

Optically Anisotropic Structure of Amides Formed by the Reformation of the Hydrogen
Bonds Induced by High Frequency Electric Field

Yasuhiro Matsuda^{*}, Yousuke Hayashi, Atsushi Sugita, and Shigeru Tasaka

Department of Materials Science and Chemical Engineering, Shizuoka University

3-5-1 Johoku, Naka-ku, Hamamatsu, Japan, 432-8561

tymatud@ipc.shizuoka.ac.jp

^{*}To whom correspondence should be addressed.

Abstract

Optically anisotropic structures of *N*-methylformamide (NMF) and some other amides formed by the reformation of hydrogen bonds were observed when alternative electric current was applied to the neat liquid. When the frequency of the applied electric field was low ($< 170\text{Hz}$), the retardation oscillated at the double frequency of the applied electric field, which was typical behavior of Kerr effect. On the other hand, the electric field with high frequency (10 MHz) induced much slower birefringence response compared to the frequency of the electric field. In order to eliminate the

influence of ionic impurity, birefringence, dielectric, and infrared measurements were carried out for NMF and some other amides applying alternative electric current of 10 MHz. The optically anisotropic structures of NMF and some other amides formed by their hydrogen bonds under high frequency electric field were discussed from the retardation, infrared spectra, and dielectric constant.

Keyword

birefringence, *N*-methylformamide, optically anisotropic structure, dielectric relaxation, IR spectroscopy, hydrogen bond

1. Introduction

Organic solvents with amide groups have large dipole moment for its electron attractive nitrogen. The high polarity makes amides to be important solvents for their strong solvating power, and the hydrogen bonds dominate the characteristics of amide solvents. Amides form specific structures such as network or chain structures by linking the molecules with hydrogen bonds, and there have been many researches on the characteristic physical properties induced by their unique structures and dynamics.

Scattering experiments [1-3] provided important information about the structures of amides. Ohtaki et al. [1] carried out X-ray diffractometry for NMF, and analyzed the results with the aid of MO calculation to determine its liquid structure. They concluded that formamide (FA), *N*-methylformamide (NMF), and *N,N*-dimethylformamide (DMF) have different liquid structures: FA has three-dimensional structure causing its high boiling point and viscosity. The hydrogen bonds of NMF induce the formation of flexible chain structure of NMF with no long ranged structure like FA. The random structure of DMF lowers the boiling and melting points.

The temperature and pressure dependence of the liquid structure of FA was also studied by Bellsient-Funel et al. [3] Although X-ray scattering experiments indicated the intermolecular distance of nitrogen and oxygen atoms decreased at higher temperature, the results of neutron scattering showed weak dependence of the structure on pressure for strong hydrogen bonds.

Spectroscopic experiments [4-6] also revealed the structural and dynamic information of amides. Holz et al. [4] measured the self diffusion coefficient of eleven organic solvents including FA and DMF by nuclear magnetic resonance (NMR) to reveal the molecular weight dependence of their dynamics.

Buchner and Yarwood [6] measured infrared (IR) spectra of NMF and DMF diluted

with carbon tetrachloride to investigate the influence of the breakage of the hydrogen bonds on the dynamics of NMF and DMF. Both the long time dynamics and short ranged potentials of NMF and DMF were changed by dilution for the decay of the molecular structure formed by hydrogen bonds.

The approach of theoretical calculation and simulation [7-10] also made great contribution to understand amides, especially their intermolecular interactions. Ludwig et al. [7] calculated the quadrupole coupling parameters of FA, and compared them with the measured values obtained by NMR. They argued that the dominant species is a six-membered ring involving hydrogen bonds. Simulations of Schiester et al. [8], Chalaris and Samios [9], and Richardi et al. [10] also revealed the structure and interaction of FA, NMF, and DMF.

The mechanism of the temporary dissociation and reformation of the network formed by hydrogen bonds were extensively studied by Barthel et al.[11] They measured the dielectric relaxation of FA, NMF, DMF, and *N,N*-dimethylacetamide (DMA) over wide range of temperature to reveal the dynamics of these amide solvents. They observed relaxation caused by the dynamics of hydrogen bonds in the dielectric spectra of FA and NMF, and argued that two characteristic times named as “dwelling time” and “waiting time” determine the relaxation behavior. The former is the time for

FA or NMF molecules to be released from the network formed by the hydrogen bonds, and the latter is the time for free molecules of FA or NMF to be trapped again to the network. This dielectric behavior suggests that the chains of FA and NMF are not a rigid framework, but the network of the molecules at the equilibrium of releasing and trapping of molecules.

