

THERMODYNAMICS OF H-BONDED COMPLEXES OF HALOALCOHOLS WITH TETRAHYDROFURAN AT LOW TEMPERATURES

MANSOOR AHMAD AND SHAHIDA SHAMIM

National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan

(Received February 27, 1990; revised March 13, 1991)

An IR study of the complexation between 2-haloethanols and tetrahydrofuran in CCl_4 has been carried out in the temperature range of $+20$ to -10° . With the change of temperature, spectra in the OH stretching region show significant changes in the absorption intensity of the free and complex bands. Thermodynamic quantities and frequency shift values measured for the interaction indicate that 2-F-ethanol has poor proton acceptor tendency as compared to other haloalcohols in the series, due to presence of strong intramolecular H-bonding. Colinear relation between ΔH° and ΔS° shows that results obtained at low temperature measurements are more reliable than those obtained at high temperature.

Key words: Thermodynamic, H-bonded, low temperature.

Introduction

Despite a huge volume of infrared spectroscopic work on H-bonding in alcohols [1-4], there have been only a few reports [5-8] dealing with the thermodynamic properties of the ternary systems particularly, systematic study on the thermodynamic consequences, in alcohol component substitution of hydrogen by different halogens, is lacking. We are interested in this aspect of hydrogen bonding.

In our previous work [9] we determined the thermodynamic quantities for the complex of 2-haloethanols with tetrahydrofuran in CCl_4 solution. It was observed that no appreciable change in the absorption intensity of the monomeric O-H band occurred within the temperature range of 30 - 45° which might be due to the evaporation losses at high temperature.

Hydrogen bonding between alcohols and some fluoroalcohols as a proton acceptors has been studied at low temperatures. The studies [13] carried out in three phases reveal that F-ethanols in CCl_4 forms only 1:1 complexes with proton acceptor in the temperature range ($+20$ to -20°).

Our present investigation deals with relative association of F, Cl, Br and I-ethanols with a proton acceptor at low temperatures.

Experimental

2-Haloethanols used in the present study were of spectroscopic grade (98-99%) from Merck and Aldrich. Analytical grade carbon tetrachloride (Merck) used as a solvent was distilled over anhydrous sodium hydroxide (B.P. = 76.4°) and was stored in dark. All the chemicals used were dried over an activated molecular sieves (4 A) immediately before use. Tetrahydrofuran used as a proton acceptor was distilled by a special method.

Tetrahydrofuran (THF). Commercial THF (Merck) was first dried over preheated molecular sieve (4 A) for 2-3 days. Then it was transferred to a flask containing sodium wire and benzophenone used as an indicator. The appearance of light blue colour showed that THF was close to dryness. Then it was refluxed for 2-4 hrs, till the contents of the flask obtained a deep purple colour. At this stage the liquid was distilled at 68° under nitrogen (dried over silica gel column) pressure.

The presence of the moisture if any was tested by collecting the distilled liquid into a container having a deep purple colour solution of sod. metal, benzophenone and THF. No change in colour of the solution indicates the complete dryness of the THF being distilled. It was collected in a predried ampoules which were sealed at the spot and they were stored in a dry box. Ampoules should not be stored for a very long period.

This method [9], applied for drying the THF was considered more easier and reliable than the one reported by Boss *et al.* [10] for two reasons; (a) Change of deep purple colour to blue colour was observed if it was exposed to atmosphere even for a fraction of a second, where in ref. [10] blue colour has been considered as a test for dryness. (b) The method used by Boss *et al.* [10] is laborious and time consuming and they used Na-K alloy as colour indicator which is rarely available.

In order to avoid moisture contamination from atmosphere, preparation of sol. and filling of cells were carried out in dry-box. For this study the dil sol. (0.02M) of 2-haloethanols were prepared in CCl_4 , where self association is negligible. Concentration of tetrahydrofuran was maintained as $0.40 \text{ mol. dm}^{-3}$ in the solution. Spectra were recorded on a Pye-Unicam SP 3-100 IR spectrophotometer over the temperature range 293 - 263 K° at intervals of 10 K° . Studies were conducted in a cell (P/N 21.00) having AgCl windows designed for the purpose where the pressure was reduced to 0.5 mm Hg .

