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Mechanisms of the anomalous Pockels effect in bulk water

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Abstract The "anomalous" Pockels effect is a phenomenon that a light beam passing between two electrodes in an aqueous electrolyte solution is deflected by an AC voltage applied between the electrodes: the deflection angle is proportional to the voltage such that the incident beam alternately changes its direction. This phenomenon, the Pockels effect in bulk water, apparently contradicts what is believed in nonlinear optics, i.e., macroscopic inversion symmetry should be broken for the second-order nonlinear optical effect to occur such as the first-order electro-optic effect, i.e., the Pockels effect. To clarify the underlying mechanism, the dependence of the effect on the electrode material is investigated to find that the Pockels coefficient with Pt electrodes is two orders of magnitude smaller than with indium tin oxide (ITO) electrodes. It is experimentally confirmed that the Pockels effect of interfacial water in the electric double layer (EDL) on these electrodes shows an electrode dependence similar to the effect in bulk water while the effects depend on the frequency of the AC voltage such that the interfacial signal decreases with frequency but the bulk signal increases with frequency up to 221 Hz. These experimental

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results lead to a conclusion that the beam deflection is caused by the refractive index gradient in the bulk water region, which is formed transiently by the Pockels effect of interfacial water in the EDL when an AC electric field is applied. The refractive index gradient is caused by the diffuse layer spreading into the bulk region to work as a breaking factor of inversion symmetry of bulk water due to its charge-biased ionic distribution. This mechanism does not contradict the principle of nonlinear optics.

Keywords Pockels effect · Electro-optic effect · water · Sagnac interferometer · electric double layer · diffuse layer · ITO · Pt

1 Introduction

The Pockels effect is the second-order nonlinear optical effect, and the first order electro-optical effect. When an external electric voltage is applied to a material, the refractive index changes linearly to the electric field by the effect [1]. This effect has been used for balanced detection of terahertz wave, and for optical switching technologies. In these technologies, crystals without inversion symmetry are commonly used because the second-order nonlinearity is prohibited for materials with macroscopic centro-symmetry [1]. It is therefore believed that the Pockels effect or second-harmonic / sum-frequency generation (SHG / SFG) could not be observed for liquid, except for interfacial liquids such as solid-liquid or gas-liquid interface where inversion symmetry is broken
[2–4].

In fact, the Pockels effects of water on the electrode surface [water in the electric double layer (EDL)] [5–7] and that at the air-water interface [8] were reported.

The EDL in an aqueous solution is a structure that appears close to a charged surface [9, 10]. It can be divided into two layers. One is a compact layer which is composed of solvents, solute molecules, and solute ions adsorbed on the electrode surface. The other is a diffuse layer which is formed by balancing two competing driving mechanisms; double-layer formation mechanism by an electric field and mechanism causing diffusion of solute-ions into the bulk layer. In the study of sum frequency generation (SFG) spectroscopy to investigate the structure of interfacial water, it is known that the inversion symmetry of the diffuse layer is broken by the anisotropic orientation of water molecules near the interface, and the SFG signal increases when the interface is positively or negatively charged by an ionic surfactant [3, 4]. The thickness of the diffuse layer is given by the Debye-Hückel length to be in nm order for 0.1 M electrolyte aqueous solution.

Thus, an intense electric field in this thin layer makes it easier to detect the Pockels effect. The Pockels coefficient in the EDL is an order of magnitude larger than that of lithium niobate [5, 6], one of the typical nonlinear optical crystals. At the air-water interface, it is suggested that the Pockels coefficient is even larger [8]. The microscopic physical mechanism of these Pockels effects of the interfacial water, however, is yet to be resolved for further experimental and theoretical researches.

Surprisingly, as an intriguing result, the Pockels effect in the bulk water region was observed [11]. In that experiment, a laser beam was aligned to travel between two electrodes immersed in aqueous electrolyte solution. When the alternating electric field was applied perpendicular to the beam axis, the direction of the beam deflection was switched synchronously with the field alternation as expected for the Pockels effect. The effect was observed even when the beam is located a few mm away from the electrode, where the macroscopic centro-symmetry is preserved definitely for the Pockels effect to be invisible. In this respect, this can be named as the “anomalous” Pockels effect.

In this paper, we propose a plausible mechanism that best explains the anomalous Pockels effects, adding further experimental results to support the mechanism. Since it requires to detect a tiny spatial gradient of the refractive index, we combined the interferometry with the means of the synchronized detection. There are several interferometers for measuring the spatial information of the optical properties such as the Fizeau interferometer, the Sagnac interferometer [12–14], the phase shifted interferometer [15]. We employed the Sagnac interferometer because of its high sensitivity. A hypothetical assumption to approach the mechanism is the idea that the physical properties of the interface affect those of the bulk region. A similar idea has also been known as the rubbing method which controls the orientation of liquid crystal by polishing the surface of the electrode [16].