In this study, we observed the formation of unique structures of NMF and some other amides under the applied electric field with high frequency. External electric field can induce the change of the network structure of NMF, because the molecules at “dwelling time” can be arranged to the external electric field for the interaction of polar groups in NMF and some other amides. In this study, we investigated the structural change of the network of amides induced by electric field by measuring the birefringence and infrared (IR) spectrum of NMF. The retardation of NMF oscillated at the double frequency as the applied electric field at low frequency (< 170 Hz), which was a typical behavior of Kerr effect. On the other hand, the retardation increased much slower than the frequency of the applied field by turning on the field, and also reversed slowly by turning off the field at high frequency of the applied field. The optically anisotropic structure slowly induced by the electric field was investigated by the IR spectra of NMF before, during and after applying the field.

2. Experimental

2-1. Sample preparation

Four amides: *N*-methylformamide (NMF), *N*-ethylformamide (NEF), *N*-methylacetoamide (NMA) and 2-acetoamideethanol (AAE) were used in this study. All the reagents were purchased from Tokyo Kasei, and used without further purification.

The electrodes in the cells to measure retardation were made of platinum wires with the diameter of 200 μm (Nilaco). Two electrodes soldered to copper wires were glued to a glass substrate. The distance between the two electrodes was fixed to be ca. 0.3 mm with a thin glass plate. Sample liquid was filled between the electrodes. A plate of calcium fluoride was used instead of a glass substrate for IR measurements to avoid the absorption of IR ray. The electrodes were made by evaporating aluminum to the substrate in vacuo.

Alternative electric field was applied to the electrodes with an electric source equipped with an amplifier. The electric source and amplifier were Model 454 of Kikusui Electronics and BWA 35-5 of Takasago Power Supply for low frequency, and Model 454A of Kikusui Electronics and 30-12C of RF Power Labs for high frequency,

respectively.

2-2. Measurements

The response of the magnitude of birefringence to alternative electric field was measured with a polarizing microscope of Nikon at crossed nicol condition. Monochromatic light (546 nm) filtered with a GIF filter was used as light source. The intensity of the transmitting light was detected with a photo diode.

IR spectra of sample liquids were obtained with an IR spectroscope (IRI-3000 of Jasco) before, during, and after applying electric field. The transmitting IR ray was measured at the resolution of 2 cm^{-1} and scan number of 32 times.

Permittivity was determined with an LCR meter (HP4284A of Hewlett Packard) at 20 Hz-1 MHz, and with a vector impedance meter (4815A of Hewlett Packard) at 1-100 MHz. The instrument was calibrated with distilled water at 20 °C.

3. Results and discussion

Fig. 1 shows the response of the birefringence of NMF to alternative electric fields. Fig. 1a illustrates the intensity of transmitting light (I) at crossed nicol condition, which

is proportional to the magnitude of birefringence of NMF under the alternative electric field at 1 Hz. Fig. 1b is the response of the intensity of transmitting light of NMF when the alternative electric field at 10 MHz was turned on at 5 s and turned off at 15 s. The symbols t and V in the figures stand for the time and applied voltage, respectively. As the ordinate indicates the absolute value of the birefringence, the birefringence of NMF shown in Fig. 1a oscillates in double phase with the applied alternative electric field (1 Hz). On the other hand, the birefringence of NMF shown in Fig. 1b increases and decreases much slower compared to the frequency of the applied field. The birefringence of NMF in Fig. 1a is a typical behavior of Kerr effect, but that in Fig. 1b suggests the slow formation of optically anisotropic structure induced by the high frequency alternative electric field.

The retardation of various liquids induced by the alternative electric field at 10 MHz was measured to verify the linear relation between the retardation (R) and applied electric field (E) as shown in Fig. 2. The retardation is defined as the product of the birefringence and the thickness of sample liquid. The retardation of NMF, NEF, and AAE increased non-linearly by increasing the intensity of applied electric field, that is, no retardation was detected below the threshold of the applied electric field (110, 70, 150 kV m^{-1} for NMF, NEF, and AAE, respectively), and the increase of the retardation

was observed only above the threshold. No retardation was observed for NMA and NEA (not shown in Fig. 2) below 185 kV m^{-1} . The non-linear behavior of the retardation in Fig. 2 is compatible with the results of dielectric measurements of amides reported previously [11], because the voltage of the applied electric field in dielectric measurements is not so high.

Fig. 3 shows the frequency (f) dependence of permittivity (χ) of NMF. While the high permittivity decreased drastically by increasing the frequency at low frequency, it was almost constant above 0.1 MHz. The high permittivity and drastic change at low frequency was caused by ionic impurity in sample liquids, and does not reflect the motion of NMF molecules. However, because the motion of ionic impurity could no longer follow the high frequency of applied electric field, its influence was diminished, and only the contribution of the optically anisotropic structure of sample liquids as shown in Fig. 1b, could be detected at high frequency. In order to elucidate the optically anisotropic structure induced by electric field, the frequency of the applied electric field in the following measurements was fixed to be 10 MHz.

