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Research Article

The Utilization of Ferrocyanide/Ferricyanide as a New Redox-Pair in the Drop Electrode System

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Abstract

Ion transfer voltammetry at liquid-liquid interfaces supported on a metallic electrode has been investigated to evaluate ferrocyanide/ferricyanide ($K_3Fe(CN)_6$ /$K_4Fe(CN)_6$) as a new redox pair in the aqueous droplet immersed into the organic phase 1,2-DCE. To this purpose, the drop system has been extended to the adsorption-desorption processes associated with the complex formation between aqueous cations and the phospholipid dipalmitoylposphatidylcholine (DPPC) at the polarizable water/1,2-DCE interface in the drop electrode system. From the cyclic voltammetry experiments, the redox couple ferrocyanide/ferricyanide has been shown to be a useful candidate for ion transfer voltammetry application in liquid-liquid soft interfaces.

Keywords
Three electrode system
Drop electrode
Ion transfer voltammetry
Adsorption
Ferrocyanide/Ferricyanide

FERROSİYANÜR/FERRİSİYANÜR’ÜN DAMLA ELEKTROT SİSTEMİNDE YENİ BİR REDOKS ÇİFTİ OLARAK KULLANIMI

Özet

Bir metalik elektrotla desteklenen sıvı-sıvı ara yüzeylerdeki iyon transfer voltametrisi çalışmalarında, ferrosiyanür/ferrisiyanür ($K_3Fe(CN)_6$/$K_4Fe(CN)_6$) yeni bir redoks çifti olarak kullanılmıştır. Sıvı-sıvı ara yüzey, metal elektrotla desteklenmiş su damlasının 1,2-DCE’den (1,2-dikloretan) oluşan organik faza daldırılması ile elde edilmiştir. Bu amaç için damla elektrot sistemi, organik fazda bulunan fosfolipit dipalmitoilfosfatidilkolin (DPPC) ile su fazında bulunan katyon arasında gerçekleşen adsorpsiyon-desorpsiyon prosesinde kullanılmıştır. Dönüşümlü voltametri çalışmalarından elde edilen sonuçlar, redoks çifti ferrosiyanür/ferrisiyanür’ün sıvı-sıvı ara yüzey voltametri çalışmaları için kullanışlı bir aday olabileceğini göstermiştir.

Anahtar Kelimeler
Üç elektrot sistemi
Damla elektrot
İyon transfer voltametrisi
Adsorpsiyon
Ferrosiyanür/Ferrisiyanür

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INTRODUCTION

ITIES (Interface between Two Immiscible Electrolyte Solutions) electrochemistry has gained plenty of attention because of its huge number of applications and has proved to be suitable for analytical applications. Liquid-liquid interfaces, also known soft interfaces, are formed between two immiscible (ideally zero-mutual miscibility) electrolyte solutions. Many researches over the last decade has been devoted to transpose liquid-liquid interfaces as practical applications including charge transfer reactions, electrochemical catalysis, adsorption and electrodeposition. Such processes find applications in electrochemical catalysis, chemical sensor, drug release, solvent extraction and energy conversion. A large number of simple and facilitated ion-transfer reactions which are of fundamental importance for many biological and technological systems can be studied at the ITIES, but not at the metal electrodes. The ambient air and most of our food are today contaminated by non-negligible quantities of heavy-metal ions such as lead, cadmium or mercury. They are released by human industrial or transportation activities. Their toxicity represents an important warning because they are continuously accumulated by living organisms. In this point of view, electrochemical studies on the transfer of heavy metal ions at liquid-liquid interfaces have also been carried out [1].

The study of ion transfer across a liquid-liquid interface modified by an adsorbed phospholipid monolayer has proven to be a topic of great interest not only because this system can simulate the half of a cellular membrane, but also because the interactions between monolayers and multiple compounds can be correlated to their lipophilicity and their electrochemical properties when controlling the potential difference across this membrane. More important, this electrochemical methodology has shown for the first time that phospholipids can act as ionophores to complex hydrophilic ions and allow their extraction to the organic phase [2].

Interfacial tension measurements as a function of the potential difference between the two phases, called electrocapillary measurements, have been used to characterize the adsorbed phospholipid monolayer. This methodology has been extended over the last thirty years to study the interactions of both neutral and/or charged species such as drug molecules with phospholipids and to determine the Gibbs energy of interaction [3-5].