2 Anomalous Pockels effect

We begin by describing the difference between the “anomalous” and “normal” Pockels effects. The normal Pockels effect is a change in the refractive index, which is proportional to the electric field. The signal we observed is different from the normal Pockels effect in that it is a deflection angle θ of light caused by a refractive index gradient, which we will discuss later in chapter 4, ”Experimental setup.” The second-order nonlinear polarization, the physical background of Pockels effect, is expressed by Eq. (1).

$$P_i \propto \chi^{(2)}_{i,j,k} F_j E_k \tag{1}$$

where P_i, F_j, and E_k are the polarization, the externally applied electric field, and the optical electric-field, respectively, with (i, j, k) denoting x, y, z components in the x,y,z axes. $\chi^{(2)}$ denotes the second-order nonlinear susceptibility. For the centro-symmetric system, when the spatial inversion operation is applied, the vector changes its sign while $\chi^{(2)}_{i,j,k}$ does not. Then, we get

$$-P_i \propto \chi^{(2)}_{i,j,k}(-F_j)(-E_k) \tag{2}$$

Equations (1) and (2) are simultaneously satisfied only when $\chi = 0$. Therefore, the second-order polarization cannot be induced from $\chi^{(2)}$. Next, the relation between the deflection angle θ and E_x is expressed as in Eq. 3. The angle

θ is proportional to the gradient of the refractive index, which characterizes the anomalous Pockels effect.

$$\theta \propto \frac{\partial}{\partial x}(\chi^{(2)} F_x) E_x \tag{3}$$

When we apply inversion operation to Eq. 3, we get Eq. 4 as below.

$$-\theta \propto \frac{\partial}{\partial(-x)}(\chi^{(2)}(-F_x))(-E_x) \tag{4}$$

The situation here is different from that with equations (1) and (2). Nontrivial $\chi^{(2)}$ may satisfy both Eq. (3) and Eq. (4) even with the medium of spatial inversion symmetry. Thus, if there is a refractive index gradient which is not inversion symmetry, the Pockels effect can be observed by detecting deflection θ. However, it is still necessary that the inversion symmetry is broken in order to make $\Delta n \propto \chi^{(2)}(F_x)$ which is the origin of the Pockels effect be nonzero. Since the mechanism of generation of the refractive index gradient and the mechanism of occurrence of the state which breaks the inversion symmetry are not fully understood, we call this phenomenon "anomalous" Pockels effect.

Intuitive understanding is obtained from Fig. 1, where the principle for the Pockels effect to occur is schematically depicted.

In bulk water as shown in Fig. 1 (a), orientation of water molecules is inverted depending on the electric-field direction. The system is shifted equivalently from the symmetrical point in such a way that the sign of Δn to be changed equivalently. (The incident light of alternating electric field direction does not discriminate the orientational direction of water molecules.) In this case, the Kerr effect could take place [17], but not the Pockels effect. For SHG/SFG, on the other hand, the polarization is asymmetrically induced by the optical electric field incident from below [as shown in Fig. 1 (a)] and can generate SHG / SFG light. This is known as electric-field induced second harmonic (EFISH) generation [18]. This difference comes from the fact that EFISH is in principle the $\chi^{(3)}$ process of (applied electric field) × (optical electric field)^2, while the Pockels effect is the $\chi^{(2)}$ process of (applied electric field) × (optical electric field).

At solid-water or air-water interface as shown in Fig. 1 (b), existence of the interface shifts the system from the symmetrical point to give rise to the field-linear component in Δn, i.e., the Pockels effect. For the Pockels effect of water in the EDL to occur, the existence of the charge alternating electrode surface is essential, which breaks the inversion symmetry before the electric field is applied. Therefore it is still questionable how the field-proportional refractive index change is generated far away from the electrode, i.e., at the place where both water molecules and the optical electric field do not know the existence of the electrode.

This question could be answered positively by the following two factors: For observation of the anomalous Pockels effect,

(1) an alternating electric field is applied between the electrodes, so that the EDL is not well developed but only transiently formed. Thus, the diffuse layer may spread into the bulk water region.

In addition,

(2) aqueous solution of electrolyte is used. Thus, there is the gradient of the ion concentration in the diffuse layer, which is positively or negatively charged.

This situation is depicted in Fig. 2. Although the electrode surface does not exist, the Pockels effect in bulk water could occur due to the existence of the charge alternating ionic distribution gradient, as well as the Pockels effect in the EDL occurs due to the existence of the charge alternating electrode surface.

We shall come back to the possible mechanism described here in Sec. 10, after presenting various experimental results which support the mechanism.

3 Electrode material dependence of the Pockels effect both in the EDL and bulk water

The proposed model in this paper is based on the hypothesis that the observed Pockels effect occurred in the EDL. Within the EDL, the centrosymmetry is broken by the existence of the interface between water and electrodes resulting in the Pockels effect. On the other hand, the bulk water located far enough from the interface is evidently centrosymmetric. Despite this condition, the Pockels effect in bulk water was visible in the previous paper [11]. According to the known theory, the Pockels effect is not expected to be observed in this region. Question arises if this is a new result that contradicts the known theory. We reported the Pockels effect in bulk water in the experimental setup where two electrodes are of different materials, a combination of indium tin oxide (ITO) and Pt electrodes in [11]. Therefore, at that time, there is a possibility that this difference causes the breakdown of the symmetry. In this paper, we present new experimental results that exclude this possibility by showing that the signals can also be detected in the cases of the combinations of ITO-ITO and Pt-Pt. We also report that the size of the Pockels effect in bulk water depends sensitively on the material of the electrodes. The Pockels coefficient in the bulk water with ITO electrodes is greater than that with Pt electrodes by two orders of magnitude. In addition, we show that the magnitude of the Pockels effect in the EDL has the same tendency as that in the bulk water about the electrode-material dependence. Based on all these experimental results, we conclude that the Pockels effect of the bulk water is closely linked to the broken symmetry in the EDL.

