Notes

Observation of Ion-Transfer of Photochemical Reaction Products of *p*-Aminodiphenylamine across an Aqueous | 1,2-Dichloroethane Solution Interface by Photo-Modulation Voltammetry with an Ultraviolet Laser

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Photo-modulation voltammetry with a 325-nm beam from a He-Cd laser was applied to an examination of a photochemical reaction of *p*-aminodiphenylamine. The photo-modulation voltammogram exhibited a peaked wave proportional to the concentration of *p*-aminodiphenylamine, and essentially agreed with a difference between linear scan voltammograms under irradiation and non-irradiation. From the absorption spectra of *p*-aminodiphenylamine and a pH dependence of the voltammograms, it was inferred that a dimer dication of *p*-aminodiphenylamine was photochemically formed and transferred from the aqueous solution to the 1,2-dichloroethane solution.
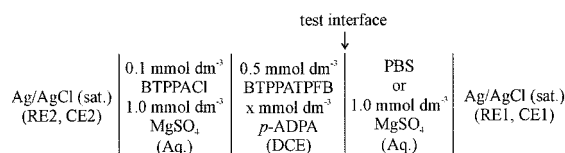
Introduction

When either of two liquid phases composing a liquid | liquid interface possesses an optical absorption in the ultraviolet region, irradiation of the interface with ultraviolet light of a proper wavelength can induce several physical or chemical phenomena at the interface and in the interfacial region, such as heating, photochemical reactions, and photoionization. Since such phenomena can modify ion-transfer across the interface through heating and the formation of new ions from the photochemical processes, good use of irradiation with ultraviolet light is expected to open a new aspect in a field of ion-transfer voltammetry at a liquid | liquid interface.[1-5] Consequently, it is assumed to be instructive to develop a technique that couples ion-transfer voltammetry with irradiation of the interface with ultraviolet light.

In a previous paper,[6] we developed thermal modulation voltammetry at an aqueous | nitrobenzene solution interface by utilizing heating with a He-Cd laser, and determined the standard entropy changes of ion-transfer for tetraalkylammonium ions. Further, we successfully detected a photodecomposed substance formed from a tetraphenylborate ion by photo-modulation voltammetry.[7] In this work, remarking that *p*-aminodiphenylamine is very soluble into 1,2-dichloroethane and readily converted to another substance under ultraviolet irradiation, we examined a photochemical reaction of *p*-aminodiphenylamine at an aqueous | 1,2-dichloroethane solution interface, using a 325-nm beam from a He-Cd laser. As a result, it has been confirmed that photo-modulation voltammetry at a liquid | liquid interface with an ultraviolet laser is a sensitive and useful technique for examining photochemical reactions in the interfacial region and identifying the photochemical reaction products.

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Experimental

Apparatus and procedure

Since the experimental apparatus for photo-modulation (PM) voltammetry used in this work was similar to that for thermal modulation (TM) voltammetry at a liquid | liquid interface,[6] it is briefly described. The electrolytic cell was machined from polychlorotrifluoroethylene (PCTFE) resin blocks, and consisted of two compartments for an aqueous solution and a 1,2-dichloroethane (DCE) solution. The two compartments were separated by a thin polyester film of 16 μm thick with a small hole of 30 μm in diameter, serving as the aqueous | DCE solution interface. The film was tightly held with screws between two sheets of silicon rubber along with the two compartments. A 325- or 442-nm beam from a He-Cd (Kimmon, IK5451R-E, KR1801C) laser was mechanically chopped at 10 Hz and introduced into the cell through an optical window from the aqueous solution side. The beam size was *ca*. 1 mm in diameter at the interface and the power was *ca*. 10 mW at 325.0 nm or *ca*. 30 mW at 442 nm. Lock-in detection was employed to detect minute currents periodically induced by the intermittent laser beam. The current signals from a four-electrode type potentiostat (Hokuto Denko, HA1010mM1A) were amplified with a lock-in amplifier (PAR, 5101) by referring to a signal supplied from the optical chopper. In addition, the phase shifter of the lock-in amplifier was fixed at 180° throughout the PM voltammetric measurements. The potential was scanned at 5 mV s^{-1} with a potential sweep unit (Fuso, Model 1104). The electrochemical system tested was as follows:

