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# Dependence of electron transfer kinetics of the ferrocene/ferrocenium couple on the viscosity in ambient temperature chloroaluminate ionic liquids[☆]

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## Abstract

The heterogeneous electron transfer kinetics of the ferrocenium/ferrocene couple have been measured throughout the basic range of composition of the ambient temperature chloroaluminate ionic liquid composed of 1-ethyl-3-methylimidazolium chloride (ImCl) and aluminum chloride. Normal and reverse pulse voltammetries with pulse times as short as 5 $\mu$s were employed. After subtraction of the background currents, the experimental voltammograms were directly compared with those calculated from the COOL algorithm using a model for reversible and quasi-reversible electron transfer reactions. The standard rate constants, uncorrected for double layer effects, were found to decrease from $0.45 \pm 0.35$ cm s$^{-1}$ at 0.95:1 to $0.027 \pm 0.004$ cm s$^{-1}$ at 0.45:1 mole ratio of aluminum chloride to ImCl. Possible factors contributing to the observed dependence are discussed. The most likely reason for the retardation of the electron transfer rate is the slow relaxation of the increasingly associated basic ionic liquid.

*Keywords:* Electron transfer; Kinetics; Ferrocene/ferrocenium couple; Chloroaluminate ionic ligands

## 1. Introduction

The low intrinsic barrier (reorganization energy) for electron transfer in metallocenes makes them particularly useful systems for studies of solvent effects on the outer sphere Gibbs activation energy and the pre-exponential factor of the rate constant [1–4]. We report here on a dependence of the electron transfer kinetics of the ferrocene/ferrocenium couple on the composition of ambient temperature chloroaluminate ionic liquids [5,6]. The viscosity of this unusual solvent, consisting of 1-ethyl-3-methylimidazolium chloride (ImCl) and $AlCl_3$, changes from 20.6 to 264 cP [7] when the $AlCl_3$/ImCl molar ratio decreases from 0.95:1 to 0.45:1. If the mole ratio of ImCl to $AlCl_3$ is greater than unity, as it is in the studies reported here, the system is considered to be basic. This drastic change of a transport property of the ionic liquid indicates significant structural transformations in the medium, even though the same ionic components, $Im^+$, $AlCl_4^-$ and $Cl^-$, are present throughout this range of solvent composition [8,9]. We were interested in what we could learn about the solvation properties of this ionic liquid from a comparison of the ferrocene electrode kinetics in it and in other solvents [4,10]. The lack of information on the dielectric properties of the ionic liquid impedes any quantitative comparisons, but even qualitative indications of dynamic solvation properties are important for the development of better physicochemical descriptions of this unusual solvent. At least two reports have experimentally shown changes in electron transfer kinetics with solution viscosity [11,12].

The heterogeneous electron transfer kinetics of the $FeCp_2^+/FeCp_2$ couple were determined by normal (NP) and reverse pulse (RP) voltammetries [13] at pulse times as short as 5 $\mu$s, using the COOL algorithm for analysis of the experimental voltammograms [14,15]. The detailed description of the experimental system and the data analysis procedures can be found in recent papers from this laboratory [10,16].

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## 2. Experimental

### 2.1. Materials

1-Ethyl-3-methylimidazolium chloride and $AlCl_3$ were synthesized and purified as described previously [17]. Proton and oxide impurities were removed according to literature procedures [18,19]. Ferrocene (Alfa) was sublimed before use. All solutions were prepared in a Vacuum Atmosphere dry-box equipped with an HE-453 Dry Train, sealed in an electrochemical cell of air-tight design with high-vacuum Teflon valves and O-ring seals, and transferred outside the dry-box. The cell and the potentiostat were then placed inside a Faraday cage to minimize noise.

### 2.2. Instrumentation

All voltammetric experiments were performed with a home built fast potentiostat, controlled by a DEC PDP8/e computer [10,16].

A platinum microdisk electrode (5 μm radius, Cypress Systems) served as the working electrode, a silver wire was used as a quasi-reference electrode, and the counter electrode was a platinum flag.

