

Charge transfer across the ionic liquid/oil interface: facilitated ion transfer and electron transfer

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Abstract

Facilitated ion transfer (FIT) and electron transfer (ET) across the ionic liquid (IL) / oil (O) interface between ethylamine nitrate (EAN) and 1,4-dichlorobutane (DCB) have been electrochemically studied. Cyclic voltammograms (CVs) for the FIT of Li^+ cation in IL by dicyclohexano-18-crown-6 (DCH18C6) across the IL/O interface formed at a micropipette tip show that the onset of the FIT current is significantly shifted due to the facilitation beyond the potential window limit and that the current is proportional to the concentration of DCH18C6 in O limited by the diffusion of DCH18C6 inside the micropipette. CVs for the ET from supporting electrolyte anions in O to NO_3^- , the IL anion of EAN, across the IL/O interface studied using a closed-bipolar cell show that NO_3^- in EAN has an ability to oxidize tetraphenylborate ions in O but not tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ions, the latter of which have more oxidation resistance.

1. Introduction

The interface between two immiscible electrolyte solutions (ITIES) has been studied for about half a century in research fields such as electroanalysis, ion extraction, phase-transfer catalysis, and electrocatalysis [1–5]. A representative ITIES is the water (W)/oil (O) interface and another example is the W/fluorous solvent interface [6–8]. The liquid/liquid interface between hydrophobic ionic liquids (ILs) and W has attracted much attention as a new class of ITIES and has been actively studied since the 2000s [9,10,19–22,11–18]. ILs are salts that are liquid around room temperature, with several characteristics such as ionic conductivity, a wide potential window at the electrode interface, high thermal stability, negligibly low vapor pressure, and flame resistance. These properties make ILs unique and different from conventional molecular liquids such as water and oil.

In the above new ITIES examples, O was replaced with other hydrophobic liquids such as fluorinated solvents and hydrophobic ILs. On the opposite, it should also be possible to replace W with other hydrophilic liquids. In 2013, the liquid/liquid interface between hydrophilic IL and O was found to be polarizable by Cousens and Kucernak using ethylammonium nitrate (EAN) as an IL [23]. This study showed that the IL/O interface is polarizable within a potential window of 150 mV. Recently, our group found another polarizable IL/O interface using 1-(3-hydroxypropyl)-3-methyl-imidazolium chloride ($C_{3OH}mimCl$) as a hydrophilic IL [24] and furthermore successfully measured the current due to ion transfer (IT) and electron transfer (ET) across the IL/O interface. By utilizing the coupling of IT and ET involved with base metal ions, we also succeeded in preparing base metal nanostructures at this liquid/liquid interface [25,26], which is possible because this two-phase system is free from water that hinders the base metal reduction.

In the present paper, we further explore the electrochemistry at the IL/O interface by investigating two charge transfer reactions, facilitated ion transfer (FIT) and ET, across the IL/O interface using EAN as an IL [23]. We will show that the current due to the transfer of Li^+ from IL to O facilitated by a crown ether

in O was successfully measured within the potential window. Regarding ET, although we already reported ET from a reducing agent in O to a metal ion in IL across the IL/O interface [24], the ET in the present study is based on the oxidizing ability of NO_3^- , which is the anion of the EAN, the IL used. We will have to be careful about this ET in the electrochemistry at the IL/O interface of EAN or possibly utilize this characteristic to oxidize the species in O.

