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Developments and Applications of Electrochemical Measurement Methods Using Light as a Probe or an Excitation Source

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In the last fifty years, many electrochemical measurement methods using light have been developed and applied to investigations of various kinds of electrode reactions. Most of these methods belong to spectroelectrochemical ones, in which light is used as a probe. On the other hand, we have intended to positively use light in the methods as an excitation source. In this article, I will first review the applications of attenuated total reflection (ATR) in the visible region to the investigations of electrode reactions, that is, the electrode reaction of a redox indicator and the deposition/stripping of Ag and Hg. In addition, the application of ATR to adsorption of water-soluble porphyrin at a glass/solution interface will be reviewed, although the adsorption is not an electrode reaction. Subsequently, the electrochemical measurement methods using laser ablation and laser heating, that is, laser ablation voltammetry (LAV) and thermal modulation voltammetry (TMV) will be reviewed together with the results obtained from the methods.

1. Attenuated total reflection^{1), 2)}

Figure 1 shows the aspect where a light beam is totally reflected at an interface between optically denser and rarer phases. When the light beam goes to the rarer phase from the denser phase with the angle of incidence, θ , more than the critical angle, θ_c , the beam is totally reflected at the interface and the evanescent wave is formed at the interface on the side of the rarer phase. At the time, if the rarer phase is opaque, the evanescent wave is absorbed by optically absorbing species contained in the rarer phase and consequently

the beam is no longer totally reflected. This optical phenomenon is called attenuated total reflection (ATR). Since the penetration depth of the evanescent wave into the rarer phase is not more than the wavelength, ATR spectroscopy is very sensitive to any optical changes at the interface. Based on this advantage, ATR has been widely applied to spectroelectrochemical studies.

1-a. ATR spectroscopy coupled with staircase voltammetry³⁾

ATR spectra were measured at every step

Fig. 1 Attenuated total reflection (ATR).

of the staircase potential scan (a minimum step voltage 2.5 mV, a minimum step interval 0.1 ms) for an electrode reaction of variamine blue (*N*-(*p*-methoxyphenyl)-phenylenediamine). A tin oxide electrode was used as the optically transparent electrode. Variamine blue is well known as a redox indicator and is oxidized on the tin oxide electrode to form a blue species in acidic solution, as shown in the following reaction scheme.

Figure 2 shows ATR spectra measured at the potentials during the staircase potential scan. As can be seen in this figure, the ATR spectra with an absorption maximum at approximately 550 nm began to emerge at the potentials more than 0.4 V vs. at SSE (sat. Ag/AgCl) and leveled off at the potentials more than 0.6 V. Taking into account that the mid potential obtained by cyclic voltammetry was 0.5 V, it could be said that this change of the spectra with the potential is reasonable.

1-b. Reflectivity change–electricity curve for electro-deposition and stripping⁴⁾

Fig. 2 ATR spectrum of variamine blue at each potential during the staircase potential scan. θ was 70° . [T. Hinoue, S. Okazaki, T. Nagaoka, K. Masuda, and T. Fujinaga, *Anal. Chim. Acta*, **136**, 385 (1982).]

The reflectivity change was measured at θ of 72° for the deposition and stripping processes of Ag and Hg on the tin oxide electrode. The reflectivity change ($\Delta R/R_0$) is expressed as follows:

$$\begin{aligned}
 \Delta R/R_0 &= 1 - R/R_0 \\
 &= \frac{1}{n_1 \cos \theta_1} \left(n_2 \alpha_2 \langle E^2 \rangle_{\text{av},2} h_2 + n_3 \alpha_3 \langle E^2 \rangle_{\text{av},3} h_3 \right). \quad (1)
 \end{aligned}$$

Here, n_1 , n_2 , and n_3 denote refractive indices of the glass reflection plate on which the tin oxide film is formed, the tin film layer, and the deposition one, respectively. θ_1 is the angle of incidence. α_i , $\langle E^2 \rangle_{\text{av},i}$, and h_i ($i = 2, 3$) are the absorption coefficient of the layer, the average light strength in the layer, and the height of the layer, respectively. This expression suggests that the reflectivity change is proportional to the height of the deposition layer that corresponds to the electricity required for the deposition, q . Figures 3 and 4 show the $\Delta R/R_0 - q$ curves measured during three successive cyclic potential scans for Ag and Hg, respectively. In the case of Ag, the difference between the reflectivity changes at the initial

Fig. 3 $\Delta R/R_0$ at 400 nm – q curve for the deposition and stripping of Ag: 1.2 mM AgNO_3 in 1.0 M KNO_3 , 10 mV s^{-1} . [T. Hinoue, S. Okazaki, and T. Fujinaga, *J. Electroanal. Chem.*, **133**, 195 (1982).]