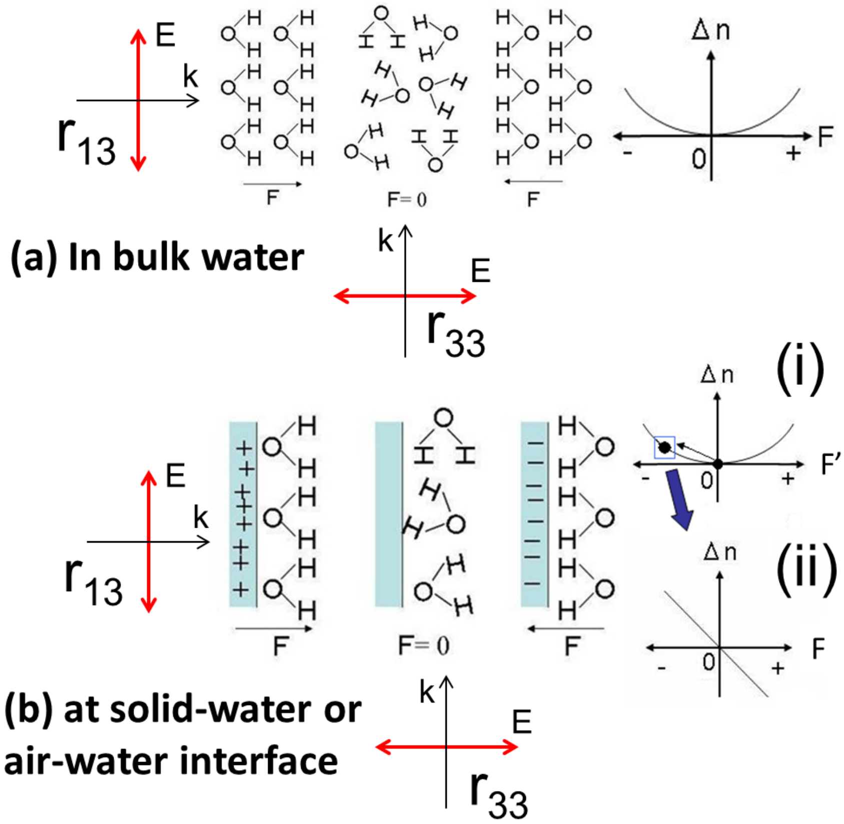

Fig. 1 Pockels effect of water requires broken inversion symmetry. (a) Bulk water. (b) Interfacial water. F:Applied electric field, k:Wavevector of incident light, E:Electric field of the incident light. In the case (b), the charged electrode breaks the symmetry. It makes the origin of the relationship between Δn and F to be shifted as shown in (i). Then, Δn vs. F becomes a locally proportional relationship as in (ii).

4 Experimental setup for the anomalous Pockels effect in bulk water

Figure 3 shows the experimental setup to detect the anomalous Pockels effect in bulk water. Laser light from a He-Ne laser (Model 32734, Research Electro-Optics, 633 nm, 3 mW) was incident on a beam splitter and divided into two directions. The beam diameter is about 1.4 mm at the detector. The transmitted beam traveled along the counter-clockwise pathway, and the reflected beam traveled along the clockwise pathway. There was a phase difference of π between the counter-clockwise beam and the clockwise beam on the photodiode due to the difference of the number of the fixed reflection. Therefore, these two beams were destructively superposed on the photodiode so that the detected

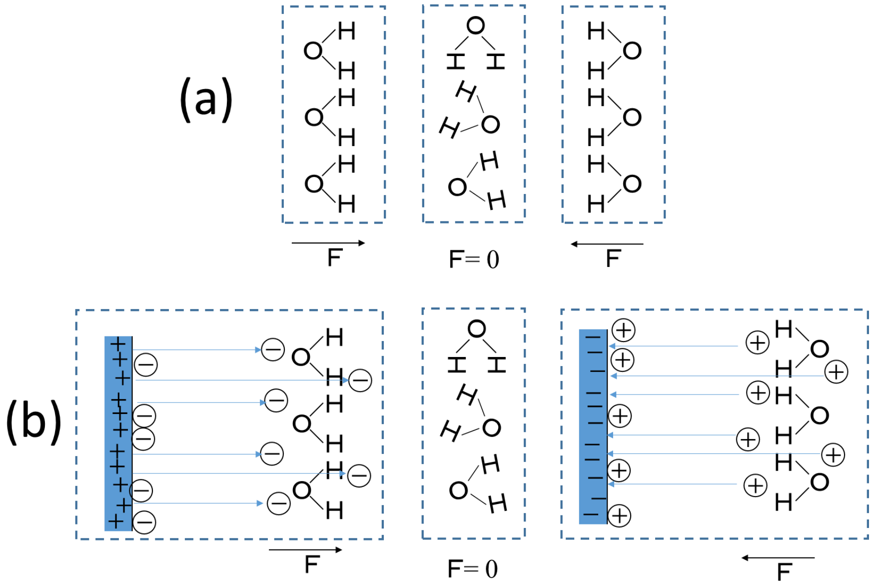

Fig. 2 The arrows show the directional vector of the electric field F produced by the electrode. (a) The case when only the orientation of molecular is considered. (b) The orientation of water molecule and the charge-biased distribution of the ions. In this figure, only the dominant ions (positive or negative) are displayed. In the case (b), the biased distribution of the ions causes the symmetry to be broken instead of the charged electrode.