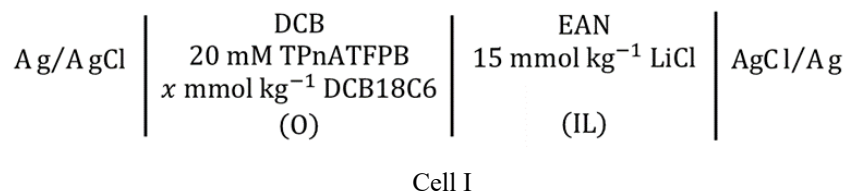
2. Experiments

2.1. Reagent

EAN, used as an IL in the present study, was prepared from ethylamine (33w% aqueous solution, TCI) and nitric acid (60w% aqueous solution, Kishida Chemical) according to the procedure described in the reference [27]. LiCl (Kishida Chemical) was dissolved in the IL. 1,4-dichlorobutane (DCB, TCI) was used as O, in which tetrapentylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TPnATFPB) was dissolved as a supporting electrolyte and dicyclohexano-18-crown-6 (DCH18C6, Aldrich) was dissolved as a ligand to form a complex with Li^+ .

2.2. Electrochemical measurements for FIT across the IL/O interface

Micropipettes with a tip inner diameter of approximately 16 μm were prepared using a glass tube (G-1, NARISHIGE) with a pipette puller (PC-100, NARISHIGE). The inner wall of the pipette was made hydrophobic using a toluene solution of dichlorodimethylsilane. DCB was injected into a micropipette as the O phase, and the micropipette tip was inserted into the IL phase. Ag wires ($\phi 0.3$ mm) coated with AgCl were inserted into the micropipette as quasi reference electrode (QRE) and into the IL phase as reference electrode (RE), respectively.



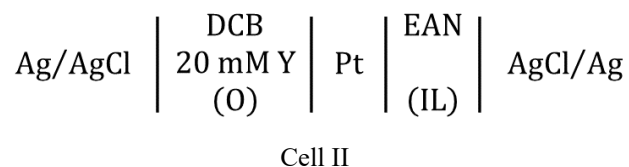
Cyclic voltammograms (CVs) were recorded with a two-electrode cell. The sweep rate was 5 mV/s. The cell diagram is shown below as Cell I (see also the schematic in Fig.S1).

The potential of the right Ag/AgCl with respect to the left Ag/AgCl in Cell I, denoted as E , was controlled with a potentiostat (ECstat-400, EC Frontier) and the current, I , defined the cation transfer from IL to O as positive, was measured. The temperature was controlled at 25°C by flowing temperature-controlled water in the water jacket of the cell.

2.3. Closed bipolar electrochemical measurements for ET across the IL/O interface

NO_3^- , the IL anion in EAN, has oxidation ability, and the redox reaction with the supporting electrolyte added to the O phase may occur within the potential window at the IL/O interface. This idea led us to perform ET experiments between NO_3^- and TFPB^- of TPnATFPB. We also tested tetraoctylammonium tetraphenylborate (TOATPB). TPB^- is also one of the most frequently used anions for supporting electrolytes in O in ITIES studies, and known to be oxidized in some conditions [28].

A Pt wire and Pt microelectrode ($\phi 10 \mu\text{m}$) were inserted into the IL and O phases, respectively, and they were connected using a conductive wire to be functionalized as a bipolar electrode. The cell diagram is shown below as Cell II (see also the schematic in Fig.S2).



where Y is TPnATFPB or TOATPB. Only the ET, not IT, across the IL/O interface can be measured in this so-called closed bipolar cell [29]. The current is limited by the electrode reaction at the microelectrode in O. CVs were recorded similarly to those with Cell I.

