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Investigation of the effects of metalloporphyrin species containing different substitutes on electron transfer at the liquid/liquid interface

Xiaoquan Lu [a,*], Hairui Zhang [a], Lina Hu [a], Cunyuan Zhao [b], Liming Zhang [a], Xiuhui Liu [a]

[a] *College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, Gansu, China*
[b] *College of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, China*

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Abstract

Scanning electrochemical microscopy (SECM) technology has been used to investigate the kinetics of heterogeneous electron transfer (ET) as a function of driving force at the interface between two immiscible electrolyte solutions (ITIES). The ET between metalloporphyrin species containing different substitutes in nitrobenzene and other redox species in the aqueous phase was studied and the rate constants were also extracted from the dependence of the steady-state current at a micrometer-sized tip electrode on the distance between the tip and the phase boundary when compared with the theoretical working curves. Corresponding to the various metalloporphyrin substitutes, SECM was demonstrated to be a useful means to study the effect of molecular structure on the kinetics of heterogeneous ET.

Keywords: Substitutes; Metalloporphyrin; Effects; Electron transfer; Liquid/liquid interface

1. Introduction

Complexes of many porphyrins with various metallic ions have been extensively studied in order to understand the biosynthetic formation and biological activity of natural compounds [1]. The continuing studies of those complexes are due to the important roles of metalloporphyrin played in biological activities as for iron complex in the haemoproteins and electroactive agents of catalytic application on mimic membranes [2–5]. A liquid/liquid interface has been suggested as a simple model for biological and artificial membranes [6]. The kinetics of the charge transfer at the ITIES could be probed directly by SECM [5,7–9]. Heterogeneous ET at a liquid/liquid (L/L) interface involves the transfer of an electron under potential control from an electron donor in one phase to an acceptor in the opposing phase. In earlier studies [10,11], the interface was under potentiostatic control and the finite potential window, which was governed by ion transfer process, limited the number of redox reaction system and also hindered further experimental operation.

Relatively few papers are devoted to the studies of the effect of different substituents of porphyrin zinc on the ET rate across the ITIES. In this work, ET between three types of porphyrin zinc and potassium ferrocyanide was investigated at the nitrobenzene/water (NB/W) interface, respectively. We also intended to calculate the electron affinities of different substitutes of porphyrin zinc to support the prediction that porphyrin zinc with different substitutes would present different electrochemical characteristic during ET reactions. As ET reactions, we evaluated their kinetics by SECM technology and found that the relationship, which were not only between rate constant and the driving force, but also among different molecular structures at the unmodified NB/W interface, obey the Bulter–Volmer equation in a rather wide potential region.

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[*] Corresponding author. Tel./fax: +86 931 7971276.
E-mail address: luxq@nwnu.edu.cn (X. Lu).

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2. Experimental section

2.1. Chemicals

Lithium chloride (LiCl) (Shanghai Runjie Chemical Reagent Co. Ltd.), nitrobenzene (NB) (Shanghai Chemical Reagent Co. Ltd.), sodium perchlorate ($NaClO_4$) (AR, Beijing Chemical Reagent Co. Ltd.) and potassium ferrocyanide ($K_4Fe(CN)_6$) were used as received without further purification. Tetrabutylammonium perchlorate ($TBAClO_4$) was synthesized with tetrabutylammonium chloride (TBACl) (AR, Aldrich) and prepared in the same method reported elsewhere [12]. 5,10,15,20-Tetraphenyl porphyrin zinc (ZnTPP), methyloxy-5,10,15,20-tetraphenyl porphyrin zinc ($ZnTPP(OCH_3)$) and mono-hydroxyl-5,10,15,20-tetraphenyl porphyrin zinc (ZnTPP(OH)) were also synthesized in our lab [13]. All chemicals were analytical grade or better. Special precautions were prepared to deal with NB and other hazardous chemicals when necessarily. Aqueous solutions with various concentrations were prepared from distilled water with LiCl and $NaClO_4$ as supporting electrolytes, while organic solutions were prepared from NB and with $TBAClO_4$ as supporting electrolyte.