Fig. 4 illustrates the IR spectra of NMF and NMA without applying electric field. The symbols ν and A in the figure stand for the wavenumber and absorbance, respectively. The most distinct difference between the two spectra is a broad peak

around 3500 cm^{-1} observed only in the spectrum of NMF. It is widely accepted that amides including NMF form associative structure by the hydrogen bonds [1-11]. In order to investigate the structural change of NMF induced by the electric field, we analyzed the peaks at 3310 , 3510 , and 1670 cm^{-1} , which were assigned to be the absorption of N-H vibration of amide groups forming hydrogen bonds, that of amide groups forming no hydrogen bonds, and that of carbonyl groups, respectively.

IR spectra of NMF before, during, and after applying the electric field are summarized in Fig. 5. The ratio of the absorbance at 3510 cm^{-1} to that at 3310 cm^{-1} was calculated to estimate the formation of hydrogen bonds of N-H. This ratio before, during, and after applying electric field was 0.681 , 0.603 , and 0.656 , respectively, which indicate the increase of the hydrogen bonds of amide groups by applying electric field. The ratio of the absorbance at 1670 cm^{-1} to that around 2870 cm^{-1} , which is assigned as the peak of the vibration of C-H in methyl groups, was also calculated to investigate the vibration of carbonyl groups, because the vibration of C-H in methyl groups is expected not to be influenced by the formation of hydrogen bonds. This ratio before, during, and after applying electric field was 2.207 , 2.299 , and 2.224 , respectively, which suggests that the vibration of carbonyl groups was suppressed by the applied electric field. These changes of IR spectrum of NMF suggest that the birefringence of NMF induced by

applying electric field with high frequency was caused by the change of molecular structure of NMF induced by the breakage and reformation of hydrogen bond.

The reversibility of the retardation and IR spectra of NMF indicates that the hydrogen bonds can be formed and dissociated reversibly. These results suggest that NMF molecules of which hydrogen bonds tentatively dissociated were aligned by the electric field to form optically anisotropic structure which was stabilized by reformed hydrogen bonds.

Fig. 6 shows the temperature (T) dependence of the absolute value of permittivity (χ) for NMF and NMA measured by dielectric measurements at 10 MHz. As the melting point of NMA is 28 °C, χ below the melting point is very low for the restricted molecular motion, and it drastically increase just below the melting point. Constant decrease of χ was observed for NMF and NMA above the melting point.

Barthel et al. [11] showed that the association number and cooperative motion of NMF decreases by increasing temperature. The decrease of χ by increasing temperature shown in Fig. 6 for NMF and NMA can be explained by the decrease of the cooperative motion of the chains of NMF.

Considering the results mentioned above, we suggest the mechanism of the formation of the optically anisotropic structure of NMF by external electric field as

follows. First, the electric field with high frequency provided the molecules with the mobility to change the structure by breaking the hydrogen bond tentatively. Optically anisotropic structure was formed by aligning the mobile molecules, and stabilized by newly formed hydrogen bonds of NMF during the application of electric field. The absence of optically anisotropic structure in NMA may be caused by the more rigid structure stabilized by stronger hydrogen bonds.

Because similar retardation behavior was also observed for NEF and AAE, the optically anisotropic structure induced by external electric field with high frequency is not peculiar to NMF, but common to some amide liquids.

4. Conclusion

The optically anisotropic structure of some amides induced by electric field with high frequency (10 MHz) was observed by measuring the retardation. Typical Kerr effect was observed for NMF under the electric field with low frequency (<170 Hz), but the retardation of NMF slowly increased by applying the electric field with high frequency, and reversed slowly by turning off the electric field. The retardation of *N*-methylformamide (NMF), *N*-ethylformamide (NEF), and 2-acetoamideethanol (AAE) increased by increasing the applied electric field above each threshold at 10 MHz.

Whereas absorption bands of N-H stretching of amide groups forming hydrogen bonds and that of amide groups forming no hydrogen bonds were observed in the IR spectrum of NMF, only the bands of N-H stretching of amide groups forming hydrogen bonds was detected in the spectrum of NMA. The reversibility of the formation and dissociation of the hydrogen bonds of NMF was confirmed by the change of its IR spectrum. The ratio of the absorbance of N-H stretching of amide groups forming hydrogen bonds to that of amide groups forming no hydrogen bonds increased by applying electric field, and again decreased by turning off the field.

It can be inferred that the optically anisotropic structure of NMF was constructed by the alignment of mobile NMF molecules of which hydrogen bonds were tentatively dissociated by external electric field.