Here, PBS denotes a phosphate buffer solution. A saturated

silver/sliver chloride reference electrode (Ag/AgCl (sat.)) was placed in the aqueous solution through a salt bridge (RE1), and a bis(triphenylphosphoranylidene)ammonium (BTPPA⁺) ion-selective electrode, which consisted of an Ag/AgCl (sat.) and a solution containing 0.1 mmol dm⁻³ BTPPACl and 1.0 mmol dm⁻³ MgSO₄, served as a reference electrode in the DCE solution (RE2). These two reference electrodes worked as counter electrodes (CE1 and CE2) as well as reference electrodes, since the currents passing through the interface were very small (< 1 nA). All voltammetric measurements were performed at room temperature (25 ± 2°C) without the IR compensation. UV-Vis absorption spectra were measured with a spectrophotometer (Shimadzu, UV-2550) by using a 1-cm optical cell made of quartz. The pH measurements for the aqueous solutions were carried out with a pH meter (Horiba, F-8 AT).

Reagents

   p-Aminodiphenylamine (*p*-ADPA) was purchased from Wako Junyaku and used without further purification. This compound, known as a head-to-tail coupling dimer of aniline, was very soluble in DCE and slightly soluble in acidic aqueous solution; moreover, it was quickly converted to another substance under irradiation at 325 nm with the He-Cd laser. Bis(triphenylphosphoranylidene)-ammonium tetrakis(pentafluorophenyl)borate (BTPPATPFB) was synthesized from bis(triphenylphosphoranylidene)-ammonium chloride (BTPPACl, Aldrich) and lithium tetrakis-(pentafluorophenyl)borate (LiTPFB, Tokyo Chemical Industry) in a 2:1 mixture of methanol and water. The precipitate of BTPPATPFB was dissolved into acetone, and then recrystallized by adding a 2:1 mixture of methanol and water to the acetone solution.[8] The 1,2-dichloroethane (DCE) used was of analytical grade, and was used after stirring with deionized water in an Erlenmeyer flask on a magnetic stirrer for longer than 2 h to be saturated with water. All aqueous solutions were prepared with deionized water, and the pH was adjusted with a 0.10 mol dm⁻³ phosphate buffer solution. All other reagents used were of analytical grade and used without further purification.

Results and Discussion

Linear scan voltammogram and photo-modulation voltammogram

   Linear scan (LS) voltammograms were measured under irradiation and non-irradiation at the interface between an aqueous solution containing 1.0 mmol dm⁻³ MgSO₄ (pH *ca.* 5) and a DCE solution containing only 0.5 mmol dm⁻³ BTPPATPFB (a blank DCE solution). The two voltammograms were almost identical with each other, which suggested that irradiation at 325 nm did not have any effects on the solvents and the supporting electrolytes composing the aqueous and DCE solutions. However, at the interface with a DCE solution containing *p*-ADPA, a slight difference was found between two LS voltammograms under irradiation and non-irradiation. As shown in Fig. 1(a), the voltammogram under irradiation (solid line) was slightly larger than that under non-irradiation (broken line) in current in the potential region more than *ca.* 0.5 V. On the other hand, photo-modulation (PM) voltammograms were measured at the interfaces with DCE solutions containing *p*-ADPA at different concentrations. Figure 1(b) shows the PM voltammograms. As can be seen in this figure, each PM voltammogram for a DCE solution containing *p*-ADPA (curves **2** - **6**) exhibited a clear peaked wave centered at 0.61 V; moreover, the signal intensity at the peak potential was proportional to the concentration of *p*-ADPA in the range of 0.10 mmol dm⁻³. These facts prove not only that PM
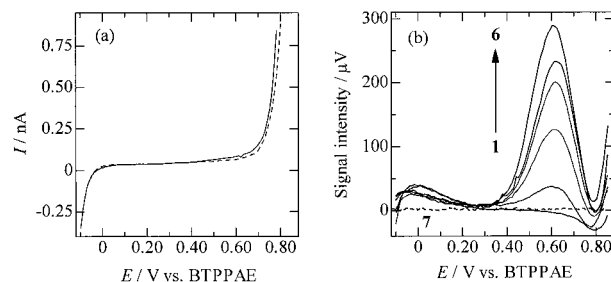

