_4
0.03	153.47	206.47	369.81
0.05	102.54	128.54	279.14
0.07	83.57	102.71	236.85
0.09	86.81	87.92	214.36
0.11	82.14	78.68	208.59
0.13	82.29	72.83	207.45
0.15	75.94	62.41	190.21

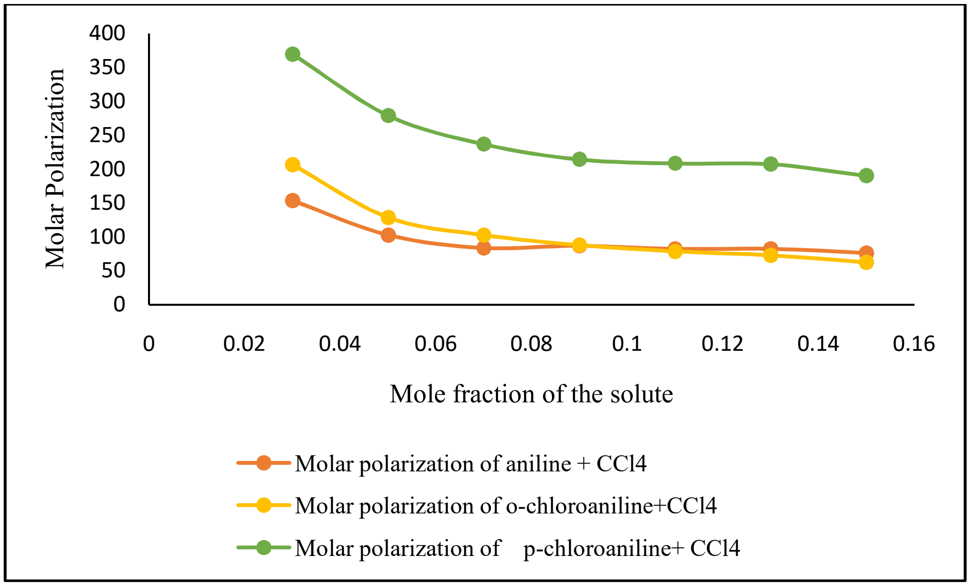

Fig.2 Molar polarization versus mole fraction of the solute

Table 4: Free energy values of 1:1 and 1:2 complexes

System	Free energy value of the complexes Kcal mol^{-1}	
	1:1	**1:2**
	-ΔG11	**-ΔG12**
Phenol+Aniline	1.2937	2.1720
Phenol+o-chloroaniline	1.1243	2.0026
Phenol+p-chloroaniline	1.0165	1.8953

3.*3 Enthalpy:*

From the enhancement dipole moment values, Huysken'sequation are used to calculate the enthalpy change. The Δμ versus Δpk_aandΔH_b for both O-H…O and O-H…N systems studied here fit only in the lower and transition portion of the sigmoidal curve, which indicates that the nature of interaction in these complexes are mainly due to the polarization effect only and may be charge transfer or proton transfer occurs in the OH….N and OH…O interaction.

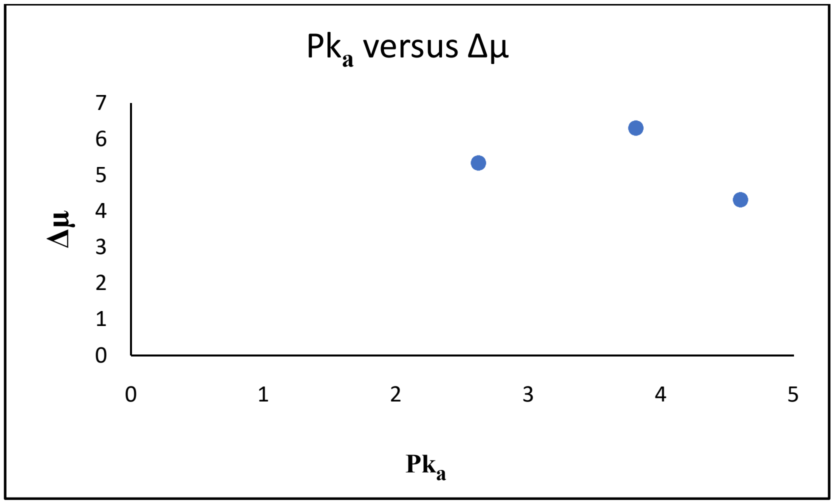

Fig 3.Pk$_a$versus Δμ

3.4 Free Energy

As seen in table 4, phenol has a strong tendency to form complexes with a variety of aniline acceptors, according to both K11 and G11 values. This finding highlights that phenol is highly associative and has high proton donating ability.The sequence of proton accepting abilities can be described as follows: aniline > o-chloroaniline> p-chloroaniline.The interacting ability of the acceptor is in the order of p-chloroaniline<o-chloroanililne<aniline.

