Near-infrared Spectroscopic Studies of the States of Water in Lyotropic Liquid Crystals

Masuo Aizawa and Shuichi Suzuki

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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The states of water in lyotropic liquid crystals of the polyoxyethylene–nonylphenylether and water system were investigated by means of near-infrared spectroscopic measurements. The states of water were classified into nonbonded, singly-hydrogen-bonded, and doubly-hydrogen-bonded states, and their relative concentrations were calculated from the intensities of the combination bands of $2\nu_1+\nu_3$ and $\nu_1+\nu_2+\nu_3$ in the temperature range from 25 to 50 °C. An increase in the hydrogen-bonded water species was found for the liquid crystal. Furthermore, the nonbonded and singly-hydrogen-bonded water species decreased, while the doubly-hydrogen-bonded water species increased in the liquid crystal structure, as compared with ordinary water. The structural properties of the liquid crystal are discussed.

Liquid crystalline structures may be prepared thermally from one component (thermotropic systems) or by the treatment of certain compounds with a controlled amount of water or other polar solvent (lyotropic systems). Lyotropic liquid crystals are strongly birefringent and may vary in texture from a turbid free-flowing fluid to a waxy substance or clear gel. A solvent is responsible for the formation of the lyotropic liquid crystals. Especially in the biological system, water plays an important role in the formation of the lyotropic liquid crystals.[1] The states of water in lyotropic liquid crystals, however, have not yet been clarified. We reported previously that the states of water involved in macromolecular gels should be classified into at least three groups, because most of the so-called free water has been found to be fairly restricted.[2–4] The present investigation was undertaken in order to determine the states of water in the lyotropic liquid crystals.

Various measurements, such as infrared and Raman spectroscopy, NMR, X-ray diffraction, and dielectric relaxation measurements, have been used in the studies of the structure of water. These methods have also been extended to aqueous solutions, and a number of structural models have been postulated for liquid water.[5] These models are generally classified into multi-state models and uniform-state models. For both a multi-state model and a uniform-state model, the degree of association of water has been the main subject of study. The vibrational spectroscopic investigation is effective, because it is extremely sensitive to the strength and extent of hydrogen bonding. The frequency of OH stretching vibrations is known to decrease in a regular manner with the strength of the hydrogen bonding. Therefore, Raman or infrared fundamental, overtone, and combination bands, which involve OH stretching, may serve as a probe of hydrogen bonding. As has been pointed out by Falk,[6] the frequencies of bending vibrations increase upon hydrogen bonding, but the shifts are much smaller, and, hence, somewhat less useful as a structural probe. As the combination bands involving OH stretching have been used successfully in quantitative investigations of the hydrogen bonding of water,[7–11] near-infrared spectroscopic analysis was carried out in this work.

The combination of nonionic surfactants and water being a typical example of how the lyotropic liquid crystals are formed, the polyoxyethylene–nonylphenylether and water system is used in this investigation. The water molecules are presumed to be strictly restricted in the lyotropic liquid crystal, because polyoxyethylene–nonylphenylether may be highly ordered and their hydrophilic sites may be hydrated. In view of the hydrogen-bonding association, the states of water in a lyotropic liquid crystal can be classified into three states: the nonbonded, singly-hydrogen-bonded, and doubly-hydrogen-bonded states. The concentrations of the nonbonded, singly-hydrogen-bonded, and doubly-hydrogen-bonded water species were calculated for this system by near-infrared spectrum analysis in the 900—1300 nm region.

Experimental

Materials. The polyoxyethylene–nonylphenylether was supplied by the Kao Atlas Co., Ltd. The average polymerisation degree of the oxyethylene residue is 13.2. This nonionic surfactant is denoted as C_9Ph_{13} in this paper.

Near-infrared Spectra. The spectra were recorded with a Shimazu SV-50A spectrophotometer. All the measurements were made with water or an aqueous solution in a 1-cm cell and with an empty cell in the reference beam. Temperature control for the sample and the reference cells was achieved with circulating water at a fixed temperature.