photocurrent ideally became zero. When the beam deflection was induced by the refractive index gradient, the distance of the two beam spots on the photodiode increased, resulting in the sharp increase of photocurrent. We applied a lock-in amplifier to detection of the small increase in the photocurrent induced by the tiny deflection angle. The relation between the photocurrent and the distance between the two beam spots on the detector was simulated by assuming that the beam intensity cross-section took a Gaussian shape. In the range of a small variation as in this experiment, the photocurrent was proportional to the beam deflection. Finally, the amount of refractive index change was calculated from the deflection angle [11]. The measured sample was 0.1 M-NaCl aqueous solution. A glass cell was placed on the optical path and it was filled with the sample. The electrodes were inserted into the sample and an AC voltage of 4 V, from 25 to 1521 Hz was applied with a function generator. ITO and Pt were used as electrodes, as depicted by A and B in Fig. 3. The measured combinations were ITO-ITO, ITO-Pt and Pt-Pt. The specification of ITO was the same as in Ref. [6]. An independent ground electrode (Pt) was set to make a three-electrode system, which did not significantly affect the result. The surface of two electrodes A and B were set to be parallel to the light path. The distance between these electrodes was 4 mm and the area of the electrodes immersed in the solution was about 1.0 cm^2 The gradient of

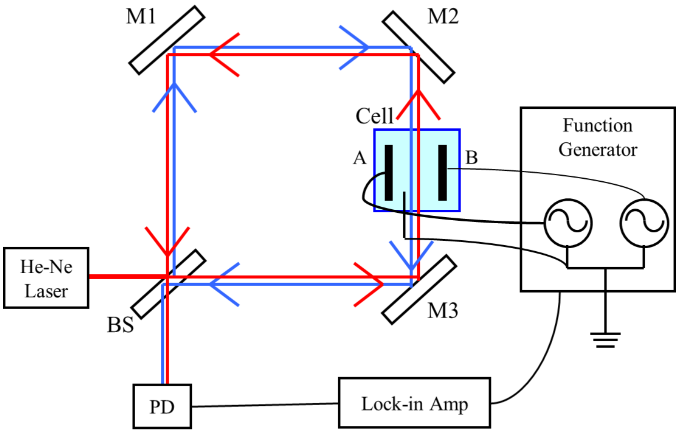

Fig. 3 Experimental setup for detecting the beam deflction produced by the Pockels effect.

the refractive index in the sample was produced by the external voltage and was detected with the photodiode in the interferometer.

5 Experimental results for the Pockels effect in bulk water

Fig. 4 (a) is a plot of the magnitude of the photocurrent response to an AC voltage as a bar graph for each electrode combination. The beam deflection was finally calculated to be 5 $\times 10^{-9}$ rad when ITO-ITO electrodes were used. By comparison of difference of photocurrent for each combination in Fig. 4, the case with ITO-ITO indicates an order of magnitude larger signal than the case with Pt-Pt. Fig. 4 (b) shows the frequency dependence of the anomalous Pockels effect signal in bulk water. Fig. 4 (c) shows the electrolyte (NaCl) concentration dependence of the signal. Fig. 4 (d) shows the dependence of the distance from the electrode surface to the beam edge. These (b), (c), and (d) are measured with ITO electrodes. We also tried to measure the dependence on the distance between the two electrodes and confirmed that the signal falls below the noise level when the distance is doubled (from 4 mm to 8 mm),

It is surprising that the size of the Pockels effect in the bulk region depends sharply on the electrode material, because the laser beam never feels what kind of material is used for the electrode. Before taking this dependence seriously, however, one should consider the possibility that the magnitude of the applied electric field in the bulk region may be different due to the difference in the impedances. To determine the Pockels coefficient with each electrode combination, we make the impedance measurement to estimate the voltage drop in the bulk region in the next section.

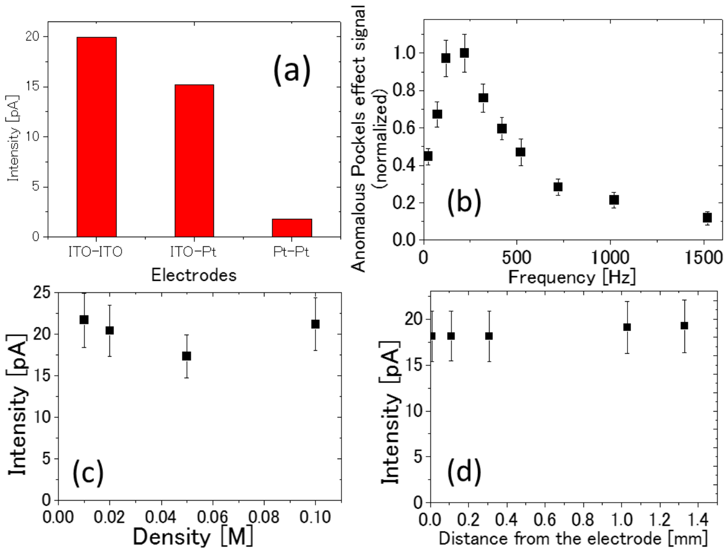

Fig. 4 The experimental results of the anomalous Pockels effect in bulk water. (a) The electrodes dependence of the signal at 221 Hz. (b) The frequency dependence of the signal. (c) Electrolyte concentration dependence of the signal at 221 Hz. (d) The signal vs. the distance from the electrode at 125 Hz. The plots (b), (c), and (d) are measured with ITO-ITO.

