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LETTERS

Refractive Indices of Water and Aqueous Electrolyte Solutions under High Magnetic Fields

Haruki Hosoda, Haruki Mori, Norihito Sogoshi, Akira Nagasawa, and Seiichiro Nakabayashi*

Department of Chemistry, Faculty of Science, Saitama University,
Shimo-Ohkubo 255, Sakura-Ku, Saitama, Japan

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The refractive index of water was measured at atmospheric pressure under magnetic fields up to 10 T and found to increase by ~0.1% with increasing magnetic field strength. In contrast, the refractive index of saturated aqueous electrolyte solutions decreased under the magnetic field. In the case of *n*-hexane, any change of the optical property by the magnetic field was not found. A possible explanation is that the lifetime of the hydrogen bond is prolonged due to the electron delocalization of a water dimer under the magnetic field.

Introduction

Water is the most ubiquitous liquid on the earth and indispensable for life and the environment. Water has many peculiar properties, including large heat of vaporization, high boiling and melting temperatures, and high solubility for charged and polar molecules.[1] The distinctive features of liquid water are mainly due to the three-dimensional hydrogen-bonding network. Recent works on water have been extended to dynamical structure studied by ultrafast laser techniques,[2,3] theoretical studies,[4−6] and the relaxation dynamics of the interfacial water near the protein surface based on neutron scattering.[7] Other recent topics are collected in the literature.[8]

While a wealth of studies on water and solutions by light absorption and scattering experiments have been reported, we pay attention to the refractive index of water in this work. Recently, several convenient commercial sensing devices based on the surface plasmon resonance (SPR) have been developed,[9−12] which can determine the refractive indices of liquid samples with very high sensitivity ($\Delta n/n < 10^{-5}$). Recent development of the SPR sensor and its application especially to the chemical and biological sensor is reviewed by Homola et al.[9] It is also promising and important for the applications to study the basic properties of water itself by this sensitive device. In this paper, the effect of the high magnetic field on the refractive indices of water and several aqueous electrolyte solutions is studied in order to obtain insight into the static structure of water.

Experimental Section

The refractive index (n) of water was measured by two methods, namely, SPR and position-sensitive detector (PSD), as shown in Figure 1 (not to scale) as a function of the magnetic field. All the measurements were carried out at ambient pressure and temperature of 25.0 °C stabilized within ±1 °C. The refractive indices of aqueous electrolyte solutions were measured by the SPR method.

Figure 1a shows a setup using an SPR sensor (Spreeta PTSPR1A170100, Texas Instruments, Inc.), which is based on the resonance between the evanescent wave and the surface plasmon.[10−12] The sensor consists of a light-emitting diode (AlGaAs, 840 nm), a molded epoxy waveguide, a sensing area (50 nm gold film), and a photodiode array. The resolution of the refractive index is 5×10^{-6}. Because of the rapid damping of the evanescent wave, this device is sensitive to the thin layer of the analyte material at the vicinity of the interface. Typical thickness is 400 nm for the water−gold interface.[12] A recommended calibration procedure was carried out so that the refractive index of ultrapure water at 25.0 °C was adjusted to

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* Author to whom correspondence may be addressed. Phone: +81-48-858-3617. Fax: +81-48-858-9424. E-mail: sei@chem.saitama-u.ac.jp.

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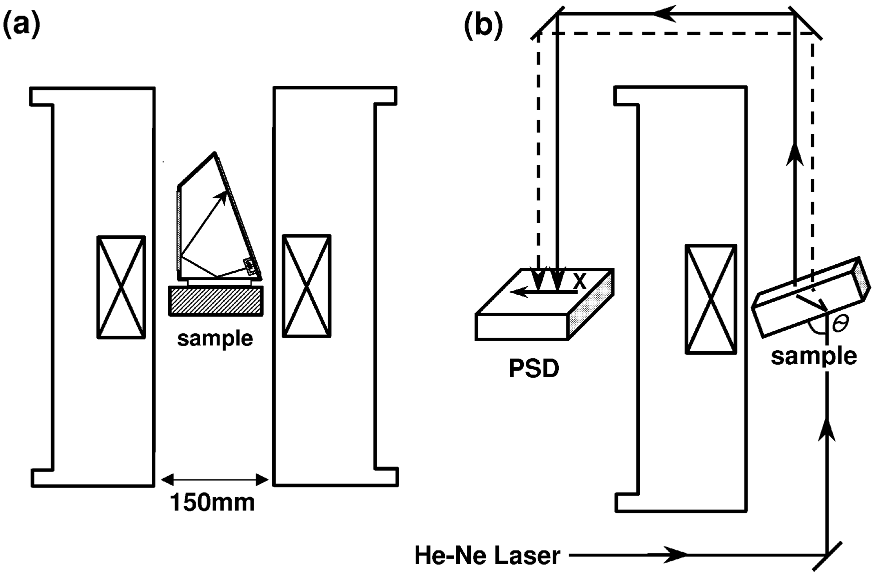