3. Results and discussion

3.1. FIT of Li^+ across the IL/O interface

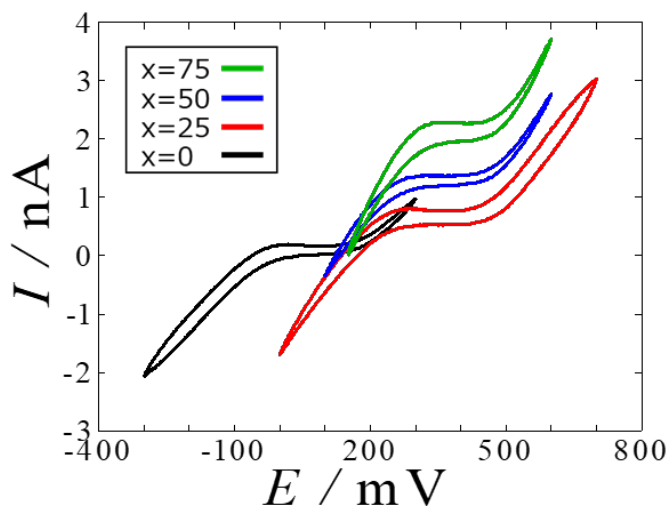


Fig.1. Cyclic voltammograms at the IL/O interface measured using Cell I. IL phase: EAN with 15 mmol kg^{-1} LiCl; O phase: DCB with $x \text{ mmol kg}^{-1}$ DCB18C6 and 20 mM TPnATFPB.

The CVs for FIT are shown in Fig.1. The potential window was 200 mV using DCB without DCH18C6 ($x = 0$). This is slightly wider than the potential window of 150 mV at the IL/O interface reported previously [23,24]. The negative current at the negative end of the potential window was attributed to the transfer of NO_3^- from EAN to DCB (IL $\rightarrow$ O), which is likely to be thermodynamically favorable compared with the other possible ITs of hydrophilic Cl^- (IL $\rightarrow$ O) and hydrophobic TPnA^+ (O $\rightarrow$ IL), judging

from the standard Gibbs energy of these ions for the W-O (nitrobenzene) two-phase system [30]. Similarly, the positive current at the positive end was attributable to the transfer of Et-NH_3^+ (EA^+) from IL to O rather than the transfer of Li^+ and TFPB^- . This discussion, the potential window limited by the ITs of EA^+ and NO_3^- , is supported by CVs where we used Cell I but replaced EAN with W or EAN-W mixtures (Fig.S4). With increasing the EAN fraction of the mixtures, the potential window of the CVs becomes narrower, indicating that EA^+ and NO_3^- determine the potential window and their standard Gibbs energies from O to IL-W become higher.

When DCB contains DCH18C6 ($x = 25, 50, 75$), the CVs in Fig.1 shifted to the higher right direction compared with the $x = 0$ case. The rightward shift, a positive potential shift, was larger with higher concentrations of DCH18C6 added to the DCB (Fig.2a). Similar positive shift was observed in the cases at the W/O interface using Cell I (Fig.S3). Also, the potential shift was confirmed with ferrocene redox on a Pt micropipette in O using the same QRE (Fig.S5). This shift is caused by the potential shift in the Ag/AgCl QRE in DCB in the presence of DCH18C6 due to the complexation of DCH18C6 with Ag^+ on the Ag/AgCl electrode and will be quantitatively discussed below in Section 3.2. The CVs also shifted upward and showed positive limiting currents, which were proportional to the concentration of DCH18C6 (Fig.2b). These limiting currents in CVs are due to the ion transfer of Li^+ , facilitated by DCH18C6 in the DCB phase.

