

# Effects of Electrolytes in a Liquid Thin Layer System

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**Abstract.** The effects of electrolytes on electrochemical behavior from an oil thin layer interposed between a graphite electrode and an aqueous solution phase were examined. A hydrophobic electroactive species, tetrachloro-1,4-benzoquinone (TCQ), in a benzonitrile (BN) layer was employed to study ion transfer properties across the BN-water interface. Experimental results showed that hydrophobic cations as well as anions could be successfully used as ionic charge carriers. The addition of various salts into either the oil layers or the aqueous solutions offers deeper insight for the electrochemistry of the liquid thin layer system. When aqueous perchloric acid is interfaced with the BN films, the perchlorate ion of tetrahexylammonium perchlorate (THAP) substantially suppresses the dissociated proton concentration in the layer by the common ion effect while there is only a little change in the total acid concentration. Further approach by theoretical calculation makes it possible to quantitatively understand the effect of the electrolytes to the electrochemical responses of TCQ, which were previously reported (Anal. Chem. 73, 337 (2001)).

**Key words :** Liquid thin layer, Ion transfer, Electrolyte, Interface

## 1. Introduction

The system of liquid thin layers interposed between graphite electrodes and aqueous solutions was recently introduced<sup>1</sup> and several reports demonstrated its potential for a variety of possible applications<sup>1-7</sup>). This method is so simple that it allows an easy approach to study on electrochemistry at liquid/liquid interfaces. A schematic sketch of a typical arrangement is shown in Figure 1. Nitrobenzene(NB)/H<sub>2</sub>O system was reported first to investigate electron transfer from electron donors in one phase to acceptors in the other one<sup>2,3</sup>). In addition to NB, a couple of oils including benzonitrile(BN) were introduced for the liquid layer<sup>4,5</sup>). In particular, BN forms thin films as stable as NB and provides a wider potential window so that electrochemical reduction process can be observed in more negative range<sup>5</sup>).

A few recent studies showed that electrocatalytic O<sub>2</sub> reduction is possible in this system<sup>5,6</sup>). Four electron reduction process was observed from O<sub>2</sub> to H<sub>2</sub>O<sup>6</sup>). As a result, numerous hydrophobic electrocatalysts, which have been considered to be practically useless due to those poor solubility in water, can be reconsidered for electrocatalytic reduction of O<sub>2</sub> in aqueous phase by this unique method. Electrochemical reduction of O<sub>2</sub> needs protons to be supplied from the aqueous phase fast enough to complete four electron reduction. A recent report showed that the concentration of proton in BN layers equilibrated with aqueous acids is even lower than that in aqueous phase<sup>7</sup>). By employing a quinone in the BN layer, it was proved that proton transfer across the BN/H<sub>2</sub>O interface is rapid enough to make proton-consuming faradaic process

sustain<sup>7</sup>). In addition, this work reported some experimental results and brief interpretation about the ionic current carried by ClO<sub>4</sub><sup>-</sup> upon the electrochemical reduction of tetrachloro-1,4-benzoquinone (TCQ)<sup>7</sup>).

In order to achieve further improvements, more knowledge is required on the ionic current accompanying faradaic process because the charge transfer at liquid-liquid interface depends remarkably on the concentration and properties of electrolytes that are present in either oil or aqueous phase. For instance, ionic current carried by cations rather than by anions and quantitative approach to the effects of hydrophobic electrolytes in the liquid thin layer are the aspects that should be explored. The present paper newly reports 1) the cationic transfer across the liquid-liquid interface upon faradaic redox events on the electrode surface, 2) the quantitative effect of the hydrophobic salt, THAP, and 3) further experimental observation and discussion about the role of ClO<sub>4</sub><sup>-</sup> as an ionic carrier.

## 2. Experimentals

### 2.1. Materials

A column of activated molecular sieves(MX1583D-1, type 3A, 8-12 mesh, EM Industries Inc.) was used to purify benzonitrile (BN) and nitrobenzene(NB) from Aldrich(HPLC grade), which was doubly distilled before electrochemical experiments. Perchloric acid (61.8% w/w, Mallinckrodt) was used as received. Water-saturated BN and BN-saturated water were prepared by agitating BN and water mixture(v/v = 1/1) and separating phases by centrifugation for 20 min. 1,1,3,3-Tetrakis-(2-methyl-2-hexyl)ferrocene(TMHF) was synthesized and provided by Prof. S. Strauss<sup>8</sup>). Tetrahexylammonium perchlorate