Figure 1. Two experimental setups for measuring the refractive indices of water and aqueous solutions (not to scale). Both measurements were carried out under the magnetic fields up to 10 T using a superconducting magnet. (a) A schematic diagram using a commercial surface plasmon resonance (SPR) sensor. The sensor comprises a light-emitting diode, a molded epoxy waveguide, a sensing area, and a photodiode array. (b) A setup using a He−Ne laser, a quartz cell, and a PSD.

1.333 000. The literature value of the refractive index of water at 840 nm and 25.0 °C is 1.327 96,[13] and thus the refractive index measured by the SPR method in this study contains a slight constant difference from the literature. This difference, however, should not affect our considerations and conclusions. The sensor was placed at the magnetic center of a superconducting magnet (JMT-10T150, Japan Superconductor Technology, Inc.), which generates the magnetic field up to 10 T. The sensor was positioned so as the gold film is perpendicular to the magnetic field.

Another setup using a He−Ne laser (633 nm) and a PSD obtained from Hamamatsu Photonics K. K. was used in order to measure the refractive index of bulk water and elucidate any surface effects for the SPR measurement. A quartz sample cell with a dimension of 12.5 × 12.5 × 45.0 mm^3 including the quartz wall thickness of 1.25 mm was placed at the magnetic center with a tilting angle (θ) between the cell and the laser beam. The laser beam passing through the cell is deflected, and the displacement of the optical path is detected by the PSD. The refractive index of water is obtained from the displacement, θ, and the refractive index of water at 633 nm; 1.331 58.[13] The small difference of the optical path due to the quartz cell itself is also taken into account. By variation of the tilting angle θ (70, 73, 75, and 77°), the consistency of the refractive index obtained was checked and the experimental error ($\Delta n/n$) was estimated to be $<1.5 \times 10^{-4}$.

Ultrapure water was prepared by a commercial water purification system (Direct-Q 5, Millipore Corp., 18.2 MΩ cm). NaCl and $NiCl_2$ (Wako Pure Chemical Industries, Ltd., GR grade) were used without further purification. The refractive index of *n*-hexane (Wako Pure Chemical Industries, Ltd., 99.5%) was also measured without further purification.

Results and Discussion

The dependence of the refractive index of pure water on the magnetic flux density (B) is shown in Figure 2. The refractive indices measured by the SPR setup (▼, n_{SPR}) and the PSD setup (●, n_{PSD}) show increases by 1.8×10^{-3} (0.14%) and 1.3×10^{-3} (0.09%) at 10 T, respectively, from the ones in the absence of the magnetic field. The increase of n_{SPR} is slightly larger than that of n_{PSD}. The origin of this discrepancy is unclear at this time, even though this could be attributed to the magnetic effect on water at the vicinity of the interface or the difference of the dielectric constant between the wavelengths of 840 nm (SPR) and 633 nm (PSD). The temperature derivative of the refractive index of water is $\sim 1 \times 10^{-4}$ deg^{-1} at room temperature in the visible region around 600 nm.[13] In the current study, the increase of n_{SPR} and n_{PSD} at 10 T exceeds the temperature fluctuation effects. Thus, the refractive indices of both of the vicinity of the interface and the bulk are increased by the magnetic field effect.

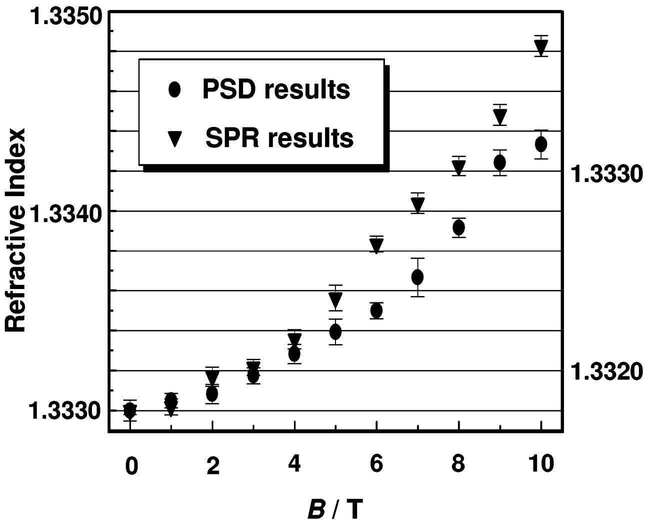

Figure 2. Refractive index of pure water plotted as a function of the magnetic field obtained by the PSD (●) setup and the SPR (▼) setup.