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[1] J. L. Fergason and G. H. Brown, *J. Amer. Oil Chem. Soc.*, **45**, 120 (1968); G. T. Stewart, *Mol. Cryst. Liq. Cryst.*, **7**, 75 (1969).

[2] J. Mizuguchi, M. Takahashi, and M. Aizawa, *Nippon Kagaku Zasshi*, **91**, 723, 961 (1970).

[3] M. Aizawa and S. Suzuki, This Bulletin, **44**, 2967 (1971).

[4] M. Aizawa, J. Mizuguchi, S. Suzuki, S. Hayashi, T. Suzuki, N. Mitomo, and H. Toyama, *ibid.*, **45**, 3031 (1972).

[5] D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford Univ. Press, London (1969), p. 254.

[6] M. Falk and T. A. Ford, *Can. J. Chem.*, **44**, 1699 (1966).

[7] K. Buijs and G. R. Choppin, *J. Chem. Phys.*, **39**, 2035 (1963).

[8] G. R. Choppin and K. Buijs, *ibid.*, **39**, 2042 (1963).

[9] O. D. Bonner and G. B. Woolsey, *J. Phys. Chem.*, **72**, 899 (1968).

[10] O. D. Bonner, and G. B. Woolsey, *ibid.*, **72**, 2512 (1968).

[11] G. R. Choppin and J. R. Downey, Jr., *J. Chem. Phys.*, **56**, 5899 (1972).

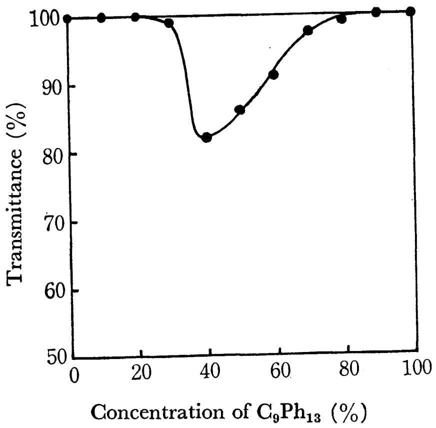

Fig. 1. Concentration dependence of transmittance at 900 nm.

Results

Near-infrared Spectra of Water in Lyotropic Liquid Crystals. Polyoxyethylene–nonylphenylether (C_9Ph_{13}) is known to form a smectic liquid crystal with less than approximately 75% of water. The transmittance measured at 900 nm in this experiment is shown in Fig. 1 for various C_9Ph_{13} contents. The transmittance becomes poor in the concentration range from 40 to 60% of C_9Ph_{13}. In the above concentration range, these mixtures form a gel at room temperature. The rheological properties of these mixtures have been reported elsewhere.[8]

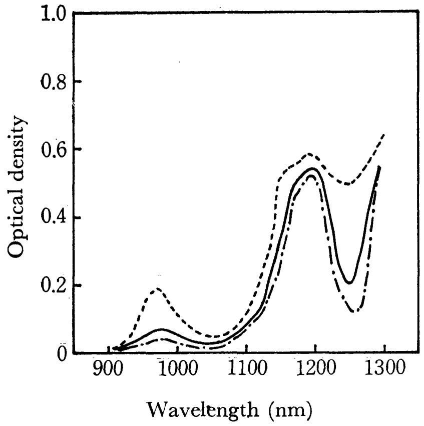

Fig. 2. Spectra of water in liquid crystals containing 60% (——), 80% (—·—) of C_9Ph_{13}, and pure water (······) at 25 °C.