5. References

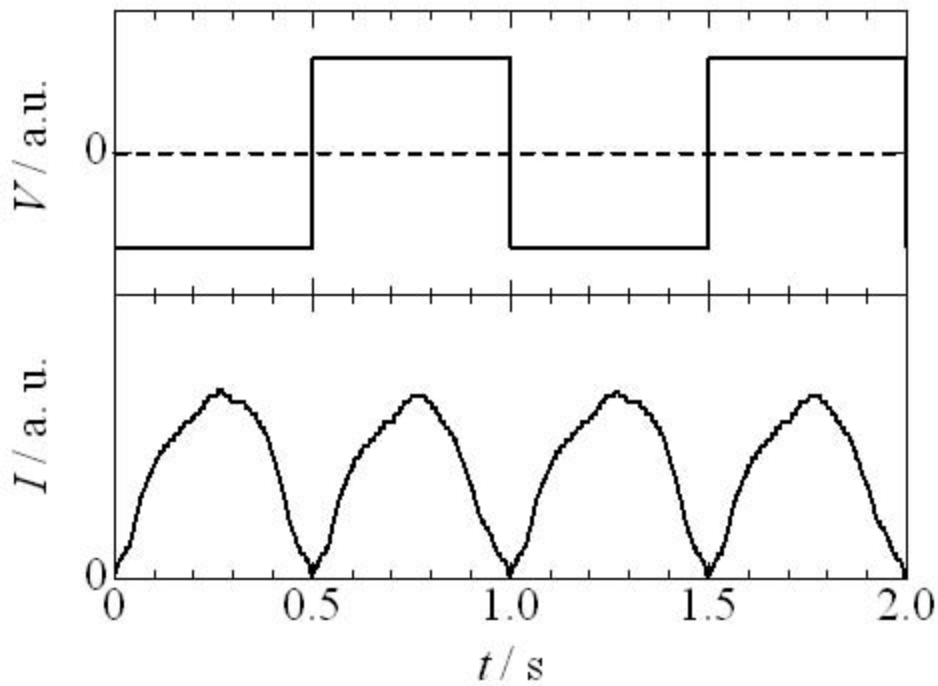
- [1] H. Ohtaki, S. Itoh, B.M. Rode, Bull. Chem. Soc. Jpn. 59 (1986) 271.
- [2] J. Neuefeind, P. Chieux, M. Zeidler, Mol. Phys. 76 (1992) 143.
- [3] M.-C. Bellisent-Funel, S. Nasr, L. Bosio, J. Chem. Phys. 106 (1997) 7913.
- [4] M. Holz, X. Mao, D. Seiferling, A. Sacco J. Chem. Phys. 104 (1996) 669.
- [5] R. Konrat, H. Sterk, J. Phys.Chem. 94 (1990) 1291.

- [6] R. Buchner, J. Yarwood, *J. Mol. Liq.* 49 (1991) 141.
- [7] R. Ludwig, F. Weinhold, T.C. Farrar, *J. Chem. Phys.* 102 (1995) 5118.
- [8] P.C. Schoester, M.D. Zeidler, T. Radnai, P.A. Bopp, *Z. Naturforsch* 50a (1995) 38.
- [9] M. Chalaris, J. Samios, *J. Chem. Phys.* 112 (2000) 8581.
- [10] J. Richardi, H. Krienke, H. Bertagnoli, P. Chieux, *Chem. Phys. Lett.* 273 (1997) 115.
- [11] J. Barthel, R. Buchner, B. Wurm, *J. Mol. Liq.* 98-99 (2002) 51.

Figure captions

- Fig. 1** The intensity of transmitting light (I) through NMF at crossed nicol condition under the alternative electric field shown in the same figures. The electric field at 1 Hz was applied to NMF through the measurement in Fig. 1a. The electric field at 10 MHz to NMF was turned on at 5 s, and turned off at 15 s in Fig. 1b. The symbols t and V in the figures stand for the time and applied voltage, respectively.
- Fig. 2** The retardation (R) of NMF, NMA, NEF, and AAE under the electric field (E) at 10 MHz with different voltage.
- Fig. 3** The frequency (f) dependence of the permittivity (χ) of NMF used in this study.
- Fig. 4** IR spectra of NMF and NMA without applying any electric field. The symbols ν and A in the figures stand for the wavenumber and absorbance, respectively.
- Fig. 5** Infrared spectra of NMF before, during and after applying electric field with high frequency (10MHz) at 2800-3700 cm^{-1} (a), and 1000-2000 cm^{-1} .

Fig. 6 The temperature (T) dependence of the permittivity (χ) at 10MHz of NMF and NMA.



magnified figure