## 3. Results

Initial experiments performed in the ionic liquids involved analysis of the time dependence of currents at times shorter than 5 μs in the absence of a faradaic process. Such measurements enable an estimate of the apparent cell time constant, the solution resistance and the double-layer capacitance [10]. For 5 μm Pt electrode, the cell time constant values increased from 1.2 μs for a 0.95:1 $AlCl_3$:ImCl molar ratio, to 2.2 μs for the most basic solvent composition (0.45:1). Estimated specific resistances were 90 and 540 $\Omega$ $cm^{-1}$, and double layer capacitance values were 33 and 10 μF $cm^{-2}$ for 0.95:1 and 0.45:1 solvent compositions, respectively. Thus, the large increase of the solution resistance at more basic solvent compositions is partly compensated for by a decrease of the double-layer capacitance so the cell time constant increases only by a factor of 2 and pulse times as short as 5 or 10 μs, depending on the $AlCl_3$:ImCl molar ratio, are accessible.

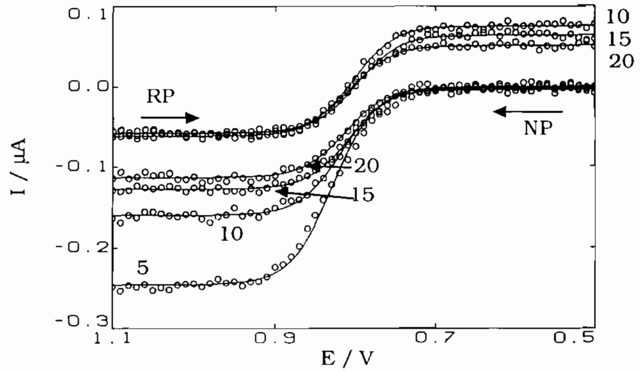

Fig. 1. Normal and reverse pulse voltammograms for 15 mM $FeCp_2$ in 0.8:1 $AlCl_3$:ImCl ionic liquid. Pulse times, μs, as indicated on the voltammograms. Generation time in RPV 50 μs. Solid lines are best fit to reversible voltammograms by COOL algorithm.

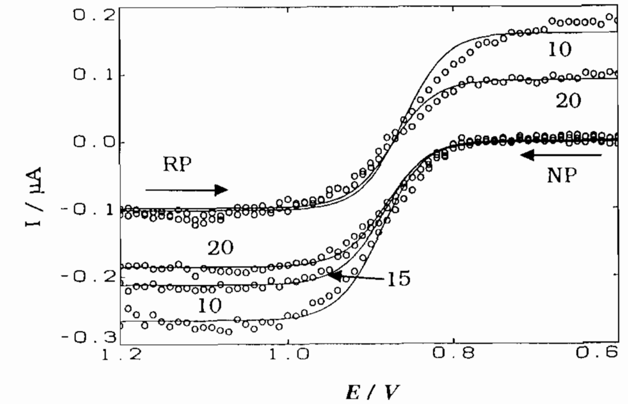

Fig. 2. Normal and reverse pulse voltammograms for 40 mM $FeCp_2$ in 0.6:1 $AlCl_3$:ImCl ionic liquid. Pulse times, μs, as indicated on the voltammograms. Generation time in RPV 50 μs. Solid lines are best fit to reversible voltammograms by COOL algorithm.

Normal and reverse pulse voltammograms for oxidation of $FeCp_2$ at 5 μm Pt electrode in 0.8:1 and 0.6:1 ionic liquids are shown in Figs. 1 and 2, together with the best fits to the reversible electron transfer model [14,15]. Parameters obtained from the data analysis, the reversible half-wave potential, $E_{1/2}{}^{r}$, and the slope, $a = nFAC(D/\pi t_p)^{1/2}$, for all four solvent compositions studied are presented in Table 1. The last two columns in Table 1 show a comparison of two values of noise calculated for each voltammogram. The initial value of noise given was obtained as a mean value of the standard deviation from straight lines of the experimental points on the initial and final linear portions of NP and RP voltammograms, while the second is the calculated standard deviation of all the points of the voltammogram from the best COOL fit. The noise of the points, usually taken from the initial and final 150 mV intervals, did not differ by more than 50%. Comparison of these two values provided a qualitative indication of the goodness of fit and, for the two less basic solvent compositions, the agreement is reasonably good. This shows that pulse voltammetry on a microsecond time scale can provide results unaffected by both the cell time constant and ohmic potential drop and the electron transfer rate for ferrocene oxidation is fast in moderately basic molten chloroaluminates; the only correction of the experimental voltammograms before analysis was a background subtraction.