Fig. 4 $\Delta R/R_0$ at 500 nm – q curve for the deposition and stripping of Hg: 1.2 mM $\text{Hg}(\text{NO}_3)_2$ in 1.0 M KNO_3 and 0.013 M HNO_3 , 10 mV s^{-1} . [T. Hinoue, S. Okazaki, and T. Fujinaga, *J. Electroanal. Chem.*, **133**, 195 (1982).]

and final potentials at each cyclic scan decreased with increasing number of the cyclic scan. In particular, the difference in the first cyclic scan was larger than those in the second and third scans. This fact can be explained by under potential deposition (UPD) of Ag on the tin oxide electrode. The first deposition

directly occurs on a fresh electrode surface of tin oxide and consequently Ag (metal) deposited at the under-potential cannot completely be stripped during the reverse potential scan. However, the second and third depositions occur on the surface partially covered with Ag. Ag deposited on Ag can be readily stripped. As a result, the difference in reflectivity change in the first cyclic scan is larger than those in the second and third cyclic scans. In the case of Hg, the electricity increased with increasing number of the cyclic scan, although the reflectivity change was kept almost constant. This behavior implies that the deposition layer of Hg is stripped by a chemical process which is not an electrode reaction. In fact, the disproportionation reaction of Hg, that is, $\text{Hg (metal)} + \text{Hg}^{2+} \rightarrow 2\text{Hg}^+$, is well known.⁵⁾ This reaction is a course of the behavior of the reflectivity change during the cyclic scan mentioned above.

1-c. Adsorption of water-soluble porphyrin at a glass-water interface in the presence of cationic surfactant^{6), 7)}

ATR spectroscopy was applied to an adsorption study at a glass-water interface. The ATR spectrophotometer used is shown in Fig. 5. The spectrophotometer was a single-beam type. The monochromatic light was reflected only once at the glass-sample solution interface and the angle of incidence was variable. Water-soluble porphyrin (5,10,15,20-tetraphenylporphyrin tetrasulfonic acid, TPPS) and cetyltrimethylammonium bromide (CTAB) were used in this work. Since TPPS exists in a

Fig. 5 Single-beam type spectrophotometer for ATR in the visible region: LS, light source (halogen lamp); M, monochromator; P, polarizer; HP, hemicylindrical ATR prism (glass); S, sample solution; PM, photomultiplier; G, goniometer; T, thermostat; PC, personal computer; L1 and L2, lenses. [J. Kobayashi, T. Hinoue, and H. Watarai, *Bull. Chem. Soc. Jpn.*, **71**, 1847 (1998).]

form of TPPS^{4-} at pH 5.9, TPPS^{4-} is not usually adsorbed on the glass surface negatively charged. However, TPPS^{4-} is adsorbed with micelles formed by CTA^+ on the glass surface, which is called *admicelle*. Figure 6 shows ATR spectra of TPPS^{4-} at the glass-water interface in the absence (a) and in the presence (b) of CTAB. Comparison between the spectra clearly shows the effect of CTAB. In the absence of CTAB, no absorption bands of TPPS^{4-} were found, which indicates that TPPS^{4-} is not adsorbed, whereas in the presence, the bands appeared at 402.5 and 417.5 nm, indicating that TPPS^{4-} is adsorbed. No bands were found in the spectrum (a), although TPPS^{4-} has a large molar absorption coefficient of approximately $5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ($\text{M} = \text{mol}^{-1} \text{ cm}^{-1}$). This is because an optical path, called an effective thickness, is extremely short ($\sim$ the wavelength) in ATR spectroscopy. The two absorption bands at 402.5 and 417.5 nm were assigned to the species of TPPS^{4-}

Fig. 6 ATR spectra of TPPS^{4-} at the glass-water interface: $[\text{TPPS}^{4-}] = 1.00 \times 10^{-6} \text{ M}$, pH 5.9. The angle of incidence was 70° . [J. Kobayashi, T. Hinoue, and H. Watarai, *Bull. Chem. Soc. Jpn.*, **71**, 1847 (1998).]

