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## A study of dimethylferrocene diffusion and electrode kinetics using microelectrode voltammetry in poly(ethylene glycol) solvent

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**Abstract** The heterogeneous electron transfer rate constant ( $k_s$ ) of dimethylferrocene (DMFc) was estimated using cyclic voltammetric peak potential separations taken typically in a mixed diffusion geometry regime in a polyelectrolyte, and the diffusion coefficient ( $D$ ) of DMFc was obtained using a steady-state voltammogram. The heterogeneous electron transfer rate constant and diffusion coefficient are both smaller by about 100-fold in the polymeric solvent than in the monomeric solvent. The results are in agreement with the difference of longitudinal dielectric relaxation time ( $\tau_L$ ) in the two kinds of solvents, poly(ethylene glycol) (PEG) and  $\text{CH}_3\text{CN}$ , indicating that  $k_s$  varies inversely with  $\tau_L$ ;  $k_s$  is proportional to  $D$  of DMFc. Both  $D$  and  $k_s$  of DMFc in PEG containing different supporting electrolytes and at different temperatures have been estimated. These results show that  $D$  and  $k_s$  of DMFc increase with increasing temperature in the polyelectrolyte, whereas they vary only slightly with changing the supporting electrolyte.

**Key words** Heterogeneous electron transfer rate constant · Diffusion coefficient · Cyclic voltammetry · Dimethylferrocene · Polyelectrolyte

### Introduction

There have been many interesting studies and applications of polymer electrolytes [1, 2]. Polymer electrolytes with high boiling points are potentially useful as solvents for electrochemical studies at elevated temperatures. Also, studies on the elucidation of their properties, such as diffusion rate and electrochemical reactivity, are of considerable importance. Although studies on mass

transport in solid state polyelectrolytes [3–5] have appeared, many problems of the kinetics of electron transfers across the interface between a solid electrode and a rigid or semirigid medium remain to be solved. The kinetics of electrode reactions in polymer electrolytes is important both practically and fundamentally. More importantly, the groups coordinating the ions are constrained in their motion by attachment to the polymer chain and this must lead to highly distinctive behavior at this interface. Further, the constrained nature of the solvent raises important questions concerning the activation mechanism of electron transfer. These polymer electrolytes offer a unique opportunity to probe some of the most fundamental aspects of interfacial electrochemistry. Solvent effects on the rates of chemical and electrochemical reactions have been studied. Recent theoretical and experimental evidence points to the influence of solvent dynamics on the nuclear barrier-crossing frequency of electron transfer reactions [6]. Polymeric solvents offer reaction media whose dynamics are on a vastly different time scale compared to monomer solvents. We can understand some fundamental problems through studying the electron transfer reaction in these solid-state polymer solvents. However, the low molecular weight poly(ethylene glycol) is a convenient liquid electrolyte at room temperature, and it is chemically similar to the amorphous conducting phase in high molecular weight polymers (solid state polymers). Because of the experimental difficulties caused by the electrode/solid-state electrolyte interface, the high resistance of the electrolyte, and uncertainty concerning the role of the surface solid-state film on the electrode, current investigations [7, 8] of electron transfer kinetics have mainly focused on the interface of the liquid polymer/electrode. This case is simpler than that of the solid state polymer/electrode, but we can obtain similar information on the solid state polymer/electrode interface. We have determined the electron transfer rate constant of ferrocene in poly(ethylene glycol) solvent by using steady state voltammograms on a Pt electrode [9]. In this paper, the heterogeneous electron transfer rate

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constant of dimethylferrocene was measured using cyclic voltammetric peak potential separations taken typically in a mixed diffusion geometry regime including both linear and partially radial diffusion [10] in the polyelectrolyte. The dependence of the heterogeneous electron transfer rate constant of dimethylferrocene on temperature and various electrolytes is also discussed.

## Experimental

### Chemicals

Poly(ethylene glycol) (PEG, average  $M = 400$ , reagent grade) was purchased from Shanghai Reagent (China), and analytical reagents such as lithium perchlorate ( $\text{LiClO}_4$ ), sodium perchlorate ( $\text{NaClO}_4$ ), and potassium perchlorate ( $\text{KClO}_4$ ) were obtained from Beijing Pure Chemical (China). Tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ , TBAP) of reagent grade was obtained from Tokyo Kasei (Japan). Dimethylferrocene (DMFc) was purchased from Sigma (USA). The PEG and salt samples were dried under vacuum at  $60^\circ\text{C}$  for 24 h without further purification before use.