On the other hand, a decrease of the $AlCl_3$:ImCl molar ratio to 0.6:1 and 0.45:1 resulted in slower kinetics for ferrocene oxidation. Deviations of experimental

Table 1
Results of the COOL fitting of pulse voltammetric data to the reversible model

| $t_p$ (μs) (s.d.×10$^3$) | $E_{1/2}^r$ (V) | $a^a$ (μA) | Noise$_{ex}^b$ (s.d.×10$^3$) | Noise$^c$ (s.d.×10$^3$) |
|---|---|---|---|---|
| 0.95:1 $AlCl_3$:ImCl (20 mM $FeCp_2$) | | | | |
| 5 | 0.671 | 0.377 | 5.2 | 5.9 |
| 10 | 0.665 | 0.280 | 4.9 | 5.8 |
| 15 | 0.660 | 0.227 | 4.9 | 5.1 |
| 20 | 0.656 | 0.190 | 3.5 | 3.9 |
| 25/5 | 0.641 | 0.351 | 8.0 | 15 |
| 25/10 | 0.652 | 0.269 | 4.5 | 5.4 |
| 0.8:1 $AlCl_3$:ImCl (15 mM $FeCp_2$) | | | | |
| 5 | 0.830 | 0.242 | 3.0 | 5.5 |
| 10 | 0.818 | 0.156 | 4.0 | 4.3 |
| 15 | 0.807 | 0.127 | 3.1 | 3.1 |
| 20 | 0.813 | 0.111 | 3.4 | 3.3 |
| 50/10 | 0.804 | 0.138 | 3.2 | 3.0 |
| 50/15 | 0.798 | 0.123 | 2.8 | 3.0 |
| 50/20 | 0.806 | 0.110 | 2.5 | 2.4 |
| 0.6:1 $AlCl_3$:ImCl (40 mM $FeCp_2$) | | | | |
| 10 | 0.887 | 0.265 | 5.3 | 9.8 |
| 15 | 0.884 | 0.213 | 3.8 | 7.1 |
| 20 | 0.882 | 0.184 | 4.0 | 5.6 |
| 50/10 | 0.860 | 0.262 | 4.4 | 14 |
| 50/20 | 0.872 | 0.189 | 4.9 | 7.5 |
| 0.45:1 $AlCl_3$:ImCl (50 mM $FeCp_2$) | | | | |
| 10 | 0.944 | 0.175 | 3.2 | 6.0 |
| 20 | 0.927 | 0.138 | 2.4 | 3.8 |
| 30 | 0.924 | 0.106 | 2.0 | 2.8 |
| 50 | 0.922 | 0.092 | 2.5 | 2.5 |
| 50/10 | 0.892 | 0.167 | 2.3 | 8.4 |
| 50/20 | 0.905 | 0.124 | 2.0 | 4.5 |
| 50/30 | 0.912 | 0.107 | 2.0 | 3.5 |

[a] The slope $a = nFAC(D/\pi t_p)^{1.2}$.

[b] Standard deviation of points from initial and final parts of the voltammogram.

[c] Standard deviation of best fit of voltagram from COOL algorithm.

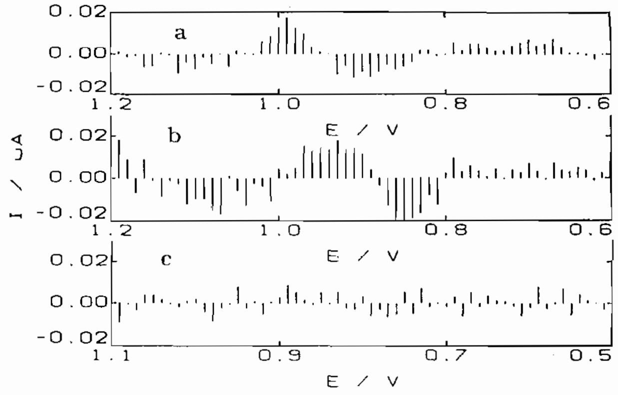

Fig. 3. Difference between fits of experimental data to reversible model calculated by COOL algorithm for NP voltammogram for $FcCp_2$ in (a) 0.45:1, (b) 0.6:1 and (c) 0.8:1 $AlCl_3$:ImCl ionic liquid. Pulse time 10 μs.