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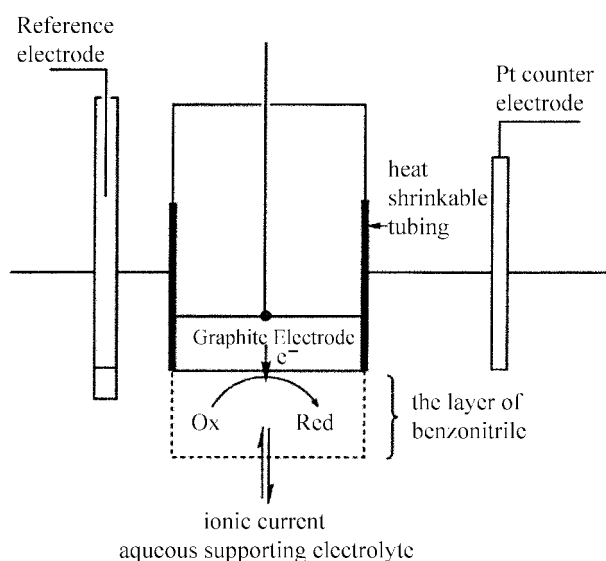


Fig. 1. Schematic view of the liquid thin layer system in this study.

(THAP, Fluka, electrochemical grade), tetrabutylammonium chloride (TBACl, Fluka, electrochemical grade) and tetrachloro-1,4-benzoquinone (TCQ, Aldrich, 99%) were used without further purification. All other reagents used in this study are the products of EM Industries Inc. Cylindrical pyrolytic graphite electrodes (Advanced Ceramics Corp.) with  $0.32 \text{ cm}^2$  of the edges of the graphitic planes exposed were mounted and pre-treated as previously described<sup>1)</sup>.

## 2.2. Apparatus and Procedures

Electrochemical experiments were performed with a Windows-driven BAS50B/W electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) using a conventional three-electrode cell. The electrochemical cells, instrumentation and the procedure employed for introducing thin layers of organic solvents on graphite electrode surfaces have been previously described<sup>1)</sup>. One drop of BN was spread over the electrode surface to produce a  $\sim 30 \mu\text{m}$  thin layer. The amount of BN for the thin films was  $1 \mu\text{L}$  throughout the experiments in this study.

## 3. Results and Discussion

### 3.1. The role of $\text{ClO}_4^-$

Ionic current at the liquid-liquid interface as well as electron transfer at the electrode surface should be considered to interpret voltammetric responses from liquid thin layer systems. Figure 2(A) shows the voltammetric response from 1,1',3,3'-Tetrakis(2-methyl-2-hexyl)ferrocene (TMHF) in thin layers and perchloric acid in aqueous phases. The symmetric reduction and oxidation waves reveal that this system behaves just like typical thin layer cells with an electroactive species. The standard ionic-transfer potentials for  $\text{H}^+$  and  $\text{ClO}_4^-$  in BN/ $\text{H}_2\text{O}$  system,  $\Delta_o^w \Phi_{\text{H}^+}^0$  and  $\Delta_o^w \Phi_{\text{ClO}_4^-}^0$ , are 0.340 and  $-0.002 \text{ V}$ , respectively<sup>7)</sup>. In other words,  $\text{ClO}_4^-$  is readily transferred across the BN/ $\text{H}_2\text{O}$  interface while  $\text{H}^+$  is thermodynamically unfavorable for the transfer from aqueous to BN phase. Thus it is reasonable that the charge flow carried by

$\text{ClO}_4^-$  mostly undertakes ionic current between the two immiscible phases. As TMHF is oxidized at the electrode surface,  $\text{ClO}_4^-$  comes into the BN layer to keep up charge neutrality. The high rate of the ionic transfer does not deform the well-defined voltammetric waves at the scan rate applied in this study,  $5 \text{ mV s}^{-1}$ . When  $\text{HClO}_4$  is replaced by  $\text{HCl}$  in the aqueous phase, the redox waves are not only largely diminished in height but also distorted in shape as shown in Figure 2(B). Two possible reasons can explain this behavior. First,  $\text{Cl}^-$  must overcome even larger potential barrier to transfer into the BN phase than  $\text{ClO}_4^-$  (c.f.  $\Delta_o^w \Phi_{\text{Cl}^-}^0 = -0.316 \text{ V}$  for NB/ $\text{H}_2\text{O}$  system<sup>9,10</sup>). Second, extremely low ionic concentration in the layer for aqueous  $\text{HCl}$  raises its resistance too much to observe the typical diffusion-controlled mass transport in thin layers.