### Apparatus and procedure

The microelectrode was prepared by sealing a Pt wire with radius of  $2.6\ \mu\text{m}$  or  $26\ \mu\text{m}$  in soft glass tubing. The microelectrode was polished with successively finer grades of  $\alpha\text{-Al}_2\text{O}_3$  ( $1\text{--}0.05\ \mu\text{m}$ ) and finally cleaned in an ultrasonic water bath. The radius of the microdisk electrode was determined voltammetrically from the plot of steady-state current versus concentration of  $\text{Fe}(\text{CN})_6^{3-}$  in  $1\ \text{M}\ \text{KCl}$  with a known diffusion coefficient. A Pt wire (diameter  $1\ \text{mm}$ ) was used as the auxiliary electrode and an Ag wire (diameter  $1\ \text{mm}$ ) as the pseudo-reference electrode. All electrochemical experiments were carried out using a conventional single-compartment Pyrex glass cell. The glass cell, with  $10\ \text{ml}$  capacity, was equipped with a jacket allowing circulation of water from a thermostat (model CS 501, China). The experimental temperature was monitored by the thermostat.

The PEG polymer solution was prepared by mixing appropriate amounts of  $\text{MClO}_4$  ( $\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Bu}_4\text{N}^+$ ) electrolyte and DMFc with stirring and sonication. The cyclic voltammetry was carried out using CV-47 (BAS, USA) and 902-PA (China) voltammograms in an earthed Faraday cage. All potentials were reported relative to the Ag pseudo-reference. All electrochemical experiments were carried out in a dry Ar atmosphere.

## Results and discussion

### Determination of the diffusion coefficient

The measurements of the diffusion coefficient of electroactive species in polyelectrolytes have been reported [3–5, 11–13]. These techniques are from the equation of chronoamperometric current ( $I$ ) at a microdisk electrode according to Shoup and Szabo [14]:

$$I = 4nFDcr\{0.7854 + 0.8862\tau^{-1/2} + 0.2146 \exp(-0.7823\tau^{-1/2})\} \quad (1)$$

$$\tau = 4Dt/r^2 \quad (2)$$

where  $c$  is the concentration of the electroactive species,  $r$  is the microdisk radius, and other symbols have their usual meanings. Equation 1 gives two limiting regimes of  $I$ , depending on the value of the dimensionless parameter  $\tau$ . When  $\tau \gg 1$ , Eq. 1 reduces to a steady-state current equation which is the same as that obtained in a slow potential sweep voltammogram under radial diffusion conditions:

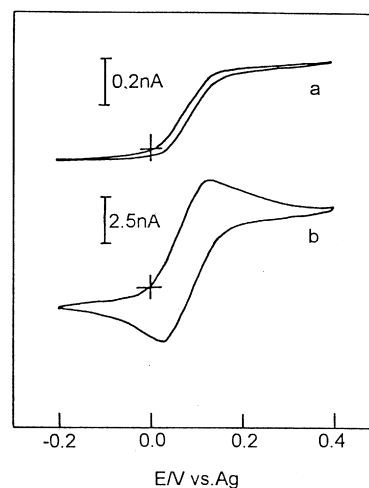
$$I = 4nFDcr \quad (3)$$

When  $\tau \ll 1$ , semi-infinite linear diffusion conditions are obtained, and Eq. 1 reduces to the well-known Cottrell equation:

$$I = \pi^{1/2}nFD^{1/2}cr^2t^{-1/2} \quad (4)$$

In our experiment the microelectrode of radius  $2.6\ \mu\text{m}$  is used and the scan rate is below  $20\ \text{mV/s}$ , so the diffusion coefficient can be obtained by Eq. 3.