associated with CTA^+ at a ratio of 1 to 4 and 1 to 7, respectively. The 1-to-4 species, $\text{TPPS}^{4-}-(\text{CTA}^+)_4$, has no charge and may be simply precipitated on the glass surface. On the other hand, the 1-to-7 species is TPPS^{4-} incorporated into the admicelle of CTA^+ . From the pH dependence of the adsorption of the 1-to-7 species, the maximum surface concentration, Γ_{max} , and the adsorption constant, $K'_{\text{ad}} (= \Gamma_{\text{max}} \times K_{\text{ad}})$ were determined to be $1.72 \times 10^{-11} \text{ mol cm}^{-2}$ and 11.7 cm , respectively. Here

$$K'_{\text{ad}} = \frac{[\text{TPPS}^{4-}(\text{CTA}^+)_{\text{admicelle}}]}{[\text{TPPS}^{4-}] \times [(\text{CTA}^+)_{\text{admicelle}}]}$$

In addition, it was also suggested that the admicelle is formed by seven CTA^+ s and one TPPS^{4-} is attached to the surface of the admicelle. At the end of this section, the schematic illustration of the adsorption of TPPS^{4-} at the glass-water interface in the presence of CTAB is shown in Fig. 7.

Fig. 7 Schematic illustration of the adsorption mechanism of TPPS⁴⁻ at the glass-water interface in the presence of the admicelles of CTAC⁺. [J. Kobayashi, T. Hinoue, and H. Watarai, *Bull. Chem. Soc. Jpn.*, **71**, 1847 (1998).]

2. Laser ablation

Laser ablation is one of physical actions caused by a strong and short laser pulse. As soon as the laser pulse hits a material, its surface is explosively etched to emit various forms of the material such as atom, molecule, ion, cluster together with light emission. Consequently, laser ablation has been used in many fields of mechanical machining, thin film manufacturing, preparation of particles and clusters, chemical analyses, light sources, medical treatments, energy etc. In electro-analytical chemistry, it has been reported that several kinds of carbon electrodes are activated by treating with laser ablation.⁸⁾⁻¹¹⁾ Figure 8 shows cyclic voltammograms of 1 mM catechol in 0.1 M H₂SO₄ on a glassy carbon

Fig. 8 Cyclic voltammograms of catechol on the glassy carbon electrode treated (a) and untreated (b) by the laser ablation: A pulse laser used was a Q-switched Nd:YAG laser. The energy was 350 mJ/pulse at 1064 nm and the pulse width was 5 ns. The diameter of the electrode was 1 mm. The scan rate was 50 mV s^{-1} .

electrode treated (a) and untreated (b) by the laser ablation. This figure clearly shows that the voltammogram on the treated electrode is well defined compared with that on the untreated electrode.

2-a. Laser ablation voltammetry

We proposed a new voltammetric technique, in which an electrode surface is successively treated (renewed) by laser ablation every several seconds, and named this technique laser ablation voltammetry (LAV).¹²⁾ Figure 9 shows the LA voltammogram of $[\text{Fe}(\text{CN})_6]^{4-}$. The voltammogram is a stationary one with a limiting current. In addition, because of the large vibration in current caused by each laser ablation, the voltammogram is like a polarogram measured with a dropping mercury electrode. The log-plot analysis of the voltammogram corrected by that of the blank solution gave the half-wave potential of 0.22 V and the slope of 59 mV. The advantages of

Fig. 9 Laser ablation voltammograms of $[\text{Fe}(\text{CN})_6]^{4-}$ in 1 M KCl (a) and the blank solution (1M KCl) (b): The working electrode used was a Pt rod of 2 mm in diameter. The pulse laser used was a Q-switched Nd:YAG laser. The energy was 350 mJ/pulse and the pulse width was 5 ns. The wavelength was 1064 nm and the spot size was 5 mm in diameter. The ablation interval was 2 s. Each arrow denotes the potential at which the current reversed its direction. [T. Hinoue, I. Watanabe, and H. Watarai, *Chem. Lett.*, **25**, 329 (1996).]

