

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

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**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*-methoxyaniline < *p*-chloroaniline < *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 presented<sup>1-4</sup>. 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  $\pm 1 \text{ cm}^{-1}$  was used for this study. Spectra were obtained at room temperature ( $25^\circ\text{C}$ ) in the region of  $4000$  to  $400 \text{ cm}^{-1}$ . 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<sup>5,6</sup> 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 method<sup>7</sup>, the equilibrium constant ( $k$ ) for the 1:1 complex is calculated by using equation

$$K = \frac{[AB]}{[A][B]} \quad (1)$$

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 substituents in presence and absence of 1-octanol respectively. The intercept of the graph in the ordinate yields  $K^{-1}$ . The changes in free energy<sup>8</sup> of systems are calculated using the equation

$$\Delta G = -RT \ln k \quad (2)$$

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  $\text{CCl}_4$  are given in Table 1.

**Table 1.** Spectral data, formation constant and free energy change of 1-octanol with *ortho* and *para* substitution of aniline in  $\text{CCl}_4$  solvent at 309 K.

| Systems      |                          | $\nu_f$ in $\text{cm}^{-1}$ | k lit $\text{mol}^{-1}$ | - $\Delta G$ kcal $\text{mol}^{-1}$ |
|--------------|--------------------------|-----------------------------|-------------------------|-------------------------------------|
| Proton donor | Proton acceptor          |                             |                         |                                     |
| 1-Octanol    | <i>o</i> -Chloroaniline  | 3494                        | 75.00                   | 2.678                               |
|              | <i>o</i> -Methoxyaniline | 3485                        | 138                     | 3.056                               |
|              | <i>o</i> -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 complexes 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 than *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-octanol<sup>9</sup>. Because of steric hindrance, it is likely to have greater probability of complex formation due to head tail linkage<sup>10</sup>. But for *ortho* position of methoxy substitute of aniline, formation constant is higher than the *para* substitute of methoxy substitute of aniline. This reveals that methoxy substitutes of aniline are under electron withdrawing groups. The free energy change and formation constant vary with *ortho* and *para* substitute of aniline with 1-octanol 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  $\text{CCl}_4$  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.

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