Solution Viscosity Effects on the Heterogeneous Electron Transfer Kinetics of Ferrocenemethanol in Dimethyl Sulfoxide−Water Mixtures

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The electrochemical kinetics for the oxidation of ferrocenemethanol ($FcCH_2OH$) over the whole composition range of dimethyl sulfoxide (DMSO)−water solutions of different viscosities (η) containing 50.0 mM $(CH_3)_4NClO_4$ (TMAP) at a Pt microelectrode was studied using scanning electrochemical microscopy (SECM). The measured diffusion coefficient, D_{FcCH_2OH}, as well as the standard rate constant of the heterogeneous electron transfer, k^0, as a function of solution composition, showed a minimum at about a DMSO molar fraction (x_{DMSO}) of 0.33, corresponding to the mixture with the maximum solution viscosity. The largest k^0 value found, 2.06 ± 0.31 cm s^{-1} in pure water (electrolyte) medium, was about 15 times larger than that obtained in the solution of $x_{DMSO} = 0.33$ (0.14 ± 0.02 cm s^{-1}). A good linear correlation between ln k^0 and ln η was observed within the solution composition range of $0.10 \leq x_{DMSO} \leq 0.60$. An excellent linear correlation between ln k^0 and ln τ_L, the longitudinal relaxation time, was also obtained with a slope equal to 1.0 when $x_{DMSO} = 0-0.60$. Unusually small rate constants found in the solutions of $x_{DMSO} \geq 0.70$ were attributed to adsorption effects at the tip and the substrate electrode. The k^0 obtained for the present system was generally found to be inversely proportional to the viscosity of the solution and directly proportional to the diffusion coefficient of the electroactive species.

Introduction

Solvent effects on the rate constants for heterogeneous electron transfer (ET) reactions (k^0) have attracted substantial attention for both theoretical calculations and experimental determinations.[1−5] The influences of the solvent on the kinetics of such reactions mainly include its effect on the magnitude of activation Gibbs energy as it is recognized by either the Marcus dielectric continuum treatment[6,7] or the mean spherical approximation (MSA) model,[8,9] as well its effect on the pre-exponential factor.[10] Since the major parameter of the pre-exponential factor, the longitudinal relaxation time τ_L, is directly related to the viscosity of the solvent,[5] explicit studies of the influence of solvent (solution) viscosity on electrochemical kinetics could provide direct tests about the involvement of the solvent dynamics in the activation step, as viscosity is a measure of solvent mobility. There have been a number of studies associated with the relationship between the ET rate constant and the solution viscosity.[5,11−18] However, most of the ET rate constants were measured under conditions where the viscosity was changed by deliberately adding electrochemically inactive materials[11−14,17] or by using different individual solvents.[18] More recently, Moressi et al.[5] have reported solvent effects on the heterogeneous kinetics of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylendiamine oxidation in nonaqueous binary solvent mixtures. By using binary solvent mixtures with different viscosity values, a continuous and gradual change in physicochemical properties of the reaction medium can be obtained. In these mixtures, solution properties, such as viscosity, showed a montonic change with solution composition and the observed changes in heterogeneous ET kinetics were mainly attributed to changes in the solvation of the reactants.

The properties of aqueous solutions of dimethyl sulfoxide (DMSO) have been studied extensively[19−27] mainly because of their unique biological features and their wide use as reaction media.[19,28] DMSO−water mixtures are especially interesting because of their pronounced microheterogeneity indicating cluster formation found with these.[29] DMSO and water can interact strongly and specifically through hydrogen bonds, and at a mole fraction of $x_{DMSO} = 0.33$, the interactions show a maximum, suggesting the existence of stoichiometrically well-defined 1DMSO:2H_2O aggregates.[21] The viscosity of the mixed solvent at this composition also shows a maximum value of about 4.4 cP at 293 K, which is about 4.4 and 1.8 times those of pure water and pure DMSO, respectively.[25] The thermodynamic and kinetic properties of an electroactive species in this binary solvent could also display a maximum or minimum at a solution composition of $x_{DMSO} = 0.33$.

Ferrocenemethanol ($FcCH_2OH$) was chosen as the electroactive species in the present study, not only because it is soluble and stable over the whole solution composition range studied, but also because it shows a simple, well-defined, one-electron chemically reversible electrochemical process at a Pt electrode in these media. Additionally, by choosing uncharged $FcCH_2OH$ as the electroactive species together with the use of tetramethylammonium perchlorate ($(CH_3)_4NClO_4$, TMAP) as the supporting electrolyte, double-layer and ion-pairing effects on the kinetics of electron transfer could be minimized.

Since the formal potential changes for $FcCH_2OH/FcCH_2OH^+$ redox couple are small over the whole range of DMSO−water (see Table 1), the effect of reactant solvation[30] differences on the standard rate constant changes should be insignificant.