6 Complex impedance measurement

The information of the voltage in the bulk water is necessary to evaluate the Pockels coefficient, which is the proportionality constant between the refractive index and the applied electric field. The experimental setup of the cell and electrodes is the same as in Fig. 3. Impedance/Gain-Phase Analyzer (Model 1260, Solatron) and Potentiostat / Galvanostat (Model 1287, Solatron) were used to measure the complex impedance. The results for three different combinations of electrodes are shown as Cole-Cole plots in Fig. 5a,b, and c. The data points circled in the graphs are corresponding to frequency of 221 Hz. The fitting curves in the graph were calculated by using an equivalent circuit shown in Fig. 5d. For simplicity, the contribution from the electrode surfaces was set as a constant phase element (CPE) [19]. In the case at frequency of 221 Hz, the voltage drop in the bulk water is estimated as 0.2 V with ITO-ITO, 2.2 V with Pt-Pt, 0.8 V with ITO-Pt. The refractive index change can be estimated by the deflection angle [11]. Finally, we get the Pockels coefficient [6] r_{33} in each case as

40 pm/V with ITO-ITO,
0.4 pm/V with Pt-Pt, and
10 pm/V with ITO-Pt.

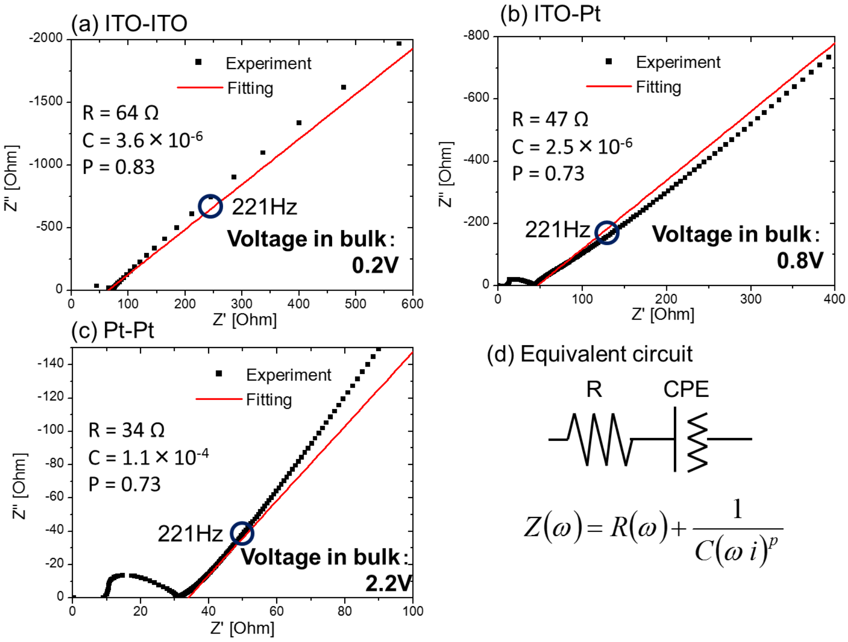

Fig. 5 a, b, c: The results and simulations of the complex impedance measurements for ITO-ITO, ITO-Pt, and Pt-Pt respectively. d: The equivalent circuit of the electrodes and aqueous solution. It consists of a DC resistance component $R(\omega)$ and a CPE component. ω : frequency of the applied electric voltage, C : capacitance, i : imaginary unit, p : CPE index ($p = 1$ makes a pure capacitor, $p = 0$ makes a pure DC resistance).

The results show that the Pockels coefficient of the bulk water with ITO-ITO electrodes is two orders of magnitude larger than the case with Pt-Pt. This difference in the Pockels coefficient is remarkable. Naturally we are tempted to examine whether the electrode material dependence of the Pockels coefficient of the interfacial water is the same. In the following sections, therefore, the Pockels effect of interfacial water on the Pt electrode is experimentally studied.

7 Experimental setup for the Pockels effect in the EDL

In our previous work [6], we measured the Pockels coefficient in the EDL by the electric field modulation transmission change spectroscopy. We measured the transmission change again to compare the signal between the case with ITO and with Pt. The experimental setup is shown in Fig. 6. A Laser-Driven Light Source (LDLS, Energetiq Technology) was used as a white light source. The aqueous solution and the ITO electrodes were the same as in Fig. 3. The Pt electrodes in Fig. 4 were prepared by sputtering. It consisted of a quartz substrate, a 5-nm-thick Cr contact layer and a 20-nm-thick Pt layer. The distance of two electrodes was 1 mm. The optical path was perpendicular to

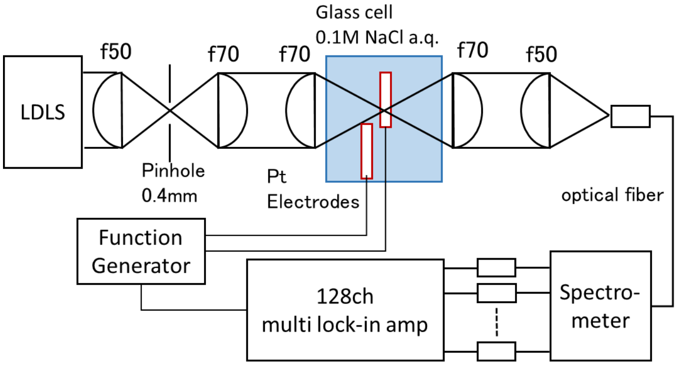

Fig. 6 The experimental setup for the electric field modulation transmittance change spectroscopy.

the electrode to which the light was incident, so that light traveled through the EDL. An AC voltage of 2 V, 21 Hz was applied to the sample. A 128-chanell lock-in amplifier [5, 6] was used to detect the transmission change spectra responding to the applied voltage.

