

Study of Electron Transfer Reactions Between a Water/1,2-Dichloroethane Interface by Scanning Electrochemical Microscopy

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Abstract: Electron transfer (ET) from ascorbic acid (AA) in aqueous to ferrocene (Fc) in 1,2-dichloroethane (DCE) was probed by the scanning electrochemical microscopy (SECM). The rate constants were extracted from the dependence of the steady-state current at ultramicro-electrode (UME, tip) on the distance between the tip and the phase boundary by comparison to theoretical working curves.

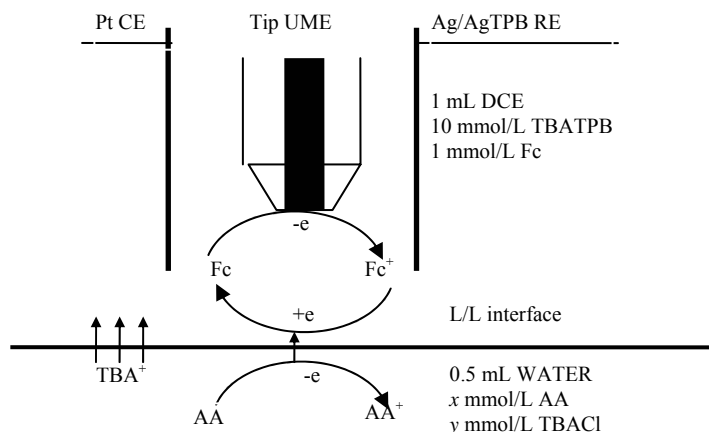
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The electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) or liquid/liquid (L/L) interface has been studied extensively during the past decades. Electron transfer (ET) between the L/L interface is a very interesting case in electrochemistry and biochemistry. But the ion transfer (IT) and electron transfer (ET) have not been clearly discriminated until scanning electrochemical microscopy (SECM) has been first employed by Bard *et al.* in 1989¹⁻⁴. From then, the kinetics of ET and IT at the ITIES were measured directly by SECM. Ascorbic acid (Vitamin C, AA), which could participate in various biochemical reactions in organism and it is a very important substance in life behavior. It was contained in food, vegetables and especially in fruits. The electrochemical oxidation of AA was studied by conventional method like cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Some electrodes or modified electrodes were employed to oxidize AA, but there is few report about ET of AA at ITIES measured by SECM.

The cell used in this work was shown as **Figure 1**. A Pt wire (25 μm diameter) was sealed in glass tubes and heated, which was used as SECM tip. The counter electrode was a Pt electrode, and Ag coated AgTPB (silver tetraphenylborate,) was used as the reference electrode. All electrochemical measurements were performed using a CHI 900 system (CH Instrument, USA). All of the experiments were carried out at room temperate (22 \pm 2 $^{\circ}\text{C}$).

We put the tip in DCE phase, which contained 1 mmol/L ferrocene (Fc) and 10 mmol/L tetrabutylammonium tetraphenylborate (TBATPB). AA acted as redox reagent in aqueous and tetrabutylammonium chloride (TBACl) served as supporting electrolyte.

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Figure 1 Schematic diagram of the electron transfer between DCE/water interface

The common ions (TBA^+) in two phase were employed to control the potential of this ideal no polarized interface.

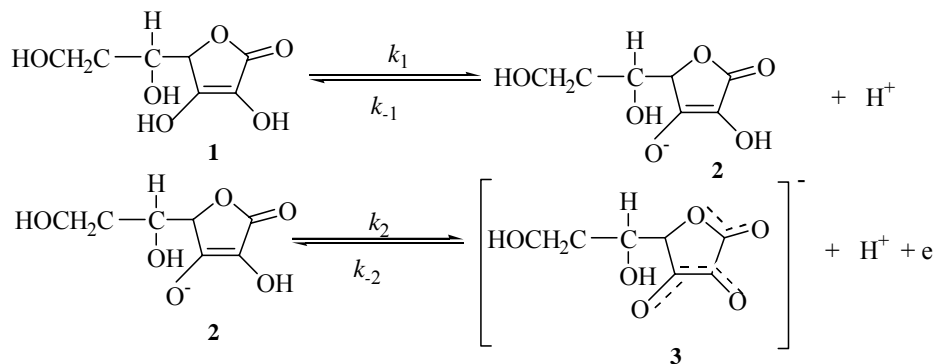
Feedback mode is the main working mode in quantitative analysis of SECM experiment data at present. When the tip approached the interface, the current of tip (i_T) increased as the distance (d) between the tip and interface decreased, which corresponded to the positive feedback mode of SECM. When the d was diminishing, the i_T was decreased, and this mode was named negative feedback mode. The approach curves (i_T - d) were recorded and the heterogeneous rate constant can be evaluated from fitting these curves with theoretical values.

In this work, we implemented the following ET reaction at the L/L interface:



The detailed mechanism of AA oxidation was shown in **Scheme 1**.

