



E-Journal of Chemistry 2010, **7(1)**, 308-310

Molecular Interaction Study of some ortho and para Substituted Anilines with 1-Octanol

M. S. MANJUNATHA* and J. SANNAPPA

Department of Physics, Yuvaraja's College, University of Mysore, Mysore-570024, Karnataka, India. manjumsphy@yahoo.co.in

Received 27 May 2009; Accepted 20 July 2009

Abstract: Interactions between *ortho* and *para* substituents of anilines such as chloroaniline, methylaniline and methoxyaniline with 1-octanol have been studied in carbon tetrachloride. The most likely association of complex between 1-octanol and substituents of anilines is 1:1 stoichiometric complex, through hydroxyl group of 1-octanol and amine group of *ortho* and *para* substituents of anilines. Interactions are studied on the bases of formation constant and free energy changes. Formation constant of the complex has been calculated using Nash method. The result shows that molecular interaction of 1-octanol as proton donor with methyl and chloride substitution of anilines in *ortho* position is smaller than the *para* position substitution of anilines. The results shows, the ability of acceptors is in the order *p*-methoxyaniline<*o*-chloroaniline<*o*-methylaniline<*o*-methylaniline<*p*-methylaniline<

Keywords: Molecular interaction, Formation constant, Free energy change, Nash method.

Introduction

Molecular interaction study between associated and non associated liquid in an inert media gives valuable information about solute-solvent and solute-solute interaction. Spectroscopic technique is a power full tool to investigate the nature of molecular complexes and hydrogen bonding. It is interesting subject to measure various thermodynamic excess functions to obtain molecular interaction. A number of attempts to develop a quantitatively accurate and physically meaning explanation of solvent induced stretching vibration frequency shifts have been presented¹⁻⁴. Alcohols are industrially and scientifically important organic compounds and their physical and chemical properties are largely determined by their hydroxyl group. In the present work, an attempt has been made to study the molecular association between free hydroxyl group of 1-octanol with different amines group of *ortho* and *para* substitutes of acceptors in carbon tetra chloride media using FTIR measurements.

Experimental

A Nicolet Avatar 360 FTIR spectrometer with a resolution of ± 1 cm⁻¹ was used for this study. Spectra were obtained at room temperature (25 0 C) in the region of 4000 to 400 cm⁻¹. The chemicals used were *o*-chloroaniline, *o*- methylaniline, *o*-methoxyaniline, *p*-chloroaniline, *p*-methylaniline and *p*-methoxyaniline of Aldrich product used without further purification. AR grade of 1-octanol and carbon tetrachloride were purified by standard procedure^{5, 6} and redistilled before used.

Results and Discussion

The FTIR spectral data of o-chloroaniline, o-methylaniline, o-methoxyaniline, p-chloroaniline, p-methylaniline and p-methoxyaniline in 1-octanol are given in Table 1. The proton acceptor of amines concentration was fixed and donor concentration varying from 0.04 was carried out. From Table 1, it is noticed that the free amine stretching band increases as the concentration of hydroxyl group increases and the intensity of amine band decreases while half width slightly increases. The observation indicates the 1:1 complex formation between hydroxyl group of 1-octanol and the amine group of aniline substituents. The FTIR spectra obtained using mixed solvent techniques indicates the formation of complexes. It indicates the existence of 1:1 complex. Using Nash method⁷, the equilibrium constant (k) for the 1:1 complex is calculated by using equation

$$K = \frac{[AB]}{[A][B]} \tag{1}$$

Where [AB] is the concentration of the 1:1 complex and [A] and [B] are the initial concentration of the proton donor and proton acceptor respectively. A graph was plotted between $Y = [A]^{-1}$ and $X = \left[1 - \frac{a}{a_0}\right]^{-1}$. Where a and a_0 are the absorbance of the carbonyl band

of aniline substitutes in presence and absence of 1-octanol respectively. The intercept of the graph in the ordinate yields K^{-1} . The changes in free energy⁸ of systems are calculated using the equation

$$\Delta G = -RT \ln k \tag{2}$$

Where R represents universal gas constant, T represents absolute temperature and k represents formation constant of the systems. The formation constant and free energy changes values for *ortho* and *para* substituents of anilines with 1-octanol systems in the inert solvent CCl_4 are given in Table 1.