LAV are as follows. 1) Since the laser ablation can instantaneously remove fouls produced during the electrolysis, the electrode surface is constantly kept fresh and consequently the voltammogram can be reproducibly measured. 2) Since the laser ablation gives a physical shock to the electrode, the diffusion layer is renewed every laser ablation and thereby the shape of the voltammogram becomes an S-shaped curve with a limiting current. 3) Activation of the electrode is expected. In particular, the advantage 1) is very effective for investigating electrode reactions of organic substances likely to foul the electrode surface.

As an example of studies by LAV, the LA voltammetric study of ascorbic acid (AA) is shown below.¹³⁾ Figure 10 shows the LA voltammograms of AA at different pHs. As can be seen in this figure, one oxidation wave can be found throughout the pH region from 1.9 to 12.2 and an additional oxidation wave appears at pHs above 6. Both waves shifts to a

Fig. 10 pH dependence of the laser ablation voltammogram for oxidation of ascorbic acid: (a) pH 1.9, (b) pH 8.0, (c) pH 12.0. The concentration of AA was 5.00 mM. The pulse laser used was the Q-switched Nd:YAG laser. The energy was 350 mJ/pulse and the pulse width was 5 ns. The ablation interval was 2 s. [T. Hinoue, N. Kuwamoto, and I. Watanabe, *J. Electroanal. Chem.*, **466**, 31 (1999).]

Fig. 11 pH dependence of the half-wave potential, $E_{1/2}$, obtained by the log-plot analysis of the LA voltammograms shown in Fig. 10. [T. Hinoue, N. Kuwamoto, and I. Watanabe, *J. Electroanal. Chem.*, **466**, 31 (1999).]

more negative potential region with increasing pH and are completely superimposed with each other at pH 12. From the pH dependence of the half-wave potential (Fig. 11) and the dissociation constants of AA, that is, $pK_{a1} = 4.0$ for $AH_2 \rightleftharpoons AH^- + H^+$ and $pK_{a2} = 11.3$ for $AH^- \rightleftharpoons A^{2-} + H^+$,¹⁴⁾ it was concluded that the first oxidation wave in the pH region from 1.9 to 5.0 was due to the electrode reaction of $AH_2 - 2e^- \rightarrow DHA + 2H^+$ and that in the pH region from 5.0 to 10.2 was due to $AH^- - 2e^- \rightarrow DHA + H^+$. Here, AH_2 , AH^- , A^{2-} and DHA denote the fully protonated AA, mono-protonated AA, unprotonated AA and dehydroascorbic AA, respectively. At pHs above 10.2, it was implied from the slope $-76 \text{ pH}^{-1} \text{ mV}$ that two electrons and two hydroxide ions were involved. On the other hand, the electrode reaction for the second oxidation wave was complicated, though the slope was -87 mV pH^{-1} . In fact, it has been reported that the second wave is strongly dependent on the structure of the electrode source.¹⁵⁾

2-b. Determination of point of zero charge¹⁶⁾

In a LA voltammogram, the potential, at which the current is zero, frequently appears. The total current, I_t , observed immediately after the laser ablation is expressed as follows:

$$I_t = (dq/dt) + I_a + I_c \quad (2).$$

Here, q is the electric charge on the electrode, I_a and I_c denote the anodic and cathodic faradaic currents, respectively. When no faradaic processes occur, $I_a = I_c = 0$. Thus, if I_t becomes 0 at a certain potential, q is 0 at the potential. Such a potential is considered to be the potential zero charge (PZC). From this anticipation, it is expected that LAV can be used as a measurement technique of PZC of a solid electrode. Figure 12 shows the cyclic and LA voltammograms measured on the Mo electrode. The cyclic voltammogram showed no waves, suggesting that no faradaic process occurred. On the other hand, the current in the LA voltammogram varied with a large amplitude every laser ablation. Such a variation in current results from agitation of the electric charge on the electrode by the laser ablation. The amplitude reduced with increasing potential, disappeared at the potential of -0.54 V , and increased again.

Based on the above consideration, the zero current potential in the LA voltammogram corresponds to PZC. The open circles in Fig. 13 indicate the zero current potentials determined by LAV and the solid circles are the PZC determined by the ac impedance method. The zero point potentials and the PZCs fairly agreed with each, which demonstrates that the zero current potential corresponds well to PZC. Figure 13 also shows

Fig. 12 A LA voltammogram and a cyclic voltammogram on a Mo electrode in phosphate buffer solution (pH 6.97). [K. Nakamura, M. Ohno, K. Umemoto, and T. Hinoue, *Chem. Lett.*, **29**, 1050 (2000).]