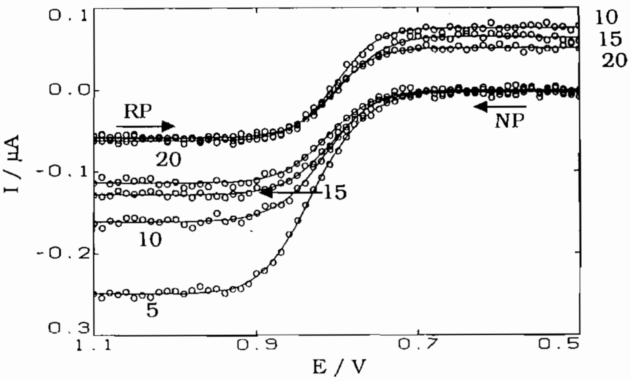

Fig. 4. Experimental voltammograms from Fig. 1 with best fit to quasi-reversible model by COOL algorithm, solid lines. Pulse times, μs, ad indicated on the voltammograms.

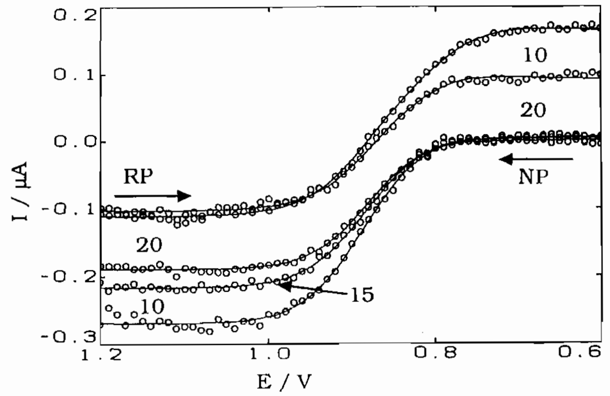

Fig. 5. Experimental voltammograms from Fig. 2 with best fit to quasi-reversible model by COOL algorithm, solid lines. Pulse times, μs, as indicated on the voltammograms.

currents from the reversible model (Fig. 2) were reflected in the noise of the fit, which became distinctly larger than the estimate of the experimental noise (Table 1). This qualitative indication was confirmed by an appearance of the characteristic pattern of the residual currents (Fig. 3) and, more importantly, by the analysis of the voltammograms with the COOL algorithm using the quasi-reversible electron transfer model (Figs. 4 and 5, Table 2). Similar fitting to the quasi-reversible model was performed for all four ionic liquid compositions. Values of the kinetic parameters from the optimization procedure for $\psi$, which in this case is a function of the parameters $\alpha$, $\kappa$, and $E_{1/2}^r$, were obtained (see Table 4). $\alpha$ is the charge transfer coefficient and $\kappa$ is $k_s/\sqrt{D}_{Fe(Cp)_2}$. Very small differences between the noise values for fits to the reversible and quasi-reversible electron transfer models for ferrocene oxidation at 0.95:1 and 0.8:1 solvent compositions and close to 0 values of the dimensionless rate parameter log $\kappa t_p^{1/2}$ indicate nearly reversible electron transfer kinetics under our experimental conditions. The same features of the fits produced by the COOL algorithm for the voltammograms measured at more basic compositions of the solvent showed distinct deviations from the reversible model. Thus, the noise of the fit was

Table 2
Results of the COOL fitting of pulse voltammetric data to the quasi-reversible model