8 Matrix method

The difference transmission spectrum was simulated by the matrix method [20, 21]. This provides both the transmittance and the reflectance of a multilayer system like Fig. 7(a). Let E_j and H_j be the electric and the magnetic field components in the j-th layer, respectively, which are parallel to the interface. The components in the adjacent layers are related by a characteristic matrix as shown below

$$\begin{pmatrix} E_{j+1} \\ H_{j+1} \end{pmatrix} = M_j \begin{pmatrix} E_j \\ H_j \end{pmatrix} \tag{5}$$

where

$$M_j = \begin{pmatrix} \cos \Delta_j & \frac{(i \sin \Delta_j)}{\eta_j} \\ i\eta_j \sin \Delta_j & \cos \Delta_j \end{pmatrix} \quad , \tag{6}$$

$$\Delta_j = \frac{2\pi N_j d_j \cos \Delta_j}{\lambda} \quad , \tag{7}$$

and η_j for P polarization and S polarization are expressed as

$$\eta_{jS} = N_j \cos \theta_j \text{ and } \eta_{jP} = N_j / \cos \theta_j \quad . \tag{8}$$

The characteristic matrix of the whole of the system is expressed by Eq. (9).

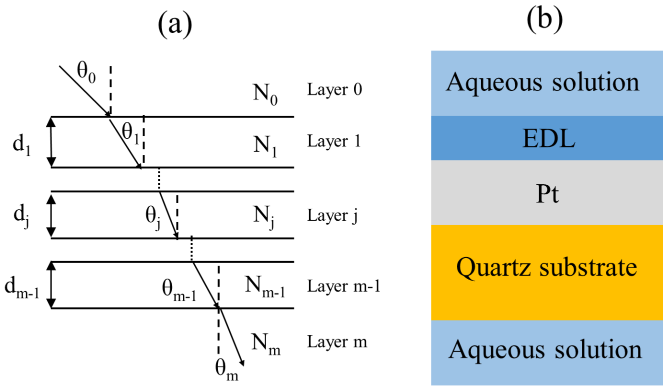

Fig. 7 Matrix method and the model of the multi-layer of the Pt electrode

$$M = M_1 \cdot M_2 \cdots M_j \cdots M_{m-1} \tag{9}$$

We define Y as E/H. Now we can connect the electric field of 0th layer and m-th layer, using $Y = E/H$, B, and C, as follows.

$$E_m \begin{pmatrix} 1 \\ Y \end{pmatrix} = M \begin{pmatrix} 1 \\ \eta_m \end{pmatrix} E_m = \begin{pmatrix} B \\ C \end{pmatrix} E_m \tag{10}$$

By using those B and C, the amplitude transmittance t is expressed as

$$t = \frac{2\eta_0}{\eta_0 B + C} \tag{11}$$

Now the energy transmittance of this multi-layer can be calculated as

$$T = Re\left(\frac{\eta_m}{\eta_0}\right) |t|^2 \tag{12}$$

We suppose that the aqueous solution, the electrode, and the EDL consist of a multi-layer as shown in Fig. 7(b). We calculated the transmittance of this system by the method explained above.

9 Experimental results for the Pockels effect of water in the EDL

The measured and simulated spectra of the transmittance change for the Pt thin film are compared in Fig. 8(a). The black line shows $\Delta T/T$, the transmittance change normalized by the original transmittance. The red line depicts the simulation of $\Delta T/T$ on the long wavelength side. The measured $\Delta T/T$ and $dT/d\lambda$, the derivative of the transmittance of the Pt electrode with respect to the wavelength, are simultaneously plotted in Fig. 8(b). The blue line shows $dT/d\lambda$ by which we can estimate how much the transmittance spectrum shifts.

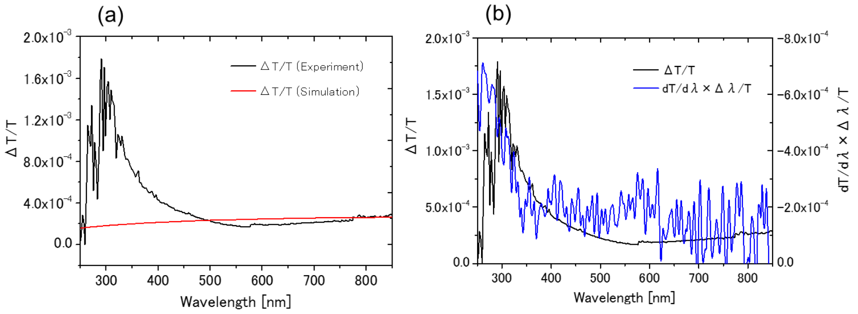

Fig. 8 The results of the electric field modulation transmittance change spectroscopy of the Pt film. (a) shows the comparison of the experimental result $\Delta T/T$ (black line) and the simulation of it (red line). (b) shows the comparison of the experimental result $\Delta T/T$ and the derivative of the transmittance with respect to the wavelength $dT/d\lambda$ (blue line).

