N–H⋯O hydrogen bonding. An FT-IR, NIR study of *N*-methylformamide–ether systems

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Abstract: This paper reports the results of an FT-IR and NIR study of *N*-methylformamide in carbon tetrachloride solution in presence of ethers as the O--electron donors, *i.e*., diethyl ether (DEE), diisopropyl ether (DiPE), methyl *t*--butyl ether (M*t*BE), dibutyl ether (DBE), dipentyl ether (DPE), tetrahydrofuran (THF) and tetrahydropyran (THP). The spectroscopic characteristics of the N–H⋯O hydrogen bonded complexes are given. In addition, the equilibrium constants for 1:1 complex formation were determined at 25 °C using Mid-IR and NIR measurements.

Keywords: hydrogen bonding; *N*-methylformamide; ethers molecular complex.

INTRODUCTION

This paper is a part of continuing and systematic investigations of secondary amides in solution from both spectroscopic[1–6] and thermodynamic[7–9] points of view. In the case of ethers, numerous measurements of the hydrogen bond formation constants have been reported.[10–13] This study should contribute to a better understanding of N-H⋯O hydrogen bonding of *N*-methylformamide (NMF) with ethers. It seemed interesting to perform experiments using two different spectroscopic techniques: Mid-IR and NIR.

EXPERIMENTAL

N-Methylformamide (Frinton, >99 %), and carbon tetrachloride (J. T. Baker, >99.9 %) were used without further purification. Diethyl ether, dibutyl ether, dipentyl ether, tetrahydrofuran, tetrahydropyran (Fluka, >98 %), diisopropyl ether (Carlo Erba >98 %) and methyl *t*--butyl ether (Riedel-de Haën >99 %) were redistilled and dried prior to use.

In order to avoid self-association, the amide concentration in the carbon tetrachloride solutions was below 0.0030 mol dm⁻³. The concentration of the ethers was varied between 0.20 and 1.0 mol dm⁻³.

The Mid IR and NIR spectra were obtained using a Thermo-Nicolet Nexus 670 instrument. A DTGS detector was employed in the Mid-IR measurements and a MCTA detector cooled with liquid nitrogen was used for the NIR measurements. The samples were placed in 1–5 cm (IR) and 10 cm (NIR) UVIRSIL cells and the spectra were recorded at 298 K. The reported frequencies and half-widths were reproducible to within 0.2 and 1 cm⁻¹, respectively. The integrated molar absorption coefficients were obtained within ±5 %. The equilibrium constants were determined with an average relative standard deviation of 6 %.

RESULTS AND DISCUSSION

The hydrogen bonding between *N*-methylformamide and ethers can be represented by the scheme given in Fig. 1.
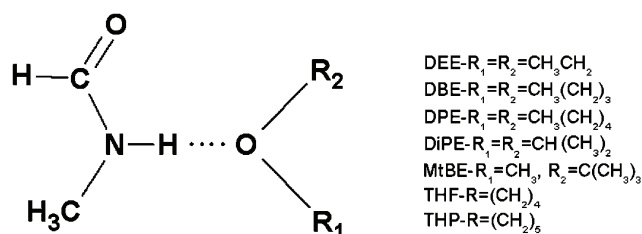

Fig. 1. Hydrogen bonded complexes between NMF and dialkyl ethers.

The equilibrium of NMF–ether hydrogen bond formation can be represented as:

$$M–H + A \rightarrow M–H\cdots A \tag{1}$$

where M–H is NMF monomer, A is an O-electron donor (ether) and M–H$\cdots$A is the molecular complex. In the case when the electron donor is present in excess over the amide concentration, then:

$$K = \frac{c_M^0 - c_M}{c_M c_A^0} \tag{2}$$

Using the Becker procedure,[14] the formation constant was determined from the absorbance of the monomer band:

$$K = \frac{A^0 - A}{A c_A^0} \tag{3}$$

where A^0 is the monomer absorbance for a carbon tetrachloride solution containing c_M^0, mol dm⁻³, of NMF and A is the absorbance of the same band for a solution with both NMF (c_M^0) and ether donor (c_A^0). The spectroscopic characteristics of the monomer (free) ν(NH) band of *N*-methylformamide are given in Table I. ν(NH) and $\nu_{1/2}$ are the wavenumber and halfwidth of the band, respect-

tively, ε and B^0 represent the molar absorption coefficient and the integrated absorption coefficient, respectively. The characteristics for the band of the corresponding first overtone are also given in Table I. In addition, the, IR and NIR spectra of NMF monomer are given in Fig. 2.

