

## FTIR Spectroscopic Studies on Molecular Interaction between Alcohols and *N,N*-dimethylacetamide

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**Abstract:** The association between alcohols and *N,N*-dimethylacetamide in carbon tetrachloride was investigated using FTIR spectroscopy at 298 K. The formation constants for 1:1 and 1:2 complexes were calculated using the method of Whetsel and Kagarise. The observed 1:1 complex values were also verified using the method of Nash. The rate of change in C=O bond moment on complexing with alcohols increased with increasing acidity of alcohols. The formation constant and values of free energy change increased with the increase in carbon chain length of alcohols, which suggested that the degree of complex formation varied with the length of the carbon chain of alcohols.

**Key Words:** FTIR spectroscopy; Hydrogen bonding; 1:1 and 1:2 complexes

Amides and alcohols have been an important group of chemicals with considerable application as starting materials for the preparation of insecticides and pharmaceutical products<sup>[1]</sup>. The study on the interaction between associated liquids in carbon tetrachloride by means of infrared spectroscopy provides valuable information about solute-solute and solute-solvent interactions. An exhaustive account of the method has been reported by Pimental and McClellan<sup>[2]</sup>. The formation of 1:1 and 1:2 hydrogen bonded complexes between *N,N*-dimethylacetamide and phenol derivatives has been reported by Zeegers-Huyskens<sup>[3]</sup> using infrared spectroscopy. Takahashi *et al.*<sup>[4]</sup> have reported the equilibrium constant for 1:1 complexes of 2-propanol and *N*-substituted acetamides using proton magnetic resonance spectroscopy. Werner *et al.*<sup>[5]</sup> have calculated the equilibrium constants and free energy changes for diethyl acetamide and *t*-butanol in benzene. Infrared spectroscopic studies of *N,N*-disubstituted amides with alcohols have been investigated by Henson *et al.*<sup>[6]</sup>. The hydrogen-bonded complexes between phenol derivatives and amides were studied by Leroux *et al.*<sup>[7,8]</sup> using infrared spectroscopy. Malathi *et al.*<sup>[9]</sup> have studied the hydrogen-bonding ability of *N*-disubstituted amides with phenol derivatives in inert solvents using FTIR spectroscopy. The aim of this study is to investigate the hydrogen bonding between free hydroxyl group of alcohols and the C=O group of *N,N*-dimethylacetamide using FTIR spectroscopy.

### 1 Experimental

Spectra were recorded using a Perkin-Elmer FTIR spectrometer with a resolution of 1 cm<sup>-1</sup> at 298 K in the wavenumber region of 4000–400 cm<sup>-1</sup> and a NaCl cell of path length 0.01 cm.

The spectrometer possesses autoalign energy optimization and a dynamically aligned interferometer. It is fitted with a KBr beam splitter, a DTGS-Detector, and an Everlgo™ mid-IR source. The processing menu contains a spectra subtraction for eliminating solvent peaks in a spectrum of a sample that is dissolved in a solvent. A base line correction was made for the spectra recorded. AR grade *N,N*-dimethylacetamide (DMA), alcohols, and carbon tetrachloride with purity >99% were purified using a standard procedure<sup>[10]</sup>.

### 2 Results and discussion

The spectral parameters were calculated by using the following relation

$$\Delta\nu = \nu_f - \nu_b \quad (1)$$

where  $\Delta\nu$  is the frequency difference between the free monomeric O—H and bonded O—H bands, and  $\nu_f$  and  $\nu_b$  are the frequencies of the free monomeric and bonded O—H bands, respectively.

Half-band width and integrated intensity were determined by the procedure described by Ramsay<sup>[11]</sup>.

Integrated intensity  $B$  is defined by

$$B = \frac{1}{cl} \int \ln\left(\frac{I_0}{I}\right) d\nu \quad (2)$$

where  $c$  is the total concentration (mol·L<sup>-1</sup>) of proton donor,  $l$  is the cell length in cm,  $I_0/I$  is the relative intensity of light transmitted, and  $\nu$  is the frequency in cm<sup>-1</sup>.