By comparison of the black line and the blue line in Fig. 8(b), we can safely conclude that the transmittance change $\Delta T/T$ on the short wavelength side is produced by the shift of the transmittance spectrum of the electrode itself.

The red line in Fig. 8(a) is calculated by the matrix method (the detail is explained in chapter. 8). The literature data of the complex refractive index of Pt [25] is used with the simulation, but the refractive index change in the Pt layer is not considered. The EDL thickness was assumed to be 2 nm [6]. The transmittance of the system in two situations, with and without applied electric voltage, are simulated. For analysis we assumed that the transmittance change is caused only by the refractive index change in the EDL. It indicates that the evaluated Pockels constant is overestimated because there should be refractive index change due to the Pt layer which is considered to be dominant on the short wavelength side. In this case, we set the amount of refractive index change in the EDL as 0.0002 to fit the simulation curve to the experimental result. This value is more than two orders of magnitude smaller than that with ITO which we reported in the past paper [6] despite of the overestimate. This fact indicates that when Pt electrodes are used, the Pockels effect in the water-electrode interface is very small.

The frequency dependence of the Pockels effect of 0.1 M NaCl aqueous solution in the EDL on the ITO electrode is shown in Fig. 9. That of the anomalous Pockels effect is also plotted in Fig. 9 for comparison. Both two vertical scales are normalized. Implications of the frequency dependence in Fig. 9 are discussed in the next section.

10 Mechanism of the anomalous Pockels effect in bulk water

A plausible model to explain the origin of the anomalous Pockels effect can readily be drawn from the two experimental findings below.

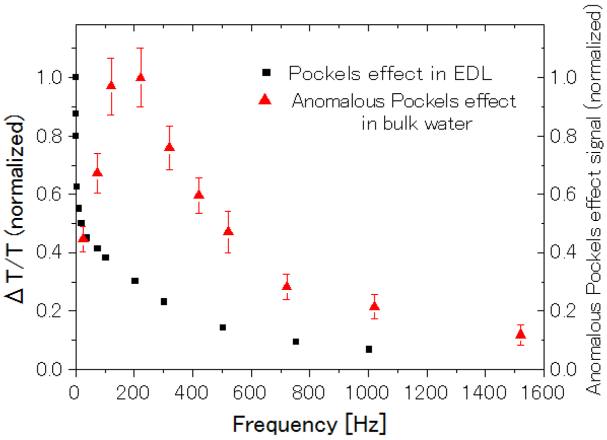

Fig. 9 The frequency dependence of the Pockels effect both in the EDL and in bulk water. The black squares show the normalized signal intensity of the Pockels effect in the EDL. The red triangles show the normalized signal intensity of the anomalous Pockels effect in bulk water. Both of data are measured with the ITO electrodes.

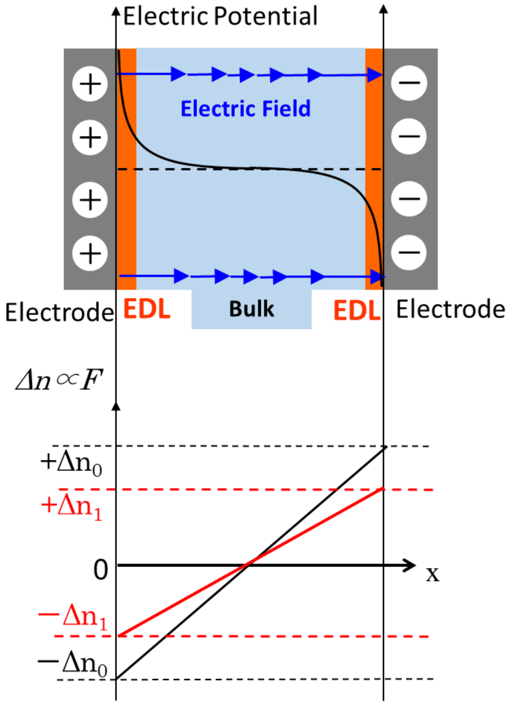

Fig. 10 The model which explains the Pockels effect at the interface is the origin of that in the bulk water.

(1) The Pockels constants of both bulk and EDL water are two orders of magnitude smaller for the Pt electrode than for the ITO electrode.

(2) As the electric-field modulation frequency is increased from zero to 200 Hz, the magnitude of the Pockels signal in the EDL water decreases while that in the bulk water increases.

That is, the Pockels effect in the bulk water is strongly correlated with that in the EDL water.

The upper half of Fig. 10 shows the schematic model of the electrodes, aqueous solution, and the graph of the electric potential. As already explained, the voltage drops drastically in the EDL so that the refractive index change there is larger than that in the bulk water. In the bulk water region, the refractive index gradient is much lower than in the EDL to be nearly constant. In fact, it is reported that the gradient of the refractive index in the bulk water is nearly constant [11]. Since the refractive index should be continuously varied from one electrode to the other, its spatial distribution can be characterized by the lower half of Fig. 10, although the actual gradient should be steeper near the both ends. The symbol Δn_0 denotes the refractive index change in the EDL on the electrodes. As the Δn is reduced from Δn_0 to Δn_1, the spatial distribution of the refractive index should change from the black line to the red line in Fig. 10. Thus, the Pockels constant in the EDL and in the bulk is positively correlated with each other. The larger Δn in the EDL becomes, so does the refractive index gradient in the bulk.