TABLE I. Spectroscopic characteristics for the monomer (free) ν(NH) band and the corresponding first overtone of *N*-methylformamide

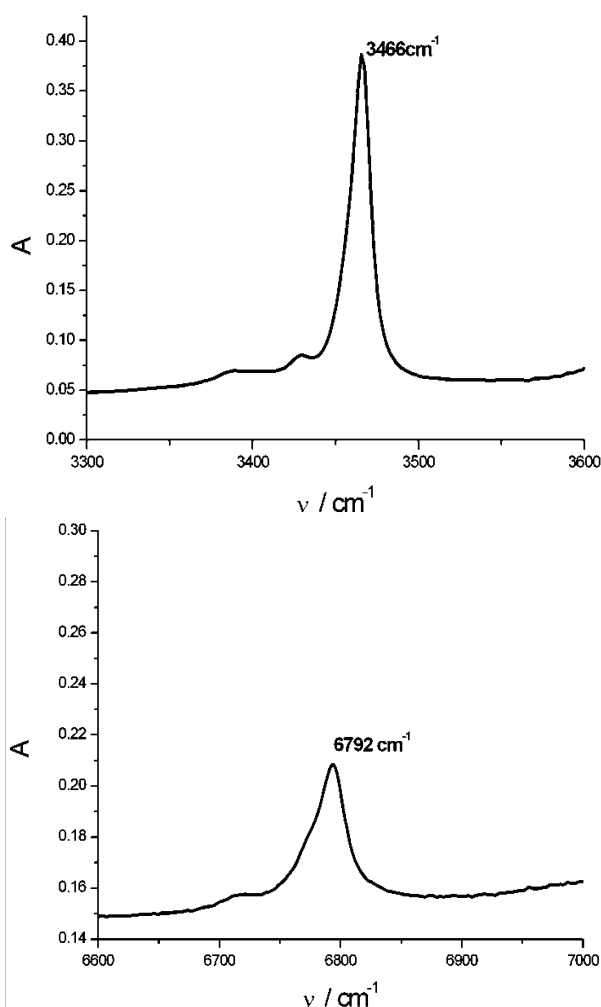| ν_0(NH) /cm^{-1}	$\nu_{1/2}$ / cm^{-1}	$\varepsilon \times 10^{-3}$ / cm^2 mol^{-1}	$B^0 \times 10^{-6}$/ cm mol^{-1}
3466.1	12	74.9	3.3
6792.8	32	17.2	0.6

Fig. 2. IR and NIR spectra of *N*-methylformamide monomer in CCl$_4$ solution, in the regions of the N–H stretching vibration band and the first overtone, at 298.15 K.

The IR spectra and the first derivative NIR spectra of NMF in the presence of different ethers are shown in Figs. 3 and 4, respectively. The spectroscopic parameters for the N–H⋯O molecular complexes obtained in the IR and NIR measurements are summarized in Table II. The equilibrium constants from both IR and NIR experiments are given in Table III.
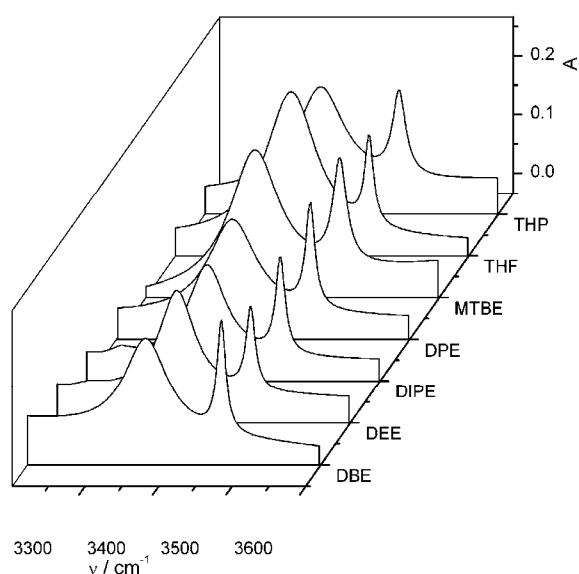