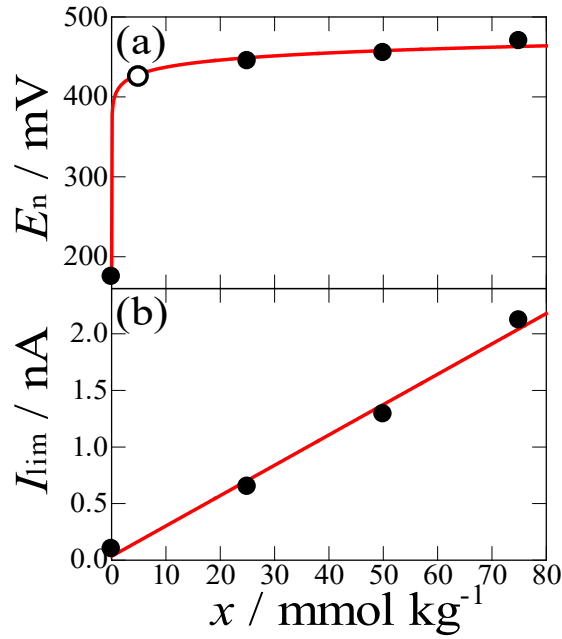


Fig.2. (a) Plots of potential E_n vs x . Here E_n is defined to be the positive edge potential where $I = I_{\text{lim},n} + 0.1$ (nA), with $I_{\text{lim},n}$ being the limiting current in the positive scan in the CVs in Fig.1. $x = C_{\text{DCH18C6}}/\rho_{\text{DCB}}$. The open circle at $x = 5$ is an estimated E_n from ferrocene redox CVs on Pt with the same QRE (Fig.S5). The red line is the fitted curve from eq 9. (b) Plots of limiting current (I_{lim}) vs x . I_{lim} is defined as the midpoint current of the limiting currents in the positive and negative scans in the CVs in Fig.1. $x = C_{\text{DCH18C6}}/\rho_{\text{DCB}}$. The red line is from the least squares regression.

In FIT across the liquid/liquid interface formed at the micropipette tip, whether the diffusion of the metal ion or the ligand toward the interface is the current-limiting process is determined by the magnitude of DCS for the two species (D is the diffusion coefficient, C is the bulk concentration, and S is the solid angle of the spherical diffusion cone inside or outside the pipette) [31–33]. In the present case, the DC term of the ligand and Li^+ are comparable. In contrast, S inside the pipette for the ligand is 4 orders of magnitude smaller than S outside for the metal ion, evaluated from the cone angle 3° for the micropipette tip (see below). Therefore, the diffusion of the ligand inside the pipette, with the significantly smaller solid angle, is the current-limiting process, which agrees with the proportionality of the limiting current and the ligand concentration (Fig.2b). This is also strongly supported by the CVs at the IL-W/O interface shown in

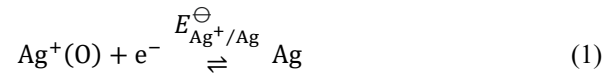
Fig.S4, in which regardless of the contents of IL-W outside the micropipette the same limiting current, 1.3nA, is observable.

Unlike CVs for FIT with a sufficiently wide potential like those at the W/O interface shown in Fig.S3, the FIT CVs in Fig.1 do not show the onset of the FIT current. This is because the IT (IL→O) of NO_3^- , determining the negative edge of the potential window, is at more positive potential than the FIT of Li^+ . The complexation constant K_f for Li^+ and DCH18C6 was reported to be $\log K_f = 5.28$ in CDCl_3 [34]. Since DCB and CDCl_3 have similar dielectric constant ϵ (9.3 and 4.8, respectively), we simply assume the same $\log K_f$ value in DCB. The negative potential shift due to the facilitation estimated from this value is $(RT/F) \ln K_f \approx 310$ mV, which is significantly greater than 200 mV, the potential window at $x = 0$ (Fig.1). This suggests that the potential for the onset of the FIT current is more negative than the negative end of the potential window, making CVs shifted upward as shown in Fig.1.

3.2. The potential shift

CVs in Fig.1 imply that DCH18C6 causes a potential shift (ΔE) of RE in O. Here, these ΔE values are thermodynamically discussed.

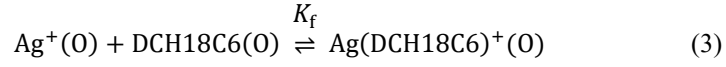
The half-reaction equation for QRE in O and the Nernst equation are written as follows.



