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Voltammetry of Mn(III) Porphyrin in Trihexyl(tetradecyl)-phosphonium Tris(pentafluoroethyl) trifluorophosphate

Supported Toluene in Contact with an Aqueous Electrolyte

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Abstract

The effect of ionic liquid on voltammetry of manganese porphyrin in toluene in contact with aqueous electrolyte was studied by cyclic and differential pulse voltammetry experiments at glassy carbon electrode modified with redox probe dissolved in toluene containing trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ionic liquid as electrolyte. This electrode was the immersed in the aqueous electrolyte solutions. UV/Vis spectroscopy of manganese porphyrin in toluene ionic liquid mixture solution was carried out, indicating a significant chloride exchange at the axial position of the complex with tris(pentafluoroethyl)trifluorophosphate anion. This complex formation was confirmed by voltammetric experiments in a single phase indicating significant decrease of manganese porphyrin diffusion coefficient. Experiments with liquid modified electrode show midpeak potential dependence on the anion of supporting aqueous electrolyte and also its concentration dependence. This effect is described by Nernst type equation. It was concluded that heterogeneous electron transfer is followed by anion expulsion and the effect of the anion results from lability of axial coordination site of the porphyrin complex enabling an exchange of strongly hydrophilic Cl^- anion to highly hydrophobic tris(pentafluoroethyl)trifluorophosphate anion. This further allows a spontaneous ion exchange between two liquid phases. The effect of anion on the manganese porphyrin voltammetry in neat toluene deposit was also noted.

Keywords: Mn tetraphenylporphyrinato, Ionic liquid, Toluene, Ion transfer, Liquid|liquid interface.

1. Introduction

Since 2000 there is a continuous interest in liquid modified electrodes (see [1-8] and refs therein). This is because of their unique property which is a well defined liquid|liquid interface. Typically, liquid deposits consist water immiscible organic solvents in a form of droplet arrays [1], single droplets [2], or thin films [3] and the electrode is immersed in an aqueous electrolyte. In majority of the studies, this organic liquid contains redox active molecules, thereby imparting redox activity of these electrodes. The electron exchange between the redox probe and the electrode leads to a charge imbalance within liquid deposit and the electrode reaction is followed by ion transfer across liquid|liquid interface. In many cases these liquid modified electrodes exhibit ion-sensitive voltammetry (see for example refs. [4-6]), because ions have different ability to pass this interface as defined by their transfer potential. If, initially, ions are not present in the organic liquid, reaction starts at a three phase junction, *i.e.* electrode|liquid|liquid formed at the circumference of the organic liquid. The electrode modification with supported organic phase [7-13] or ionic liquid [14-17] removes this restriction, because electron transfer reaction zone is not limited to the three phase junction. Moreover, it has been recognized that the addition of the electrolyte to the organic liquid deposit may change the mechanism of the overall electrode process, in particular ion transfer across liquid|liquid interface [7,10,16,17].

The majority of the studies were performed with electrodes modified by a non-coordinating redox probe solution in hydrophobic polar solvents like nitrobenzene, 1,2-dichloroethane or 2-nitrophenyl octyl ether (see for example [2,6,7,9,11]). The use of weakly polar non-coordinating solvent or solvent mixture like kerosene [18], toluene [16,19] or 1,2-dichlorobenzene [12,13] for electrode modification was rather rare. For instance, the voltammetry of 1,3,5-tris[4-[(3-methylphenyl)phenylamino]phenyl]benzene dissolved in toluene droplets deposited on the electrode surface exhibits some anion sensitivity in the presence of nitrate or pechlorate anions [18]. In our earlier study we reported that voltammetry of the electrode modified with t-butylferrocene in toluene shows no ion sensitivity due to expulsion of electrogenerated cation into the aqueous solution [16]. However, addition of hydrophobic ionic liquid, *i.e.* trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)-trifluorophosphate ($P_{14,6,6,6}FAP$) (Scheme 1) to toluene deposit promotes anion insertion into organic liquid deposit [16].