In addition to the simple reaction in which electron transfer is solely involved, proton-consuming system deserves to be investigated in terms of electrocatalytic reduction of  $\text{O}_2$ . The difference between  $\text{ClO}_4^-$  and  $\text{Cl}^-$  for this system can be also seen in the faradaic processes that need protons. The tetrachloro-1,4-benzoquinone (TCQ) as a proton-consuming electroactive species was proven to be useful to study the proton transport from the aqueous phase<sup>7)</sup>. With aqueous perchloric acid, TCQ is reduced through the mechanism that involves two electrons and two protons<sup>7,11)</sup>. Figure 3(A) shows the reduction peak with symmetric bell shape appears at around  $+0.4 \text{ V}$  when the BN layer is interfaced with aqueous  $\text{HClO}_4$ . The area under the peak is equivalent to the charge of  $3.7 \times 10^{-4} \text{ C}$ , which is very close to that calculated from the assumption that all TCQs in the layer are reduced,  $3.9 \times 10^{-4} \text{ C}$ . Both the symmetric shape and the area under the reduction peak unequivocally indicate that TCQ in the layer is completely reduced. In addition, the current at more negative

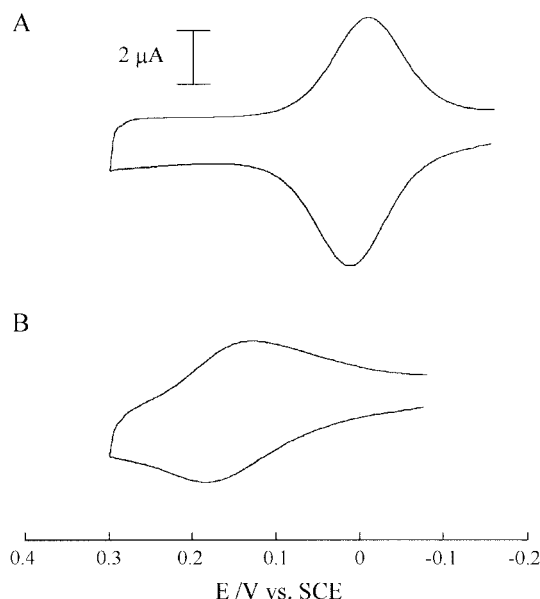


Fig. 2. Cyclic voltammograms of 1.1 mM tetrakis(2-methyl-hexyl)ferrocene in BN thin layers that are interfaced with the aqueous media of 1.0 M  $\text{HClO}_4$  (A) and 1.0 M  $\text{HCl}$  (B), respectively. No electrolyte is initially added to the BN layer. Scan rate is  $5 \text{ mV s}^{-1}$ .

potential than +0.2 V in the voltammogram is nearly the same as the background, indicating actually no faradaic current owing to the reduction of residual TCQ in the layer. On the other hand, aqueous HCl brings about seriously distorted wave, decrease in peak height and the long tail of faradaic current in the negative potential region as demonstrated in Figure 3(B). The charge from the peak area is  $1.9 \times 10^{-4}$  C, which is significantly less than that calculated. Even at a slow scan rate,  $5 \text{ mV s}^{-1}$  in this study, electrochemical reduction of TCQ in the BN layer is not completed. The ionic current, for which  $\text{Cl}^-$  carries charge, is unable to keep up the electron transfer at the electrode surface. Thus the apparent voltammetric response is limited by the rate of charge transfer at the BN/ $\text{H}_2\text{O}$  interface. Moreover, the concentration of  $\text{Cl}^-$  in the BN layer is too low to secure the conductance of the layer for the appropriate control of electrochemical potential. Lack of  $\text{Cl}^-$  results in low proton concentration in the layer, which hampers the proton-involved reduction.