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TABLE 1: Kinetic Parameters Obtained for the Oxidation of 1.00 mM $FcCH_2OH$ in Different Molar Fractions of DMSO Aqueous Solutions Containing 50.0 mM TMAP at a 5.06-μm-diameter Pt Electrode ($T = 293$ K, except for τ_L Values for 298 K)

x_{DMSO}	η^a (cP) (±0.55%)	D ($\times 10^6$, cm^2 s^{-1}, ± 3%)	I_T^C (L)	L	m_0 ($\times 10^2$, cm s^{-1})	k^0 (cm s^{-1} ±15%)	$E^{0\prime}$ (mV vs Pt, ±3 mV)	α (±0.02)	τ_L^e (ps)
0	1.002[b]	7.8	3.95	0.204	15.51	2.06	48	0.20	0.44[f]
0.10	2.152	3.7	4.00	0.200	7.452	1.93	50	0.19	0.38
0.20	3.455	2.5	3.99	0.201	5.022	0.43	70	0.32	2.16
0.30	4.31	2.0	4.06	0.197	4.088	0.20	75	0.31	3.94
0.33	4.383	1.9	4.02	0.199	3.845	0.14	71	0.36	4.47
0.37	4.354[c]	2.0							
0.40	4.267	2.2	3.93	0.205	4.353	0.17	79	0.40	4.66
0.50	3.838	2.5	4.04	0.198	5.085	0.19	80	0.40	4.35
0.60	3.398	2.7	4.03	0.199	5.479	0.34	86	0.34	2.44
0.70	2.967	2.9	3.99	0.201	5.826	0.28	81	0.32	1.10
0.80	2.627	3.1	4.05	0.198	6.320	0.19	91	0.33	0.83
0.90	2.478[c]	3.4	4.01	0.200	6.866	0.17	94	0.35	0.66
1.00	2.47[d]	3.7	3.94	0.204	7.340	0.17	160	0.36	0.50

[a] Viscosity from ref 25 unless otherwise stated. [b] From ref 36. [c] Interpolated values. [d] From ref 35. [e] Longitudinal relaxation time taken or interpolated from ref 21 unless otherwise stated. [f] Longitudinal relaxation time from ref 15.

The scanning electrochemical microscope (SECM) has been proven to be very powerful for the determination of the rate constant of very fast electrochemical processes.[31,32] As will be indicated below, the oxidation of $FcCH_2OH$ at a Pt electrode in the DMSO−water system is a very rapid process; as a result the SECM with a micrometer-size Pt tip was chosen for the measurement of the rate constant in the current study.

In the present paper, the electrochemical kinetics for the oxidation of $FcCH_2OH$ over the whole composition range of DMSO−water solutions containing 50.0 mM TMAP as supporting electrolyte at a Pt microelectrode were investigated by the SECM technique. The ET rate constant was shown to be inversely proportional to the solution viscosity and the solvent longitudinal relaxation time, and directly proportional to the diffusion coefficient of the electroactive species.

Experimental Section

Chemicals. Dimethyl sulfoxide (DMSO, AR, water content ≈0.02%, Mallinckrodt), ferrocenemethanol ($FcCH_2OH$, 97%, Aldrich), tetramethylammonium perchlorate (TMAP, >99%, Fluka), hexaammineruthenium(III) chloride ($Ru(NH_3)_6Cl_3$, 99%, Strem), potassium ferricyanide ($K_3[Fe(CN)_6]$, AR, Aldrich), sodium phosphate ($Na_3PO_4 \cdot 12H_2O$, AR, Sigma), and potassium chloride (KCl, AR, Aldrich) were used directly without further purification. All solutions were freshly prepared with deionized water (Milli-Q, Millipore). The electroactive species ($FcCH_2OH$) concentration and the supporting electrolyte (TMAP) concentration used in the different DMSO−water solutions were always 1.00 and 50.0 mM, respectively.

Electrodes. The platinum electrode tip for SECM was constructed from a 5-μm-diameter Pt wire (Goodfellow Corp., PA) as described previously.[32,33] The size of the Pt disk was determined via eq 1 shown below,[33] using both $Ru(NH_3)_6Cl_3$ (0.09 M Na_3PO_4)[33] and $K_3[Fe(CN)_6]$ (0.10 M KCl)[34] as standard solutions for steady-state voltammetric measurements.

$$i_{T,\infty} = 4nFDc^0a \qquad (1)$$

where $i_{T,\infty}$ is the steady-state limiting current to the tip electrode far from any substrate, n is the number of electrons transferred per molecule, F is Faraday's constant, D is the diffusion coefficient of the electroactive molecule, c^0 is its bulk concentration, and a is the radius of the Pt tip. The electrochemically determined result of $a = 2.53$ μm was further confirmed via a high-magnification optical microscope. The RG value ($RG = R_g/a$, where R_g is the radius of the insulating glass surrounding the tip of the radius a) of the tip electrode was around 3. A 3.0-mm-diameter macrodisk Pt electrode polished with a 0.05 μm alumina slurry (Buehler Ltd., Lake Bluff, IL) was used as the SECM substrate. Both the counter and the reference electrodes used were Pt wire. Classical reference electrodes, such as a saturated calomel electrode (SEC) and a Ag/AgCl electrode, are probably not suitable for use in these solvent mixtures, since DMSO can easily penetrate the frit of the reference electrode and react with water,[19] resulting in the drift of the reference electrode potential.