From the frequency dependence of the Pockels effect in the EDL (black squares in Fig. 9), the cutoff frequency is estimated to be 5-10 Hz. This corresponds to the time constant of τ approximately 20 to 40 ms, i.e., the formation time of the EDL. This value is reasonable in view of the formula for the voltage and concentration dependent time constant derived in Ref. [22], where the time-dependent development of EDLs is studied in detail by Morrow et al. The measurement of the anomalous Pockels effect in bulk water is performed around 220 Hz where the signal intensity becomes maximum (red triangles in Fig. 9). It is certain that the EDL is transiently formed under this condition.

It can be seen that the frequency dependent peak for the anomalous Pockels effect is shifted by about 200 Hz from that for the Pockels effect signal in the EDL. Below 100 Hz, the signal intensity of the anomalous Pockels effect tends to be attenuated as the frequency decreases, but the concrete value is not plotted because the signal intensity is buried below the noise floor, which increases with decreasing frequency. The data we have shown so far such as the concentration-, location-, and electrode-dependences have all been carried out from 125 to 221 Hz where the signal intensity is maximum. The attenuation of the signal strength with frequency in the EDL can be explained by the EDL being insufficiently developed (resulting in the thicker diffuse layer) because the formation of the EDL cannot follow fast alternation of the polarity of the field. The frequency dependence of the anomalous Pockels effect in bulk water is composed of two factors. One is an increase in the distribution ratio of the voltage drop to the bulk region due to the expansion of the EDL (diffuse layer) with increasing frequency. This effect is dominant at low frequencies to increase the signal magnitude. The other is that the formation of ion distribution in the bulk region cannot follow the fast alternation of the field direction. This effect is dominant at high frequencies to decrease the signal magnitude. Around 220 Hz where the two effects are balanced, the signal intensity is maximized and a spatial distribution where the electric field gradient is close to constant is formed, resulting in nearly constant position dependence in Fig. 4 (d).

It is also not obvious why no significant electrolyte-concentration dependence is observed in the range of 0.01 M to 0.1 M as shown in Fig. 4 (c). By remarked contrast, the magnitude of the Pockels effect in the EDL shows the dependence of the square root of the concentration M such as $M^{1/2}$ [5, 6]. Since the thickness of the diffuse layer is given by the Debye-Hückel length $\lambda_D = 0.304M^{-1/2}$ nm, the field strength in the EDL increases proportionally to $M^{1/2}$, so that the $M^{1/2}$ dependence in the Pockels effect in the EDL is reasonable. Nearly constant concentration dependence for the anomalous Pockels effect, on the other hand, might be explained as follows. As the concentration M is decreased, the formation time of the diffuse layer increases as about $M^{-1/2}$ [22] or M^{-1} [23] and the thickness of the well-developed diffuse layer increases as $M^{-1/2}$, so that the diffuse layer spreads more and more into the bulk region as M is decreased to keep the anomalous Pockels effect nearly constant. Rich information may be obtained if the concentration and location dependences are measured and compared at all frequencies, but this is left for a future task.

The strong dependence on the electrode materials is an important result for clarifying the microscopic mechanism of the Pockels effect of water in the EDL. Previously Kanamaru et al. [7] reported that the Pockels constants of water on the GaN electrode is smaller than that on the ITO electrode. The present result indicates that the constant on the Pt electrode is much smaller than on the ITO and GaN electrodes. In addition, recently the Pockels effects of polar organic solvents on the ITO electrode were reported [24] to suggest that the hydrogen bond is important for the Pockels effect to take place. The electrode material dependence revealed in the present paper also agrees with this suggestion, possibly providing a significant step for resolving the mechanism.

11 Conclusion

In this paper, we have reported the dependence of the anomalous Pockels effect in bulk water on the electrode materials. The experimental results denote that the Pockels coefficient in the bulk water in the case with ITO electrode is two orders of magnitude greater than that with Pt electrodes. Similarly, it is found that the Pockels effect of interfacial water in the EDL on ITO is orders of magnitude larger than on Pt. Based on these observations, it is concluded that the Pockels effect in bulk water is caused by the existence of the Pockels effect in the EDL. In other words, the Pockels effect in bulk water is one of the expressions of the fact that the physical property of the bulk water and the water-electrode interface are mutually correlated. This is because the refractive index gradient in the bulk water region (anomalous Pockels effect) is induced by the refractive index change of water on the electrode surface (Pockels effect in the EDL). The refractive index gradient is generated in the process of transient formation of the EDL with an alternating electric field. The diffuse layer transiently spreads into the bulk water region accompanied by the charge-alternating ionic distribution gradient. This distribution induces the electric-field gradient to produce the refractive index gradient under broken inversion symmetry due to the charged ionic distribution. This model is well supported by the anticorrelated frequency dependence between the bulk and EDL signals. To finally resolve the mechanism, however, further study is required such as the study of the position and electrolyte concentration dependences of the anomalous Pockels effect in a wide range of frequency.

12 Conflicts of interest

There are no conflicts of interest to declare.

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