Here, we will show that such ionic sensitivity can be achieved for a redox probe having ligand coordinating sites (e.g. porphyrinato metal complexes) and the observed effect is

different than for a bulk solution voltammetry. Until now such redox probes have been studied on electrodes modified with strongly coordinating solvents such as benzonitrile [20], 4-(3-phenylpropyl)pyridine [21-24] or ionic liquid [17]. However, it is already known that toluene has been recognized as a suitable solvent for voltammetric studies of the redox probes sparingly soluble in more polar solvents [25-29] and hydrophobic phosphonium–phosphate ionic liquid $P_{14,6,6,6}FAP$ [30] represents one of the possible electrolytes [29]. As a redox probe 5,10,15,20-tetraphenyl-21H,23H-porphine manganese(III) chloride $(Mn(III)TPP^+Cl^-)$ was selected, because it exhibits ion sensitive voltammetry when dissolved in 4-(3-phenylpropyl)pyridine deposit [21-24]. Contrary to the earlier study [16], this work is focused on the system where electroreduction of a charged reactant to a neutral molecule occurs. Electrochemical studies in the biphasic systems are preceded by a single phase study of $Mn(III)TPP^+Cl^-$ in toluene-$P_{14,6,6,6}FAP$ mixture in order to evaluate its interactions with this ionic liquid and elucidate mechanism of the electrode process.

2. Experimental

2.1. Chemicals

$(Mn(III)TPP^+Cl^-)$ and toluene (anhydrous, 99%+) were obtained from Aldrich. Ferrocene (Fc) and tetrahexylammonium perchlorate (THxAP) were obtained from ABCR. $P_{14,6,6,6}FAP$ and KPF_6 (98+%) were obtained from Merck. Salts: NaF, NaSCN, KBr, KCl, NaSCN, $NaClO_4$ and KNO_3 (all of analytical grade) were purchased from POCh. Salts: LiCl, NaCl, RbCl and CsCl were purchased from Fluka. All chemicals were used without further purification. Water was filtered and demineralised with the ELIX system (Millipore).

2.2. Instrumentation and procedures

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with PGSTAT30 Autolab (Eco Chemie, NL) electrochemical system. The DPV experimental parameters were: modulation time 0.05 s, interval time 0.5 s, step potential 0.005 V and modulation amplitude 0.025 V. The start potential in CV and DPV experiments was usually chosen as the most positive point in the potential window.

For the one-phase experiments in toluene containing $P_{14,6,6,6}FAP$ or THxAP, a platinum ultramicroelectrode (Pt UME) of 10 μm diameter was employed. A platinum and silver wire served as counter and quasi-reference electrode, respectively. Ferrocene served as an internal

standard. Before each measurement, the electrode was polished with 0.05 μm Al$_2$O$_3$ (Buehler) aqueous suspension and then sonicated in water. The organic solution was deaerated with pure argon (99.9%) for at least 15 min prior to measurements.

As a substrate for organic liquid deposit a GC disc embedded in Teflon cylinder (nLab) was used as a working electrode. Its geometric surface area was 0.031 cm^2. GC disc was polished with 1, 0.3 and 0.05 μm Al$_2$O$_3$ (Buehler) aqueous suspension and then sonicated in water. The electrode was modified by deposition of 2 μl of toluene solution (containing 1 mM Mn(III)TPP$^+$Cl$^-$ and 0.4 M P$_{14,6,6,6}$FAP or 0.1 M THxAP) diluted with acetonitrile (1:25 v/v). After evaporation of acetonitrile the liquid deposit formed irregular shimmering stain on the GC surface. The electrode together with platinum wire and Ag/AgCl/KCl$_{sat}$ electrode were immersed into the aqueous salt solution. The solution was deareated with pure argon (99.9%) prior to measurements. All experiments were performed at room temperature (22-23°C).

Electronic absorption spectra were recorded on Nicolet Evolution 300 UV-Visible spectrophotometer (Thermo) with a 2 mm path length cuvette.

3. Results and discussion

3.1 Voltammetry and UV/Vis spectroscopy of Mn(III)TPP$^+$Cl$^-$ in P$_{14,6,6,6}$FAP-toluene mixture

First, the electrochemical behavior of Mn(III)TPP$^+$Cl$^-$ in P$_{14,6,6,6}$FAP-toluene mixture and for comparison in THxAP solution in toluene was studied by cyclic voltammetry at Pt ultramicroelectrode. Sigmoidal shaped curves in the positive and negative potential range refer to one-electron oxidation of Fc and one-electron reduction of Mn(III)TPP$^+$Cl$^-$, respectively, under steady-state diffusion conditions (Fig. 1). Two important features of the voltammogram should be highlighted: (i) large ratio of anodic (Fc) to cathodic (Mn(III)TPP$^+$Cl$^-$) current, and (ii) hysteresis recorded when MnTPP is reduced and re-oxidized. The former feature can be explained by different diffusion coefficients (D) of Mn(III)TPP$^+$Cl$^-$ and Fc. To the best of our knowledge, the diffusion coefficient of Mn(III)TPP$^+$Cl$^-$ in toluene was not reported in the literature. Taking 600 pm and 320 pm as the radii of Mn(III)TPP$^+$Cl$^-$ and Fc [31], respectively, one can estimate D from the Stokes-Einstein equation [32]:

$$D = \frac{kT}{6\pi\eta a} \tag{1}$$

where k is the Boltzmann constant, T is a temperature, η is a dynamic solution viscosity and a is a hydrodynamic radius of diffusing species assuming their spherical shape. Viscosity of 0.1