Infrared spectral parameters for alcohols (1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol) in carbon tetrachloride solution at 298 K are given in Table 1. Alcohols in carbon tetrachloride exhibit two hydroxyl bands in the region of

**Table 1** Spectral data of alcohols in carbon tetrachloride at 298 K

Alcohol	$\nu_1/\text{cm}^{-1}$	$\nu_2/\text{cm}^{-1}$	$\Delta\nu/\text{cm}^{-1}$	$\Delta\nu_{1/2}$	$10^{-3}B/(\text{mol}^{-1}\cdot\text{cm})$
1-butanol	3634	3350	284	18	3.05
1-pentanol	3636	3350	286	22	2.83
1-hexanol	3637	3350	287	25	1.98
1-heptanol	3638	3350	288	30	1.73
1-octanol	3641	3350	291	33	1.56
1-decanol	3642	3350	292	36	1.41

3700–3200  $\text{cm}^{-1}$ : one is attributed to the free O—H group and appears as a sharp band near 3638  $\text{cm}^{-1}$  and the other is attributed to the bonded O—H group and appears as a broad band around 3350  $\text{cm}^{-1}$ [12]. The free monomeric O—H band frequency ( $\nu_1$ ), frequency difference between the free monomeric O—H and bonded O—H bands ( $\Delta\nu$ ), and half-band width ( $\Delta\nu_{1/2}$ ) increase with increase in the length of carbon chain of alcohol, whereas the reverse trend is observed for integrated intensity ( $B$ ). But the frequency of the polymeric absorption band of alcohols in carbon tetrachloride (3350  $\text{cm}^{-1}$ ) is not influenced by the length of the alcohol chain. Similar observations were reported by Liddel and Becker[13]. For the binary mixture of DMA with carbon tetrachloride, the carbonyl (C=O) band was observed at 1661  $\text{cm}^{-1}$ [9].

In the ternary systems, the concentration of the proton acceptor (DMA) was fixed at 0.03  $\text{mol}\cdot\text{L}^{-1}$  and the concentration of the proton donor (alcohol) varies from 0.03 to 0.15  $\text{mol}\cdot\text{L}^{-1}$ . For DMA in carbon tetrachloride, a single band representing the free C=O band was found at 1661  $\text{cm}^{-1}$ . With the addition of alcohol, a new band appears at 1654  $\text{cm}^{-1}$  and the intensity of the original band decreases. The position of the two bands does not alter. This is indicative of the existence of an equilibrium involving the free C=O and the hydrogen bonded complex (1:1). As the concentration of alcohol is increased further, another band appears at wavelength of approximately 1654–1648  $\text{cm}^{-1}$  and the original high-frequency band disappears. This new low-frequency band may be ascribed to the 1:2 complexes formed between the proton acceptor and the proton donor.

The formation constants for 1:1 ( $K_{11}$ ) and 1:2 ( $K_{12}$ ) complexes

of amide-alcohols systems were calculated using the method of Whetsel and Kagarise[14]. The procedure adopted to calculate the spectra of the individual complexes is as follows.

$$K_{11} = \frac{[AB]}{[A][B]}, \quad K_{12} = \frac{[AB_2]}{[AB][A]} \quad (3)$$

where A represents the proton acceptor and B represents the proton donor, when the  $K_{11}$  and  $K_{12}$  values are available, one can calculate the relative concentrations of the three species: 1:1 complex [AB], 1:2 complex [AB<sub>2</sub>], and free carbonyl species [A] at different concentrations of alcohol, as shown in Table 2 for DMA-alcohol systems. To ensure that the values of 1:1 formation constants obtained were accurate, they were also determined using the method of Nash[15]. In this method, a graph is plotted between  $Y=[A]^{-1}$  and  $X=(1-(a/a_0))^{-1}$ , where  $a$  and  $a_0$  are the absorbances of the carbonyl band of amide in the presence and absence of alcohol, respectively, the intercept of the graph in the ordinate yields  $K$ .

The free energy change ( $\Delta G^0$ ) of the systems were calculated using the following relation[16]

$$\Delta G^0 = -RT \ln K \quad (4)$$

where  $R$ ,  $T$ , and  $K$  represent the universal gas constant, absolute temperature, and formation constant of the relative systems, respectively.