The near-infrared spectra of water in liquid crystals containing 60 and 80% of C_9Ph_{13} at 25 °C are presented in Fig. 2. The spectrum of pure water is illustrated as a reference. As has been reported by Buijs and Choppin,[7] the absorption band at 977 nm can be assigned to the combination band of $2\nu_1+\nu_3$, and the bands at 1160 and 1200 nm, to that of $\nu_1+\nu_2+\nu_3$, where ν_1 (symmetric stretching), ν_2 (bending), and ν_3 (asymmetric stretching) are the fundamental vibrations. As for the bands around 1200 nm, the three peaks at 1160, 1200, and 1250 nm were assigned to the bands of the water species involving 0, 1, and 2 hydrogen bondings respectively.[7] As the temperature is raised, the bands have been observed to become sharper and to shift toward the blue, so as to approach a constant wavelength asymptotically. On the contrary, the formation of hydrogen bonding is known to shift the water bands toward the red.[9–10]

As is shown in Fig. 2, the peak of $2\nu_1+\nu_3$ in the lyotropic liquid crystals was observed to shift to a longer wavelength compared with that of ordinary water. In addition, the peak height at 1160 nm attributed to the monomeric water species is suppressed. These spectra suggest that the monomeric water species decrease in the liquid crystals. The association degree of water in the liquid crystals was surveyed by the quantitative analysis of both the $2\nu_1+\nu_3$ and $\nu_1+\nu_2+\nu_3$ bands.

Hydrogen Bonding of Water in the Liquid Crystal. The band of $2\nu_1+\nu_3$ was analysed in order to estimate the association degree of water. As has been described above, the band of $2\nu_1+\nu_3$ can be expected to shift to a longer wavelength in the liquid crystals because of the decrease in monomeric water species.

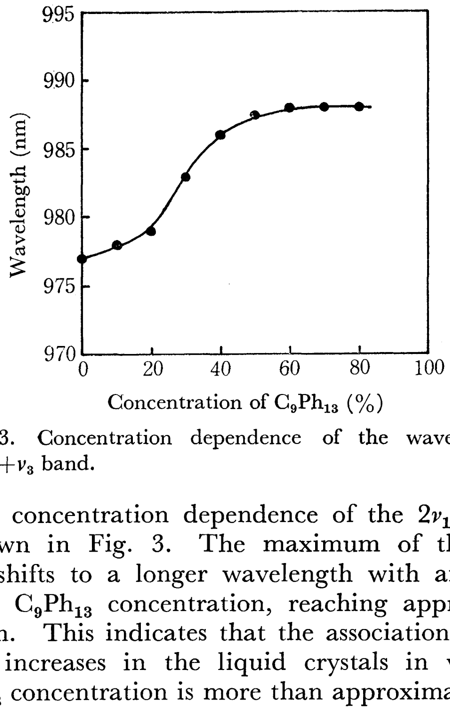

Fig. 3. Concentration dependence of the wavelength at $2\nu_1+\nu_3$ band.

The concentration dependence of the $2\nu_1+\nu_3$ band is shown in Fig. 3. The maximum of the $2\nu_1+\nu_3$ band shifts to a longer wavelength with an increase in the C_9Ph_{13} concentration, reaching approximately 988 nm. This indicates that the association degree of water increases in the liquid crystals in which the C_9Ph_{13} concentration is more than approximately 30%.

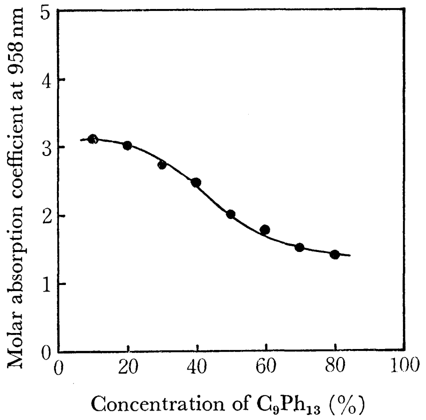

Fig. 4. Molar absorption coefficients at 958 nm for various concentrations of C_9Ph_{13}.