M solution of $P_{14,6,6,6}FAP$ is virtually as of pure toluene (0.56 mPa s [29]). Then it is possible to calculate a steady-state current i_{ss}:

$$i_{ss} = 4nFDcr \qquad (2)$$

where n is the number of electrons involved in the electrode reaction, F is the Faraday constant, c is a bulk concentration of redox probe and r is a radius of an electrode.

Different behavior manifested in i_{ss} and D values of these redox probes can be clearly seen (Table 1). The oxidation current of Fc is in fair agreement with the calculated value, whereas the reduction current of $Mn(III)TPP^+Cl^-$ is 54 % of the calculated one. The latter result may suggest that ellipsoidal shape of porphyrin molecule should be taken into account in calculation of diffusion coefficient. However, the obtained value differs only by 10% from experimentally determined diffusion coefficient of zinc tetraphenylporphyrin in toluene [33]. When $P_{14,6,6,6}FAP$ is replaced with THxAP, the reduction current of $MnTPP^+Cl^-$ is increased by 42% whereas the oxidation current of Fc is decreased by only 1.8%. Moreover, the experimentally determined D value for $MnTPP^+Cl^-$ is 80% of the calculated one. Therefore, one may conclude that the decrease of diffusion coefficient with the addition of ionic liquid consisting of large FAP^- anion is caused by its spontaneous exchange with chloride anion axially coordinated to $Mn(III)TPP^+$:

$$Mn(III)TPP^+Cl^- + FAP^- \leftrightarrows Mn(III)TPP^+FAP^- + Cl^- \qquad (3)$$

Diffusion coefficient of $Mn(III)TPP^+FAP^-$ is expected to be smaller than for $Mn(III)TPP^+Cl^-$ due to considerable difference in size of these anions (487 pm for FAP^- anion [34], 167 pm for Cl^- [35]) hence, the reduction current should be lower in the presence of the ionic liquid. Moreover, if reaction (3) is spontaneous, FAP^- will stabilize the oxidized form of porphyrin which should exhibit more negative half-wave potential than the reduced form. This can be manifested in the hysteresis observed on the voltammogram presented in Fig. 1 and not seen in THxAP solution.

Indeed, the weak axial binding of anions to $Mn(III)TPP^+$ in aprotic polar solvents has been already reported [36,37]. To verify this hypothesis, the UV-Vis spectra of $Mn(III)TPP^+Cl^-$ in toluene were recorded for different concentrations of $P_{14,6,6,6}FAP$ (Fig. 2). Clearly, the spectrum is affected by the addition of the ionic liquid. The effect of $P_{14,6,6,6}FAP$ concentration increase is most pronounced for the Soret bands (VI, Va and V). Upon addition of $P_{14,6,6,6}FAP$ all absorption bands lose intensity. Additionally, a blue shifted shoulder of band V appears. The effect of $P_{14,6,6,6}FAP$ addition is also visible for the Q bands (IV, III) (inset in Fig. 2). Most importantly, the increase of the absorbance ratio corresponding to IV and III bands and the blue

shift of their position (Fig. 3) can be considered as a signature of anion exchange at the axial position [37]. This confirms the equilibrium described by Eq. (3) which is shifted to the right when ratio of the FAP$^-$ to Cl$^-$ concentration is larger than 10^3. Interestingly, this behavior is qualitatively similar to those observed in supported more polar solvents such as tetrahydrofurane [37] or pyridine [36]. Clearly, the observed effect provides strong evidence for axial ligation and explains the low value of pophyrin complex diffusion coefficient.

3.2. Voltammetry of Mn(III/II)TPP at liquid modified electrode.

The cyclic voltammograms recorded at GC electrode, modified with MnTPP$^+$Cl$^-$ solution in P$_{14,6,6,6}$FAP-supported toluene, immersed in an aqueous KCl solution exhibits well-developed peaks with cathodic-to-anodic peak current ratio of *ca.* 1 being constant during subsequent cycles (Fig. 4). They can be attributed to reversible redox process of the Mn(III)TPP$^+$ metal complex:

$$\text{Mn(III)TPP}^+_{(org)} + e^- \leftrightarrows \text{Mn(II)TPP}_{(org)} \tag{4}$$
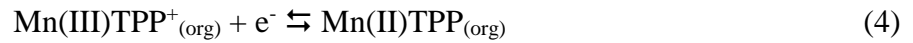
The observed stability of the voltammograms indicates the ion transfer across liquid|liquid interface that ensures electroneutrality within the organic phase.