The integrated intensities ( $A_s/(\text{cm}^2\cdot\text{mol}^{-1}\cdot\text{s}^{-1})$ ) of the C=O band were calculated using the relation[17]:

$$A_s = \frac{2.303}{Cd} \int_{\nu_1}^{\nu_2} \lg \left[ \frac{I_0}{I} \right] d\nu \frac{C^1 M}{\rho T N_A} \quad (5)$$

where  $\nu_1$  and  $\nu_2$  are the upper and lower frequencies in  $\text{cm}^{-1}$ , respectively, of the absorption band,  $C$  is the concentration ( $\text{mol}\cdot\text{L}^{-1}$ ) of the carbonyl molecules, and  $d$  is the cell thickness in cm.  $C^1$  is velocity of light,  $M$  is the molecular weight,  $\rho$  is the density,  $T$  is the absolute temperature, and  $N_A$  is Avogadro's number.

Using the integrated intensity values and assuming that the vibration is a pure stretching mode, the change in bond moment on stretching is calculated from the relation[18]:

$$\frac{d\mu}{dr} = \left( \frac{1}{m_C} + \frac{1}{m_O} \right)^{-1/2} \frac{d\mu}{dQ}, \quad \frac{d\mu}{dQ} = \pm \left( \frac{3C^1 A_s}{\pi} \right)^{1/2} \quad (6)$$

where  $m_C$  and  $m_O$  are the masses of carbon and oxygen atoms, respectively, and  $d\mu/dQ$  is the change in dipole moment ( $\mu$ ), with

**Table 2** Carbonyl vibrational frequencies, formation constant, and free energy change for 1:1 and 1:2 complexes of alcohols with *N,N*-dimethylacetamide (DMA) in  $\text{CCl}_4$  at 298 K

Alcohol	$\nu/\text{cm}^{-1}$					Formation constant ( $\text{L}\cdot\text{mol}^{-1}$ )			Free energy change ( $\text{kJ}\cdot\text{mol}^{-1}$ )		
	$\nu_{\text{C=O}}$	$\nu_{\text{C=O}}$	$\Delta\nu_{\text{C=O}}$	$\nu_{\text{C=O}}$	$\Delta\nu_{\text{C=O}}$	Nash method	Whetsel and Kagarise method		Nash method	Whetsel Kagarise method	
	(free C=O)	(1:1 complex)	(1:1 complex)	(1:2 complex)	(1:2 complex)		$K_{11}$	$K_{11}$		$K_{12}$	$\Delta G_{11}^0$
1-butanol	1661	1654	7	1648	13	25.23	24.82	5.00	8.00	7.96	3.99
1-pentanol	1661	1654	7	1647	14	27.21	26.48	10.00	8.18	8.12	5.70
1-hexanol	1661	1654	7	1647	14	30.85	29.64	10.00	8.50	8.40	5.70
1-heptanol	1661	1654	7	1648	13	33.48	32.85	10.00	8.70	8.65	5.70
1-octanol	1661	1654	7	1648	13	35.65	35.11	15.00	8.85	8.82	6.71
1-decanol	1661	1654	7	1647	14	39.44	38.82	20.00	9.10	9.07	7.42

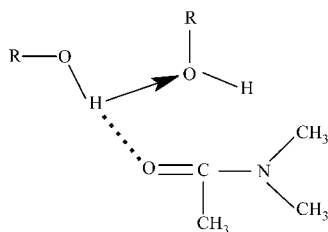
the normal coordinate ( $Q$ ).

The carbonyl vibrational frequencies, formation constants (using the methods of Nash and of Whetsel and Kagarise), and free energy change for 1:1 and 1:2 complexes of alcohols with *N,N*-dimethylacetamide (DMA) in  $\text{CCl}_4$  are shown in Table 2. The formation constants determined using the above-mentioned two methods for all the systems studied are in good agreement with each other.