As the characteristic band for liquid monomeric water has been reported to be 958 nm, the absorbance at 958 nm may serve as a measure of the amount of liquid monomeric water. If the hydrogen-bonding association increases in the liquid crystals, the molar absorption coefficient at 958 nm can be expected to decrease in the liquid crystals. In Fig. 4, the molar absorption coefficient at 958 nm is shown for various concentrations of C_9Ph_{13} at 25 °C. A marked suppression of the molar absorption coefficient at 958 nm was observed in the liquid-crystal phase. Thus, it is reasonable to state that most of the monomeric water species disappear because of the strong interaction between C_9Ph_{13} and water in the liquid crystals.

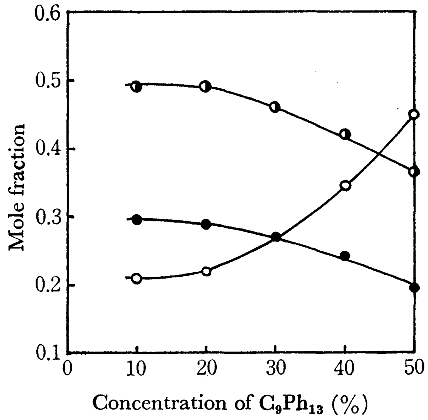

Fig. 5. Mole fractions of nonbonded (—●—), singly-bonded (—◐—), and doubly-bonded (—○—) water species in various concentrations of C_9Ph_{13}.

The relative amounts of nonbonded, singly-bonded, and doubly-bonded water species can be calculated according to the method of Buijs and Choppin.[7] In Fig. 5, C_0, C_1, and C_2, which are the relative concentrations of nonbonded, singly-bonded, and doulby-bonded water species respectively, are presented for various C_9Ph_{13} concentrations at 25 °C.

A baseline in the range from 1100 to 1300 nm was constructed so as to deduct the contribution of the strong band of water at 1447 nm and the sharp band of C_9Ph_{13} at 1200 nm. The baseline was calculated from a sum of the exponentials, $A=A_1e^{d_1(\lambda-\lambda_0)}+A_2e^{d_2(\lambda-\lambda_0)}$, for the band at 1447 nm[7] and by multiplying the observed molar absorption coefficients of C_9Ph_{13} at 1160, 1200, and 1250 nm with the molar concentration of the liquid crystals. The molar absorption coefficients of C_9Ph_{13} were then determined in the temperature range surveyed. The influence of the band at 980 nm was disregarded. The quantitative correction becomes difficult in the concentrated liquid crystals because of the marked disturbance by the band of C_9Ph_{13}. Therefore, C_0, C_1, and C_2 were calculated in the concentration range from 0 to 50% of C_9Ph_{13}.

As was expected, not only C_0 but also C_1 decreases with an increase in the C_9Ph_{13} concentration. A decrease in C_0 and C_1 was observed in the liquid crystals containing more than 30% of C_9Ph_{13}. In contrast with C_0 and C_1, an increase in C_2 was found in the above liquid crystals. Thus, most of the water in the liquid crystals is singly- or doubly-hydrogen-bonded and the monomeric water species are reduced compared with ordinary water. An increase in the doubly-bonded water species is characteristic in this system.

Temperature Effect on the States of Water in the Liquid Crystal. The physicochemical properties, such as the viscosity and birefringence of the liquid crystal, show a drastic change at approximately 40 °C. Such a drastic change may be caused by the structural change in the liquid crystal. Therefore, the states of water can be expected to show anomalous changes accompanying the above changes.

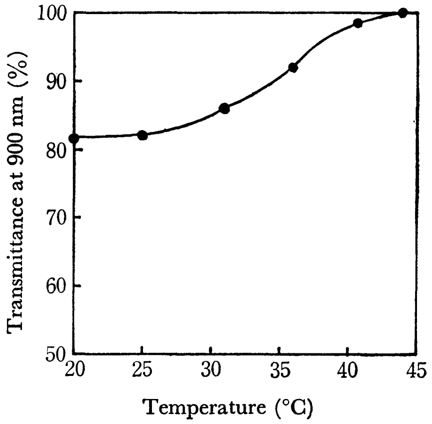

Fig. 6. Temperature dependence of transmittance at 900 nm for the liquid crystal containing 40% of C_9Ph_{13}.