At first, the electroreduction of Mn(III)TPP$^+$ is expected to be accompanied by a transfer of the cations from the aqueous to the organic phase. Therefore redox potential should depend upon the nature and concentration of the aqueous cations, $c_{cat+(aq)}$ [38]:

$$E_{\text{Mn(II/III)TPP}} = E^{o'}_{\text{Mn(II/III)TPP}} + \Delta^{org}_{aq}\phi^o_{\text{Cat}^+} + \frac{RT}{F}\ln c_{\text{Cat}^+\text{(aq)}} + \frac{RT}{F}\ln\frac{2}{c^*_{\text{Mn(III)TPP}}} \tag{5}$$

where $\Delta^{org}_{aq}\phi^o_{\text{Cat}^+}$ is a standard potential of transfer of a cation from the aqueous to the organic phase, $c^*_{\text{Mn(III)TPP}}$ is the initial concentration of the porphyrin and the other symbols have their usual meaning. The standard transfer potential describes an affinity of a cation to an organic phase and is defined as [39]:

$$\Delta^{org}_{aq}\phi^o_{\text{Cat}^+} = -\frac{\Delta^{org}_{aq}G^o_{\text{Cat}^+}}{zF} \tag{6}$$
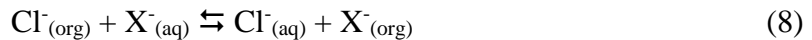
where $\Delta^{org}_{aq}G^o_{\text{Cat}^+}$ is a standard Gibbs energy of transfer of the cation from the aqueous to the organic phase and z is a charge number of the cation. Here, its values for nitrobenzene are used, because of the lack of data for toluene.

The slope of the plot of $E_{\text{Mn(II/III)TPP}}$ vs. $\Delta_{\text{aq}}^{\text{NB}}\phi_{\text{Cat}^+}^{\text{o}}$ (Fig. 5) is close to zero indicating that cations of the aqueous supporting electrolyte do not participate in the charge compensation process. This behavior is different than for Fe(III) iron tetraphenylporphyrin in nitrobenzene deposit [38], presumably due to lower polarity of the organic phase. The transfer of Cl⁻ anions across liquid|liquid interface represents another possibility. The Cl⁻ anions are produced by the porphyrin complex dissociation (Eq. 7) or the anion exchange (Eq. 3):

$$\text{Mn(III)TPP}^+\text{Cl}^-_{\text{(org)}} + e^- \leftrightarrows \text{Mn(II)TPP}_{\text{(org)}} + \text{Cl}^-_{\text{(org)}} \tag{7}$$
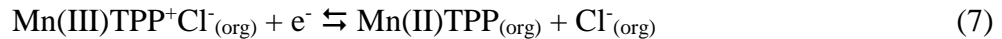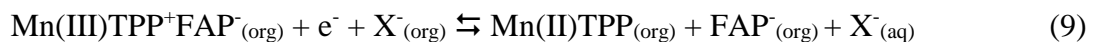
Then the lack of $E_{\text{Mn(II/III)TPP}}$ anion dependence should be indicative of this mechanism. Interestingly, the position of the voltammetric signal depends on the anion (X⁻) present in the aqueous solution (Fig. 6). Clearly, it is more difficult to electroreduce Mn(III)TPP⁺ in the toluene deposit when more hydrophobic anions are present in the aqueous phase. Therefore more complex mechanism than Cl⁻ transfer has to be considered.

Comparison of the Gibbs energies of Cl⁻ transfer and those of other anions (Table 2) shows that it is likely that Cl⁻ anions can be replaced spontaneously by more hydrophobic (with more negative $\Delta_{\text{aq}}^{\text{org}}G_{\text{X}^-}^{\text{o}}$ value) ones:

$$\text{Cl}^-_{\text{(org)}} + \text{X}^-_{\text{(aq)}} \leftrightarrows \text{Cl}^-_{\text{(aq)}} + \text{X}^-_{\text{(org)}} \tag{8}$$

Since the voltammograms are clearly affected by the aqueous electrolyte, one can exclude transfer of FAP⁻ anion as the charge compensation process. Instead, we suggest that the overall electrode process consists of the electron transfer reaction followed by X⁻ anion transfer to maintain electroneutrality within the bulk organic phase:

$$\text{Mn(III)TPP}^+\text{FAP}^-_{\text{(org)}} + e^- + \text{X}^-_{\text{(org)}} \leftrightarrows \text{Mn(II)TPP}_{\text{(org)}} + \text{FAP}^-_{\text{(org)}} + \text{X}^-_{\text{(aq)}} \tag{9}$$

This explains why the porphyrin reduction is facilitated in the presence of more hydrophilic anions.