$$E_{\text{QRE}} = E_{\text{Ag}^+/\text{Ag}}^\ominus - \frac{RT}{F} \ln \frac{1}{[\text{Ag}^+]} \quad (2)$$

where E_{QRE} is the electrode potential of QRE in O, $E_{\text{Ag}^+/\text{Ag}}^\ominus$ is the standard electrode potential, $[\text{Ag}^+]$ is the concentration of Ag^+ , R is the gas constant, T is the temperature and F is the Faraday constant. Here we neglect the activity coefficient for simplicity. Since the relation of E_{QRE} with E is written as $E = \phi^{\text{IL}} - \phi^{\text{O}} - E_{\text{QRE}} + \text{const.}$, E_n , a measure of the potential shift shown in Fig.2a is similarly written as $E_n = -E_{\text{QRE}} + \text{const.}$

The reaction equation for the complex formation of Ag^+ and $\text{Ag}(\text{DCH18C6})^+$ is:



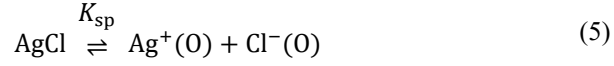
where K_f is the complexation constant written as follows.

$$K_f = \frac{[\text{Ag}(\text{DCH18C6})^+]}{[\text{Ag}^+][\text{DCH18C6}]} \quad (4)$$

with $[\text{DCH18C6}]$ and $[\text{Ag}(\text{DCH18C6})^+]$ being the concentrations of DCH18C6 and $\text{Ag}(\text{DCH18C6})^+$, respectively.

The Ag/AgCl QRE in O works by the AgCl dissolution from the AgCl surface at a low concentration. The AgCl solubility in a hydrophobic IL is several tens M [35] and that in DCB will be lower. As the concentration of DCH18C6 increases, the concentration of Ag^+ decreases due to the complexation, which causes a positive potential shift of QRE in O as shown in eq 2.

The reaction equation for the dissolution of AgCl in O is:



where K_{sp} is the solubility product of AgCl in O.

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] \quad (6)$$

The following equation is for the mass balance of DCH18C6 using the formal concentration of DCH18C6 in O (C_{DCH18C6}), which we control in the experiments.

$$C_{\text{DCH18C6}} = [\text{DCH18C6}] + [\text{Ag}(\text{DCH18C6})^+] \quad (7)$$

Another mass balance equation for AgCl gives the following equation:

$$[\text{Ag}^+] + [\text{Ag}(\text{DCH18C6})^+] = [\text{Cl}^-] \quad (8)$$

Combining eqs 4, 6, 7, and 8 yields the cubic equation for $[\text{Ag}^+]$.

$$K_f[\text{Ag}^+]^3 + (1 + C_{\text{DCH18C6}}K_f)[\text{Ag}^+]^2 - K_fK_{sp}[\text{Ag}^+] - K_{sp} = 0 \quad (9)$$

which we can solve with a known parameter C_{DCH18C6} and variable parameters K_f and K_{sp} to obtain $[\text{Ag}^+]$ and therefore E_{QRE} (by using eq 2). By fitting eq 9 to the E vs x plots (Fig.2a) in which x was approximated to be $C_{\text{DCH18C6}}/\rho_{\text{DCB}}$ (ρ_{DCB} is the density of neat DCB, 1.16 g/cm³), $\log K_f$ was estimated to be 11.6. This value is higher than the $\text{Ag}(\text{DCH18C6})^+$ complex formation constant ($\log K_f = 4.64$) in MeOH [36], which qualitatively agrees with the fact that DCB is less polar than MeOH (dielectric constant ϵ 8.9 vs. 33 at 25°C). The fitting also gave $\log K_{sp} = -12.2$, which is lower than those in water and in a hydrophobic IL, again agreeing with the low polar nature of DCB.