Following the pioneering work of Marken et al. [6-8] and Compton et al., [9, 10] ion transfer voltammetry at liquid-liquid interfaces supported on a metallic electrode has also been investigated. Similar to that reported by Ulmeanu et al., [11] a liquid-liquid interface was formed by immersing a platinum electrode fully covered by an aqueous droplet containing a fixed concentration of a redox pair into a 1,2-DCE solution. Using this simple approach, the standard Gibbs transfer energies of amino acids and small peptides across the water-DCE interface can be determined [12].

The redox couple used in the drop electrode systems has a significant effect on the results obtained, especially the complex formation process. In order to verify the strong effect of the cation contained in the aqueous drop in this process, the $IrCl_6^{-2}$ / $IrCl_6^{-3}$ redox couple we used previously was replaced by the redox couple $K_3Fe(CN)_6$, $K_4Fe(CN)_6$. Thus, in this paper, a three-electrode system is utilized for testing a new redox pair adding the aqueous phase to the mainly the desorptive process of a phospholipid from the water–DCE interface.

MATERIAL AND METHOD

Chemicals. The phospholipid employed is dipalmitoyl posphatidylcholine (DPPC) and it was used without further purification. Bis(triphenylphosphoranylidene) ammonium tetrakis (pentafluorophenyl) borate (BTPPATPFB) and bis(triphenylphosphoranylidene) ammonium tetrakis(4-chlorophenyl) borate (BTPPATPBCl) were used as organic phase salts. These salts were obtained by methathesis of bis(triphenylphosphoranylidene) ammonium chloride (Fluka) with lithium tetrakis(4-chlorophenyl) borate (Sigma Aldrich) and potassium tetrakis(4-chlorophenyl) borate (Fluka), respectively. A similar procedure was used to preparation of tetraethylammonium tetrakis(4-chlorophenyl) borate (TEATPBCl) from tetramethylammonium chloride (Fluka) and potassium tetrakis(4-chlorophenyl) borate. $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, Hydrochloric acid (HCl), Calcium chloride ($CaCl_2XH_2O$), Lithium chloride anhydrous (LiCl), bis(triphenylphosphoranylidene) ammonium chloride (BTPPACl) and 1,2-dichloroethane (1,2-DCE) were used as received from Fluka. The aqueous and organic phases were prepared with deionized water (Milli-Q, Millipore Corp.) and 1,2-DCE, respectively.

Apparatus and Electrochemical Measurements. A drop of a volume of 10 µl of an aqueous solutions contains an equimolar mixture of oxidized and reduced iron species, namely $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ was depositing using a syringe on the Pt disc electrode mounted in a Teflon holder (Metrohm, CH). The size of the droplet is required to ensure that the entire electrode surface is covered. The electrode with its droplet turned over and immersed immediately into a 1,2-DCE (of a certain volume) including a supporting electrolyte. A Pt wire was used as the counter electrode, and an Ag wire coated with AgCl was used as the organic phase reference electrode. The platinum electrode surface was polished with alumina (1.0, 0.3 and 0.05 µm) just before starting to each experiment. Then, the disc electrode surface was rinsed well with water and acetone. Figure 1 shows the schematic diagram of the electrochemical cell used in the experiments. Detailed description of the electrochemical cell employed has been reported elsewhere [11]. All experiment was performed at room temperature.

The cyclic voltammetry (CV) measurements were conducted using a 4-electrodes potentiostat with a standard 3-electrode configuration. TEATPBCl was employed as a reference electrolyte to change potential differences into Galvani potential scale by adding at the end of each experiment. Half wave potential of the reference is 0.048 volt against to Ag/AgCl reference electrode.

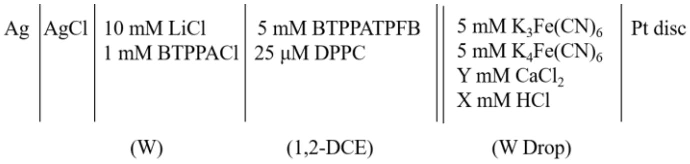


Figure 1. Electrochemical cell employed in the drop system. The double line indicates the interface between water drop and DCE.