Table 1. Spectral data, formation constant and fee energy change of 1-octanol with *ortho* and *para* substitution of aniline in CCl₄ solvent at 309 K.

Systems		γ_f in cm ⁻¹	k lit mol ⁻¹	- ΔG kcal mol ⁻¹
Proton donor	Proton acceptor	7 f in cin	K III IIIOI	- AG Keal IIIoi
1-Octanol	o-Chloroaniline	3494	75.00	2.678
	o-Methoxyaniline	3485	138	3.056
	o-Methylaniline	3479	148.38	3.101
	<i>p</i> -Chloroaniline	3481	50.00	2.426
	<i>p</i> - Methylaniline	3469	150	3.107
	<i>p</i> - Methoxyaniline	3459	195.23	3.271

An examination of Table 1 shows that the formation constant for the hydrogen bonded of *ortho* and *para* aniline with 1-octanol is in the order of p-methoxyaniline < o-chloroaniline < o-methylaniline < o-methoxyaniline <p-chloroaniline. K values for methyl substitute of aniline and chloride substitute of aniline in ortho position are smaller then para substitution of aniline. This shows that molecular interaction has greater steric hindrance involving free rotation of molecules. The complex formation is relatively more in 1-octanol⁹. Because of steric hindrance, it is likely have greater probability of complex formation due to head tail linkage¹⁰. But for *ortho* position of methoxy substitute of aniline, formation constant is higher then the para substitute of methoxy substitute of aniline. These reveals that methoxy substitutes of aniline are comes under electron withdrawing groups. The free energy change and formation constant vary with ortho and para substitute of aniline with 1-octanol is suggests that the strength of intermolecular interaction occurs in the ternary mixture. Proton acceptor ability is in the order p-methoxyaniline < o-chloroaniline < o-methylaniline < o-methoxyaniline < p-chloroaniline < p-methoxyaniline.

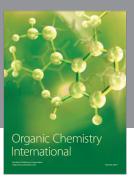
Conclusion

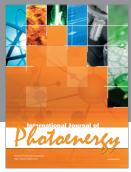
The formation constant and free energy change of *ortho* and *para* substitute of amines with 1-octanol in ccl4 are carried out. From this study one may conclude that the strength of intermolecular bond formed between the ortho and para substitute of amines and 1-octanol is shown that the tendency of molecular interaction is relatively more in para substitute than that of ortho substitute of anilines.

References

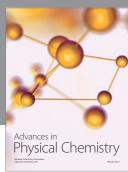
- 1. Navarro R, Hernanz A and Bratu I, J Mol Struct., 1995, 348, 253.
- 2. Symons M C R, Chem Soc Rev., 1983, 12, 1.
- 3. Bratu I, Grecu R, Constantinescu R and Iliescu T, Spectrochim Acta Part A., 1998,
- Streck R and Barnes A J, Spectrochim Acta A., 1999, 55(5), 1049. 4.
- 5. Hernandez B, Gavira-Vallejo J M, Navarro R and Hernanz A, J Mol Struct., 2001, **565,** 259.
- 6. Riddick J R and Bunger W B, Organic Sovents, Wiley Intersciences, New York, 1970.
- Nash C P, J Phys Chem., 1960, 64, 632. 7.
- Vinogradov C R H, Hydrogen Bonding, van Nostrand Reinhold Company, New 8. York, 1971.
- 9. Chandra A K and Basu S, Trans Frarday Soc., 1960, 56, 632.
- 10. Das J K, Dash D K, Acharya S and Swain B B, Jpn J Appl Phys., 1996, 35, 453.

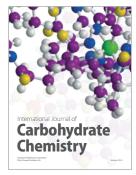
















Submit your manuscripts at http://www.hindawi.com