3.3. Limiting current of FIT

Fig. 1 shows that the limiting current (I_{lim}) varies with the concentration of DCH18C6 added to the O phase. Since the present CVs using a micropipette are limited by the diffusion inside the micropipette, the I_{lim} of Li^+ FIT can be expressed using a modified version of the Saito equation [37].

$$I_{\text{lim}} = \tan \frac{\theta}{2} \cdot 4FC_{\text{DCH18C6}}D_{\text{DCH18C6}}r_{\text{in}} \quad (10)$$

where θ is the conical angle of the micropipette tip, C_{DCH18C6} is the concentration of DCH18C6 in the O phase (approximated to be $x\rho_{\text{DCB}}$ with ρ_{DCB} being the density of neat DCB, 1.16 g/cm³), D_{DCH18C6} is the diffusion coefficient of DCH18C6 in O, and r_{in} is the inner radius of the micropipette tip. In eq 10, the term $\tan \frac{\theta}{2}$ is introduced and attached to the original Saito equation, which expresses the fraction of the conical geometry against the hemispherical one in the oblate spheroidal coordinate (derivation is in Supporting Information). A magnified view of the micropipette tip used in the experiment is shown in Fig.S6, with which θ and r_{in} were estimated to be 3° and 8 μm , respectively. D_{DCH18C6} was estimated to be $4.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ by applying the Stokes-Einstein relation $D\eta = \text{const}$ for a solute in different solvents with a reported value $5.05 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for D_{DCH18C6} in ethanol at 25°C [38] and the viscosity η data for DCB and ethanol (1.46 and 1.14 mPa s at 20°C respectively). By substituting these parameter into eq 10,

$I_{\text{lim}}/C_{\text{DCH18C6}}$ was estimated to be $3.2 \times 10^{-11} \text{ A m}^3 \text{ mol}^{-1}$, which is 39% higher than $2.3 \times 10^{-11} \text{ A m}^3 \text{ mol}^{-1}$ obtained from the I_{lim} vs x plot (Fig.2b). The θ value of 2.2° would reproduce the experimental value if we boldly assume that the systematic error only comes from θ , neither from D_{DCH18C6} or r . Aside from the accuracy of the parameter values, there are still several possible reasons for the discrepancy. Beattie et al. in a previous paper [39] observed a limiting current higher than that from the expected diffusion geometry outside the W/O interface formed at the micropipette tip, suggesting that a possible reason for the increase in the limiting currents could be an expansion of the interfacial area with the interface bulging out from the ideal disk shape at the micropipette tip. This type of bulging out may also occur for the IL/O interface in the present study, lowering the limiting current. Another possible reason is the discrepancy in the geometry; the micropipette cone could be thin at the bottom (far from the tip) compared with the ideal shape in the oblate spheroidal coordinate, which makes the current lower than the prediction by eq 10.

3.4. Closed bipolar electrochemical experiment for ET

The closed bipolar experiment (Section 2.3) allows us to observe the ET involved with the redox reaction between the IL and O phases as a current. The recorded CVs are shown in Fig.3.

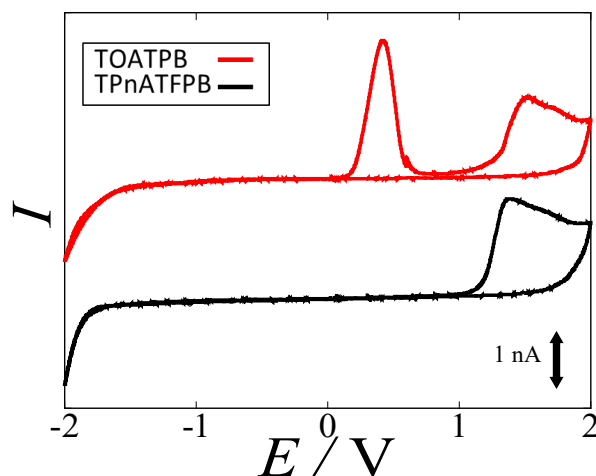
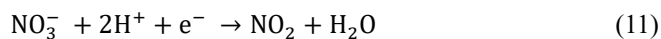


Fig.3 Cyclic voltammograms at the IL/O interface measured using the Cell II. O phase: DCB with 20 mM TOATPB (red) or 20 mM TPnATFPB (black).