2.2. Electrodes and electrochemical cells

A three-electrode arrangement was used. The reference electrode (Ag/AgCl) was prepared by coating AgCl onto an Ag wire, and platinum (Pt) wire was adopted as counter electrode without any further treatment. The working electrode was Pt ultramicroelectrode (UME), which was prepared by heat-sealed Pt wire (25 μm diameter, Kunming Institute of Precious Metals.) in borosilicate glass capillaries at vacuum state, and then polished and sharpened as previous description [14] until the characterized ratio of the tip, R_G ($=r_g/a$, where r_g is the tip radius and a is the radius of Pt wire) was between 5 and 6. To make the tip approach the interface more closely and avoid the glass sheath contacting the phase interface, a smaller RG (<10) is significant and necessary. The tip was polished with 0.3 and 0.05 μm alumina power, rinsed with ethanol and water, respectively and dried with nitrogen prior to each measurement. The SECM cell was described previously [15], which was like traditional instrument except for its much smaller diameter (the diameter of the glass cell is 0.6 cm), and both volumes of water and organic phases are 0.3 mL during each experiment. Before application, the cell has to be silanized by marinating it in chlorotrimethylsilane for 12 h to make NB easily laid on the top of the aqueous phases. The small size of the cell not only decreased the NB evaporating, but also provided sufficient convenience to make NB as the top phase.

2.3. SECM apparatus and procedures

Cyclic voltammetry (CV) and SECM measurements were performed with a commercially available SECM instrument (CHI 900, CH-instrument Co. Ltd, Austin, USA). The experimental system for investigation of ET at the interface can be represented as follows:

$$\begin{aligned}&\mathrm{Ag/AgCl/0.3\ mL,\ 0.1\ M\ LiCl},\ x\ \mathrm{mMNaClO_4},\\&y\ \mathrm{mMK_4Fe(CN)_6//NB\ 0.3\ mL,\ 10\ mM\ TBAClO_4},\\&\mathrm{1\ mMZnTPP(ZnTPP(OCH_3)\ or\ ZnTPP(OH))/tip}\end{aligned}$$

The working electrode-UME was placed in the upper phase (NB solution) throughout all the measurements, and applying the cyclic voltammetry to record the signals at the tip from the redox species. Subsequently, the tip was biased at a potential in the diffusion-controlled region. Approach curves, where tip current (i_T) was monitored as a function of distance (d), were obtained by moving the tip toward the liquid/liquid interface. The tip current (i_T) was normalized by the diffusion limiting current $i_{T,\infty}$ ($= 4nFDCa$, where D represents the diffusion coefficient, C is the concentration of the redox couple, a is the electrode radius, and F is Faraday constant). All approach curves were gained by the feedback mode and the whole experiments were conducted at the ambient laboratory temperature (22 ± 2 °C).

3. Results and discussion

The electrochemical properties formal potential of the redox couples in NB were obtained from the cyclic voltammogram at the Pt UME vs a Ag/AgCl electrode immersed in the bottom phase (aqueous solution). In order to avoid the complication of diffusion effect of the second phase [16,17], the program of SECM about liquid/liquid feedback experiments often employed a high concentration of reactants in organic phase comparing with that of the mediator in aqueous phase. However, because of the low concentration ratio $K_r(C^*_{H_2O}/C^*_{NB})$ in our work, the diffusion of both redox couples had to be considered, which gave an evidence to the procedure proposed by Barker et al. [8]. Moreover, by reason of the small value of K_r, mass transfer which limited the experimental accessibility of the rate constants can be overcome in some extent, and the application of relative lower concentrations of the reactants in the aqueous phase was theoretically predicted to have considerable advantages for decreasing the ET reaction rate and causing the fast kinetic limited approach curves to be more readily distinguished from one another. The constant composition approximation is dependent on both K_r and r (D_w/D_o). When the diffusion coefficient of redox species in water is greater than that of reactants in organic solution, the constant composition model is valid to the lower K_r and the concentrations of $K_4Fe(CN)_6$ in water are varied in a relative wide range. In our systems, the measured values of D_{ZnTPP}, $D_{ZnTPP(OCH_3)}$, $D_{ZnTPP(OH)}$ and $D_{K_4Fe(CN)_6}$ are $2.9 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$, $2.8 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$, $2.7 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$ and $6.7 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$, respectively, and $r = D_{K_4Fe(CN)_6}/D_{ZnTPP}$, $D_{K_4Fe(CN)_6}/D_{ZnTPP(OCH_3)}$, $D_{K_4Fe(CN)_6}/D_{ZnTPP(OH)} \approx 2.3, 2.4, 2.5$.