The results from  $\text{ClO}_4^-$  and  $\text{Cl}^-$  give clear lessons. First, the apparent voltammetric responses from this system must be interpreted on the consideration of ionic current at the liquid-liquid interfaces, which may act as a limiting factor to the net current. Second, the properties of ionic current can be reasonably understood by the concepts and tabulated data from conventional liquid-liquid electrochemistry based on classical thermodynamics. With the thermodynamic data (e.g.  $\Delta_o^w \Phi^0$ ), the electrochemical behavior can be predicted in the presence of ions other than  $\text{ClO}_4^-$  or  $\text{Cl}^-$ . Third, ionic concentration in the layer as well as charge transfer across the liquid-liquid interface should be counted in building up a liquid thin layer system. Four,  $\text{ClO}_4^-$  is suitable for studies with this

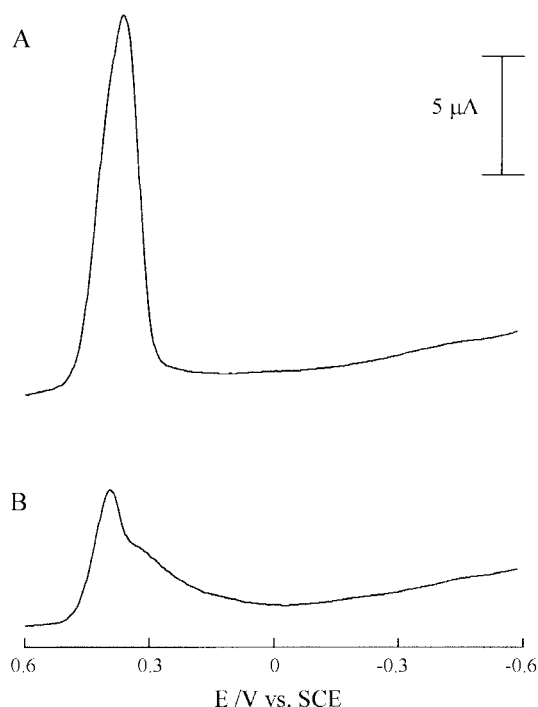


Fig. 3. Cyclic voltammograms from the thin layer systems of 2.0 mM TCQ in BN|1.0 M  $\text{HClO}_4$  aq.(A) and 2.0 mM TCQ in BN|1.0 M HCl aq.(B). Scan rate is  $5 \text{ mV s}^{-1}$ .

system because of its chemical inertness and small absolute value of  $\Delta_o^w \Phi^0$ , especially for BN/ $\text{H}_2\text{O}$  system.

### 3.2. Cationic charge carrier

The electrochemistry of the liquid thin layer system, in which cations carry the charge for ionic current, is also interesting. Figure 4 shows a voltammogram from the system composed of aqueous TBACl solution and TCQ in BN thin layer. The symmetric peak around +0.2 V is due to the reduction of TCQ that involves no proton but one electron<sup>7,11</sup>. The radical anions produced by the reduction around +0.2 V take up another electron around 0.4 V without protonation. The absence of the peak due to oxidation of hydroquinone at far positive potential region implies that consecutive reductions produce dianionic quinone.

Another feature of the voltammetric behavior in Figure 4 is that the oxidation peak around +0.2 V is much smaller than the reduction one with respect to the first electron transfer. The repetitive cycling by reversing the scans at the potential between the first and second peak, at 0 V, gives very symmetric reduction and oxidation waves, which diminish only a little even after several cycles. This means that radical anionic TCQ is very stable in the BN layer and never leach out. Considerable amount of TCQ is lost as a result of second electron transfer. Probably, the high hydrophilicity of dianionic TCQ is responsible for the loss.

In this system, hydrophobic  $\text{TBA}^+$  ( $\Delta_o^w \Phi_{\text{TBA}^+}^0 = -0.250 \text{ V}$  for NB/ $\text{H}_2\text{O}^{10}$ ) prefers being in the oil layer. However, owing to strongly hydrophilic  $\text{Cl}^-$  ( $\Delta_o^w \Phi_{\text{Cl}^-}^0 = -0.316 \text{ V}$  for NB/ $\text{H}_2\text{O}^{10}$ ), it is supposed that large part of  $\text{TBA}^+$  and  $\text{Cl}^-$  are still present in aqueous phase. Considering the similarity between NB and BN in terms of physical properties as solvents, about 70% of TBACl is expected to reside in aqueous side. It is not surprising that hydrophobic  $\text{TBA}^+$  will play the

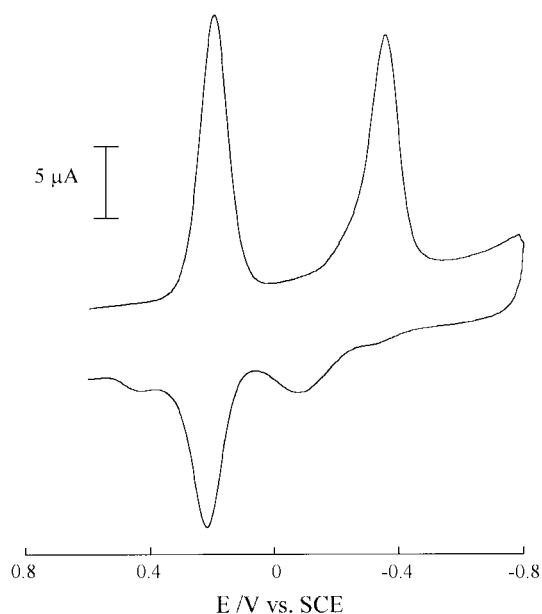


Fig. 4. Cyclic voltammograms from the thin layer systems of 2.0 mM TCQ in BN|0.05 M TBACl aq.