Fig. 13 Zero current potentials obtained by LAV (open circles) and PZCs (solid circle) determined by the ac impedance method (1 kHz) in phosphate buffer solutions with different pHs. [K. Nakamura, M. Ohno, K. Umemoto, and T. Hinoue, *Chem. Lett.*, **29**, 1050 (2000).]

the pH dependence of the PZC on the Mo electrode. The PZC linearly decreased with respect to pH with a slope of -61.9 mV pH^{-1} . This linear decrease may be due to the acid–base equilibrium on the oxide layer of the Mo electrode, since it is likely that high temperature and pressure induced by the laser ablation form the oxide layer.

3. Laser heating

In general, when a material absorbs light,

heat generates through a non-radiative process. Based on this heat generation, we can heat only an electrode in a solution using a laser beam of an excellent directionality. On the other hand, the standard potential of an electrode reaction, E° , depends on the temperature, and its temperature coefficient gives the standard entropy change, ΔS° . For the electrode reaction of $\text{Ox} + ne^- \rightleftharpoons \text{Red}$,

$$\Delta G^\circ = -nFE^\circ. \quad (3)$$

Here ΔG° is the standard Gibbs energy change.

From the relation of $G = H - TS$,

$$(\partial G / \partial T) = -S. \quad (4)$$

Accordingly,

$$\Delta S^\circ = nF (\partial E^\circ / \partial T). \quad (5)$$

From Eqs. (3), (4), and (5), the standard entropy change can be determined by measuring the standard potentials at different temperatures and subsequently calculating its temperature coefficient. Such a procedure is a classical one for determining the standard entropy change, and has been often carried out by potentiometry.

3-a) Thermal modulation voltammetry with a solid electrode¹⁷⁾

We proposed a voltammetric technique for examining the standard entropy change, using the laser heating mentioned previously, and have been developing new voltammetry, called, thermal modulation voltammetry (TMV). Figure 14 shows the principle of TMV. For simplicity, only the case where the standard entropy change is positive is shown. The solid curve (a) corresponds to a linear sweep voltammogram including a Nernstian oxidation wave measured at the temperature T . When the

Fig. 14 Principle of thermal modulation voltammetry. [T. Hinoue, R. Harui, T. Izumi, I. Watanabe, and H. Watarai, *Anal. Sci.*, **11**, 1 (1995).]

temperature is changed from T to $T + \Delta T$, the voltammogram is shifted to the positive potential region to be the broken curve (b), as expected from Eq. 5. When the temperature is periodically changed and the difference between the currents at T and $T + \Delta T$ is recorded as a function of the potential, the resultant curve becomes the dashed curve (c). The curve (c) corresponds to a thermal modulation (TM) voltammogram. On the other hand, even in the case of a linear sweep voltammogram including a nernstian reduction wave, the solid curve (d), corresponding to the voltammogram at T , shifts to the positive potential region to be the broken curve (e), corresponding to the voltammogram at $T + \Delta T$. The difference between them results in the dashed curve (f). The curves (c) and (f) are not entirely symmetric, since the diffusion coefficient increases with the temperature and thus the limiting current increases. In order to perform the principle of TMV, we composed

Fig. 15 Apparatus for thermal modulation voltammetry: The upper is a schematic diagram of the apparatus, and the lower is a flow electrolytic cell. [T. Hinoue, R. Harui, T. Izumi, I. Watanabe, and H. Watarai, *Anal. Sci.*, **11**, 1 (1995).]

an apparatus for TMV shown in Fig. 15. The laser beam from the Ar^+ ion laser (10 mW at 488 nm) is chopped at a frequency of 50 Hz with the mechanical chopper and the intermittent beam is generated. The intermittent beam impinges upon the Pt microelectrode 10 μm in diameter in the flow electrolytic cell through the cover glass and the sample solution. The current signal from the potentiostat is amplified with the lock-in amplifier and the output signal from the lock-in amplifier is recorded as a function of the potential. TM voltammograms obtained in this way are shown in Fig. 16, together with the linear sweep voltammograms. The voltammograms of (a) and (b) were measured for sample solutions containing 5.0 mM $[\text{Fe}(\text{CN})_6]^{4-}$ and 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-}$,

