Fourier Transform Near -Infrared Study of Dissociation and Thermodynamic Properties of N-Methylacetamide in a Carbon Tetrachloride Solution

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Fourier transform near-infrared (FT-NIR) spectra have been measured for N-methylacetamide (NMA) in a carbon tetrachloride solution over a temperature range of 283-348K. With increasing temperature, the intensity of a band at 6805 cm^{-1} due to the first overtone of a NH stretching mode of the monomeric form increases while those of bands near 6550 cm^{-1} and 6375 and 6270 cm^{-1}, assignable to the first overtones of stretching modes of free end NH and hydrogen-bonded NH groups of the asscociated forms, respectively, decrease. These observations show that the associated forms dissociate into the monomers as the temperature increases. By calculating the difference spectra, which are free from the contributions from the hydrogen-bonded species, the temperature-dependent change in the peak height of the NH overtone of the monomer is estimated, and then the degree of dissociation and thermodynamic parameters for the process of dissociation are determined and discussed.

KEY WORDS: FT-NIR / N-Methylacetamide / Near infrared / Overtone / Thermodynamic
          properties / Hydrogen bonding

INTRODUCTION

Near-infrared (NIR) spectroscopy has recently become more and more important in va-
rious fields, and a large amount of literature is available on its applications to agricultural
and food sciences, polymer and chemical engineering, and medical and pharmaceutical sci-
ences.[1-4] However, its applications to basic chemical problems are still very limited probably
because detailed spectral analsyses of standard compounds have not been well carried out.
Therefore, we have started systematic investigations of NIR spectra of simple organic com-
pounds such as fatty acids,[5,6] alcoholes,[7,8] and amino acids[9] by use of Fourier transform
(FT) NIR spectroscopy (FT-NIR). The use of FT-NIR enables us to obtain highly accurate
spectra both in wavenumbers and absorbance scale, making the spectral analyses more re-
liable.

We previously demostrated that FT-NIR spectroscopy has great potential in the quantita-
tive investigation of the process of dissociation of fatty acids[5,6] and alcoholes.[7] In this paper
we report FT-NIR study of N-methylacetamide (NMA), which has been extensively investi-
gated as the simplest model containing a -CO-NH- group by using various techniques such as
infrared,[10,11] Raman,[10] and ultraviolet[10] spectroscopy, measurements of a dipole moment,[10]
and electron diffraction.[12] It has been well known that NMA takes a trans structure in solids

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and solutions and vibrational assignments in the infrared region have been established with the aid of the calculation of normal vibrations.[11-13] Two research groups used NIR spectroscopy to determine dimerization constants of NMA in solutions,[14,15] but they measured the spectra only at room temperature and their results were different from each other.

We measured FT-NIR spectra of NMA in a diluted carbon tetrachloride solution in the temperature range of 283 - 343 K. The temperature-dependent spectral changes clearly show that the concentration of the monomeric species increases with increasing temperature. By analyzing the first overtone of the NH stretching mode of the monomeric species we determined the equilibrium constants K at different temperatures and their thermodynamic parameters (ΔH, ΔS) for the process of dissociation of NMA into the monomers in the CCl_4 solution.

EXPERIMENTAL

Material: NMA (purity greater than 99.0%) was purchased from Aldrich Chemical Company, Inc. and used without further purification. The melting point of NMA is 301 K.[16] Carbon disulfide free carbon tetrachloride (CCl_4, its purity greater than 99%, Dojin Co. Ltd.) was used without purification too.

FT-NIR spectra: All FT-NIR measurements were performed at a 8 cm^{-1} resolution with a JEOL JRS 6500N FT-Raman spectrophotometer equipped with an InGaAs detector. Details of the spectral measurements and computer processing were the same as those reported previously.[5]
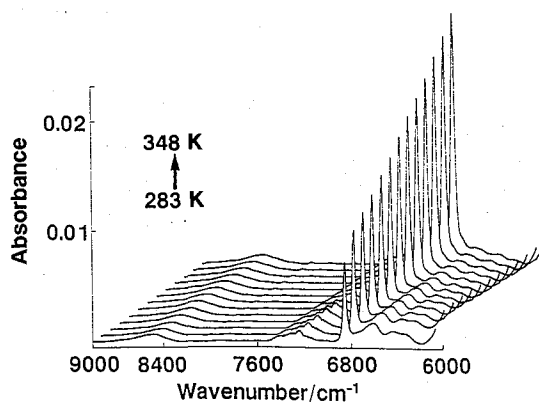
RESULTS AND DISCUSSION

Fig.1 FT-NIR spectra in the 9000-6000 cm^{-1} region of NMA in the CCl_4 solution (0.216M) measured over the temperature range of 283-348 K.

