



## **EFFECT OF HYDROGEN BONDING ON THE INFRA-RED STUDY OF DONOR-ACCEPTOR COMPLEX BETWEEN ALCOHOL AND IODINE**

**S. K. BARUAH\* and R. UPADHAYA**

Department of Chemistry, Dibrugarh University, DIBRUGARH – 786 004 (Assam) INDIA

### **ABSTRACT**

The present study is based on the effect of solute such as iodine on H-bonding in aliphatic alcohols. Alcohols form charge transfer complexes with halogens. Several parameters like dimerisation constant ( $K_d$ ) and thermodynamic parameters like free energy ( $\Delta G$ ) at laboratory temperature for self associated alcohols as well as equilibrium constant ( $K$ ), free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) at different temperatures for charge transfer complexes are evaluated from IR spectra in solvent like carbon tetrachloride. In the adduct of 1 : 1 between alcohol and Iodine, the dimeric form around  $3500\text{ cm}^{-1}$  vanishes with the result that the broad band shift to higher frequency region. With the increase of temperature the value of equilibrium constant in the 1 : 1 adduct goes on decreasing suggests the stability of charge transfer interaction is low at low temperature.

**Key words:** Dimerization constant, Thermodynamic parameters, Hydrogen bonding.

### **INTRODUCTION**

Over the years several excellent reviews have been published covering different aspects of hydrogen bonding<sup>1-4</sup>. The most prominent effect of H-bonding on the vibrational spectrum is the shift of the absorption of the A-H stretching mode and its overtones to low frequencies. This spectral change was observed for a number of compounds which form intermolecular H-bonds, e.g. acetyl acetone benzoyl acetate, salicyl aldehyde and 0-nitrophenol<sup>5-9</sup>. Hadzi et al<sup>10</sup> found that the intensity and frequency of  $\nu_s$  of an alcohol are dependent on concentration and temperature. Simultaneously, a systematic study of the IR spectra of many amines, alcohols and phenols was done by earlier workers<sup>11-16</sup> and they generalized that the IR spectra provides a criterion for directing chelation through hydrogen<sup>17-21</sup>. IR spectroscopy is the most important method because of the sensitivity of vibrational mode to the presence of hydrogen bonds.

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\* Author for correspondence; E-mail: dpttchemistry@yahoo.com

In the present study, attempt has been made to correlate the effect of presence of solute on hydrogen bonding with parameters like  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  in a particular solvent.

## EXPERIMENTAL

### Material purification

Iodine (AR) was purified by sublimating a mixture of iodine, calcium oxide and potassium iodide.

Carbon tetrachloride is purified by distillation at its boiling point. Methanol (AR), propanol (AR) butanol (AR), amyl alcohol (AR) and allyl alcohol (AR) were purified by distillation at their boiling points:

### Preparation of the solution

Solutions of each of the alcohols of concentration 1M in carbon tetrachloride were prepared. Iodine solution in carbon tetrachloride ( $5 \times 10^{-3}$  1) M was also prepared.

The IR spectra of the experimental solutions were recorded in the range of 3000-4000  $\text{cm}^{-1}$  using Perkin – Elmer IR spectrophotometer. The dimerisation constant  $K_d$  and Gibb's free energy ( $\Delta G$ ) were calculated from the following equations (1) and (2) respectively.

$$A_{\nu} = \frac{\epsilon_A}{2K_d} \frac{C_A^0}{A} \frac{\epsilon_A l^2}{2K_d} \quad \dots(1)$$

Where  $l$  = Path length of the cell

$\epsilon_A$  = Extinction coefficient

$A_{\nu}$  = Absorbance

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

## RESULTS AND DISCUSSION

Alcohols are supposed to be mild donors. It can form charge transfer complexes with halogens since methanol is less viscous which prefers greater participation in charge transfer interaction with iodine. In case of Methanol – Iodine system at low concentration the frequency shift of the free OH is constant while the frequency shift of the bonded OH

shift towards higher frequency region. The low value of equilibrium constant  $K$  signifies the weak nature of bonding in hydrogen bonded  $-I_2$  CT complexes (Table 1).

**Table 1: Dimerization constant (K), free energy ( $\Delta G$ ), Enthalpy ( $\Delta H$ ) and Entropy change ( $\Delta S$ )**