Electrochemical Measurements. All electrochemical measurements were performed with a CHI 900 SECM system (CH Instruments, Austin, TX). A 3-mL Teflon cell was employed with either three or four electrodes connected to the SECM bipotentiostat. To acquire the approach curves for the oxidation of $FcCH_2OH$ in the different DMSO−water media, the Pt tip was initially brought close to the substrate (about 50 μm away), held there for 20 s, and then slowly approached (0.025 μm s^{-1}) the substrate, until a 4-times positive feedback tip current was achieved. The potential values of the tip and the substrate, which were determined by cyclic voltammetry in the bulk solution, were held at around +0.35 V and −0.15 V vs Pt, respectively. The steady-state voltammograms at the Pt tip were immediately recorded at this tip/substrate separation distance by scanning the tip potential between about −0.15 and +0.35 V vs Pt at a constant substrate potential of −0.15 V vs Pt. The recorded voltammograms were used for the calculation of the kinetic parameters. Unless otherwise stated, the scan rate used was 20 mV s^{-1}. All experiments were conducted under ambient temperature conditions, 20 ± 2 °C.

Data Analysis. The kinetic parameters (standard rate constant k^0, formal potential $E^{0\prime}$, and electron-transfer coefficient α) were extracted by fitting the experimentally obtained steady-state voltammograms to the theory (see next section), using the nonlinear least-squares curve fitting function provided by Origin 6.0 (Microcal Software, Inc., MA).

Results and Discussion

Dependence of Diffusion Coefficient on Viscosity. The diffusion coefficients of $FcCH_2OH$ (D_{FcCH_2OH}) in solutions with different mole fractions of DMSO (x_{DMSO}) containing 50.0 mM TMAP were derived from eq 1. The steady-state limiting current of the bulk solution ($i_{T,\infty}$) was obtained from an ultramicrodisk Pt electrode with $a = 2.53$ μm. The measured D_{FcCH_2OH}, together

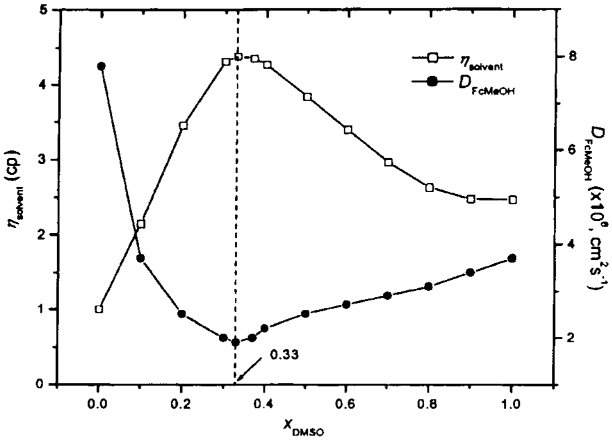

Figure 1. Variations of solvent viscosity (η) and the measured diffusion coefficient for $FcCH_2OH$ (D_{FcCH_2OH}) with the mole fraction of DMSO (with water).

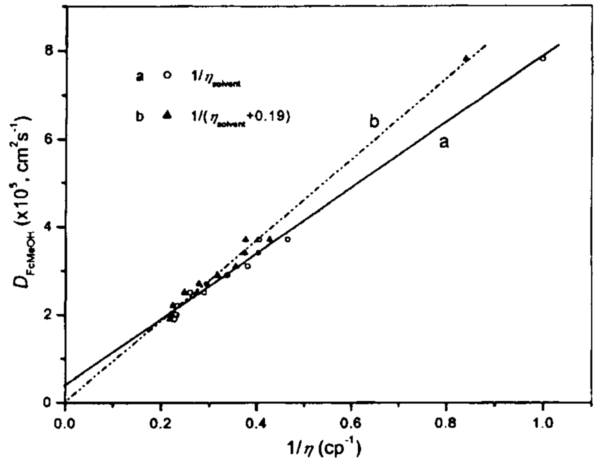

Figure 2. Plots of the diffusion coefficient, D_{FcCH_2OH}, as a function of the reciprocal viscosity, $1/\eta$, for $FcCH_2OH$ in different fractions of DMSO−water solutions containing 50.0 mM TMAP as the supporting electrolyte.