Fig.1 shows the FT-NIR spectra in the 9000-6000 cm^{-1} region of NMA in the CCl$_4$ solution (0.216M) measured over temperature range of 283-348 K. Of particular note in Fig.1 is that the intensity of a band at 6805 cm^{-1} increases while those of bands near 6550, 6375, and 6270 cm^{-1} decrease with increasing temperature. As for spectral features near 8500 and 7200 cm^{-1}, the intensities are nearly temperature-independent. According to the literature,[1-3] the features near 8500 and 7200 cm^{-1} are assigned to the second overtones of CH stretching modes and combination modes of the CH vibrations, respectively. The temperature-dependent bands at 6805 cm^{-1}, 6550 cm^{-1}, 6375 and 6270 cm^{-1} are attributable to the first overtone of the NH stretching vibrations of the monomer form, that of free end NH groups of the associated forms, and those of their hydrogen-bonded NH groups, respectively. The band assignments for the NH groups were confirmed by measuring FT-NIR spectra of NMA in pure liquid at various temperatures. The appearances of two bands assignable to the hydrogen-bonded NH groups suggest the coexistence of at least two kinds of associated forms. Probably, one of them is dimeric form.
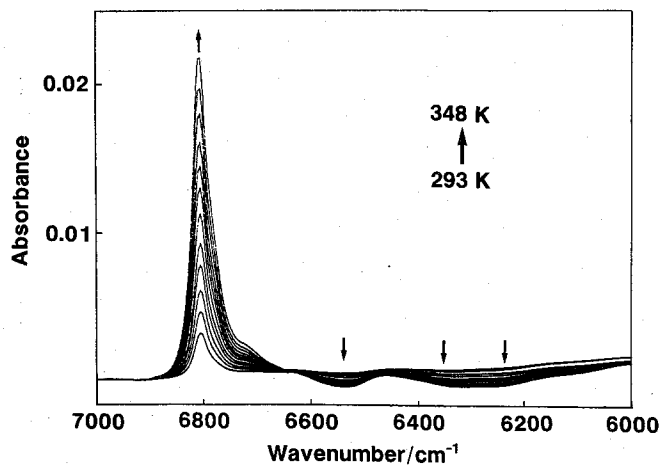

Fig.2 Difference spectra in the 7000-6000 cm^{-1} region of NMA in the CCl$_4$ solution over the temperature range of 293-348 K. The spectra were calculated by subtracting the spectrum at 283 K, as a reference.

In Fig.2 are exhibited the difference spectra in the 7000-6000 cm^{-1} region of NMA in the CCl$_4$ solution. Those spectra were calculated by subtracting the spectrum at 283 K, as a reference. Fig.2 clearly shows that the associated species dissociate into the monomers as the temperature increases.

In order to estimate the degree of dissociation and thermodynamic parameters for the dissociation process, we calculated a series of spectra which are free from the contributions from the hydrogen-bonded NMA. The results are shown in Fig.3. To obtain
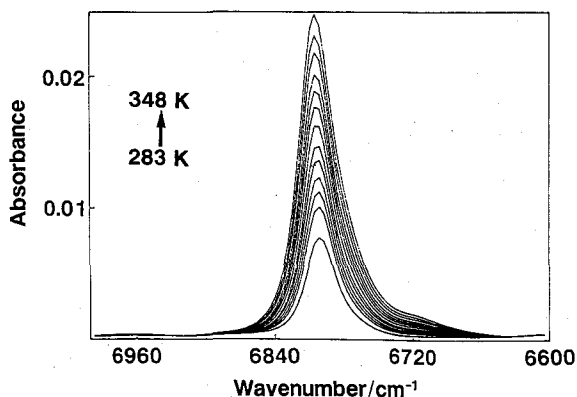
Fig.3 Difference spectra in the 7000-6000 cm⁻¹ region of NMA in the CCl₄ solution
over the temperature range of 283-348 K.

the spectra, first, the spectrum of NMA in pure liquid measured at 303 K (very close to the melting point) was subtracted from all the raw spectra. Then, the difference spectra were calculated by the same method as described before.[5]
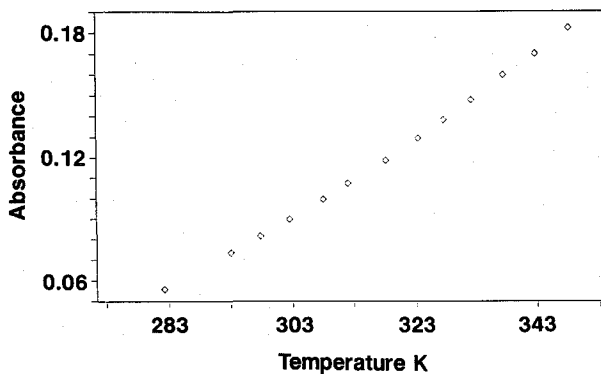

Fig.4 Temperature dependence of the peak height of the NH first overtone of the
NMA monomeric form in the CCl₄ solution.

