

Title: Novel redox probes for electrochemistry at the three-phase junction

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Abstract

This thesis aimed to investigate the electrochemistry of different compounds at the organic|aqueous|electrode three-phase interface. For three-phase electrochemistry, I used the microdroplet based three-phase electrode (TPE) configuration and TPE configuration created in microfluidic devices.

In the microdroplet based TPE system, a microdroplet volume of a water-immiscible organic solvent containing a neutral lipophilic redox compound (without supporting electrolyte) is deposited on the working electrode and immersed in the aqueous electrolyte. The electron transfer across the electrode|organic interface results in the ions transfer from aqueous to the organic phase to maintain the electroneutrality in the organic droplet. This method enables determining the lipophilicity of different transferring ions at various organic|aqueous interfaces. Further, the lipophilicity of moving ions can be correlated with their biological and pharmacological activities. Additionally, the lipophilic|hydrophilic interface formed at TPE is the simple design of complex biological systems, hence studying electrochemistry of biologically relevant compounds and ions at TPE is required.

The first section of my work concerns the use of different quinones for cation transfer studies. Generally, electroactive organic and metallorganic compounds have been used to study ion transfer at TPE system. However, the redox behaviour of biologically essential compounds is not often studied at the TPE setup. Hence, I studied the reduction of essential quinone derivatives such as 1-aminoanthraquinone (AQ), and 2,3-dichloro-1,4-naphthoquinone (NQ) at glassy carbon (GC) working electrode|n-octyl-2-pyrrolidone (NOP)|aqueous electrolyte three-phase interface for cation transfer studies. Both AQ and NQ functional groups are present in various biomolecules, and the activities of these biomolecules depend on the redox behaviour of the quinone moieties (AQ and NQ). At the three-phase junction, AQ exhibited a single step two-electron reduction to AQ^{2-} , which was supported by the cations transfer from the aqueous to NOP. However, NQ reduction occurred in two steps; in the first step (NQ to $NQ^{\bullet-}$ radical anion), $NQ^{\bullet-}$ transferred to the interface with the reduction potential dependent on the hydrophobicity of the aqueous anion due to salting-out effects. In the second reduction ($NQ^{\bullet-}$ to NQ^{2-}), cations transferred from the aqueous phase to NOP. With AQ and NQ, the cation transfer potential depends on the ionic

potential of the aqueous cation due to the ion-pair formation between the transferred cation with the reduced quinone in NOP.

The second section comprises the study of 7,7,8,8-tetracyanoquinodimethane (TCNQ) for cation transfer at GC|NOP|aqueous TPE configuration. TCNQ is an organic redox probe, employed in the studies of heterogeneous electron and alkylammonium cation transfer across the organic|aqueous interfaces. To examine TCNQ's applicability for TPE cation transfer reactions, it is essential to investigate for both inorganic and organic cations. Consequently, I studied the reduction of TCNQ at GC|NOP|aqueous three-phase interface for both inorganic and organic cations transfer reactions. At the three-phase junction, the reduction of TCNQ to $\text{TCNQ}^{\cdot-}$ and TCNQ^{2-} leads to the reduced TCNQ anions ($\text{TCNQ}^{\cdot-}$ and TCNQ^{2-}) expulsion to water instead of cation transfer from the aqueous phase to NOP. TCNQ anion expulsion was confirmed by the decrease of current in the continuous scans, and the reduction potentials did not depend on the nature of the aqueous cation. Moreover, the reduction potential of TCNQ to $\text{TCNQ}^{\cdot-}$ varied with the hydrophobicity of the aqueous anion because of the salting-out effect when $\text{TCNQ}^{\cdot-}$ transferred to the water. Therefore, TCNQ is not a suitable redox probe for TPE cation transfer studies.

The third part of my work includes the three-phase anion transfer studies using a highly lipophilic mononuclear ruthenium(II) complex $[\text{Ru}^{\text{II}}(\text{LR})(\text{L})]^0$ having two tridentate ligands of 2,6-bis(1-(2-octyldodecan)benzimidazol-2-yl)pyridine (LR) and 2,6-bis(benzimidazol-2-yl)pyridine (L). So far, commercially available decamethylferrocene (DMFc) and tetraphenylporphyrinato-metal complexes (TPP-metal) have been used for anion transfer studies. It is known that the expulsion of oxidised DMFc to water is possible when the aqueous phase contains hydrophilic anions (Cl^-); also, TPP-metal complexes interact with the transferring nucleophilic anions (F^- and SCN^-). Thus, a new, highly lipophilic non-interacting redox probe is needed. Therefore, during my internship in Japan, I synthesised $[\text{Ru}^{\text{II}}(\text{LR})(\text{L})]^0$ complex and investigated the anion transfer studies at GC|nitrobenzene(NB)|aqueous TPE setup. The oxidation of $[\text{Ru}^{\text{II}}(\text{LR})(\text{L})]^0$ to $[\text{Ru}^{\text{III}}(\text{LR})(\text{L})]^+$ in NB is followed by the anion transfer from the water to NB. Anion transfer was verified by examining the dependence of oxidation potential on the hydrophobicity and concentration of the aqueous anion. Usually, Ru complexes are not used in anion transfer studies since they do not undergo $\text{Ru}^{\text{II/III}}$ oxidation before the water oxidation at TPE. In this work, by choosing bis(benzimidazolyl)pyridine based ligands, the lower $\text{Ru}^{\text{II/III}}$ oxidation potential and high lipophilicity of $[\text{Ru}^{\text{II}}(\text{LR})(\text{L})]^0$ complex was achieved.

The last section of the thesis constitutes the investigation of the ion transfer voltammetry in the microfluidic TPE setup of different geometries. In the microfluidic device, the parallel flow of the organic|aqueous interface across the microband electrode creates the three-phase junction; which is used to study the ion transfer across the interface in hydrodynamic condition. D. Kaluza et al. from our group have performed a comparison ion transfer study between a droplet-based TPE system and a microfluidic TPE system. Also, they investigated the strange effect of flow rate

with the limiting current in three-phase cyclic voltammetry. To contribute further, I tried to examine the voltammetry in the T-junction microfluidic TPE system; where one phase is stationary, and the other is flowing. I fabricated different models of T-junction and chemically hydrophobised the microchannel to have the stationary organic phase and flowing aqueous phase. The interface was not stable at T-junction and always moved back-and-forth. Hence the ion transfer voltammetry was not reproducible. Besides, increasing the hydrophobicity and providing PDMS micropillar structures to the organic microchannel could not able to prevent the tiny back-and-forth vibration of the interface.