Figure 1 shows typical voltammograms of DMFc in the polyelectrolyte  $\text{PEG} \cdot \text{LiClO}_4$ . Curve a is obtained by using a  $2.6\ \mu\text{m}$  Pt electrode at a scan rate of  $10\ \text{mV/s}$ . The diffusion coefficient of DMFc in the polyelectrolyte can be estimated according to Fig. 1 and Eq. 3. Each value of the diffusion coefficient was estimated with five scan rates ( $5, 8, 10, 15, 20\ \text{mV/s}$ ) to improve the statistics. Table 1 shows these diffusion coefficients of DMFc in different polyelectrolytes and at different temperatures. In Table 1, the  $D$  values of DMFc were found to be not very different in the polyelectrolytes  $\text{PEG} \cdot \text{LiClO}_4$ ,  $\text{PEG} \cdot \text{NaClO}_4$ , or  $\text{PEG} \cdot \text{KClO}_4$ , but smaller in the polyelectrolyte  $\text{PEG} \cdot \text{Bu}_4\text{NClO}_4$ . These plots of  $\log D$  versus  $T^{-1}$  are shown in Fig. 2, which also indicates that the  $D$  value of DMFc increases with increasing temperature. The temperature dependence of  $D$  can be explained by the free volume model. The model shows that, as the temperature increases, the expansivity of the material produces local empty space, free volume, into



**Fig. 1** Cyclic voltammograms for  $10\ \text{mM}$  dimethylferrocene (DMFc) in the polyelectrolyte  $\text{PEG} \cdot \text{LiClO}_4$  (100:1) at  $30^\circ\text{C}$ :  $a\ v = 10\ \text{mV/s}$ ,  $r = 26\ \mu\text{m}$ ;  $b\ v = 15\ \text{mV/s}$ ,  $r = 26\ \mu\text{m}$

**Table 1** The diffusion coefficients and heterogeneous electron transfer rate constants of dimethylferrocene in different supporting electrolytes (O:Li = 100:1)

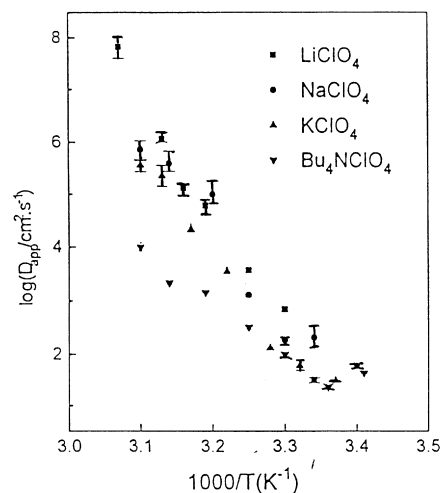
MClO <sub>4</sub>		T (°C)						
		20	25	30	35	40	45	50
LiClO <sub>4</sub>	$D \times 10^7$ (cm <sup>2</sup> /s)		1.49 ± 0.05 (26 °C)	2.84 ± 0.04	3.57 ± 0.05	4.78 ± 0.18	6.06 ± 0.14	7.82 ± 0.22
	$k_s \times 10^3$ (cm/s)		1.16 ± 0.16 (26 °C)	2.80 ± 0.20	4.14 ± 0.88	6.54 ± 0.17	8.08 ± 0.42	
	$E_a$ (kcal/mol)				13.77			
	$D \times 10^7$ (cm <sup>2</sup> /s)	1.77 ± 0.04 (21 °C)	2.31 ± 0.22 (26 °C)	2.27 ± 0.08	3.11 ± 0.04	5.00 ± 0.25	5.59 ± 0.24	5.86 ± 0.20
NaClO <sub>4</sub>	$k_s \times 10^3$ (cm/s)		2.68 ± 0.24 (26 °C)	3.20 ± 0.05	4.55 ± 0.19	5.09 ± 0.18	6.33 ± 0.25	7.61 ± 0.21
	$E_a$ (kcal/mol)				8.28			
	$D \times 10^7$ (cm <sup>2</sup> /s)							
KClO <sub>4</sub>	$D \times 10^7$ (cm <sup>2</sup> /s)	1.48 ± 0.02 (23.4 °C)	1.77 ± 0.13 (28 °C)	2.12 ± 0.04 (32 °C)	3.55 ± 0.09 (38 °C)	4.33 ± 0.11 (42 °C)	5.35 ± 0.20 (46 °C)	5.55 ± 0.10
	$k_s \times 10^3$ (cm/s)	1.49 ± 0.13 (23.4 °C)	2.39 ± 0.10 (28 °C)	3.22 ± 0.25 (32 °C)	3.57 ± 0.95 (38 °C)	4.22 ± 0.08 (42 °C)	5.71 ± 0.60 (46 °C)	6.73 ± 0.10
	$E_a$ (kcal/mol)				9.38			
	$D \times 10^7$ (cm <sup>2</sup> /s)		1.35 ± 0.07	2.00 ± 0.05	2.51 ± 0.04	3.16 ± 0.03	3.33 ± 0.06	4.00 ± 0.09
TBAP	$k_s \times 10^3$ (cm/s)		0.52 ± 0.10	1.28 ± 0.10	2.18 ± 0.22	2.47 ± 0.10	3.07 ± 0.30	3.83 ± 0.14
	$E_a$ (kcal/mol)				11.53			
	$D \times 10^7$ (cm <sup>2</sup> /s)							