Liquid N₂ was used as a refrigerant. Temperature of the cell was controlled by the copper-constantan thermocouple and was measured with a variable temperature unit SPECAC having ± 1.0 K° accuracy. 10-15 Minutes were allowed to attain the desired temperature. Temperature cycling has been applied in recording the spectra to check the reproducibility of the results.

Treatment of data. Free and intra bands were resolved by graphical separation method. OH stretching frequency of unbounded OH group was determined in CCl₄ solution. Frequency shifts ($\Delta\nu = \nu_{\text{unbonded in CCl}_4 \text{ sol.}} - \nu_{\text{bonded with THF}}$) are reported in Table 1.

Band area (A) due to complexes were calculated from equation 1 [11].

$$A = 2.303 \times \pi \times D \times \nu^{a_{1/2}} \dots \dots \dots (1)$$

where D and $\nu^{a_{1/2}}$ are absorbance and apparent half-band width of the band due to complex. True integrated intensities (T) were calculated from equation 2.

$$T = K \frac{1}{Cl} \log \left(\frac{I_0}{I} \right)_{\text{max}} \nu^{a_{1/2}} \dots \dots \dots (2)$$

where K is correction factor for instrumental effect on the band shape. The value of K tabulated by Ramsey [11] for various values of $\log \left(\frac{I_0}{I} \right)_{\text{max}}$ and $S/\nu^{a_{1/2}}$ were used. S is the effective slit-width of spectrometer (5.6 cm⁻¹ in the present case) and I is the path length of the cell.

The equilibrium constant (K_{11}) for complexation of alcohols (A) with base (b) tetrahydrofuran,



was calculated from expression

$$K_{11} = \frac{C_{\text{complex}}}{C_A C_B} \dots \dots \dots (3)$$

where the concentrations are molar concentrations at equilibrium and the activity coefficients have been neglected for dilute solution. Concentrations of alcohol and base used were the known initial concentrations while the concentration of

complex was calculated as follows:-

$$C_{\text{complex}} = A/T \times 1 \dots \dots \dots (4)$$

Thermodynamic quantities were obtained from the Van't Hoff equation 5.

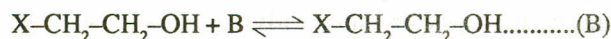
$$\Delta G^\circ = -RT \ln K_{11} = \Delta H^\circ - T\Delta S^\circ \dots \dots \dots (5)$$

The best values of ΔH° and ΔS° , together with their correlation coefficients, were obtained by the least-square method.

Relationship [12] between $\log K_{11}$ vs. $1/T$, ΔH° vs ΔS° , ΔH° vs. $\Delta\nu$ and ΔG° vs ΔS° (Figs 2,3) were used to explain the stability and strength of the complex formed.

Discussion

IR spectra (Fig. 1) show that in the ternary mixture, the decrease in temperature causes a significant increase in the intensity of the complex band while a simultaneous decrease in the monomer band is observed, indicating a strong shift in equilibrium to the right.



Since all the complex bands in CCl₄ are smooth, one can say

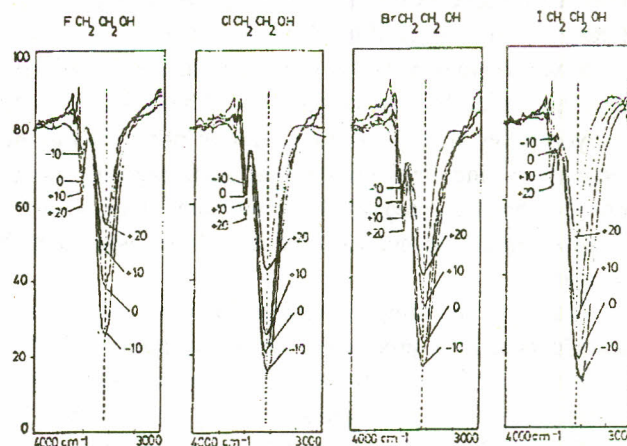


Fig. 1. Effect of temperature on 2-haloethanols. THF complexes (...) shows the position of complexed bands.