Fig. 1 Linear scan voltammograms and photo-modulation voltammograms at the aqueous | 1,2-dichloroethane solution interface. The linear scan voltammograms (a) were measured under irradiation (solid line) at 325 nm with a He-Cd laser and non-irradiation (broken line). The concentration of *p*-aminodiphenylamine in the 1,2-dichloroethane solution was 0.10 mmol dm⁻³. The photo-modulation voltammograms (b) were measured at the interface with 1,2-dichloroethane solutions containing different concentrations of *p*-aminodiphenylamine. Curves **1** to **6** (solid line) show the voltammograms for concentrations of 0, 0.02, 0.04, 0.06, 0.08, and 0.10 mmol dm⁻³, respectively. Curve **7** (broken line) shows a photo-modulation voltammogram measured at the interface with a 1,2-dichloroethane solution not containg *p*-aminodiphenylamine under irradiation at 442 nm with the He-Cd laser. The scan rate and the modulation frequency were 5 mV s⁻¹ and 10 Hz, respectively.

voltammetry is very sensitive to a slight difference between the currents under irradiation and non-irradiation, but also that the peaked wave arises from *p*-ADPA. Further, the slight difference between the LS voltammograms under irradiation and non-irradiation or the clear appearance of a peaked wave in the PM voltammogram implies that certain ions were formed from *p*-ADPA under irradiation, which were transferred across the interface. From the fact that the LS voltammogram under irradiation was larger in current than that under non-irradiation in the positive direction, the ion-transfer occurring at the interface is assumed to be a cation-transfer from the aqueous solution to the DCE solution, or an anion-transfer from the DCE solution to the aqueous solution, according to the convention used in this work. It is discussed in more detail in the following section whether the transferring ion is an anion or a cation. On the other hand, all of the PM voltammograms in Fig. 1(b), including the voltammogram for a DCE solution not containing *p*-ADPA (curve **1**), show convex and concave waves around 0 and 0.8 V, respectively. These waves probably arise from the thermal effect on ion-transfers of BTPPA⁺ and TPFB⁻, serving as a supporting electrolyte in the DCE solution. In fact, the polyester film for the micro-interface absorbs the 325-nm beam, and hence the absorbed light would be converted to heat. Fortunately, since the He-Cd laser had another beam at 442 nm, transparent to the film, a PM voltammogram was measured by changing the wavelength from 325 to 442 nm. As a result, the waves vanished away from the PM voltammogram (curve **7**), confirming that the convex and concave waves were caused by the thermal effect.

UV-Vis absorption spectra of a 1,2-dichloroethane and an acidic aqueous solution of p-aminodiphenylamine