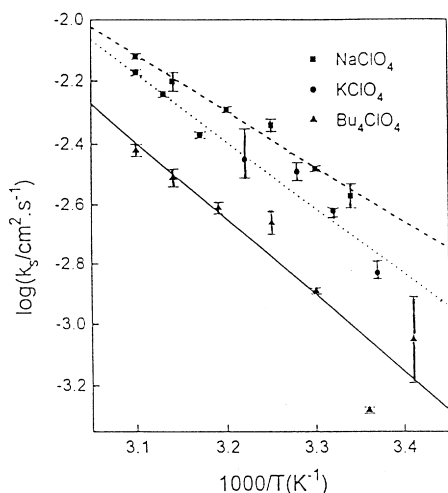
which ionic carriers, solvated molecules, or polymer segments can move freely. The  $D$  value increases with increasing temperature owing to the increasing amount of free volume.

#### Determination of the heterogeneous rate constant

Microdisk electrodes have a convenient application in the study of electrode kinetics owing to their advantageous properties in reducing the charging current and the distortion of the voltammetric waveform. Therefore, previous authors [15–17] have reported some techniques of electrode kinetics measurements using microdisk electrodes. We [9] have estimated the electron transfer rate of ferrocene in PEG · LiClO<sub>4</sub> using steady-state voltammograms, but the technique requires the availability of a series of electrodes with different radii, and the potential measurements to be accurate to 1 mV or better. The latest paper [18] suggested that the heterogeneous electron transfer rate constants could be measured using cyclic voltammetric peak potential separations taken typically in a mixed diffusion geometry regime including both linear and partially radial diffusion in a polyelectrolyte, as shown in Fig. 1b. The cyclic voltammetric peak separation  $\Delta E_p$  is obtained from Fig. 1b, then the dimensionless peak separation  $\Delta \xi_p = (nF/RT)\Delta E_p$  can be calculated. In addition, the dimensionless diffusion parameter  $p = (nFvr^2/DRT)^{1/2}$  can be obtained if  $D$  of the electroactive species is known.

From  $p$ ,  $\Delta \xi_p$  and table 1 in Lavagnini et al. [10] the dimensionless kinetic parameter  $\Lambda' = k_s r/D$  can then be obtained. Thus  $k_s$  of the electroactive species can be estimated from the  $\Lambda'$  value. Table 1 gives these heterogeneous electron transfer rate constants of DMFc at different temperatures and in different polyelectrolytes. These plots of  $\log k_s$  versus  $T^{-1}$  are shown in Fig. 3. Figure 3 and Table 1 show that  $k_s$  of DMFc increases with increasing temperature, and the plot of  $\log k_s$  versus  $T^{-1}$  is linear. The activation barriers ( $E_a$ ) of DMFc are

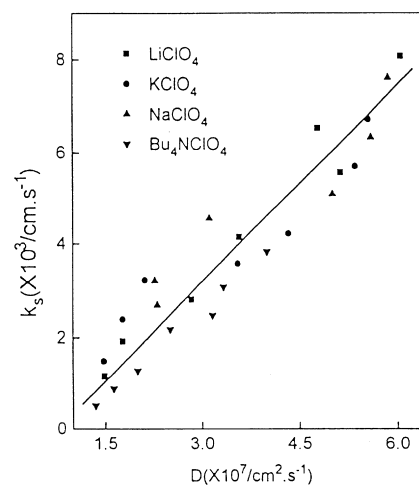
**Fig. 2** Temperature dependence of the diffusion coefficient of DMFc in different supporting electrolytes