Fig.4 shows a temperature-dependent change in the absorbance (peak height) due to the monomer band. The concentration of the monomer form can be given by Beer's law;

$$A_m = \varepsilon_m \cdot b \cdot C_m \tag{1}$$

where A_m, ε_m, b, and C_m are the absorbance due to the monomeric form, its molar absorption coefficient (here, $\varepsilon_m = 1.63$ $M^{-1} \cdot cm^{-1}$; cited from ref.15), optical path length of the cell, and the concentration of the monomer form, respectively. Knowing $_cm$ from equ. (1), one can obtain the concentration of the associated forms (C_b) from equ. (2).[14]

$$C_0 = C_m + C_b \qquad (2)$$

where C_0 and C_b are total concentration of NMA in the CCl_4 solution and concentration of the associated forms, respectively. Then, the degree of dissociation of NMA in the CCl_4 solution, α, can be determined by equ. (3)
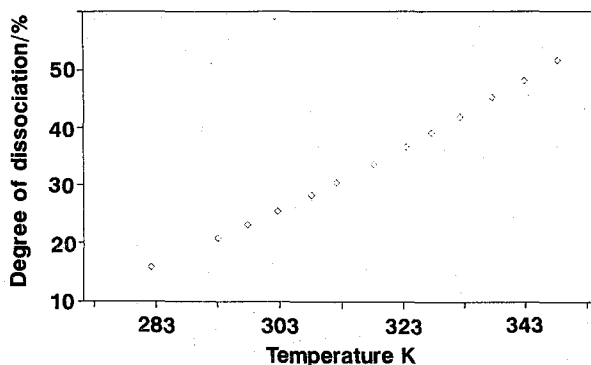
$$\alpha = \frac{C_m}{C_0} \cdot 100\% \qquad (3)$$

Fig.5 Temperature dependence of the degree of dissociation of NMA in the CCl_4 solution.

In Fig.5 is plotted the degree of dissociation of NMA in the 0.216M CCl_4 solution vs. absolute temperature.

Klotz and Franzen[14] and Krikorian[15] proposed formulas to calculate dimerization constants K of the process of the formation of NMA dimers. We slightly modified the formula proposed by Krikorian[15] and rewrote as following;

$$K = \lim_{C_b \to C_0} \frac{C_m^2}{C_b} \qquad (4)$$

From equ. (4) we calculated the equilibrium constants K for the process of the dissociation of NMA in CCl_4 solution at different temperatures. In Fig.6 is shown the plot of logarithm of the equilibrium constant K vs. inverse of the absolute temperature.
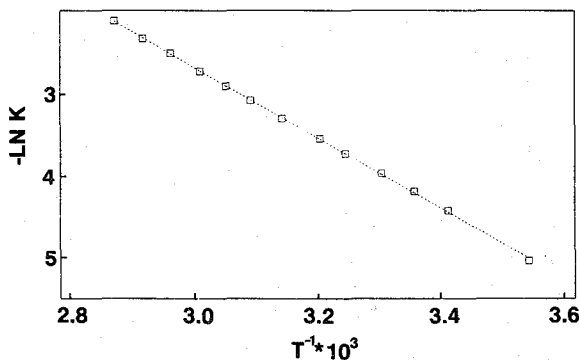
Fig.6 Plot of logarithm of the equilibrium constant (ln K) against inverse of absolute
temperature (1/T) for values determined by employing the peak heights with
the straight line fitted to the experimental points for NMA.

Good straight line is obtained and from the parameters of the line one can determine enthalpy
(ΔH^0=18.0 KJ·mol^{-1}) and entropy (ΔS^0=41.6 J· K^{-1}· mol^{-1}) for the process of the dissociation
of NMA in the 0.216M CCl$_4$ solution. The results are in good agreement with reported
data.[14]

In summary, the present study has demonstrated that FT-NIR is powerful in investigat-
ing the dissociation and thermodynamic properties of NMA. This kind of examinations may
provide new insight into the spectral analyses of proteins, polypeptides, and polyamides.
More thorough FT-NIR studies of the structure and the results thermodynamic properties of
NMA in pure liquid as well as in solution are now in progress in our laboratory and the
results will be published soon.

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