   In order to examine whether the transferring ion is an anion or a cation, absorption spectra were measured with changing time of irradiation at 325 nm. The spectra of DCE and acidic aqueous solution containing *p*-ADPA are shown in Fig. 2. The pH of the aqueous solution was adjusted to 2.35 with a phosphate buffer. Before irradiation, the spectrum of the DCE
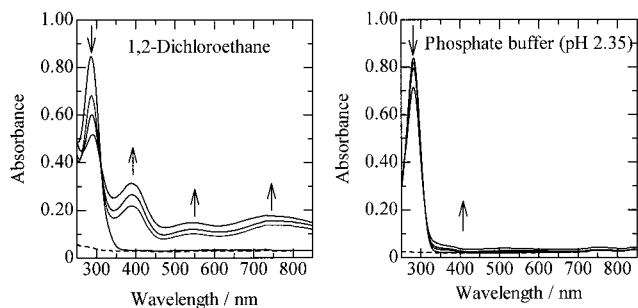
Fig. 2 Time course of the absorption spectra of a 1,2-dichloroethane and aqueous phosphate buffer (pH 2.35) solution containing *p*-aminodiphenylamine during irradiation at 325 nm with a He-Cd laser. The spectra were recorded before and after 5, 10, and 30-min irradiation by using a 1-cm optical cell. The concentrations of *p*-aminodiphenylamine in the 1,2-dichloroethane and aqueous phosphate buffer solution were 0.050 and 0.065 mmol dm^{-3}, respectively. All of the spectra of the aqueous phosphate buffer solution in this figure are normalized to those for a concentration of 0.050 mmol dm^{-3}. The broken lines indicate the absorption spectra of the 1,2-dichloroethane and aqueous phosphate buffer solution not containing *p*-aminodiphenylamine.
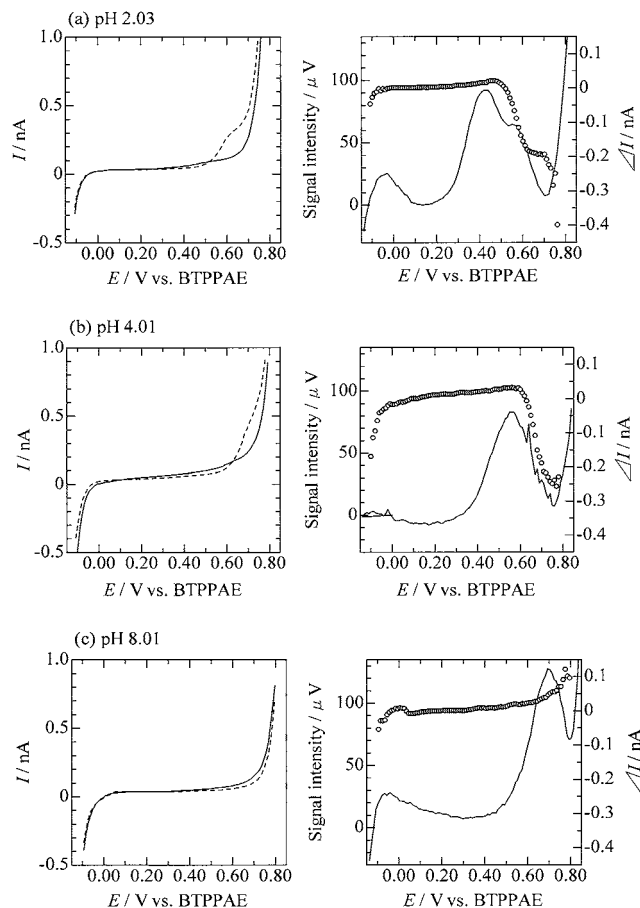

Fig. 3 pH dependence of the linear scan and photo-modulation voltammogram. The left figures show the linear scan voltammograms under irradiation (solid line) at 325 nm with the He-Cd laser and non-irradiation (broken line). The right figures show photo-modulation voltammograms. The dotted lines in the right figures represent difference voltammograms between the linear scan voltammograms under irradiation and non-irradiation. The pH of the aqueous solution was adjusted with 0.10 mol dm^{-3} phosphate buffer. The concentration of *p*-aminodiphenylamine was 0.10 mmol dm^{-3}.