Similar anion sensitivity was reported for fullerene C_{60} dissolved in 1,2-dichlorobenzene deposit in contact with the aqueous electrolyte [12,13]. By analogy, one can write following Nernst type equation for porphyrin redox potential (see ref. [13]):

$$E_{\text{Mn(II/III)TPP}} = E_{\text{Mn(II/III)TPP}}^{\text{o}'} + \Delta_{\text{aq}}^{\text{org}}\phi_{\text{X}^-}^{\text{o}} + \frac{RT}{F}\ln c_{\text{X}^-_{\text{(org)}}} - \frac{RT}{F}\ln c_{\text{X}^-_{\text{(aq)}}} + \frac{RT}{F}\ln\frac{c_{\text{Mn(III)TPP}^+}}{c_{\text{Mn(II)TPP}}} \tag{10}$$

where $\Delta_{\text{aq}}^{\text{org}}\phi_{\text{X}^-}^{\text{o}}$ denotes the standard potential of transfer of X⁻ from water to toluene and the other symbols have their usual meaning. Again, its values for anion transfer from water to

nitrobenzene ($\Delta_{\text{aq}}^{\text{NB}}\phi_{X^-}^{\text{o}}$) are used as a measure of hydrophobicity of the anions [3-5, 40-42]. If the electron transfer is exclusively followed by transfer of the anion X^-, the unity slope of $E_{\text{Mn(II/III)TPP}}$ vs. $\Delta_{\text{aq}}^{\text{NB}}\phi_{X^-}^{\text{o}}$ dependence has to be observed. In contrast, if the Cl^- ion transfer across liquid|liquid interface dominates, no anion effect (slope = 0) is expected.

As can be seen in Fig. 7 (circles), the dependence of $E_{\text{Mn(II/III)TPP}}$ vs. $\Delta_{\text{aq}}^{\text{NB}}\phi_{X^-}^{\text{o}}$ is linear with a slope close to unity for the anions more hydrophobic than Cl^-, wheras in the presence of F^- and SO_4^{2-} anions this trend is not followed. This confirms the proposed mechanism being responsible for anion sensitivity. In the presence of most hydrophilic anions the reduction of the porphyrin is followed by Cl^- expulsion from the organic to the aqueous phase:

$$Mn(III)TPP^+FAP^-_{(org)} + Cl^-_{(org)} + e^- \leftrightarrows Mn(II)TPP_{(org)} + FAP^-_{(org)} + Cl^-_{(aq)} \tag{11}$$
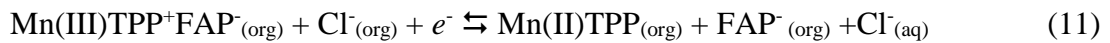
A further proof for the anion-transfer-mechanism is provided by linear $E_{\text{Mn(II/III)TPP}}$ vs. $\log c_{X^-_{(aq)}}$ dependence shown in Fig. 8. Although, according to Eq. (10), the slope of -0.059 V dec^{-1} is expected, a slightly less negative value was found for the aqueous solutions containing ClO_4^- (-0.049 V dec^{-1}) and Cl^- (-0.046 V dec^{-1}) anions. This may indicate that more than single ionic species transfer across a liquid|liquid interface in a charge compensation process [12]. For example, in a light of results presented by Quentel et al. [17] some contribution of FAP^- expulsion to the aqueous phase can be considered. Nevertheless, the negative slope of linear $E_{\text{Mn(II/III)TPP}}$ vs. $\log c_{X^-_{(aq)}}$ plot (Fig. 8) confirms the direction of ion transfer across liquid|liquid interface

In order to further examine the role of the ionic liquid in the overall process, the experiments with electrode modified with $Mn(III)TPP^+Cl^-$ solution in neat toluene were carried out. No signal of porphyrin redox process was detected when the aqueous phase contained relatively hydrophilic electrolytes (0.1 M KCl or CsCl) contrary to the situation when $P_{14,6,6,6}FAP$ was dissolved in the organic phase (Fig. 4). This result indicates that the addition of the ionic liquid allows $Mn(III)TPP^+Cl^-$ complex to be dissociated, making subsequent electron and ion transfer reaction possible within accessible potential window. Clearly the comparison of both experiments confirms the existence of equilibrium involving Cl^- and FAP^- anion exchange at coordination site of porphyrin (Eq. 3.).