| $t_p$ ($\mu$s) | $E_{1/2}^r$ (V) | $\alpha$ | log $\kappa t_p^{1/2}$ | $k_s$ (cm $s^{-1}$) | $a^a$ ($\mu$A) | Noise[e] (s.d.$\times 10^3$) |
|---|---|---|---|---|---|---|
| 0.95:1 $AlCl_3$:ImCl[b] | | | | | | |
| 5 | 0.668 | 0.419 | 0.15 | 0.62 | 0.380 | 5.5(5.2) |
| 10 | 0.664 | 0.732 | 0.55 | 1.1 | 0.271 | 7.0(4.9) |
| 15 | 0.657 | 0.541 | 0.11 | 0.33 | 0.228 | 5.0(4.9) |
| 20 | 0.651 | 0.515 | 0.35 | 0.24 | 0.191 | 4.0(3.5) |
| 25/5 | 0.639 | 0.579 | −0.44 | 0.16 | 0.366 | 8.8(8.0) |
| 25/10 | 0.643 | 0.545 | −0.04 | 0.28 | 0.271 | 4.8(4.5) |
| Av.[c] | 0.654 | 0.55 | | | | |
| s.d.[d] | (0.011) | (0.10) | | | | |
| 0.8:1 $AlCl_3$:ImCl[b] | | | | | | |
| 5 | 0.803 | 0.559 | −0.52 | 0.11 | 0.247 | 2.9(3.0) |
| 10 | 0.813 | 0.361 | 0.06 | 0.29 | 0.158 | 4.0(4.0) |
| 15 | 0.802 | 0.438 | 0.03 | 0.22 | 0.128 | 3.0(3.1) |
| 20 | 0.807 | 0.564 | −0.05 | 0.16 | 0.114 | 3.2(3.4) |
| 50/10 | 0.798 | 0.973 | 0.10 | 0.32 | 0.141 | 3.3(3.2) |
| 50/15 | 0.793 | 0.751 | 0.03 | 0.22 | 0.121 | 2.8(2.8) |
| 50/20 | 0.801 | 1.00 | 0.21 | 0.28 | 0.109 | 2.4(2.5) |
| Av.[c] | 0.806 | 0.48[e] | | | | |
| s.d.[d] | (0.005) | (0.10) | | | | |
| 0.6:1 $AlCl_3$:ImCl[b] | | | | | | |
| 10 | 0.865 | 0.430 | −0.38 | 0.065 | 0.275 | 6.0(5.3) |
| 15 | 0.864 | 0.412 | −0.35 | 0.058 | 0.220 | 3.6(3.8) |
| 20 | 0.866 | 0.419 | −0.28 | 0.059 | 0.189 | 3.5(4.0) |
| 50/10 | 0.858 | 0.640 | −0.56 | 0.043 | 0.279 | 4.7(4.4) |
| 50/20 | 0.861 | 0.565 | −0.40 | 0.045 | 0.193 | 4.8(4.9) |
| Av.[c] | 0.863 | 0.49 | | | | |
| s.d.[d] | (0.003) | (0.10) | | | | |
| 0.45:1 $AlCl_3$:ImCl[b] | | | | | | |
| 10 | 0.916 | 0.467 | −0.50 | 0.028 | 0.182 | 3.0(3.2) |
| 20 | 0.905 | 0.504 | −0.43 | 0.024 | 0.142 | 2.5(2.4) |
| 30 | 0.911 | 0.435 | −0.22 | 0.031 | 0.108 | 2.0(2.0) |
| 50 | 0.913 | 0.385 | −0.10 | 0.032 | 0.094 | 2.0(2.5) |
| 50/10 | 0.890 | 0.576 | −0.54 | 0.026 | 0.175 | 2.5(2.3) |
| 50/20 | 0.893 | 0.533 | −0.40 | 0.025 | 0.127 | 2.0(2.0) |
| 50/30 | 0.897 | 0.596 | −0.39 | 0.021 | 0.108 | 1.8(2.0) |
| Av.[c] | 0.863 | 0.49 | | | | |
| s.d.[d] | (0.003) | (0.10) | | | | |

[a] Slope $a=nFAC(D/\pi t_p)^{1/2}$.
[b] Data from Table 1.
[c] Average.
[d] Standard deviation.
[e] Without RPV data.

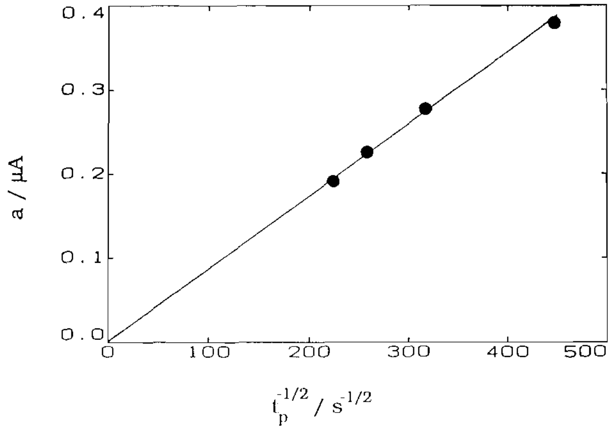

Fig. 6. Dependence of experimental slope, $a=nFAC(D/\pi t_p)^{1/2}$ for 20 mM $FeCp_2$ in 0.95:1 $AlCl_3$:ImCl ionic liquid on $t_p^{-1/2}$.