with the solvent viscosity ($\eta_{solvent}$) taken or interpolated from the literature,[25,35,36] are collected in Table 1. The variation of D_{FcCH_2OH}, as well as $\eta_{solvent}$, with x_{DMSO} is plotted in Figure 1. While solvent viscosity shows a nonmonotonic function of composition passing through a maximum at $x_{DMSO} = 0.33$, the profile of diffusion coefficient versus x_{DMSO} shows a minimum at the same mixed solvent composition of $x_{DMSO} = 0.33$. This is consistent with the Stokes−Einstein equation[37]

$$D = kT/6\pi r\eta \tag{2}$$

where k is Boltzmann's constant, r is the hydrodynamic radius of the diffusing species, and η is the solution viscosity. Accordingly, a straight-line plot of D_{FcCH_2OH} vs $1/\eta$ is expected (Figure 2). By fitting eq 2 with the measured diffusion coefficients, we found that the addition of 50.0 mM TMAP to the solvent resulted in an average increase of the solvent viscosity of about 0.19 cP (Figure 2b). A hydrodynamic radius of 2.24 Å for $FcCH_2OH$ was deduced from Figure 2b and eq 2. This value is close to, but slightly larger than, the bond length of Fe−C in ferrocene (2.03 Å).[38]

Determination of Rate Constant. Many techniques such as fast scan cyclic voltammetry,[33] ac impedance/admittance voltammetry,[12,15,18,39] and rotating disk electrode measurements[17] can be used to measure the heterogeneous ET rate constant. Steady-state SECM with a micrometer-size tip electrode, however, has been recently shown to be a powerful method of studying very rapid electron-transfer processes,[31,32] especially where solution resistance effects are significant and surface processes decrease the precision of transient measurements. As seen below, because the electron-transfer process of $FcCH_2OH$ in DMSO−water media at a Pt tip is very rapid, SECM with a 5-μm-diameter Pt tip was chosen for the determination of $FcCH_2OH$ kinetic parameters. On the basis of previous studies,[31,32,40] for finite kinetics at the tip and diffusion-controlled mediator regeneration at the substrate, the voltammogram at the tip in dimensionless form for a reduction reaction can be described as

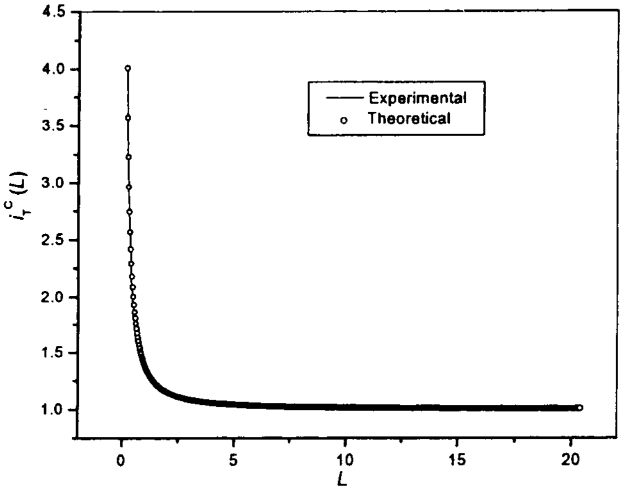

Figure 3. Tip approach curve fitting. The experimental approach curve (solid line) was obtained for the oxidation of 1.00 mM $FcCH_2OH$ at a 5.06-μm-diameter Pt tip using a macrodisk Pt as the substrate in a DMSO−water solution with $x_{DMSO} = 0.50$ and 50.0 mM TMAP, and the theoretical one (open cycle) derived from eq 5 of the main text. The experimental limiting current was taken from the range of L = 15−20.

$$i_T(E,L)/i_{T,\infty} = I_T^C(L)/(\theta + 1/\kappa) \tag{3}$$

where $i_T(E,L)$ is the tip current at the tip potential E when the tip is held from the substrate at a distance d or L ($L = d/a$, where L is the dimensionless tip/substrate distance, and a is the radius of the tip), $i_{T,\infty}$ is the limiting current of the bulk solution as expressed in eq 1, $I_T^C(L)$ ($=i_T(L)/i_{T,\infty}$) is the normalized tip current at L under limiting current conditions, $\theta = 1 + \exp[nf(E - E^{0\prime})]D_o/D_R$, $f = F/RT$, $n = 1$ for $FcCH_2OH$ oxidation, and $\kappa = k^0 \exp[-\alpha f(E-E^{0\prime})]m_0$. For SECM the effective mass-transfer coefficient, m_0, is a function of L and is given by[31]

$$m_0 = 4D_oI_T^C(L)/\pi a \tag{4}$$

For a conductive substrate, the experimental approach curve can be fitted to the following equation[32,41]

$$I_T^C(L) = k_1 + k_2/L + k_3 \exp(k_4/L) \tag{5}$$

where k_1, k_2, k_3, and k_4 are constants, which depend slightly on the RG value of the tip. In the present study, the experimental approach curves obtained at a Pt tip with $RG \sim 3$ show a good fit to eq 5 with $k_1 = 0.633\,49$, $k_2 = 0.674\,76$, $k_3 = 0.365\,09$, and $k_4 = -1.428\,97$.[41] That is, the constants used for $RG = 1.51$ in the literature are probably the best ones to fit our experimental data. Figure 3 illustrates such an example of an approach curve for the system with $x_{DMSO} = 0.50$. From this