Fig. 3. IR spectra of *N*-methylformamide in the presence of seven different ethers at the same concentration.
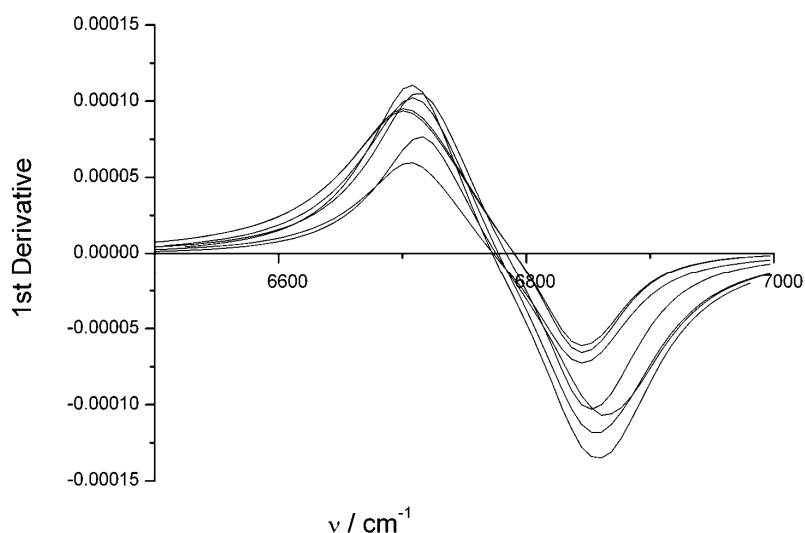

Fig. 4. First derivative NIR spectra of NMF in the presence of different ethers.

TABLE II. Spectroscopic parameters for the N–H⋯O hydrogen bonded complexes obtained in IR spectroscopy

O-electron donor	$\Delta\nu$ / cm^{-1}	$\nu_{1/2}$ / cm^{-1}	$\varepsilon \times 10^{-3}$ / cm^2 mol^{-1}	$B^0 \times 10^{-6}$ / cm mol^{-1}
Dibutyl ether	101.3	83	73.3	8.2
Diethyl ether	99.0	71	88.5	8.5
Diisopropyl ether	106.5	92	202.8	23.4
Dipentyl ether	102.6	77	62.3	6.7
Methyl *t*-butyl ether	113.5	71	116.8	11.5
Tetrahydrofuran	101.8	75	97.2	9.9
Tetrahydropyran	102.9	75	96.6	10.7

TABLE III. The equilibrium constants from both IR and NIR measurements

O-electron donor	K / dm^3 mol^{-1}	
	IR	NIR
Dibutyl ether	0.84	0.76
Diethyl ether	1.23	1.11
Diisopropyl ether	0.85	0.97
Dipentyl ether	0.92	0.79
Methyl *t*-butyl ether	0.72	0.99
Tetrahydrofuran	1.44	1.56
Tetrahydropyran	1.22	1.27

The obtained IR spectroscopic parameters clearly indicate N–H⋯O hydrogen bonding between NMF and the ethers.

The stability of molecular complexes increases in the order: M*t*BE < DBE DiPE <DPE <THP < DEE < THF. The differences in the stability of the N–H⋯O complexes for the five studied dialkyl ethers can be interpreted using the Taft equation:[15]

$$\log K_{298} = \log K_{298}^0 + \rho\sigma^* + \delta E_S \qquad (6)$$

where K_{298}^0 represents the formation constant of the complex with dimethyl ether and σ^* and E_S represent the inductive and steric factors for the alkyl groups, respectively. If $\log K_{298}$ is correlated with both σ^* and E_S, a good correlation is obtained:

$$\log K_{298} = 0.2 + 0.280\sigma^* - 0.182 E_S , \quad R = 0.95 \qquad (7)$$

Several investigators[10–13] obtained equilibrium constants for hydrogen bonding between phenols and various (cyclic and aliphatic) ethers and they established that donor-acceptor interactions are sensitive to both steric and inductive effects.