A possible explanation for the increase of the refractive index of water is that the hydrogen bond is stabilized under the magnetic field. From a classical electromagnetical point of view, diamagnetism is explained by the antiparallel magnetization of a molecule to the external magnetic field by the electromagnetic induction. It is well known that Pauling explained the diamagnetism of aromatic hydrocarbons by a molecular-size ring current model.[14] Since diamagnetism of a molecule depends on the extent of electron distribution, the electron delocalization

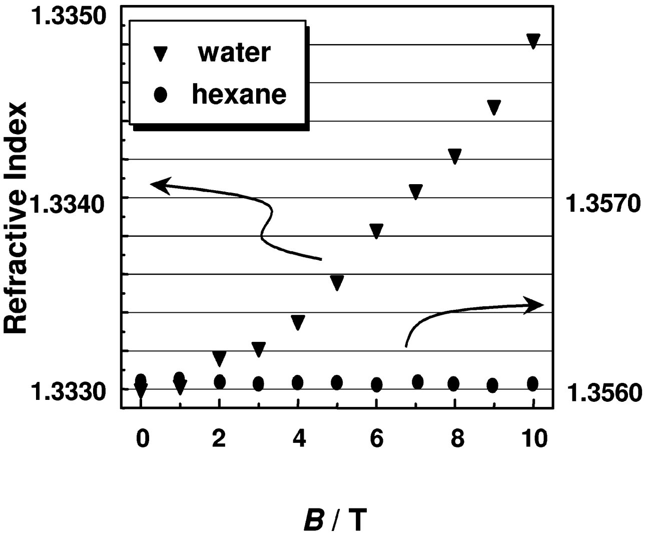

Figure 3. Refractive index of *n*-hexane plotted against the magnetic field (●) measured by the SPR method. The refractive index of water measured by the SPR method is reproduced for clarity (▼).

of hydrogen-bonded molecules should increase its diamagnetism. Therefore, the hydrogen bond should become more stable under the magnetic field. Iwasaka et al.[15] found that the frequency of the higher harmonic vibrations of water shifts toward the longer wavelength under 14 T. In comparison to the spectra of water at higher pressures, they suggested the enhancement of hydrogen bond under the high magnetic fields. The enhancement of hydrogen-bond strength should lead to the change of the electronic absorption, which affects the refractive index in the near-IR region. According to the electronic spectra of ice in the vacuum ultraviolet region,[16] the increase in the absorption of the first electronic excited states of the crystalline hexagonal ice from the one of amorphous ice was observed. The increase in the absorption due to the formation of hydrogen bonds should cause the increase of the refractive index via the Kramers−Kronig relation. The present observation strongly indicates that the lifetime of hydrogen bonds is prolonged.

In Figure 3, the refractive index of *n*-hexane (n_{hexane}) is plotted against B (●) measured by the SPR method. The result of pure water (n_{water}) by the SPR method is reproduced for clarity (▼). While n_{water} gradually increases with B, n_{hexane} does not change up to 10 T. This difference supports the hypothesis that hydrogen bonds are stabilized under magnetic fields. Moreover, the refractive index of ethanol under the magnetic field (unpublished data) was measured and shows little dependence on B. This may mean that although ethanol forms hydrogen bonds, they are not stabilized significantly under the magnetic fields since number of hydrogen bonds per molecule for ethanol is smaller than that for water.

Figure 4 shows the dependences of the refractive indices of aqueous electrolyte solutions on B as measured by the SPR method. Each mark represents the following electrolyte solutions: NaCl solutions at concentrations of 5.0 M (□) and 0.50 M (○) and $NiCl_2$ solutions at concentrations of 2.5 M (■) and 0.40 M (●). The refractive index of pure water (n_{water}) is again reproduced for clarity (▼). The figure indicates that (1) the refractive indices of electrolyte solutions increase with the increase of its concentration in the absence of the magnetic field and (2) the slope of the $n-B$ curves is positive at lower concentrations and negative at higher ones.