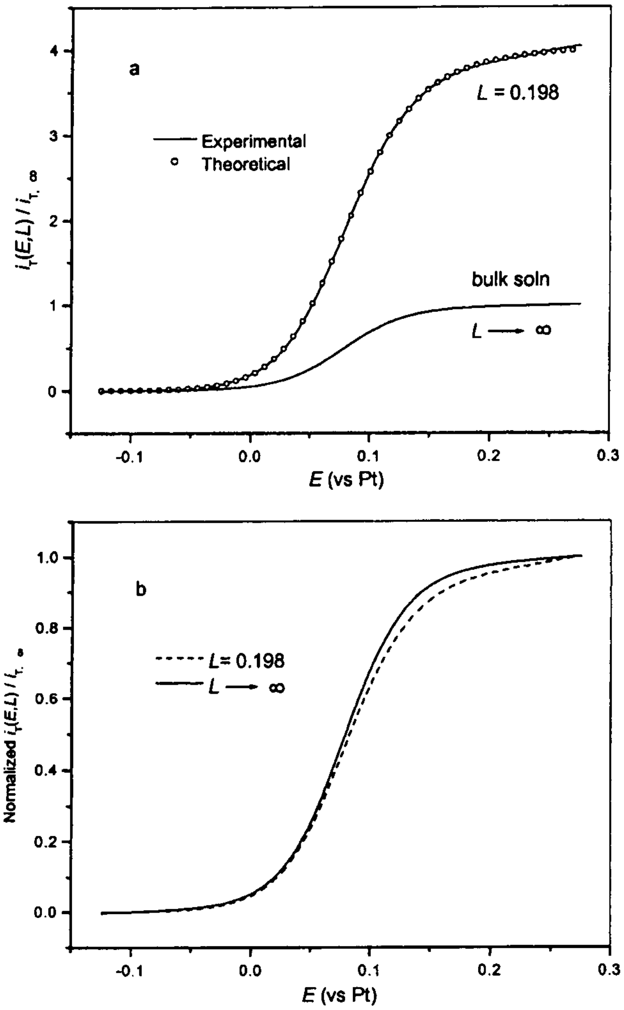

Figure 4. (a) Tip voltammogram fitting. The experimental voltammogram (solid line, $L = 0.198$) was obtained for the oxidation of 1.00 mM $FcCH_2OH$ at a 5.06-μm-diameter Pt tip using a macrodisk Pt as the substrate in a DMSO−water solution with $x_{DMSO} = 0.50$ and 50.0 mM TMAP, and the theoretical one (open cycle) derived from eq 3 of the main text after fitting to the experimental data using a nonlinear least-squares method. (b) Normalized experimental tip voltammogram from (a), showing the derivation of the tip voltammogram obtained at a small tip/substrate separation from the voltammogram obtained from the bulk solution.

figure, a maximum dimensionless positive feedback current of $I_T^C(L) = 4.04$ was obtained. Consequently, a minimum value of $L = 0.198$ or $d = 0.501$ μm can be extracted from either eq 5 or Figure 3. The calculation of the effective mass-transfer coefficient m_0 is straightforward at this tip/substrate separation, according to the related equation and data shown earlier. Table 1 summarizes the maximum $I_T^C(L)$, L, and m_0 values obtained for the oxidation of $FcCH_2OH$ with different DMSO−water solutions at a Pt tip with $RG \sim 3$ and $a = 2.53$ μm.

As described in the Experimental Section, the standard rate constant k^0, the electron-transfer coefficient α, and the formal potential $E^{0\prime}$ were evaluated by fitting the experimentally obtained $i_T(E,L)/i_{T,\infty}$ vs E curve to eq 3 with the assumption that $D_o = D_R$. Figure 4a demonstrates the quality of the fit. The kinetic parameters obtained for the different DMSO−water compositions are listed in Table 1. Figure 4b presents the normalized voltammograms derived from the experimental data shown in Figure 4a. Clearly, the voltammogram obtained at $L = 0.198$ or $d = 0.501$ μm deviates from that obtained from the bulk solution ($L \rightarrow \infty$), confirming that when the tip/substrate separation, d, is small, the electrode process is eventually controlled by heterogeneous kinetics.

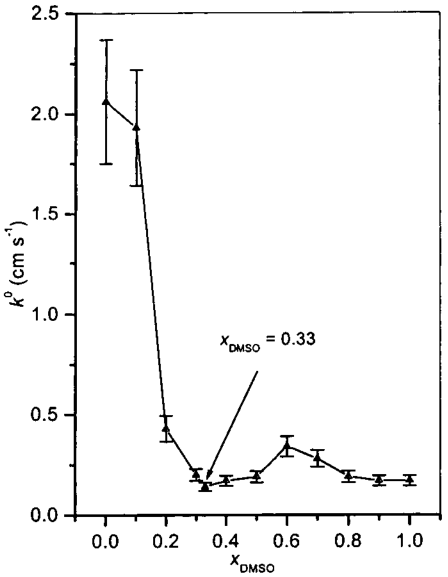

Figure 5. Plot of the experimental ET rate constant, k^0, as a function of the solution composition, x_{DMSO}, for the oxidation of 1.00 mM $FcCH_2OH$ at a 5.06-μm-diameter Pt electrode.