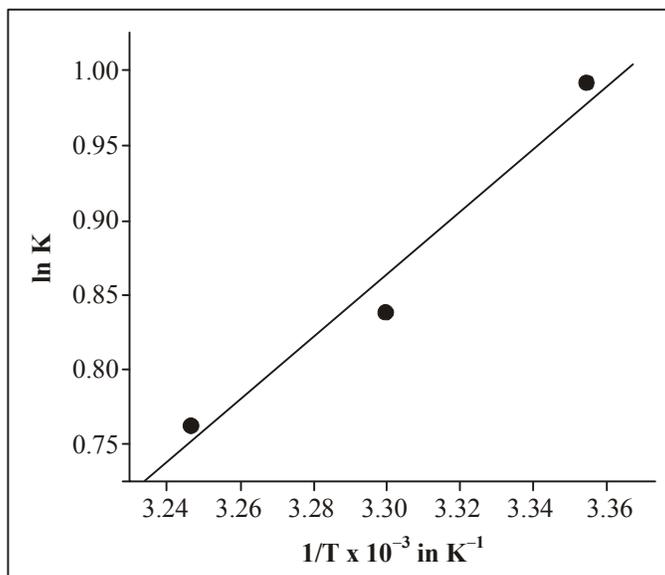
| Hydrogen bonded donor acceptor complex | Solvent          | Temp. in K | Equilibrium constant $\text{dm}^3 \text{mol}^{-1}$ | $\Delta G$ in KJ/ Mol. | $\Delta H$ KJ/ Mole | $\Delta S$ JK <sup>-1</sup> Mol. <sup>-1</sup> |
|--|------------------|------------|--|------------------------|---------------------|--|
| Methanol-I <sub>2</sub>                | CCl <sub>4</sub> | 298        | 2.65   | -2.45                  |                     |  |
|  |                  | 303        | 2.31   | -2.11                  | -17.56              | -50.77   |
|  |                  | 308        | 2.14   | -1.91                  |                     |  |
| Propanol-I <sub>2</sub>                | CCl <sub>4</sub> | 298        | 3.49   | -3.7                   |                     |  |
|  |                  | 303        | 2.65   | -2.04                  | -107.58             | -89.4  |
|  |                  | 308        | 1.527  | -5.2                   |                     |  |
| Butanol-I <sub>2</sub>                 | CCl <sub>4</sub> | 298        | 1.52   | -1.06                  |                     |  |
|  |                  | 303        | 1.45   | -0.536                 | -6.15               | -17.126  |
|  |                  | 308        | 1.40   | -0.872                 |                     |  |

Value of dimerisation constant (k) free energy ( $\Delta G$ ), Enthalpy ( $\Delta H$ ) and Entropy change ( $\Delta S$ ) of the system.

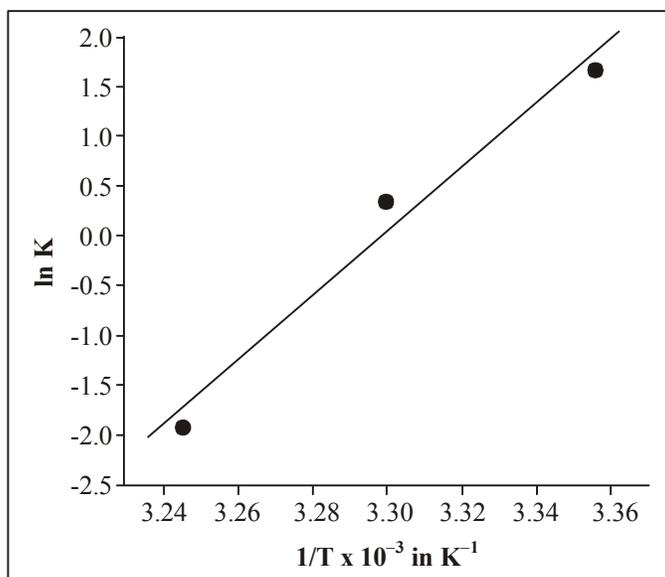
From the Table 1, it is observed that the entropy change ( $\Delta S$ ) is much higher in CH<sub>3</sub>OH-I<sub>2</sub> than that in propanol -I<sub>2</sub> and butanol -I<sub>2</sub> system which suggests more participation of charge transfer because one can expect the dimeric form in the methanol-I<sub>2</sub> system. But in case of Butanol-I<sub>2</sub> system one cannot ignore the formation of trimeric form of hydrogen bonding which slows down the charge-transfer process for these alcohols.

Enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) change for CT complexes in all the system reveals the fact that in methanol-I<sub>2</sub> system charge transfer is more significant to any other system.

As soon as iodine is added to methanol solution in CCl<sub>4</sub> the dimeric behaviour of H-bonding slowly vanishes. This proves the absence of the band around 3520 cm<sup>-1</sup>. The frequency shift of the bonded OH- shift to about 45 cm<sup>-1</sup>. Same observations were seen in case of propanol-I<sub>2</sub> and Butanol-I<sub>2</sub> system but frequency shift for bonded OH are rather high in comparison to methanol-I<sub>2</sub> system. In case of Amyl alcohol-I<sub>2</sub> and Allyl alcohol-I<sub>2</sub> systems the frequency shift of the bonded -OH are rather high with the existence of dimeric behaviour of H-bonding.



**Fig. 1: Graphical plot of  $\ln k$  against  $1/T$  for Methanol-I<sub>2</sub> system**



**Fig. 2: Graphical plot of  $\ln k$  against  $1/T$  for Propanol-I<sub>2</sub> system**

The loss of dimeric form in the adduct manifests the interaction of free-donor-acceptor rather than the H-bonded donor. This is also due to the non-bonding electrons on oxygen which does take part in the complex formation with I<sub>2</sub> molecule.

The increasing value of intensity i.e.  $\epsilon_{\max} = 10^4$  indicates strong participation in charge transfer interaction in these complexes.

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