In this case, IT (TBA^+ transfer) is not rate limiting step to reaction (1). The following equations can be used to extract the heterogeneous rate constants (k_f) from the experimental i_T - d curves⁴:

Scheme 1 The proposed mechanism for oxidation of ascorbic acid

$$I_T^c = 0.68 + 0.78377/L + 0.3315\exp(-1.0672/L) \quad (2)$$

$$I_T^{\text{ins}} = 1/(0.15 + 1.5358/L + 0.58\exp(-1.14/L) + 0.0908\exp[(L-6.3)/(1.017L)]) \quad (3)$$

$$I_S^k = 0.78377/[L(1+1/\Lambda)] + [0.68 + 0.3315\exp(-1.0672/L)]/[1+F(L,\Lambda)] \quad (4)$$

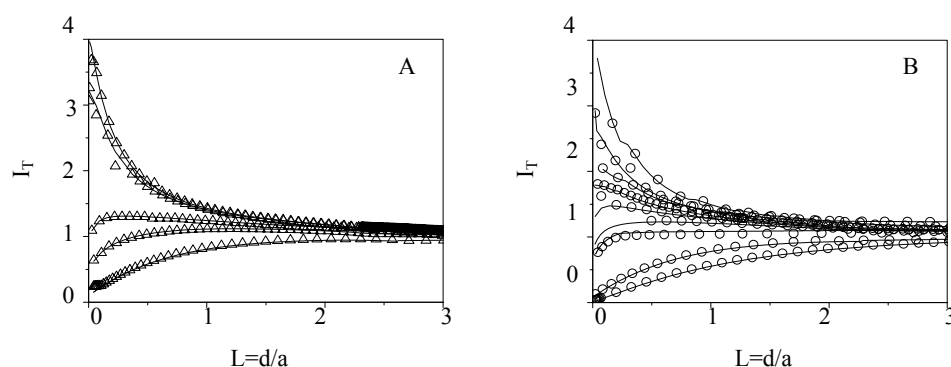
$$I_T^k = I_S^k(1 - I_T^{\text{ins}}/I_T^c) + I_T^{\text{ins}} \quad (5)$$

where I_T^c , I_T^k , I_T^{ins} represent the normalized tip currents for diffusion-controlled regeneration of a redox mediator, finite substrate kinetics, and insulating substrate, respectively, at a normalized tip – substrate separation, $L=d/a$. I_S^k is the kinetically controlled substrate current, $\Lambda=k_f d/D$, where k_f is the apparent heterogeneous rate constant, D is the diffusion coefficient of the redox mediator in the top phase, and $F(L,\Lambda) = (11 + 7.3\Lambda)/[\Lambda(110 - 40L)]$. These current are normalized by the tip current at an infinite tip – substrate separation ($i_{T,\infty}$), $i_{T,\infty} = 4nFDac$.

Equation (4) and (5) were used to fit the families of approach curves obtained at different concentrations of AA and TBACl in the water phase (**Figure 2**). Good agreement between theory (solid line) and experiment data (symbols) were found in figure. The obtained k_f values within the range $0.00004 \sim 0.05 \text{ cm}^2/\text{s}$ from a diffusion of Fc in DCE of $1.21 \times 10^{-5} \text{ cm}^2/\text{s}$ obtained by steady-state voltammetry⁵.

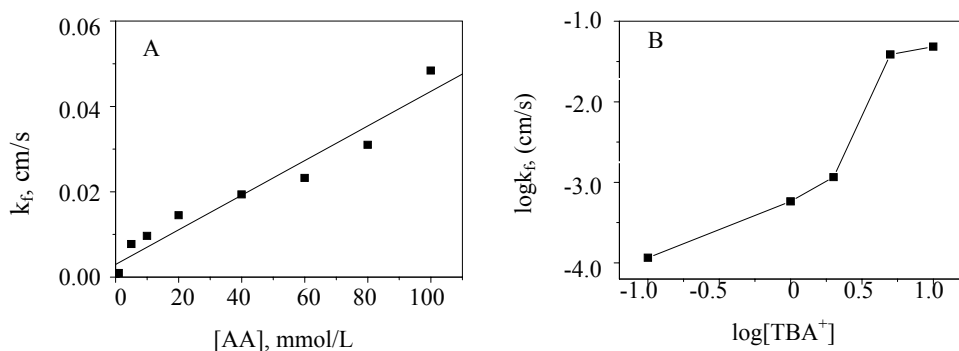
At a given concentration of AA, the apparent rate constant depends on the potential drop across the ITIES, which increases with a increase of the $[\text{TBA}^+]_w$ and $[\text{AA}]$ (**Figure 2**). By the increasing of $[\text{AA}]$, the diffusion from aqueous to interface accelerated. So the interface has more AA than bulk solution, the rate constant of ET increased. At lower concentration of TBA^+ , the potential drop was more negative to the reaction (1),

Figure 2 SECM normalized approach curves for a 12.5 μm Pt tip. The DCE phase contained 1mmol/L Fc and 10 mmol/L TBATPB.



The aqueous phase contained x mmol/L AA and y mmol/L TBACl. From top to bottom, for (A) $x=20$, $y=10, 5, 2, 1, 0.1$; (B) $y=10$, $x=100, 80, 60, 40, 20, 10, 5, 1$. All of the approach rate were $1 \mu\text{m}/\text{s}$.

Figure 3 Dependence of the effective heterogeneous rate constant on [AA] (A) and [TBA⁺] (B). (The other parameters see **Figure 2**)



The k_f decreased accordingly (**Figure 3**).

We have used the SECM to investigate ET occurring at the ITIES *via* a bimolecular reaction between redox species confined to different solvent. The potential drop at the ITIES was controlled by the concentrations of common ions (TBA⁺) in both phases, providing a controllable driving force for the ET reaction. This method could be used in other similitude of biosystems.

Acknowledgments

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