RESULT AND DISCUSSION

At the interface between two immiscible liquids, like water and oil, a potential difference is established by solvent dipole orientation in the vicinity of the interface and the existence of excess free charges close to it. This potential difference can be derived by the equality of the electrochemical potential of species i in each phase: $\tilde{\mu}_i^w = \tilde{\mu}_i^o$

where, $\tilde{\mu}_i^w = \mu_i^{0,w} + RT\,ln\,a_i^w + z_iF\varphi^w$

Here, $\tilde{\mu}_i^w$ stands for the electrochemical potential, $\mu_i^{0,w}$standard electrochemical potential, z_i the charge and a_i^w the activity of the species i dissolved in water. At the same time φ^w represents the Galvani potential in the aqueous phase. An equivalent expression can be obtained for the species i in the organic phase. Thus, the galvanic potential difference between the water and the organic phase can be obtained:

$$\Delta_o^w\varphi = \varphi^w - \phi^o = \Delta_o^w\varphi_i^0 + \frac{RT}{z_iF}\;ln\left(\frac{a_i^o}{a_i^w}\right)$$

This equation can be rewritten by including the activity coefficients (γ_i^o, γ_i^w)

$$\Delta_o^w\varphi \;= \Delta_o^w\varphi_i^{0'} + \frac{RT}{z_iF}ln\left(\frac{c_i^o}{c_i^w}\right)$$

where $\Delta_o^w\varphi_i^{0'}$ represents the so-called formal transfer potential:

$$\Delta_o^w\varphi_i^{0'} = \Delta_o^w\varphi_i^0 + \frac{RT}{z_iF}ln\left(\frac{\gamma_i^o}{\gamma_i^w}\right)$$

In consequence, when the potential is varied, the flow of the current will occur to maintain the electrochemical equilibrium according to the Nernst equation. In the presence of an ion susceptible of being transferred across the interface, like tetramethylammonium (TMA^+), a current density proportional to the mass transport of the ion toward the interface as well as to its concentration will be observed. Thus, from simple electrochemical experiments, ion transfer voltammograms can be obtained. In principle, when the oxidation at the platinum electrode of an electroactive species, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ takes place, an ion transfer reaction must occur in order to maintain the electroneutrality balance (Figure 2).

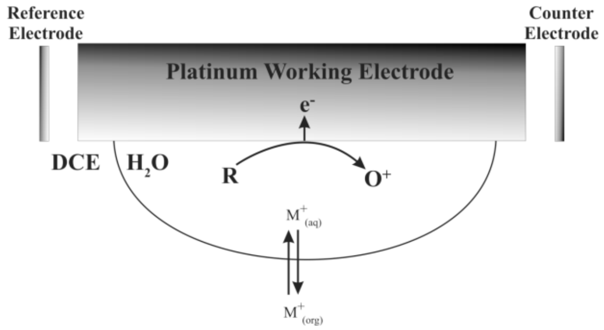
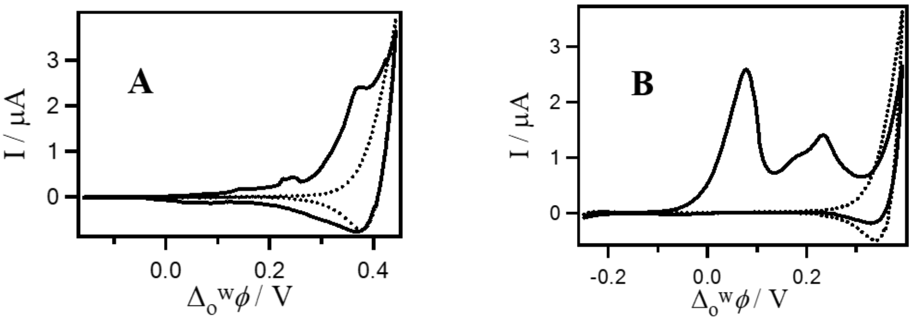


Figure 2. Schematic representation of the droplet method in which an aqueous droplet contains an electroactive species R, which is oxidized to O^+ accompanied by the transfer of cations M^+ from a water to DCE.