TABLE 1. THERMODYNAMIC PROPERTIES OF 2, HALOETHANOLS -TETRAHYDROFURAN SYSTEM IN CCl₄. (C_A = 0.02 mol. dm⁻³, C_B = 0.4 mol. dm⁻³).

	2,F-ethanol	2,Cl-ethanol	2,Br-ethanol	2,I-ethanol
$-\Delta H$ KJ.mol ⁻¹	72.309 (± 2.46)	52.034 (± 2.29)	47.598 (± 0.24)	72.815 (± 5.98)
$-\Delta G^\circ$ KJ. mol ⁻¹	1.132	4.628	4.604	3.330
$-\Delta S^\circ$ J.mol ⁻¹ degree ⁻¹	250.652 (± 8.84)	161.796 (± 8.27)	146.749 (± 0.85)	237.143 (± 21.49)

Note: Values given in the parenthesis are standard deviation.

that spectra do not allow a distinction between different complex species (1:1, 1:2, etc).

As it can be seen from Fig. 1 that the complexed bands in the ternary mixture exhibits fine symmetric form and one may reasonably assume for the presence of only 1:1 type of complexes. Same observations have been obtained in case of high temperature measurements [9].

Temperature decrease, however, does not only influence the OH band intensities but also shifts the monomer and complex absorptions to lower frequencies.

Schrems *et al.* [13] noted that within the temperature range of +20 to -20° the monomer OH bands shift at an average rate of $0.08 \text{ cm}^{-1}\text{K}^{-1}$ and the complex bands with $0.27 \text{ cm}^{-1}\text{K}^{-1}$ for the complexes of different fluoroalcohols with DME in CCl_4 . The shifts noted in complexed OH bands for 2-haloethanols varies in the range $0.66\text{--}0.72 \text{ cm}^{-1}\text{K}^{-1}$ from F-through I, while no reasonable shift was observed in monomeric OH bands for the temperature range studied (+20 to -10°). It is apparent from $\Delta\nu$ values (Fluoroethanol = 200 cm^{-1} , chloroethanol = 210 cm^{-1} , bromoethanol = 212 cm^{-1} , iodoethanol = 220 cm^{-1}) that the shifts in νOH increase linearly with the size of the atom. Higher $\Delta\nu$ value indicates that 2, I-ethanol has

better affinity for intermolecular association with tetrahydrofuran as compared to other alcohols. Similar trend has been reported in case of $\text{RF}\dots\text{HOCH}_2\text{CH}_2\text{I}$.

Linear plots of $\text{Log } K_{11}$ vs. T^{-1} obtained by least square method are presented in Fig. 2. Slopes of these plots indicate that population of the alcohol base complexes is same for both the systems, having 2, F-ethanol and 2, I-ethanol. The heat of formation and other thermodynamic parameters were calculated from Van't Hoff equation. Best fit values for ΔH° and ΔS° along their standard deviations are summarized in Table. High values of ΔH° for 2, F- and 2, I-ethanol strongly support the above mentioned conclusion.

Relationships [12] between thermodynamic parameters provide significant information about the strength and stability of the associated species. Figure 3 show moderately linear relationship between these parameters. In Fig. 3(d), ΔH° vs. $\Delta\nu$ indicates that Badger - Bauer rule [12] is not applicable to the present system. While ΔH° vs. ΔS° shows better compensation relation for all the alcohols except that of 2, I-ethanol.