solution exhibited an absorption band at 286 nm, which agrees well with literature data.[9–11] The band at 286 nm decreased in absorbance with increasing irradiation time, but new bands grew at 388, 550, and 730 nm. This time course of the spectrum was quite similar to that reported in a spectroelectrochemical study on the electrooxidation of *p*-ADPA in an acid solution (0.5 mol dm^{-3} H$_2$SO$_4$),[11] except for the band at 550 nm. According to the spectroelectrochemical study, *p*-ADPA is oxidized to a radical cation at a platinum electrode, and then the two radical cations are coupled to form a dimer dication. The dication is further oxidized with two electrons and two hydrogen ions at the electrode to form a diimine, called Willstätters blue imine (WBI). Assuming that the photochemical reaction occurring in the DCE solution is similar to the electrooxidation mechanism, the transferring ion across the interface must be a cation, probably the dimer dication. Consequently, taking account of the conclusion in the previous section, namely, the ion-transfer is a cation-transfer from the aqueous solution to the DCE solution, or an anion-transfer from the DCE solution to the aqueous solution, the following ion-transfer mechanisms are proposed: (1) The dimer dication, which is formed on the DCE solution side at the interface under irradiation, is distributed to the aqueous solution along with certain anions, and then transferred from the aqueous solution to the DCE solution. (2) Because *p*-ADPA is oxidized under irradiation to form the dimer dication, an oxygen molecule contained in the DCE solution is reduced to the radical anion and/or the dianion, and they are then transferred from the DCE solution to the aqueous solution. Although the mechanism is still obscure, the former mechanism may be true, taking account of the pH dependence of PM voltammogram described later. On the other hand, the spectrum of the aqueous solution of pH 2.35 exhibited an absorption band at 281 nm before irradiation, which suggests that most of the *p*-ADPA (Ph-NH-Ph-NH$_2$) exists as *p*-ADPAH$^+$ (Ph-NH-Ph-NH$_3$$^+$).[9] This suggestion is also supported from a pK_a value of 4.4 for the acid-base equilibrium of *p*-ADPAH$^+$ $\rightleftharpoons$ *p*-ADPA + H$^+$.[12,13] While the spectrum of the aqueous solution of *p*-ADPA did not vary as greatly as that of the DCE solution upon increasing the irradiation time, the band at 281 decreased and the spectrum

slightly increased in absorbance in the wavelength range above 310 nm, particularly, around 380 and 740 nm. It is therefore expected that the dimer dication is formed under irradiation in the aqueous solution as well.

pH dependence of a linear scan and a photo-modulation voltammogram

As described above, the pK_a value of *p*-ADPA has been reported to be 4.4.[12,13] Consequently, the distribution of *p*-ADPA between the aqueous and DCE solution depends on the pH of the aqueous solution. In order to examine the pH dependence of LS and PM voltammograms, the voltammetric measurements were carried out at the interfaces with aqueous solutions of different pH values from *ca*. 2 to 10 under both irradiation and non-irradiation. Figure 3 shows typical LS voltammograms and the corresponding PM voltammograms measured at pH 2.03 (a), 4.01 (b), and 8.01 (c). Under non-irradiation (broken line), while the LS voltammograms at pH 2.03 and 4.01 exhibited waves at *ca*. 0.60 and 0.67 V, respectively, the voltammogram at pH 8.01 exhibited no wave. Since a large fraction of *p*-ADPA is distributed as *p*-ADPAH$^+$ to the aqueous solutions at pH values lower than the pK_a, the
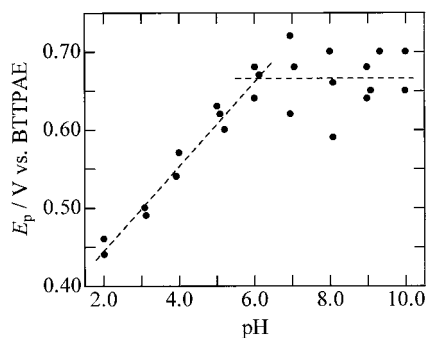
Fig. 4 pH dependence of the peak potential in the photo-modulation voltammogram. The pH of the aqueous solution was adjusted with 0.10 mol dm^{-3} phosphate buffer. The slope, $\Delta E_p/\Delta pH$, was 0.056 V/pH in the pH region from 2 to 6.