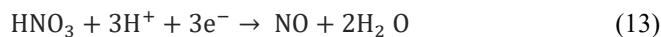
Since the IL and O phases are separated by an electron conductor in this cell, only the ET, not the IT, can be observed as the current across the interface. The red line is the CV of the O phase with TOATPB added, and the black line is the CV of the O phase with TPnATFPB added. The “potential window” of these CVs, spanning from -1.8 V to $+1.2$ V, is significantly wider than 200 mV at the normal IL/O interface (Fig.1), because the IT is inhibited for this cell. CV with TOATPB (red) shows a positive current in the positive scan around $+0.2$ V, while that with TPnATFPB (black) shows no such current. These CV behaviors agree with the difference between the two anionic species in anodic decomposition potential at the electrode; the anodic decomposition potential for TPB^- is around 0.4 V (vs Fc/Fc^+) which is 1 V more positive than that for TFPB^- [39]. Therefore, in the present E and I definitions, the oxidative decomposition of TPB^- should appear as a positive current at 1 V more negative than that of TFPB^- . This coincides with the positive current onset in Fig.3; $+0.2$ V for TPB^- and $+1.2$ V for TFPB^- . Since the positive current at $+1.2$ V also appears for the TPB^- case, this current is likely to be also caused by the oxidation of other species such as quaternary ammonium cations and DCB. The positive current for the TOATPB case, corresponding to ET from O to IL, suggests a possible redox reaction as follows.



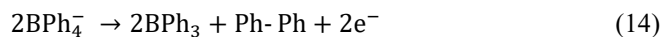


where TPB^- is denoted as BPh_4^- to describe its oxidative decomposition [28]. Eq 11 is known as the reduction reaction of NO_3^- in a concentrated nitric acid. Here in the present case, H^+ is supplied by EA^+ .

Another possible reduction reaction is:



This reaction will be minor, if it occurs, because we detected generated NO_2 (eq 11) as described below. Eq 12 is taken from the literature in which the oxidation reaction of TPB^- was examined in several solvents [28]. The study reported that in dichloromethane (DCM), which has a low donor number and low dielectric constant, like DCB used in the present study, TPB^- is oxidized partially reversibly as in eq 12, although the paper did not describe the subsequent chemical reactions in DCM. From the results of several previous studies on the TPB^- oxidation at the electrode [39] and in liquid bulk [40], a possible total TPB^- oxidation reaction including the subsequent chemical reactions could be:



Actually, mass spectrometry analysis (GC-EI) for DCB containing TOATPB after being in contact with IL (see the upper right image in Fig. 4 below) confirmed the existence of Ph-Ph in the oil phase, although BPh_3 was not discernible in the mass spectra.

To verify the reduction of NO_3^- described in eq 11; EAN and DCB were placed in a sample tube to form an interface, where DCB contained either TOATPB or TPnATFPB. The two sample tubes were heated up to 80°C to promote the reaction and left for 5 hours. The photographs for the two-phase system are shown in Fig.4.