When the aqueous phase contains more hydrophobic anions like ClO_4^- or PF_6^-, the well-resolved peaks can be seen on the DPV curves (not shown). This indicates that axially coordinated Cl^- anion can be replaced by more hydrophobic ones and electrode reaction obeys

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anion-expulsion mechanism as observed for $P_{14,6,6,6}$FAP supported toluene deposit. This is also confirmed by approximately linear dependence of $E_{Mn(II/III)TPP}$ vs. $\Delta_{aq}^{NB}\phi_{X^-}^o$ with slope not much below unity. The irregularity observed for neat toluene deposit in the presence of SCN$^-$ anions might be due to their specific binding to Mn(III)TPP$^+$ [21]. It is not observed in the presence of the ionic liquid probably due to the existence of relatively strong Mn(III)TPP$^+$FAP$^-$ complex.

It should be also noticed that in the presence of PF$_6^-$, ClO$_4^-$, NO$_3^-$ and Br$^-$ anions the Mn(III/II)TPP redox potential in $P_{14,6,6,6}$FAP supported toluene deposit is more negative with respect to the neat toluene. This confirms a strong axial coordination of the FAP$^-$ anion to porphyrin (Eq. (3)) stabilizing its cation.

4. Conclusions

It has been shown that the electrochemical behavior of Mn(III/II)TPP solution in $P_{14,6,6,6}$FAP supported toluene in contact with aqueous electrolyte can be described by mechanism consisting electron transfer followed by anion expulsion. This behavior is different than observed for majority of similar systems where heterogeneous electron transfer is followed by counterion insertion or expulsion of the produced form of the redox probe [5-7,15,16]. The reported mechanism results from lability of axial coordination site of the redox probe enabling an exchange of strongly hydrophilic Cl$^-$ anion to highly hydrophobic FAP$^-$ anion. This further allows a spontaneous ion exchange between two liquid phases to occur and enable to obtain voltammetric signal when such hydrophilic anions as F$^-$ or SO$_4^{2-}$ are present in aqueous phase. The observed anion effect is similar to that observed for the same porphyrin in strongly coordinating solvent deposit (4-(3-phenylpropyl)pyridine) [21-23]. However, here anion-dependent voltammetry results from axial ligand exchange coupled to ion transfer across liquid|liquid interface. Additional evidence was provided by UV-Vis spectroscopy and voltammetric experiments of Mn(III/II)TPP in toluene – ionic liquid mixture. The importance of axial anion ligation to Mn(III/II)TPP complex is further confirmed by its anion sensitive voltammetry in neat toluene deposit.

It is of major importance that the presence of the liquid|liquid interface reverses the anion effect on the redox potential observed in the single phase experiments [36,37]. Namely, in a biphasic arrangement the redox potential is shifted towards more negative values for more hydrophobic anions. In the future, toluene-based media could be employed to extract anions from the aqueous solutions or to pump hydrophobic anions from one aqueous phase to another.

Acknowledgements

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Caption to Scheme and Figures

Scheme 1. The structure of trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)-trifluorophosphate ($P_{14,6,6,6}FAP$) used in this study.

Fig. 1. Cyclic voltammogram recorded at Pt UME (10 μm diameter) in the toluene solution containing: Mn(III)TPP$^+$Cl$^-$ (3.5 mM), Fc (3.4 mM) and $P_{14,6,6,6}FAP$ (0.1 M). Scan rate was 10 mV s^{-1}. Arrows indicate a scanning direction.

Fig. 2. UV-Vis spectra for 5×10^{-5} M Mn(III)TPP$^+$Cl$^-$ solution in neat toluene (solid), and in the presence of 0.022 M (dashed), and 0.05 M (dotted) $P_{14,6,6,6}FAP$.

Fig. 3. The effect of $P_{14,6,6,6}FAP$ concentration ($c_{P14,6,6,6FAP}$) on the position (λ_{max}), and the absorbance ratio of IV (filled circles) and III (filled squares) Q bands (A(IV)/A(III))

Fig. 4. Cyclic voltamograms (15 subsequent cycles) recorded at GC electrode immersed in 0.1 M KCl aqueous solution. GC electrode was coated with toluene solution containing 1 mM Mn(III)TPP$^+$Cl$^-$ and 0.4 M $P_{14,6,6,6}FAP$. Scan rate was 10 mV s^{-1}.