The transimittance at 900 nm is a suitable measure for following the structural transition of the liquid crystal. The temperature dependence of the transmittance at 900 nm is shown in Fig. 6 for the liquid crystal containing 40% of C_9Ph_{13}. Though this liquid crystal shows a poor transmittance at room temperature, it gives excellent transparency above approximately 40 °C. A kind of structural transition may occur around this temperature.

If such a structural transition is caused by dehydration, the relative concentration of the monomeric water species, C_0, will increase. The temperature effect on the relative concentrations of nonbonded, singly-bonded, and doubly-bonded water species is shown in Fig. 7

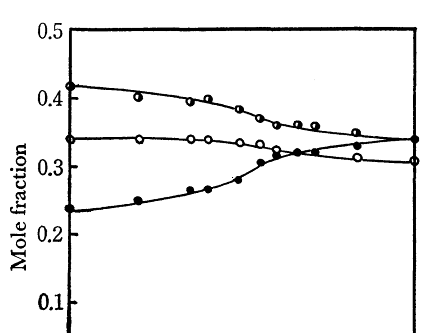

Fig. 7. Temperature dependence of mole fractions of nonbonded (—●—), singly-bonded (—◐—), and doubly-bonded (—○—) water species in the liquid crystal containing 40% of C_9Ph_{13}.

for the liquid crystal containing 40% of C_9Ph_{13}. The relative concentration of the nonbonded water species, C_0, increases gradually with an increase in the temperature. Accompanying the temperature dependence of C_0, the relative concentrations of the singly-bonded and doubly-bonded water species, C_1 and C_2, decrease with an increase in the temperature. These changes indicate that a marked dehydration of C_9Ph_{13} occurs with the structural transition in this temperature range.

Discussion

The spectrum analysis of the combination bands, $2\nu_1+\nu_3$ and $\nu_1+\nu_2+\nu_3$, has revealed that the degree of hydrogen-bond association increases in the lyotropic liquid crystals compared with ordinary water. For instance, in the liquid crystal containing 50% of C_9Ph_{13}, only 18% of the water is nonbonded, whereas approximately 32% of the water is nonbonded in ordinary water at 25 °C. In addition, the relative concentration of the doubly-hydrogen-bonded water species exceeds that of the singly-hydrogen-bonded ones in the liquid crystal. Such an increased degree of hydrogen-bond association, especially doubly-hydrogen-bond association, may be closely related to the mechanism of the liquid-crystal formation.

One of the possible explanations for the increase in the doubly-hydrogen-bonded water species is the hydration to the ether bonds of the polyoxyethylene chain. Each hydrogen atom of water can be linked with the oxygen atom of an ether bond in the polyoxyethylene chain. Water molecules may be bridged between two polyoxyethylene chains by hydrogen bonding. Gel formation may be caused by such a water bridge. This explanation is supported by the temperature dependence of the concentration of the doubly-hydrogen-bonded water species. The hydrogen bonds dissociate markedly around 40 °C, at which temperature the gel recovers fluidity. Moreover, it has been reported that this liquid crystal changes its birefringence from positive to negative with a phase transition of the liquid crystal at approximately 40 °C.[9] Therefore dehydration is thought to occur around 40 °C and to give fluidity.

The C_9Ph_{13} and water system is known to form smectic liquid crystals. The molecules in the smectic structure may be arranged in neat rows within individual layers or the molecules within a layer may be randomly distributed. The orientation of the C_9Ph_{13} and water molecules, however, cannot be determined by this method. The mobility and orientation of water molecules in lyotropic liquid crystals are now under investigation.

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12) S. Kuroiwa, *Kogyo Kagaku Zasshi*, **63**, 1384 (1960).
13) S. Kuroiwa, *ibid.*, **70**, 2103 (1967).