Table 3
Diffusion coefficients and Stokes-Einstein products of ferrocene

| $AlCl_3$·ImCl mole ratio | $10^7$ $D$ ($cm^2$ $s^{-1}$) | $10^7$ $D\eta/T$ (g cm $s^{-2}$ $K^{-1}$) |
|---|---|---|
| 0.95:1 | 10 | 6.9 |
| 0.8:1 | 6.3 | 7.4 |
| 0.6:1 | 2.5 | 7.7 |
| 0.45:1 | 0.81 | 7.2 |

Table 4
Standard heterogeneous rate constant of ferrocene

| $AlCl_3$:ImCl mole ratio | $k_s$ (cm $s^{-1}$) | s.d.[a] (cm $s^{-1}$) | $\eta$ (g $cm^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 0.95:1 | 0.45 | 0.35 | 0.21 |
| 0.8:1 | 0.20 | 0.08 | 0.35 |
| 0.6:1 | 0.054 | 0.009 | 0.92 |
| 0.45:1 | 0.027 | 0.004 | 2.6 |

[a] Standard deviation.

clearly smaller for the quasi-reversible model, and the values of log $\kappa t_p^{1/2}$ were negative (Table 2). Calculations of the apparent heterogeneous rate constant from $\kappa t_p^{1/2}$ required a knowledge of the diffusion coefficient of ferrocene in all solvent compositions. These were calculated from linear dependence of the slope, $a$, on $t_p^{-1/2}$ as shown in Fig. 6. With the low diffusion coefficients in the ionic liquid the deviations from linear diffusion are negligible on the microsecond time scale. Therefore, diffusion coefficients were calculated from the lines passing through the origin. The values thus obtained are collected in Table 3, together with the Stokes–Einstein products $D_\eta/T$. Finally, the standard heterogeneous rate constant $k_s$, was calculated from the $\kappa t_p^{1/2}$ values optimized by the COOL algorithm and the diffusion coefficients. Values for $k_s$ are shown in Table 2. Lack of any electrical double-layer data precluded corrections of the apparent rate constant values. However, it has been found [20] that the electron transfer rate for ferrocene oxidation is insensitive to double-layer effects. All the $k_s$ values obtained at the various compositions of the ionic liquid, their standard deviations, and values of solvent viscosity are shown in Table 2 and Table 4.