Fig. 5. Effect of the aqueous cations on the DPV peak potential for Mn(III)TPP$^+$Cl$^-$. The dashed line indicates theoretical slope in case of cation transfer mechanism. The DPV curves were recorded at GC electrode immersed in the aqueous solutions containing various chloride salts (0.1 M). GC electrode was coated with toluene solution containing 1 mM Mn(III)TPP$^+$Cl$^-$ and 0.4 M $P_{14,6,6,6}FAP$. Values of $\Delta_{aq}^{NB}\phi_{Cat^+}^{o}$ were taken from [35].

Fig. 6: Cyclic voltammograms obtained at GC electrode with a 0.08 μl deposit of 1 mM Mn(III)TPP$^+$Cl$^-$ and 0.4 M $P_{14,6,6,6}FAP$ solution in toluene, immersed into 0.1 M aqueous solution of KPF$_6$, KNO$_3$ and KCl. Scan rate was 10 mV s^{-1}.

Fig. 7. Effect of the aqueous anions on the DPV peak potential for Mn(III)TPP$^+$Cl$^-$. The dashed line indicates theoretical slope in case of anion transfer mechanism. The DPV curves were recorded at GC electrode immersed in the aqueous solutions containing various salts (0.1 M).

GC electrode was modified with 0.08 μl deposit of 1 mM Mn(III)TPP$^+$Cl$^-$ solution in toluene with 0.4 M P$_{14,6,6,6}$FAP (circles) and pure toluene (triangles). Values of $\Delta_{aq}^{NB}\phi_{X^-}^o$ were taken from [35].

Fig. 8. Plot of the peak potential, E_p, vs. the logarithm of the anion concentration in the aqueous solution, $\log c_{X^-(aq)}$. The E_p values were taken from DPV curves obtained at GC electrode modified with 0.08 μl deposit of 1 mM Mn(III)TPP$^+$Cl$^-$ and 0.4 M P$_{14,6,6,6}$FAP solution in toluene immersed into 0.1 M NaClO$_4$ (diamonds) and KCl (squares) aqueous solution.

Table 1. Comparison between the experimental and calculated diffusion coefficients and steady-state currents, i_{ss}, for Fc (3.4 mM) and Mn(III)TPP$^+$Cl$^-$ (3.5 mM) in toluene containing P$_{14,6,6,6}$FAP or THxAP.

	0.1 M P$_{14,6,6,6}$FAP / toluene		0.1 M THxAP / toluene	
	exp	calc	exp	calc
D (Fc) / cm^2 s^{-1}	1.6×10^{-5} ^{a}	1.2×10^{-5} ^{b}	1.2×10^{-5} ^{a}	1.2×10^{-5} ^{b}
D (Mn(III)TPP$^+$Cl$^-$) / cm^2 s^{-1}	3.5×10^{-6} ^{a}	6.5×10^{-6} ^{b}	5.2×10^{-6} ^{a}	6.5×10^{-6} ^{b}
i_{ss} (Fc) / nA	10.2	8.1 ^{a}	8.0	8.1 ^{a}
i_{ss} (Mn(III)TPP$^+$Cl$^-$) / nA	2.4	4.4 ^{a}	3.4	4.4 ^{a}
i_{ss} (Fc) / i_{ss} (Mn(III)TPP$^+$Cl$^-$)	4.3	1.8	2.2	1.8

^{a} calculated from Eq. (2)

^{b} calculated from Eq. (1)

Table 2. Standard Gibbs energies of anion transfer from water to nitrobenzene, $\Delta_{aq}^{NB} G_{X^-}^o$ [35], and standard Gibbs energies of ion-exchange reaction calculated for reaction (8), $\Delta_r G^o$.

	ClO$_4^-$	SCN$^-$	NO$_3^-$	Br$^-$	Cl$^-$	F$^-$	SO$_4^{2-}$
$\Delta_{aq}^{NB} G_{X^-}^o$ / kJ mol^{-1}	7.9	15.8	25.2	27.8	38.2	68.9	176.4
$\Delta_r G^o$ / kJ mol^{-1}	-30.3	-22.4	-13.0	-10.4	0.0	30.7	138.2