**Fig. 3** Temperature dependence of the heterogeneous rate constant of DMFc with different supporting electrolytes

obtained according to the Arrhenius equation and are shown in Table 1. These heterogeneous rate constants for the  $\text{DMFc}^{0/+}$  reaction in  $\text{PEG} \cdot \text{MClO}_4$  are in sharp contrast to that of the kinetics results in a monomeric fluid electrolyte medium:  $k_s$  of DMFc is found to be about 0.25 cm/s (18 °C) in acetonitrile solvent using the same method. The values of  $k_s$  shown in Table 1 are ca. 100-fold lower. These results indicate that the medium affects electron transfer. Generally, the elementary chemical transformation reaction occurs in a solvent cage. Dipolar coupling between an electron-transfer reaction and the solvent dipole serves to couple the solvent dipole fluctuation or relaxation rate to the barrier-crossing rate for electron transfer. In a polymer solvent, the solvent dipoles are constrained by the segmental (or subsegmental) mobility of the polymer chains to which they are logically attached, and the relaxation or fluctuation times for such dipoles will be longer than those of monomeric fluid solvents. According to Zhang's paper [19], these longitudinal dielectric relaxation times of a polymer solvent are significantly longer than those of a typical monomeric solvent. On the other hand, the type of electrolyte may affect the relaxation time or  $\tau_L$  because the electrolyte can change the viscosity of the solvent, and  $\tau_L$  is proportional to the viscosity of the solvent. The relaxation time for  $\text{MPEG} \cdot 400$  ( $\tau_L = 22$  ps) is 100-fold larger than that for  $\text{CH}_3\text{CN}$  ( $\tau_L = 0.2$  ps). So the  $k_s$  values should be 100-fold different. The experimental results show that the  $k_s$  values of DMFc in  $\text{PEG} \cdot \text{LiClO}_4$  are about 100-fold lower than in  $\text{CH}_3\text{CN} \cdot \text{LiClO}_4$ , even without considering the effect of temperature and the concentration of the supporting electrolyte.

Figure 4 is the plot of  $k_s$  versus the diffusion coefficient for DMFc in various polyelectrolytes. It shows that the slope is nearly unity and the value of  $D$  for DMFc is proportional to the value of  $k_s$ . This demonstrates that the DMFc reaction kinetics respond in a sensitive way to diffusive characteristics of the solvent medium, and insofar as the dynamics of solvent dipolar relaxations in-



**Fig. 4** The plot of heterogeneous rate constants of DMFc versus diffusion coefficients in different supporting electrolytes

fluencing the barrier crossing frequency vary in a parallel manner to solute diffusive characteristics, solvent dynamics control of the electrode reaction is indicated by these results.

Finally, it should be mentioned that the experiments are performed using the BAS system, utilizing the automatic iR compensation method. Since the rate constants of electroactive species are not very fast in polyelectrolytes, the remaining uncompensated resistance constitutes a minor effect. The uncompensated resistance effects in the polymer solvent are noticeable but not very larger [18, 20] because of using a micro-electrode: for example, according to Wooster's paper [20], the most reliable value of  $k_s$  for  $[\text{Co}(\text{bpy})_3]^{3+/2+}$  is  $1.6 \times 10^{-2}$  cm/s in  $\text{MPEG} \cdot 400$  at 68 °C, using the highest level of feedback compensation, but the apparent  $k_s$  is only slightly lower ( $1.1 \times 10^{-2}$  cm/s) without compensation. This indicates that the former resistance compensation method was unnecessary.

## Conclusions

Cyclic voltammograms under mixed spherical/semi-infinite linear diffusion at a microdisk electrode is used for measurement of heterogeneous rate constants in polyelectrolytes as a simple technique. The values of  $k_s$  are smaller in polymer solvents than those in a monomeric solvent. These indicate that the solvent (ether) dipoles are constrained by the segmental mobility of the polymer chains. So the relaxation times for such dipoles will be longer than those in monomeric solvents. The dependences of  $k_s$  and  $D$  on temperature are observed. The plot of  $\log k_s$  versus  $T^{-1}$  is linear, and values of  $E_a$  are obtained in different polyelectrolytes.  $k_s$  is proportional to  $D$  of DMFc in polyelectrolytes.

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