Dependence of Rate Constant on Viscosity. It has been reported previously[5,11−18] that the standard rate constant of an electroactive species is inversely proportional to the viscosity of the solution. As a result, the rate constant should, in principle, correlate with the diffusion coefficient of the same solution (see eq 2). Figure 5 shows such a correlation of rate constant with solution composition (hence, diffusion coefficient) for the present system. Obviously, in the absence of DMSO, the oxidation of $FcCH_2OH$ at a Pt tip has the fastest ET rate constant, 2.06 cm s^{-1}. With an increase in the amount of DMSO, the rate constant decreases dramatically and reaches a minimum value of 0.14 cm s^{-1} at $x_{DMSO} = 0.33$. At larger DMSO amounts, the rate constant increases gradually until $x_{DMSO} = 0.60$. This tendency of the rate constant change with the solution composition is consistent with the behavior of the variation of D_{FcCH_2OH} with x_{DMSO} (Figure 1). Interestingly, beyond $x_{DMSO} = 0.60$ the rate constant slowly decreased and essentially attained a constant value of about 0.17 cm s^{-1} in the region of $x_{DMSO} = 0.90−1$. As will be discussed later, this unexpected behavior is caused by electrode surface problems, i.e., the adsorption of $FcCH_2OH$ and $FcCH_2OH^+$ on both the Pt tip and Pt substrate during the course of the measurements at high mole fractions of DMSO.

Figure 6 shows the correlation of ln k^0 with ln $\eta_{solvent}$ for the oxidation of $FcCH_2OH$ at a Pt electrode over the whole range of solution composition. Except for the first point with $x_{DMSO} = 0$ and the last four points with $x_{DMSO} \geq 0.70$, a good linear relationship between ln k^0 and ln $\eta_{solvent}$ was found, and followed the equation

$$\ln k^0 = 3.37 - 3.55 \ln \eta_{solvent} \qquad \text{(regression coefficient} = 0.983) \quad (6)$$

Dependence of Rate Constant on the Longitudinal Relaxation Time of the Solvent. The standard rate constant can be presented as[5,15,18,39]

$$k^0 = A\tau_L^{\ -\theta} \exp(-\Delta G^*/RT) \qquad (7)$$

in which A is the portion of the preexponential factor that is

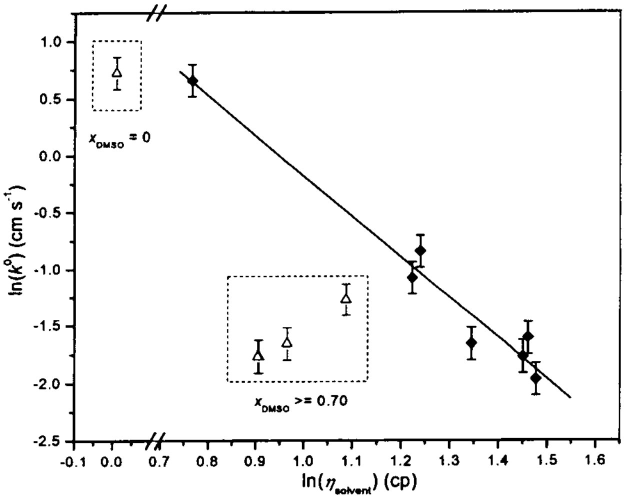

Figure 6. Linear correlation of the experimental ET rate constant, ln k^0, with the viscosity of the solvent used, ln η, for the oxidation of 1.00 mM $FcCH_2OH$ at a 5.06-μm-diameter Pt electrode, in the solution composition range of $0.10 \leq x_{DMSO} \leq 0.60$. For comparison, the data enclosed in dashed boxes for $x_{DMSO} = 0$ and $x_{DMSO} \geq 0.70$ are also included.

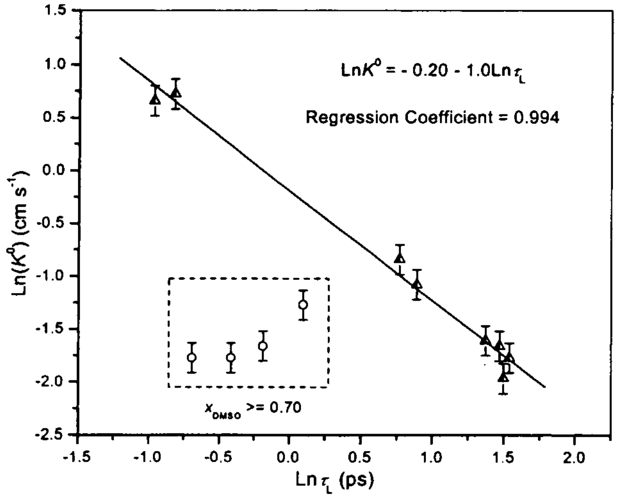

Figure 7. Linear correlations between the experimental rate constant, ln k^0, and the theoretical longitudinal relaxation time, ln τ_L, for the oxidation of 1.00 mM $FcCH_2OH$ at a 5.06-μm-diameter Pt electrode, in the solution composition range of $0 \leq x_{DMSO} \leq 0.60$. For comparison, the data enclosed in the dashed box for $x_{DMSO} \geq 0.70$ are also included.