role of the charge carrier through the BN/H<sub>2</sub>O interface, taking account of the large  $\Delta_o^w \Phi_{Cl^-}$ . The well-defined two reduction peaks in Figure 4 result from ionic transfer by TBA<sup>+</sup> that moves rapidly enough to keep up the faradaic current. Furthermore, the high content of TBACl in the layer makes its resistance negligible so that it helps obtain the well-defined voltammograms. Consequently, hydrophobic cations with hydrophilic counter anions can be a successful choice for charge carriers as well.

### 3.3. Effect of hydrophobic electrolyte in the BN layer

Experiments with electrolytes in aqueous phase provide valuable information as described above. The other case, hydrophobic electrolytes in the oil layer, remains to be addressed. In this study, a couple consisting of very hydrophobic cation, THA<sup>+</sup>, and amphiphilic anion, ClO<sub>4</sub><sup>-</sup> was chosen. Assuming the differences between NB/H<sub>2</sub>O and BN/H<sub>2</sub>O system are negligible, THAP is supposed to be present predominantly in the BN layer ( $\Delta_o^w \Phi_{THA^+}$  is -0.472 V for NB/H<sub>2</sub>O<sup>10</sup>). The aqueous phase contains various concentrations of HClO<sub>4</sub>.

The previous paper<sup>7)</sup> reported the change in voltammetric behavior due to the presence of THAP in the BN layer. When THAP is added to the BN layer, the reduction wave producing hydroquinone diminishes a little and shifts to more negative potential whereas the peak generating radical anionic quinone appears. This behavior implies that the concentration of proton is substantially lowered by THAP. However, the paper did not present quantitative analysis to interpret this experimental results.

From the relationship between standard Galvani potential difference ( $\Delta\phi^0$ ) and activities of H<sup>+</sup> ( $a_{H^+}$ ) and ClO<sub>4</sub><sup>-</sup> ( $a_{ClO_4^-}$ ), the following equations are driven<sup>9,10)</sup>. The superscripts of the activity symbols stand for the corresponding phases. w and o denote aqueous and organic phase, respectively.

$$\Delta\phi = \frac{\Delta\phi_{H^+}^o + \Delta\phi_{ClO_4^-}^o}{2} + \frac{RT}{2F} \ln \frac{a_{H^+}^o a_{ClO_4^-}^w}{a_{H^+}^w a_{ClO_4^-}^o} \quad (1)$$

$$\text{Since } a_{H^+}^w = a_{ClO_4^-}^w, a_{H^+}^o = a_{THA^+}^o = a_{ClO_4^-}^o,$$

$$\Delta\phi = \frac{\Delta\phi_{H^+}^o + \Delta\phi_{ClO_4^-}^o}{2} + \frac{RT}{2F} \ln \frac{a_{H^+}^o}{a_{H^+}^w + a_{THA^+}^o} \quad (2)$$

Assuming the activity coefficients are unity, activities can be replaced by formal concentrations.

$$\Delta\phi = \frac{\Delta\phi_{H^+}^o + \Delta\phi_{ClO_4^-}^o}{2} + \frac{RT}{2F} \ln \frac{[H^+]_o}{[H^+]_o + [THA^+]_o} \quad (3)$$

Equation (1) is rearranged to the following expression.

$$[H^+]_o = [H^+]_w \exp \left\{ \frac{F}{RT} (\Delta\phi - \Delta\phi_{H^+}^o) \right\} \quad (4)$$

Inserting equation (3) for  $\Delta\phi$  in equation (4) yields

$$[H^+]_o = [H^+]_w \exp \left\{ \frac{F}{RT} \left( \frac{\Delta\phi_{ClO_4^-}^o - \Delta\phi_{H^+}^o}{2} \right) \right\} \left( \frac{[H^+]_o}{[H^+]_o + [THA^+]_o} \right)^{1/2} \quad (5)$$