From Table 2, it is evident that the values of formation constant and free energy changes decrease in the order: 1-decanol > 1-octanol > 1-heptanol > 1-hexanol > 1-pentanol > 1-butanol. This indicates that the tendency of complex formation in higher chain alcohol, i.e. 1-decanol is relatively larger. Because of steric hindrance, it is likely that long-chain alcohols will have greater probability for complex formation due to head-tail linkage<sup>[19]</sup>, whereas for relatively smaller molecules, this tendency is weakened due to the switching mechanism, i.e. the relatively low energy associated with the breaking of the  $\text{O}-\text{H}\cdots\text{O}=\text{C}$  hydrogen bond can be explained in terms of the "switching mechanism" (Fig.1). This mechanism explains that the bond will break when another alcohol molecule approaches with its oxygen atom oriented favorably for "switch". This third oxygen atom from the alcohol molecule will lower the energy barrier for breaking the hydrogen bond below that required in the absence of the third atom<sup>[20]</sup>.

Similar conclusions were reported for the mixture of alcohols with *N,N*-dimethylformamide in benzene<sup>[21]</sup>. The acidity of proton donor decreases in the order of 1-decanol > 1-octanol > 1-heptanol > 1-hexanol > 1-pentanol > 1-butanol<sup>[22]</sup>. Therefore, the strongest hydrogen bond would be expected to be formed between 1-decanol with *N,N*-dimethylacetamide in carbon tetrachloride and weakest hydrogen bond between 1-butanol with *N,N*-dimethylacetamide in carbon tetrachloride, which is reflected by the higher formation constant and free energy change in the former system.

The integrated intensity values and the rate of change of dipole moment were calculated at the concentration of alcohols at which the DMA was completely bonded, as evidenced from the disappearance of the free  $\text{C}=\text{O}$  bond. The ratio of the rate of change of dipole moment with respect to bond length for the complexed  $\text{C}=\text{O}$  and for the free  $\text{C}=\text{O}$  is given in Table 3. The results of this study show that the increasing acidities of the proton donor shift the relative position of the peak of the 1:1 and 1:2 complexed  $\text{C}=\text{O}$ <sup>[9]</sup>.



**Fig.1 Configuration of hydrogen bond switching for *n*-butanol with DMA**

**Table 3 Integrated intensity and dipole moment derivative of carbonyl stretching vibration of alcohols with *N,N*-dimethylacetamide in  $\text{CCl}_4$  at 298 K**

Alcohol	$A_s$ (free $\text{C}=\text{O}$ )	$A_s$ (1:1 complex)	$(d\mu/dr)$ (free $\text{C}=\text{O}$ )	$(d\mu/dr)$ (1:1 complex)	$(d\mu/dr)$
					$(d\mu/dr)$ (free $\text{C}=\text{O}$ )
1-butanol	5.87	6.05	4.10	5.81	1.42
1-pentanol	6.52	6.79	4.32	6.29	1.46
1-hexanol	6.82	7.06	4.42	6.54	1.48
1-heptanol	7.12	7.38	4.52	6.98	1.55
1-octanol	7.55	7.81	4.65	7.39	1.59
1-decanol	8.29	8.52	4.87	8.15	1.67

$A_s$ : intensity of  $\text{C}=\text{O}$  in  $\text{CCl}_4$  (in  $10^{-7} \text{ cm}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ );

$(d\mu/dr)$ : dipole moment derivative of  $\text{C}=\text{O}$  in  $\text{CCl}_4$  (in  $10^{-10} \text{ esu}$ )

Several authors<sup>[23-26]</sup> have discussed the nature of these interactions on the basis of polarization interactions. If one of the two  $sp^2$  hybrid orbital of the oxygen in the carboxyl group is collinear with the  $\text{O}-\text{H}\cdots\text{O}$  axis, the interaction between the polar  $\text{O}-\text{H}$  and the  $\text{C}=\text{O}$  is maximum. Then, the  $\text{O}-\text{H}$  bond induces a moment in the highly polarizable lone-pair charge cloud and enhances the IR intensity. The integrated intensity measurements of the complexed and uncomplexed carbonyl bands recorded in this study showed an increase of 10%–40% in the bond moment derivatives (Table 3). This shows that polarization interaction is more dominant than electron transfer alone. A similar but enhanced charge in the polarity of the  $\text{O}-\text{H}$  bond is also expected, resulting in a further increase in dipolar increment on complexation.

### 3 Conclusion

The formation of the complex between alcohols and *N,N*-dimethylacetamide in carbon tetrachloride was carried out using FTIR spectroscopy at 298 K. From this study, it may be concluded that the higher chain alcohol has greater proton-donating ability compared with the lower-chain alcohols.

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