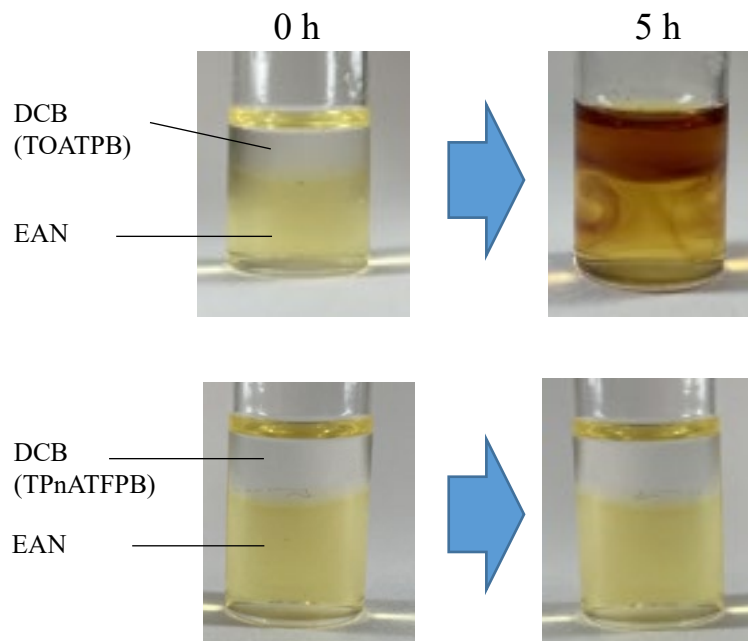
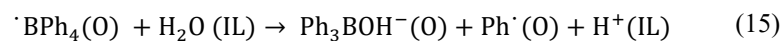


Fig.4 Photographs for the IL-O two phase system in which O contains TOATPB (upper) and TPnATFPB (lower) at 20 mM, before (left) and after (right) the 5h reaction at 80°C.

Thus, the O phase was colored only when TOATPB was added, implying that the redox reaction (eqs 11,12) occurred and the generated NO_2 was transferred from IL to O. It should be noted that even at room temperature, this coloration was visible in 72 hours only for the TOATPB case. This indicates a clear difference in reactivity between TPB^- and TFPB^- . The UV-Vis spectrum for the colored O phase in Fig.5(a) shows a peak at 350 nm. The spectrum agrees with that for NO_2 in MeCN [41]. To confirm that this peak indicates NO_2 , we generated NO_2 gas by heating PbNO_3 [41] and dissolved it in DCB. Fig.5(b) shows the UV-Vis spectrum for the DCB dissolved in NO_2 . This confirms that NO_3^- in EAN is in a redox reaction as in eqs 11, 12. At first glance, the ET associated with this redox reaction appears to disrupt the charge balance of each liquid phase. Therefore, another charge transfer, which counter-balances the ET, should occur. A possible reaction would be:



This reaction results in IT of OH^- from IL to O, triggered by the generated H_2O and BPh_4^- by eqs 11 and 12, respectively, and coupled with ET (eqs 11, 12).

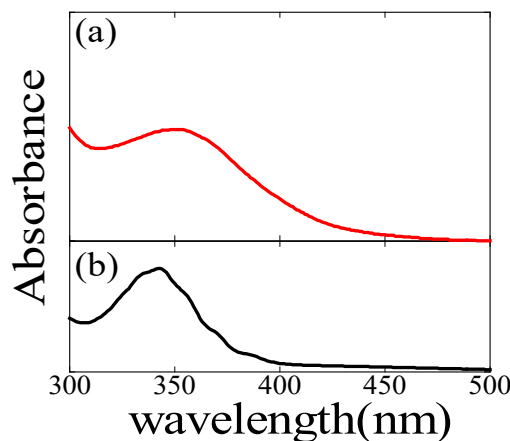


Fig.5 UV-Vis absorption spectra for (a)DCB with TPB^- after the reaction (upper right in Fig.4) and (b) NO_2 gas [39] dissolved DCB.

4. Conclusions

FIT and ET across the IL / O interface have been studied by recording CVs. The limiting current of FIT of Li^+ cation in IL across the IL/O interface is proportional to the concentration of DCH18C6 in O limited by the diffusion of DCH18C6 inside the micropipette. CVs of ET across the IL/O interface illuminated that NO_3^- in EAN has the ability to oxidize TPB^- in O but not TFPB^- , the latter of which has more oxidation resistance. These results suggest that the EAN/DCB interface is a useful oxidation reaction field under non-aqueous conditions. One of the future research directions would be to produce oxidized species that is impossible to do in the presence of water, by utilizing the IL/O interface as a water-free reaction field.

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Author Declarations

The authors have no conflicts to disclose.

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