Recently, this electrochemical system has been extended not only to the ion transfer processes but also to the adsorption-desorption processes associated with the phospholipid interfacial complex formation [13, 14]. It has been observed that the interfacial tension diminishes in the presence of the phospholipid at potentials where the adsorption occurs. However, as the potential increases, the desorption of charged complexes of DPPC takes place, resulting in a potential-dependent drop shape phenomenon. This is the case that we get from the electrochemical experiments, as shown in Figure 3. This figure shows how the aqueous drop shape changes during the potential scan using the electrochemical cell in Figure 1.

Figure 3. Video snapshots of aq. droplet immersed into DCE in presence of DPPC 25 µM containing BTPPATPFB 5 mM. Aqueous droplet composition in the electrochemical cell=$K_3Fe(CN)_6$ 5mM, $K_4Fe(CN)_6$ 5 mM and HCl 10 mM and Y=0.

Figure 4 shows the voltammograms connected with the ion transfer in presence and in absence of the phospholipid DPPC. Only very little current flow occurred within the potential window in absence of DPPC, which was the result of the charging current. Outside the potential window in absence of the phospholipid, the ions of the support electrolyte begin to transfer from the phase they are in to the opposite phase, and this causes the background current to increase. The right side of the curve means that the aqueous phase is made positive, as assigning the polarity of the interface is traditionally done with respect to the aqueous phase. In other words, the potential window (dotted lines in the voltammograms) is limited at negative potentials by the transfer of the aqueous anions, i.e. $Fe(CN)_6^{3-}$ or $Fe(CN)_6^{4-}$, which is in turn connected with the reduction of $Fe(CN)_6^{3-}$. However, the oxidation of $Fe(CN)_6^{4-}$ is accompanied by the transfer of potassium ions at the positive side of the potential window.



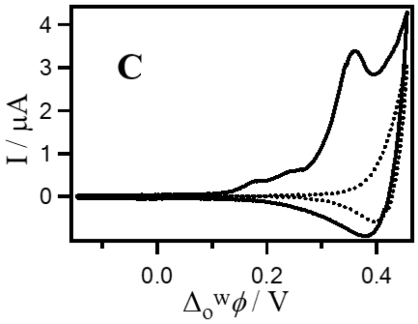


Figure 4. Cyclic Voltammograms of the supporting electrolyte 5 mM BTPPATPFB with the Cell in the absence (dotted lines) and presence (solid lines) of DPPC in 1,2-DCE. A: X=0, Y=0; B: X=10, Y=0; C: X=0, Y=10. Scan rate was 5 mV/s. Ion transfer voltammograms were recorded 30 min. after adding DPPC into 1,2-DCE solution.

When we look at the voltammogram, there is no increase in current flow in the absence of the phospholipid in the organic phase. But, when we include the phospholipid in the organic phase 1,2-DCE, the current increases considerably towards the positive potential values above of about 0.15 V. This can be explained by the fact that the phospholipid in the organic phase is first adsorbed at low potential values (more negative potentials) at the interface. As shown in Figure 4, When potential scanning is started, the phospholipid adsorbed on the interface begin to desorb into the organic phase across the interface.

However, aqueous ions in the aqueous phase can form a complex with the phospholipid molecules in adsorbed form. This situation seems to be in accordance with the literature previous studies [2, 15]. Therefore, the positive current signal in the voltammogram is probably due to the desorption of the phospholipid and the ion transfer assisted by aqueous ions to the organic phase.

It has also been found that voltammograms are time dependent; that is, the balancing time has a important effect on the total charge during forward scan. However, after thirty minutes, voltammograms can always be obtained with high reproducibility, which ensures that steady state has been reached in this time interval. In fact, adsorption is a diffusion-controlled process and absolute surface coverage will be proportional to square root of the time. Therefore, the voltammograms in the Figure 4 were recorded after a 30-minutes stabilization time, which are reproducible voltammetric signals.

CONCLUSION

We have already studied about the drop shape phenomenon at the polarizable liquid-liquid interfaces [14]. In that work, we used two different compounds, namely K_2IrCl_6/K_3IrCl_6 or $FeSO_4/Fe_2(SO)_3$, as a redox pair in aqueous phase. However, in this current work, we have shown electrochemical proof for the utilization of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ as a new redox pair in aqueous ion-lipid complexes adsorbed at the interface between DPPC and the ions in the aqueous phase ions. In other words, the redox pair $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ has confirmed the strong influence of the cations present in the aqueous droplet used to form polarizable liquid-liquid interface with 1,2-DCE phase.

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