Without the magnetic field, the variation of the refractive indices of electrolyte solutions from that of pure water increases in sequence of 0.50 M NaCl (0.009) < 0.40 M $NiCl_2$ (0.011) < 5.0 M NaCl (0.034) < 2.5 M $NiCl_2$ (0.035). It is intriguing that the increase of the refractive index is dominated by $[Cl^-]$ at higher concentrations. The color of the aqueous $NiCl_2$ solution is green due to the formation of $[Ni(H_2O)_6]^{2+}$,[17] and therefore its refractive index is expected to be dependent on $[Ni^{2+}]$ due to the Kramers−Kronig relations. The results, however, show the refractive index depends more strongly on $[Cl^-]$ than on $[Ni^{2+}]$ and $[Na^+]$ at higher concentrations. The solutions of 2.5 M $NiCl_2$ and 5.0 M NaCl are near the saturation; NaCl/aq, 5.6 M and $NiCl_2$/aq, 6.0 M. At this concentration, the solution is dominated by ionic atmospheres, and the extent of ion-pair formation becomes large.[18] The refractive index at 840 nm seems to correlate to Cl^-, possibly due to the change or the appearance of the electronic states of Cl^- perturbed by ion-pair formation or complexation with cations. It should be noted that in the case of a concentrated $NiCl_2$ solution, the formation of $[Ni(H_2O)_5Cl]^+$ is reported.[19]

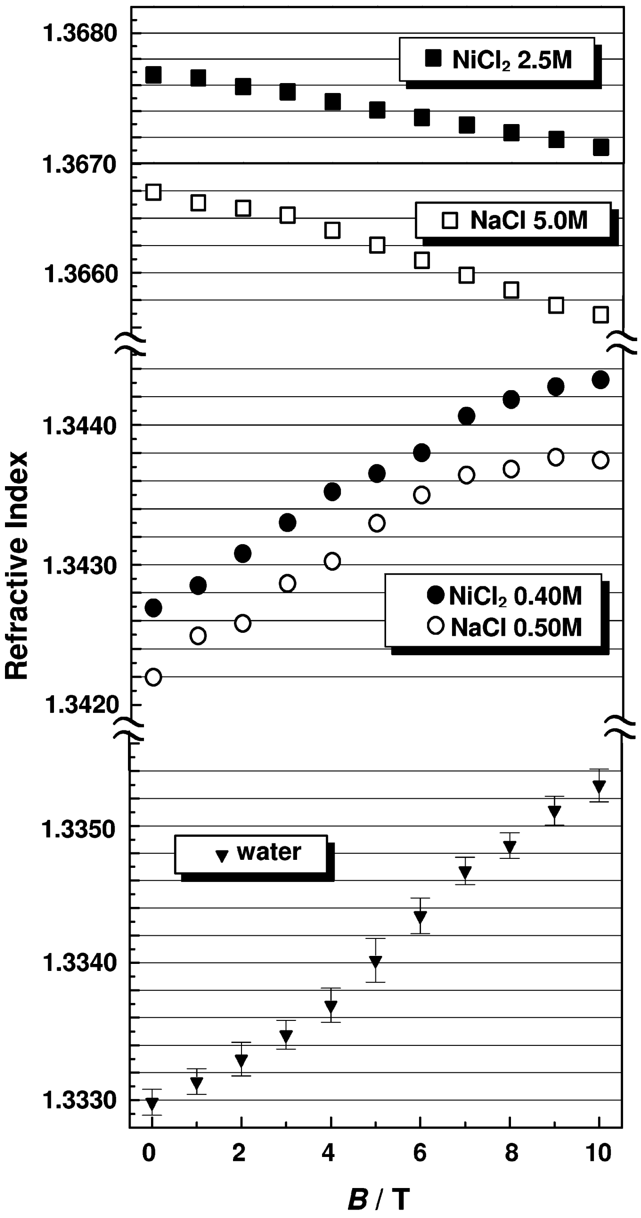

Figure 4. Refractive indices of aqueous solutions of 2.5 M $NiCl_2$ (■), 5.0 M NaCl (□), 0.40 M $NiCl_2$ (●), and 0.50 M NaCl (○) plotted against the magnetic field, measured by the SPR method. The refractive index of pure water measured by the SPR method is again reproduced for clarity (▼).