Scheme 1
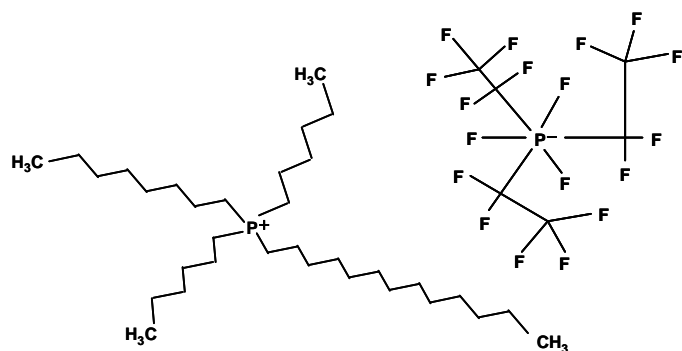
Fig. 1.
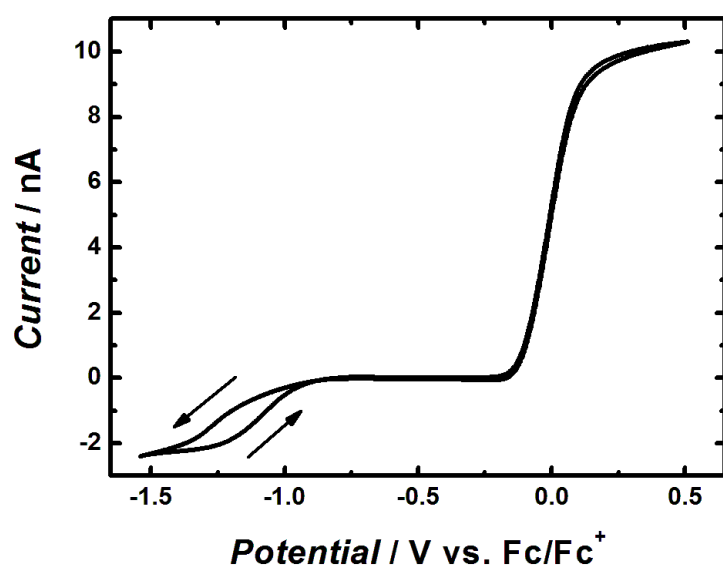
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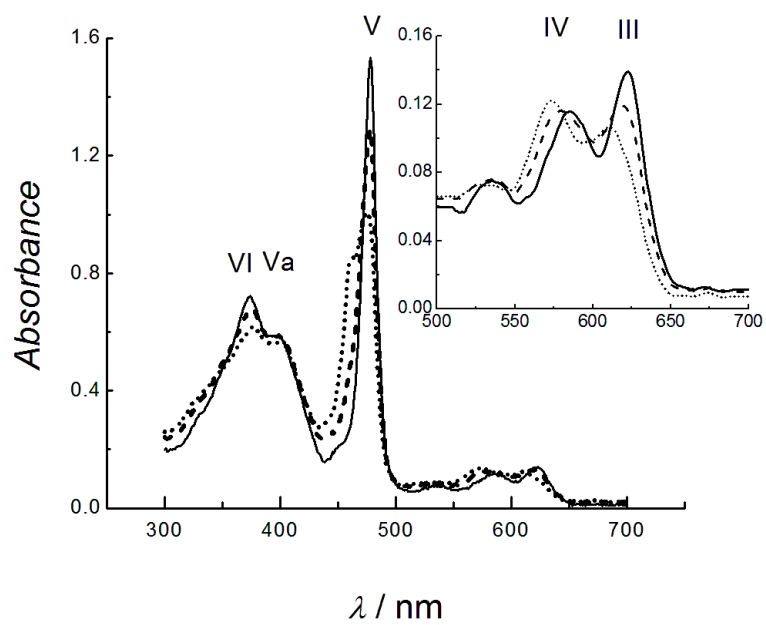
Fig. 3.
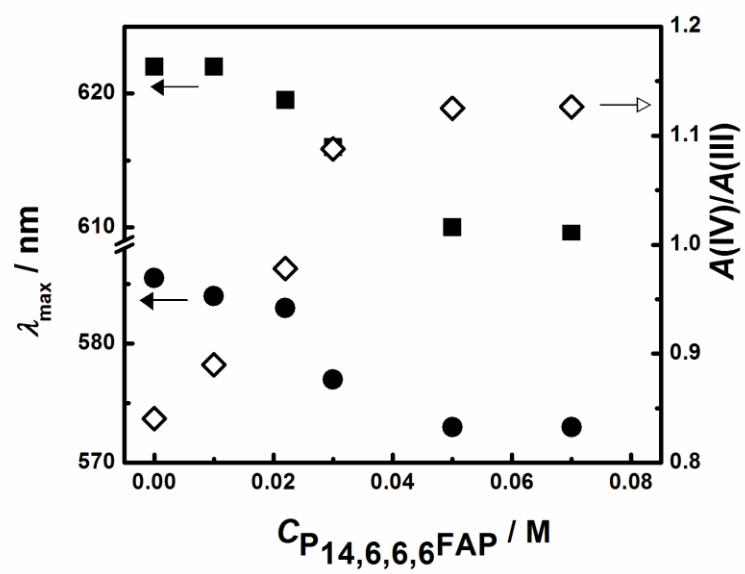
Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

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