Fig. 16 Thermal modulation voltammograms and cyclic voltammograms for $[\text{Fe}(\text{CN})_6]^{4-}$ (a) $[\text{Fe}(\text{CN})_6]^{3-}$ (b) and the blank solution (c). The electrode used was the Pt electrode of 10 mm in diameter. The scan rate was 10 mV s^{-1} . The details are described in the text. [T. Hinoue, R. Harui, T. Izumi, I. Watanabe, and H. Watarai, *Anal. Sci.*, **11**, 1 (1995).]

respectively. The voltammograms of (c) was measured for a blank solution containing 1 M KCl and 5.0 mM KCN. All the linear sweep voltammograms showed a well-defined shape and all the TM voltammograms showed the peaks in the same direction (upturned) at approximately the half-wave potentials, as can be expected from Fig. 14. In addition, taking account into that the standard entropy change

of the electrode reaction, $[\text{Fe}(\text{CN})_6]^{3-} + e^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$ is known as $-175 \text{ J K}^{-1} \text{ mol}^{-1}$,¹⁸⁾ it is reasonable that the peaks of the TM voltammograms were upturned. In this work, we did not determine the standard entropy. However, we applied TMV to ion transfer voltammetry to practically determine values of the standard entropy change of ion transfer.

3-b. Thermal modulation voltammetry at a liquid/liquid interface^{19), 20)}

TMV was applied to ion transfer voltammetry at a liquid/liquid interface to determine the standard entropy change of ion transfer. In TMV at a liquid/liquid interface, the principle and the apparatus were basically the same as those of TMV with a solid electrode mentioned above, except for a heating source (a laser) and an electrolytic cell. The intersectional view of the electrolytic cell for TMV at a liquid/liquid interface is shown in Fig. 17.

The organic phase (nitrobenzene, NB) and the aqueous phase (W) were separated with a polyester film 16 μm thick with a micro-hole 30 μm in diameter. A He-Cd laser was used as the heating source. The laser beam (13.0 mW at 325.0 nm) was mechanically chopped and was introduced to the micro-hole at the NB/W interface. The aqueous phase is transparent at 325.0 nm, whereas the NB phase is opaque. Consequently, the laser beam is entirely absorbed in the NB phase, as soon as the beam enters the NB phase through the aqueous phase. The absorbed light energy is converted to heat in the NB phase to warm the interfacial region. In this way, the temperature is periodically

Fig. 17 Electrolytic cell for TMV at a nitrobenzene (NB) / aqueous solution (W) interface.

changed at the chopping frequency (10 Hz in this work). The current for ion transfer is modulated by the periodic temperature change and the amplitude of the modulated current is amplified with the lock-in amplifier. The modulation amplitude is recorded as a function of the potential and thus a TM voltammogram is obtained.

The expression was proposed to concretely obtain values of the standard entropy change from TM voltammograms. The expression was basically derived by differentiating an S-shaped current–voltage curve, that is, a nernstian linear sweep voltammogram with respect to the temperature, T .

$$\Delta S_{tr}^{\circ, O \rightarrow W} = \frac{2RT}{D_W} \times \left(\frac{dD_W}{dT} \right) \times \left(\frac{\Delta T_d}{\Delta T_i} \right) \times \left[1 - 2 \left(\frac{\Delta I_{E1/2}}{\Delta I_l} \right) \right] \quad (6)$$

Here $\Delta S_{tr}^{\circ, O \rightarrow W}$ is the standard entropy change of ion transfer from the organic phase to the aqueous one. D_W is the diffusion coefficient of an ion of interest in the aqueous phase. (dD_W/dT) is a temperature coefficient of the diffusion coefficient, which was determined from a slope of the limiting current vs. temperature plot. ΔT indicates the temperature change amplitude caused by the periodic laser heating. The $(\Delta T_d/\Delta T_i)$ represents a ratio of the averaged amplitude in the diffusion layer to that at the interface. In practice, the ratio was experimentally obtained by measuring the TM voltammogram of a standard ion (tetraethylammonium ion), the standard entropy change of which is already known. $\Delta I_{E1/2}$ and ΔI_l are the signal intensities of the TM voltammogram at the half-wave potential and at the potential in the limiting current region, respectively (see Fig. 18). Practically, ΔI_l was the averaged value at the potentials in the limiting current region.