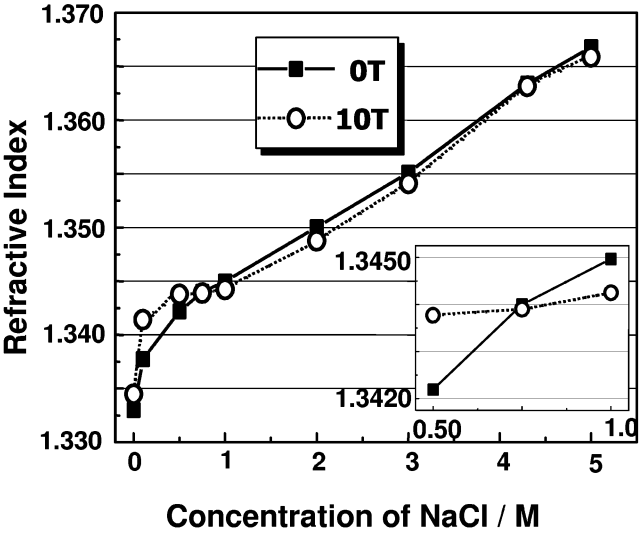

Figure 5. Refractive index of the aqueous NaCl solution measured by the SPR method plotted against the concentration in the absence (■) and the presence (○) of the magnetic field of 10 T. The magnified view ranging from 0.50 to 1.0 M is shown in the inset.

The changes of the refractive indices of the solutions at 10 T from the ones without the magnetic field are −0.0006 (2.5 M $NiCl_2$), −0.0010 (5.0 M NaCl), 0.0016 (0.40 M $NiCl_2$), and 0.0014 (0.50 M NaCl), respectively, as is shown in Figure 4. The slope of the $n-B$ curves of these electrolyte solutions also seems to be dependent on $[Cl^-]$ rather than $[Na^+]$ or $[Ni^{2+}]$ at higher concentrations. Although the paramagnetism of Ni^{2+} due to unpaired 3d electrons is important, the refractive index under 10 T shows little difference between the paramagnetic species (Ni^{2+}) and the diamagnetic species (Na^+). Therefore, the $n-B$ curves obtained should originate from Cl^-.

Although the complex magneto-optical behavior of electrolyte solutions cannot be explained easily, we can presume that two species bear the different $n-B$ curves, e.g., the one dominant at higher concentrations and the other at lower concentrations. Possible candidates for the higher concentrations are a hydrate complex or ion pair containing more than one chloride ion, since the absolute value of n and the negative dependence of n on B is dominated by $[Cl^-]$ at higher concentrations for both of the $NiCl_2$ and NaCl solutions. In addition, there are no distinct differences between the two cations. The origin of the $n-B$ curve at lower concentrations should be water itself. According to the three-zone model by Frank and Wen,[20] ions hydrated by water (A zone) are further surrounded by a weakly interacting “destructured” region (B zone), where water molecules are neither oriented to the core ion nor hydrogen bonded to each other. Around them is bulk water (C zone), in which water molecules are structured by hydrogen bonds. Thus, the $n-B$ curve at lower concentrations is considered to be the one for bulk water (C zone) superimposed by another for the ionic species (A or B zones). For the saturated solutions, the $n-B$ curve should be purely dominated by the hydrated ions or the ion pairs.

The refractive index of aqueous NaCl (n_{NaCl}) solution is plotted against its concentrations (c_{NaCl}) with (○) and without (■) the magnetic field of 10 T in Figure 5, as measured by the SPR method. The n_{NaCl} increases rapidly up to ~0.5 M, and above which it increases linearly in both of the absence and the presence of the magnetic field. The $n_{NaCl}-c_{NaCl}$ curves at 0 and 10 T cross at 0.75 M (see the inset of Figure 5). The figure clearly shows the occurrence of the tradeoff between two bearers of the different magneto-optical behaviors at concentrations of 0.5−0.75 M.

Conclusion

The refractive indices of water and aqueous electrolyte solutions were measured. The refractive index of pure water under 10 T increases by ~0.1% from the one without the magnetic field. It is proposed that the hydrogen bond of water is stabilized under the magnetic field. Therefore, the optical properties of the ultraviolet absorption and the refractive index should increase. Aqueous electrolyte solutions at higher concentrations show the decrease of the refractive index under 10 T, which is possibly explained by the formation of a hydrate complex or an ion-pair containing more than one chloride ions.

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