The high entropy change of the F-ethanol-THF complex shows that the "complex" is more ordered as compared to others in the series. A relatively smaller ΔS° for 2, I-ethanol

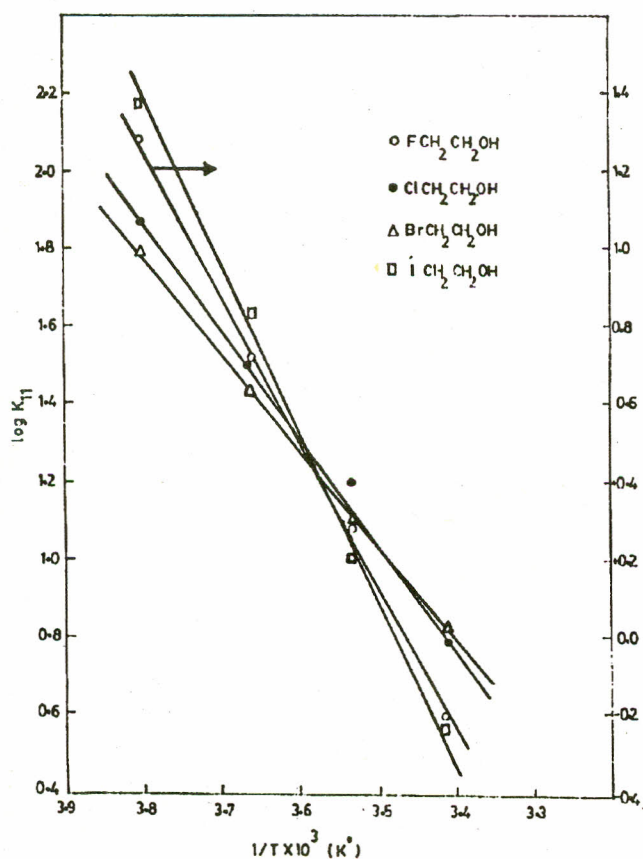


Fig. 2. Plots of $\text{Log } K_{11}$ vs. $1/T$ for 1:1 complexes of 2-haloethanols with THF in CCl_4 .

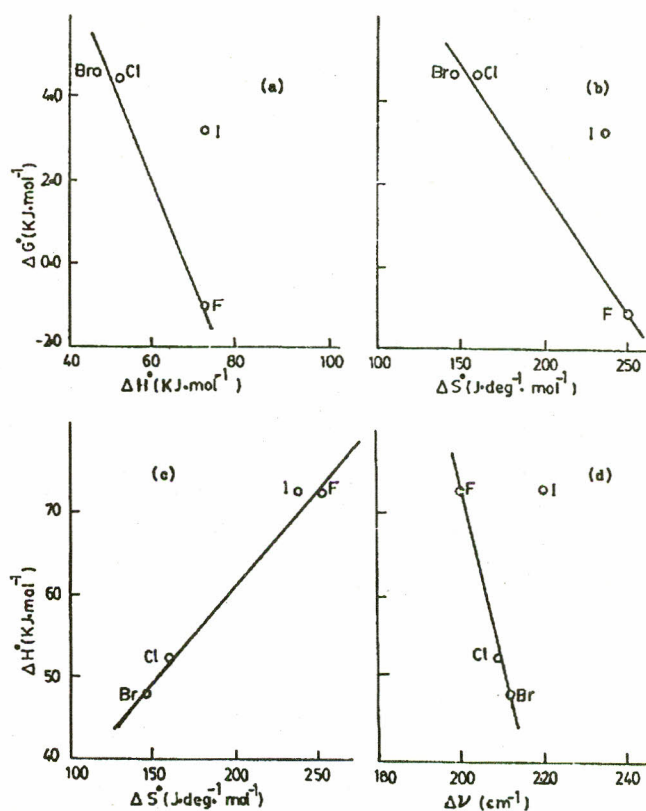


Fig. 3. Plots of (a) ΔG° vs. ΔH° (b) ΔG° vs. ΔS° (c) ΔH° vs. ΔS° (d) ΔH° vs. $\Delta\nu$ for the 2-haloethanols -- THF complexes.

suggests a poor order in the aggregates. The disorderliness and lower stability of the complex may be attributed to weak intramolecular H-bonding and large size of iodine.

Acknowledgement. Shahida Shamim is gratefully acknowledged of the Directorate of Education N.W.F.P. Pakistan.

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