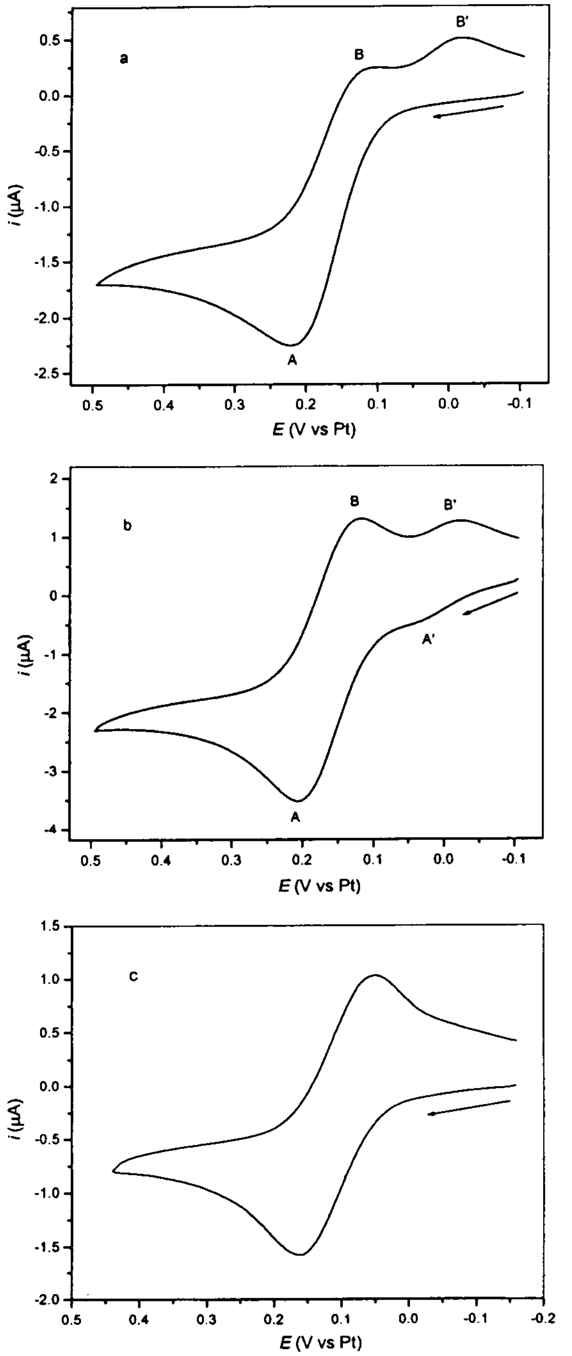

Figure 8. Voltammograms obtained for the oxidation of 1.00 mM $FcCH_2OH$ in a pure DMSO (50.0 mM TMAP) solution (a) at a 3-mm-diammeter Pt substrate with a scan rate of 10 mV s^{-1}, (b) same as (a) but using a scan rate of 50 mV s^{-1}, and (c) same as (a) but for solution $x_{DMSO} = 0.30$.

approximately independent of the solvent, τ_L is the longitudinal relaxation time, θ is a fraction between 0 and 1 that depends on the degree of reaction adiabacity and the relative sizes of the inner- and outer-sphere reorganization energies, and ΔG^* is the Gibbs activation energy containing inner- and an outer-sphere reorganization energy components. Consequently, a linear relation between ln k^0 and ln τ_L with a slope of $-\theta$ is expected, i.e.

$$\ln k^0 = (\ln A - \Delta G^*/RT) - \theta \ln \tau_L \qquad (8)$$

For the present study system, the τ_L values taken or interpolated from the literature[15,21] and obtained mainly from theoretical simulations are given in Table 1. The ln k^0 as a function of ln τ_L is plotted in Figure 7. Clearly, a very good linear correlation between the two parameters is observed within the solution composition range of $0 \leq x_{DMSO} \leq 0.60$, with a slope equal to -1.0. This suggests that the reaction currently studied is strongly adiabatic and the contribution of inner-sphere reorganization energy is negligible.[5] Note also that, unlike the case presented in Figure 6, the rate constant of $FcCH_2OH$ obtained from pure water (electrolyte) now lies on the straight line. This might be primarily due to the relatively large longitudinal relaxation time in this solution (Table 1).