Fig. 18 $\Delta I_{E1/2}$ and ΔI_l in Eq. (6): $E_{1/2}$ and E_l indicate the half-wave potential and the potential in the limiting current region. The curve is the TM voltammogram when the standard entropy change is negative.

Fig. 19 Linear sweep voltammograms (a) and thermal modulation voltammograms (b) of ion transfer: 1, blank solution (1.00 mM MgSO_4 in the aqueous phase and 0.5 mM BTPPATPFB in the NB phase); 2, TMA^+ ; 3, TEA^+ ; 4, TPrA^+ ; 5, TBA^+ . The concentrations of the tetraalkylammonium ions were all 0.5 mM. [T. Hinoue, E. Ikeda, S. Watariguchi, and Y. Kibune, *Anal. Chem.*, **79**, 291 (2007).]

Figure 19 shows the linear sweep voltammograms (a) and the TM voltammograms (b) for four kinds of tetraalkylammonium ions, that is, TMA^+ , TEA^+ , TPrA^+ and TBA^+ , which are transferred from the aqueous phase to the NB phase. The half-wave potential of the linear sweep voltammogram shifted to the more negative potential with lengthening alkyl chain, which indicates that the tetraalkylammonium ion becomes more hydrophobic with increasing length of the alkyl chain. In addition, the limiting current decreased with the alkyl chain. This fact suggests that the diffusion coefficient

decreases with increasing chain length. On the other hand, the shape of the TM voltammogram suggested that the standard entropy change was shifted from a positive value to a negative one with increasing length of the alkyl change. The standard entropy changes obtained from Eq. (6) are listed in Table 1. The tendency of the standard entropy change with the alkyl chain length can be explained based on the model by Frank and Wen.²¹⁾ The alkylammonium ion with a short alkyl chain such as TMA^+ is an ion that tends to destroy the structure of water. With increasing alkyl chain length, the ion becomes bulkier and as a result the ion weakens the destructive nature of the structure, rather has a tendency of the constructive nature.

Table 1 The standard entropy changes of ion transfer of the tetraalkylammonium ions¹⁹⁾

ion	$\Delta S_{tr}^{o,w} / \text{J K}^{-1} \text{mol}^{-1}$
TMA^+	+85.2
TEA^+	$+11.4 \pm 10.8$
TPrA^+	-53.6 ± 24.5
TBA^+	-89.5 ± 14.6

Figure 20 shows the plot of the standard entropy change against the standard Gibbs energy change of ion transfer for tetraalkylammonium ions and 1-alkylpyridinium ones from the aqueous phase to the NB phase.²²⁾ The relationships are linear. The larger the standard Gibbs energy change, the smaller the standard entropy change. This relationship suggests that more hydrophobic ions are more constructive to the structure of water in both cases of tetraalkylammonium ions and 1-alkylpyridinium ones.

Fig. 20 Relationships between $\Delta S_{tr}^{o \rightarrow W}$ and $\Delta G_{tr}^{o \rightarrow W}$ for (●) tetraalkylammonium ions, (■) tetraalkylpyridinium ions²⁾ and (▲) 1-alkylpyridinium ions. [R. Watanabe, Y. Terauchi, M. Sakaue, and T. Hinoue, *Anal. Sci.*, **30**, 595 (2014).]

So far, several improvements have been achieved for the apparatus for TMV.^{22), 24)} One is the use of a semiconductor laser, which is a compact and can be electrically controlled. This improvement not only dissolved the use of the mechanical chopper but also made the apparatus compact. Visible light from the semiconductor laser hardly deteriorates the polyester film separating the two phases in the electrolytic cell. Although the NB phase does not absorb the visible light from the semiconductor laser, the addition of crystal-violet tetrakis(4-chlorophenyl)borate, serving as a supporting electrolyte, allows the NB phase to absorb the visible light. This is also available when 1,2-dichloroethane (DCE) is used as solvent of the organic phase. Another improvement was employing a micro-hole array with many micro-holes to increase the NB/W interfacial area. By increasing the number of the micro-holes, the current for ion

transfer increases approximately 100 times. Based on these improvements, we will develop TMV in the future.

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