waves in the LS voltammograms at pH 2.03 and 4.01 are obviously assigned to the ion-transfer of p-ADPAH$^+$ from the aqueous solution to the DCE solution. However, the LS voltammograms were markedly changed upon irradiating at 325 nm with the He-Cd laser (solid line). A comparison of the LS voltammograms under irradiation and non-irradiation at pH 2.03 or 4.01 indicates that the wave almost vanished and the currents increased in the potential region less positive than that in which the wave had appeared under non-irradiation. This fact suggests that p-ADPAH$^+$ existing on the aqueous solution side at the interface was changed to another cation under irradiation, and then the cation was transferred from the aqueous solution to the DCE solution. The cation formed under irradiation was probably a dimer of p-ADPA with two positive charges, described in the previous section. The PM voltammograms at pH 2.03 and 4.01 exhibited peaked waves centered at 0.43 and 0.56 V, respectively. In addition, each PM voltammogram essentially agreed with a difference voltammogram between the two LS voltammograms under irradiation and non-irradiation, which are shown in the right figures. In other words, the increase or decrease in the signal intensity of the PM voltammogram reasonably corresponded to that in the current of the difference voltammogram. On the other hand, the peak potential of the PM voltammogram linearly increased with a slope of 0.056 V/pH in the pH region from 2 to 6, although it was approximately constant in the pH region from 6 to 10, as shown in Fig. 4. Assuming that the pH dependence of the peak potential corresponds to that of the half-wave potential of the LS voltammogram for ion-transfer of p-ADPAH$^+$, the slope of 0.056 V/pH can be explained by the fact that the half-wave potential shifts to a more positive potential with a slope of 0.059 V/pH at 298 K for acid-base dissociation with one hydrogen ion. As described above, the LS voltammogram under non-irradiation exhibited no wave at pH 8.01 (see Fig. 3). This is supported from an expectation that most p-ADPA exists as an electrically neutral species in the DCE solution at this pH. However, the LS voltammogram under irradiation was slightly larger in current than that under non-irradiation in the potential region more than 0.5 V, which can also be confirmed from the difference voltammogram. Assuming that the change in current between the LS voltammograms under irradiation and non-irradiation at pH 2.03 or 4.01 is due to the formation of the dimer cation from p-ADPAH$^+$ and its ion-transfer, it is expected that the increase at pH 8.01 is also due to ion-transfer of the dimer cation formed under irradiation from the aqueous solution to the DCE solution. That is, the dimer dication formed on the DCE solution side at the interface is once distributed to the aqueous solution with certain anions, and then transferred across the interface. On the other hand, the PM voltammogram at pH 8.01 exhibited a peaked wave at 0.70 V. As described above, the PM voltammograms at pH 2.03 and 4.01 agree fairly well with the difference voltammograms. Consequently, the appearance of the peaked wave on the PM voltammogram at pH 2.03 or 4.01 essentially results from a difference between the currents under irradiation and non-irradiation, that is, from a difference in current arising from the photochemical reaction of p-ADPA. However, the appearance at pH 8.01 is assumed to be concerned with not only the photochemical reaction of p-ADPA, but also the thermal effect for the ion-transfer of TPFB$^-$, serving as a supporting electrolyte in the DCE solution.

Conclusion

Using linear scan voltammetry and photo-modulation voltammetry at an aqueous | 1,2-dichloroethane solution interface with a 325-nm beam from a He-Cd laser, we examined a photochemical reaction of p-aminodiphenylamine. As a result, it was assumed that a dimer dication of p-aminodiphenylamine was formed at the interface under irradiation, and was then transferred from the aqueous solution to the 1,2-dichloroethane solution. Such results suggest that photo-modulation voltammetry is available for examining the mechanism of a photochemical reaction and identifying ionic species photochemically formed at a liquid | liquid interface,

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