CONCULSION:

In the present investigation, all the complexes examined exhibited ΔH_bvalues within the range of 49.01 to 67.98 KJ mol^{-1}. These values, calculated for the 1:1 complexes, fall within the transition region of the sigmoidal curve and are relatively high. This suggests the presence of polarization interactions. Based on the aforementioned findings, it can be inferred that the increase in dipole moment of the complexes is primarily attributed to the polarization effect. The investigation also explored the possibility of charge transfer or proton transfer in the complexes.The values of effective dipole moment μ_{ab} for phenol and aniline with CCl_4 is less than that of phenol and o-chloroaniline with CCl_4 and phenol and p-chloroaniline with CCl_4 whichIndicatesaniline is highly associative than p-chloroaniline. The calculated μ_{ab} values of all the systems in the 'Trans' form are found to be higher than the 'Cis' form. Hence 'Cis' form may be taken as the most favourable structure of the 1:1 complex which has the

most stable configuration of the 1:1 complex for which the potential energy is minimum. In the FTIR study, it was observed that as the concentration of phenol increases, the intensity of the amine band decreases, and the half width of the band slightly increases. This behaviour suggests the presence of a 1:1 complex. Additionally, when the concentration of phenol is raised, the intensity of the free OH band also increases.

REFERENCES:

1. XieMeng-Xia , Liu Yuan, Studies on the hydrogen bonding of aniline's derivatives by FT-IR, SpectrochimicaActa Part A, 2002; 58: 2817-2826
2. Sivashankar P, Umamaheswari A, Formation Constant and Free Energy Values of 1:1Complexes of 1-Bromohexane, 1-Bromodecane, 1-Bromooctane withO-Nitro Phenol In CS_2 ,IJSRR 2018; 7(4): 736-743.
3. V. Satheesh, M. Jeyaraj, J. Sobhanadri, Dielectric studies of allyl alcohol with (i) pyridine, (ii) 1-4 dioxane, (iii) phenol Hydrogen bonded complexes, Jou.of Mol. Liq, 1995; 64(3): 247-261.
4. YoshikiYomogida, Ryusuke Nozaki, Dielectric study of acetophenone and its derivatives, Jou. Of Mol. Liq. 2009; 149(3): 101-104.
5. P.J. Singh, K.K.Gupta Fluid structure and molecular interaction of acetone derivatives, Pramana J. phys. 2004; 62 (5):1129-1137.
6. RajniMisra, Amar Singh et. el., Thermodynamics of H- bond through dielectric data analysis, Phy and Che of Liq., 1985; 14(3): 189-198.
   J. Phys. A Proc. Indian Assoc. Cultiv. Sci. 2000; A 74: 471-478.
7. S.L. Abd-EI messieh, Effect of solvent viscosity on the dielectric relaxation of some acetophenone derivatives, Jou. ofMol.Liq. 2003; 105: 37-51.
8. M. Malathi, R. Sabesan, S. Krishnan, Dielectric Studies of H-bonded complexes of farmamide and acetamide with substituted phenols, Jou. of Mol. Liq.,2004; 109:11-18.
9. P. Krishnamurthy, PhD Thesis, Department of Physics, AnnamalaiUniversity,India, 2003.
10. A. Uma maheswari, S. Balamuralikrishnan, Dipole moment studies of molecular complexes of 1-heptanol and 1- octanol with amyl acetate and anisole in carbontetrachloride system, J. Annamalai Univ. Sci., (2004) 85-90.
11. K.K. Gupta, A.K. Bansal, P.J. Singh et. el,Temperature dependence of dielectric relaxation of rigid polar molecules acetophenone , pyridine and their mixtures in dilute solutions of benzene, Indian J Pure&AppliedPhys, (2003)41: 57-63.

12. D.Devika and S. Balamuralikrishnan, Dipole moment studies of some substituted Benzaldehyde with 1-Octanol, IntJou.of Tech Res. and applications, 2015; 5: 112-115.
13. P.L. Huyskens, H.M. Vanbrabant-Govaerts, Structrual differences between hydrogen-bonded complexes of enamino ketones and amino ketones in benzene solution, Journal of Molecular Structure 1982; 84 (1-2): 141-151.
14. T. Indira, G. Parthipan,T. Thenappan, Dipole moment studies of complexes of alcohols with ethyl bromide, Journal of MolecularLiquids, 2009; 150 (1-3): 22-24.
15. Baliah, V. and Aparajithan, K., “Dipolemoments of poly phenylenepolyethers and polyphenylene poly sulphides”, J. Ind. Chem. Soc., 1991; 68: 593-598.
16. T. Thenappan, M. Subramanian,Dielectric studies of hydrogen bonded complexes of alcohols with nitriles ,Materials Science and Engineering B, 2001; 86(1): 7–10.
17. Balamuralikrishnan S and Umamaheswari A.,Dipole moment studies of some substituted anilineswith phenols, Jou. of Mol. Liquids, 2006; 124: 19-22.