In order to determine the possible contribution of the charge transfer mechanism to the associations in this study, the correlation between donor ionization potential, I_D, and the function of the frequency shift, $(\nu_0/\Delta\nu)^{1/2}$, was examined.

Puranik and Kumar,[16] based on the Mulliken perturbation theory,[17] proposed a relationship between I_D and $(v_0/\Delta v)^{1/2}$. For the same acceptor and a series of electron donors, the relationship has a simple form:

$$I_D = C_1(\frac{v_0}{\Delta v})^{1/2} + C_2 \tag{8}$$

where v_0 is the frequency of the NH monomer band; C_1 and C_2 are constants for a given acceptor. The plot of I_D *vs.* the experimental $(v_0/\Delta v)^{1/2}$ for *N*-methyl-formamide–electron donors (except MTBE and DPE) is given in Fig 5.
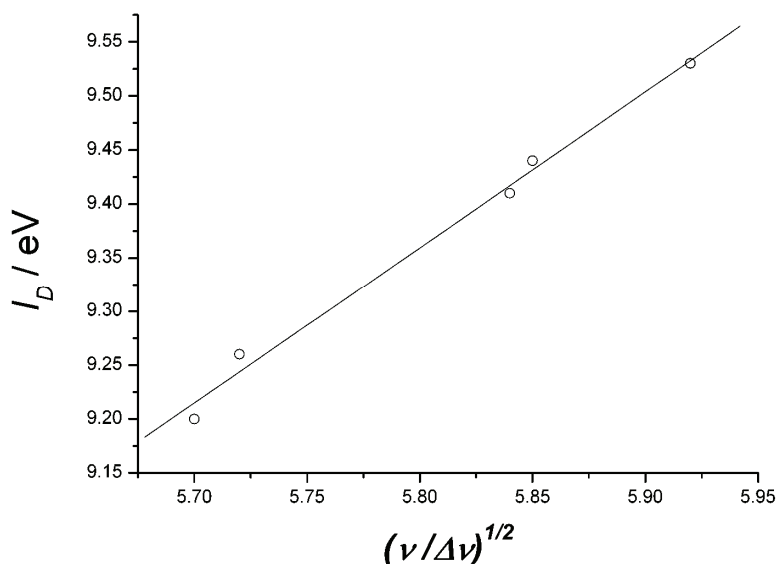

Fig. 5. Plot of I_D *vs.* experimental $(v_0/\Delta v)^{1/2}$ for *N*-methylformamide–electron donors.

The following equation was obtained based on the least-squares treatment of the data in Table II.

$$I_D = 1.444(\frac{v_0}{\Delta v})^{1/2} + 0.98 \, , \, R = 0.99 \tag{9}$$

The linear relationship between the donor ionization potential (I_D) and the function, $(v_0/\Delta v)^{1/2}$, indicates that the charge transfer mechanism significantly contributes to the hydrogen bonding in the studied systems.

A comparison of the equilibrium constants obtained in this study with those obtained for *N*-methylpropionamide–ether complexes[5,6] showed that the constants for N–H···O hydrogen bonding in NMF–ether complexes are significantly higher. The difference in the stability of NMF and *N*-methylpropionamide complexes with ethers can be attributed to the more expressed steric hindrance in the latter complexes.

An attempt was made to estimate the equilibrium constant using Eq. (3) applied to the monomer first overtone. The equilibrium constants from the IR and NIR measurements agreed quite well.

ИЗВОД

N-H⋯О ВОДОНИЧНА ВЕЗА. FT-IR И NIR СПЕКТРОСКОПСКО ИСПИТИВАЊЕ СИСТЕМА *N*-МЕТИЛФОРМАМИД–ЕТРИ

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За карактеризацију особина молекулских комплекса *N*-метилформамида са седам различитих етара праћене су промене на основној валентној (истежућој) траци NH вибрације и траци првог вишег тона. Одређене су спектроскопске карактеристике и константе формирања 1:1 молекулских комплекса на 25 °C коришћењем FT-IR и NIR техника.

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