In theory, the τ_L can be also calculated on the basis of the following equation[5,42]

$$\tau_L = 3V_m(\epsilon_\infty/\epsilon_0)\eta/RT \qquad (9)$$

where V_m is the molar volume of the medium, η is the viscosity, and ϵ_∞ and ϵ_0 are the high-frequency and the static permittivities, respectively. We have indeed tried to calculate the τ_L values of the media studied using experimentally measured ϵ_∞ and ϵ_0 data,[20,43] and plotted ln k^0 against ln τ_L. However, we did not find a good linear correlation between the two parameters over the entire solution region of $0 \le x_{DMSO} \le 0.60$ (not shown).

When the variations in V_m, ϵ_∞, and ϵ_0 with the composition of solvent mixtures are much lower than the variations of η with x_{DMSO}, the influence of V_m, ϵ_∞, and ϵ_0 on k^0 becomes negligible. Thus, a linear correlation of ln k^0 with ln η is observed (see Figure 6 and eq 6). This behavior has been seen in a number of papers published recently.[5,13,14,17,18]

Influence of Adsorption on Rate Constant. As shown in Figures 5−7 and Table 1, the experimentally measured ET rate constants for the oxidation of $FcCH_2OH$ at a Pt tip are much smaller than those expected on the basis of the relevant theory when $x_{DMSO} \ge 0.70$, and we have not included these in our analysis of the results. By examining voltammograms obtained at the Pt tip as well as the Pt substrate, we found, in relatively high mole fraction of DMSO solutions, particularly in pure DMSO (electrolyte) solution, that the reactant $FcCH_2OH$ and its oxidized product $FcCH_2OH^+$ can adsorb on the electrode surfaces. Adsorption at the macroelectrode/electrolyte solution interface[44] can give rise to enhancement of peak currents, shifting of peak potentials, wave splitting, and other phenomena.[45−48] For example, if the product or reactant is strongly adsorbed, a separate peak may occur prior to or after the normal diffusion peak.[48] Accordingly, as shown in Figure 8a, at a relatively slow scan rate of 10 mV s^{-1}, an enhanced oxidation peak (peak A relative to peak B) and a separated postwave on the reverse scan (peak B′) are observed at the macrodisk Pt substrate. When the scan rate is increased from 10 to 50 mV s^{-1} (Figure 8b), a pair of small waves appeared at about 0.010 V vs Pt (peaks A′ and B′), but in this case only a minor difference in the two major peak currents were found (peak A to peak B), as would be expected from theory. A classical reversible voltammogram was seen when a scan rate faster than 500 mV s^{-1} was used (not shown). Based on these results, we conclude that the electroactive species $FcCH_2OH$ weakly adsorbs onto the Pt surface while its oxidized product $FcCH_2OH^+$ strongly adsorbs, when $x_{DMSO} \ge 0.70$. This adsorption can affect the heterogeneous electron-transfer rate, for example by slowing down the reaction at the portions of the electrode that are blocked by adsorbate.

The behavior of the steady-state voltammograms at an ultramicrodisk electrode (5-μm-diameter Pt) was also slightly different for solutions of $x_{DMSO} \ge 0.7$ (not shown). At lower mole fractions of DMSO, the voltammogram was normal with a smooth limiting current plateau. However, at the higher DMSO concentrations, the limiting current plateau was noticeably “noisier” and the forward and back scans showed a greater hysteresis. This suggests some surface effects that vary with time.

Conclusions

Detailed experimental examinations of the electrochemical kinetics for the oxidation of $FcCH_2OH$ over the whole composition range of DMSO−water solutions containing 50.0 mM TMAP at a Pt microelectrode have been carried out. Profiles of the measured diffusion coefficient and the solvent/solution viscosity as a function of solution composition show inverse proportionality predicted by the Stokes−Einstein equation. The kinetic parameters, namely, the standard rate constant k^0, at the formal potential of the reaction $E^{0\prime}$, and the electron-transfer coefficient α, were evaluated by fitting the tip voltammogram with the tip held in close proximity to a Pt substrate. The largest and the smallest rate constants found are 2.06 ± 0.31 and 0.14 ± 0.02 cm s^{-1}, which correspond to pure water (electrolyte) and $x_{DMSO} = 0.33$ solutions, respectively. Good linear correlations between ln k^0 and ln η as well as ln k^0 and ln τ_L were observed. Unusually small rate constants were found when $x_{DMSO} \ge 0.70$, which is believed to be associated with the adsorption of reactant and product at the tip electrode. With an increase in the DMSO concentration, the formal potential slightly shifted positive with respect to a Pt quasireference electrode. The electron-transfer coefficient with values between 0.19 ± 0.02 and 0.40 ± 0.02 were estimated on the basis of the nonlinear least-squares fitting.

The results demonstrate that the previously observed variation of heterogeneous electron-transfer rates with viscosity holds, even in this unique solvent mixture where cluster formation and nonmonotonic variation of viscosity with composition exist.

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