By taking  $A = \exp \left\{ \frac{F}{RT} \left( \frac{\Delta\phi_{ClO_4^-}^o - \Delta\phi_{H^+}^o}{2} \right) \right\}$  in equation (5) can be rearranged to equation (6).

$$[H^+]_o^2 + [THA^+]_o [H^+]_o - [H^+]_w^2 A^2 = 0 \quad (6)$$

The solution of this simple quadratic equation is as shown in (7).

$$[H^+]_o = \frac{\sqrt{[THA^+]_o^2 + 4[H^+]_w^2 A^2} - [THA^+]_o}{2} \quad (7)$$

Using the relationship of charge balance in the thin layer,  $[ClO_4^-]_o = [H^+]_o + [THA^+]_o$ ,

$$[ClO_4^-]_o = \frac{\sqrt{[THA^+]_o^2 + 4[H^+]_w^2 A^2} + [THA^+]_o}{2} \quad (8)$$

Because HClO<sub>4</sub> in BN is a weak acid ( $K_a = 2.9 \times 10^{-4}$ )<sup>7)</sup>, predominant portion of the total acid is present in the undissociated form. From equation (7) and (8),

$$[HClO_4]_o = \frac{[H^+]_o [ClO_4^-]_o}{K_a} = \frac{[H^+]_w^2 A^2}{K_a}$$

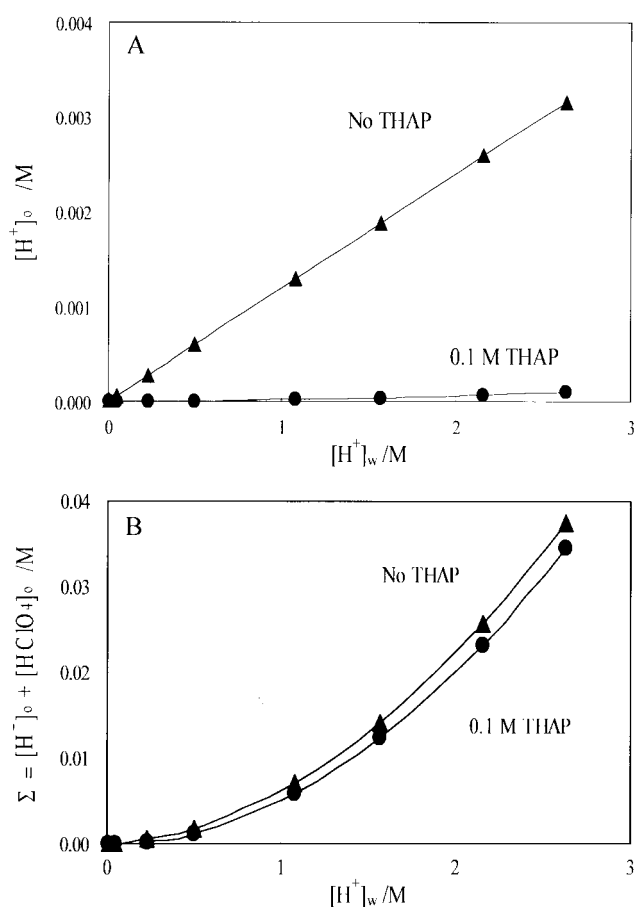
As A value ( $= 1.2 \times 10^{-3}$ ) is known<sup>7)</sup>, both the concentrations of undissociated and of dissociated acid are the function of the concentrations of aqueous perchloric acid ( $[H^+]_w$ ) and of THAP in the BN layer ( $[THA^+]_o$ ). Now, the total acid concentration ( $\Sigma = [H^+]_w + [THA^+]_o$ ) can be evaluated. Figure 5 shows the dependence of  $[H^+]_o$  and  $\Sigma$  on  $[H^+]_w$ . Figure 5(A) clearly illustrates that THAP brings about substantial suppression of  $[H^+]_o$ .  $[H^+]_o$  in the presence of THAP is about 100 fold lower than that in the absence. However, only a little decrease in the total concentration of the acid ( $\Sigma$ ) is observed as shown in Figure 5(B) because most part of the acid exists in the undissociated form. In summary, the change in the voltammetric responses of TCQ in the presence of THAP<sup>7)</sup> is attributed to the increase of pH by common ion effect.

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**Fig. 5.** Calculated dissociated (A) and total acid concentration (B) in BN layer with and without hydrophobic electrolyte, 0.1 M THAP. Triangles and circles denote acid concentrations in the absence and presence of THAP, respectively.

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