## 4. Discussion

Normal and reverse pulse voltammetric experiments with pulse times as short as 5 $\mu$s enabled determination of the heterogeneous electron transfer kinetics of the ferrocenium/ferrocene couple throughout the basic range of composition of the ambient temperature chloroaluminate ionic liquid. Statistical treatment of the voltammograms using the objective fitting procedure of the COOL algorithm [14,15] revealed small deviations of the experimental voltammograms measured at less basic solvent compositions, 0.95:1 and 0.85:1 $AlCl_3$:ImCl mole ratio, from the reversible electron transfer model. It is noteworthy that at the lower rates of diffusion in these viscous ionic liquids the oxidation of ferrocene is nearly diffusion controlled on the microsecond time scale at the fastest pulse times employed. The values of $\kappa t_p^{1/2}$ determined at 0.95:1 and 0.8:1 ionic solvent compositions, Table 2, are higher than those observed in the acetonitrile solutions at the same time scale of the experiment [10], even though the electron transfer rate in the latter solvent is ~3 times faster than in the chloroaluminate ionic liquid. On the other hand, at more basic solvent composition, the deviations of the voltammograms from the reversible electron transfer model were significant, the optimized values of $\kappa t_p^{1/2}$ were distinctly smaller than 1, see Table 2. It is important to note that even at very basic compositions of the ionic liquid, with their higher viscosities and resistivities, the pulse voltammetric data did not require corrections for ohmic potential drop. The accuracy of these experiments was limited by lower signal to noise ratio, resulting from smaller faradaic and larger background currents, than those observed previously in more common aprotic solvents [10]. However, within these error limits, neither standard deviations of the reversible half-wave potential, nor differences between $E_{1/2}^r$ for the normal and reverse pulse waves, Table 2, depended clearly on the solvent resistance, increasing by a factor of 6 between 0.95:1 and 0.45:1 ionic liquid composition. The dependence of the standard heterogeneous rate constant for $FeCp_2$ oxidation at Pt electrode on the reciprocal of the viscosity of the solvent is illustrated in Fig. 7. It distinctly deviates from a linear dependence, indicating probable deviations of the properties of the ionic liquid from the ideal Debye behavior [21] (vida infra). Nevertheless, the electron transfer kinetics exhibits a distinct dependence on the ionic liquid composition, even though the constancy of the formal potential of the ferrocenium/ferrocene couple suggests only weak, or composition independent solvation, in this system [22]. Independence of the $E°$ for $FeCp_2$ oxidation measured against the quasi-reference silver electrode, Table 2, agrees quite well with that expected for the silver electrode in the basic chloroaluminate ionic liquid [23]. The experimental slope of the dependence of $E_{1/2}^r$ versus log $C_{Cl^-}$ was $0.217 \pm 0.011$ V, while the theoretical dependence for the electrode stoichiometry $Ag + 4Cl^- = AgCl_4^{3-}$ is 0.236 V. The weak or constant solvation in the studied system renders unlikely an explanation of the observed kinetics by the dependence of the outer-shell component of the free energy of activation for the electron transfer on the solvent composition. Therefore, we turn to the dependence of the pre-exponential factor of the rate constant for the electron transfer on the solvent dynamic effects as the most likely reason for the observed behavior. Unfortunately, there is no data on dielectric properties of the chloroaluminate ionic liquid and even an estimation of the Debye relaxation time, $\tau_D$, from the Debye equation would probably be only a rough approximation in this unusual medium. There have been several experimental [8,24,25] and theoretical [26] studies indicating composition dependent association of ambient temperature chloroaluminate ionic liquids involving contributions from hydrogen bonding between chloride and imidazolium ions. Structured liquids usually exhibit more than one dielectric relaxation time [21] and deviate from the Debye model. A qualitative comparison between the kinetic data observed in the present system and those observed in other solvents [4,10] shows clearly that the macroscopic viscosity, $\eta$, is only a limited indication of the effects of the ionic liquid dielectric relaxation on the barrier crossing frequency for the outer-sphere electron transfer. Thus, the rate constant, $k_s$, obtained in the 0.95:1 ionic liquid is similar to the value observed in much less viscous dichloromethane, for which $\eta$ is 0.4 cP. An analogous comparison for the 0.8:1 melt and such solvents as DMSO and propylene carbonate, with viscosities of 2.2 and 2.4 cP, respectively, suggest relatively fast solvent relaxation in not very basic ionic liquids. It has already been reported for other structured solvents [27] that faster solvent relaxation modes can be involved in the electron transfer because of the 'structure breaking' due to electrostatic interactions in the vicinity of both the charged solute and the electrode surface. The most basic ionic liquid compositions are more viscous than any other electrochemical solvent, and thus even such qualitative comparisons are impossible. Nevertheless, the very slow electron transfer rates observed there, Table 4, indicates increasingly slow relaxation of the highly associated basic ionic liquid.

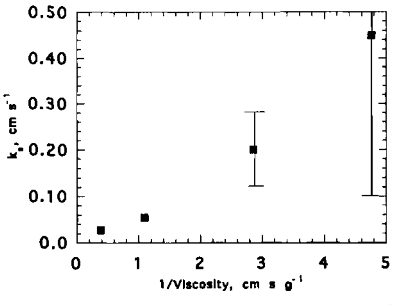

Fig. 7. Dependence of the standard rate constant, $k_s$, for $FeCp_2$ oxidation on the reciprocal of the kinematic viscosity of the $AlCl_3$:ImCl ionic liquid.

A plot of the log of the rate constant against the log of the reciprocal of the viscosity is linear, with a slope of 1.1 and a correlation coefficient of 0.96, suggesting that the reaction is adiabatic. Thus, a deviation from adiabaticity for the behavior observed in this system is much less likely than the solvent dependence of the outer-shell component of the free energy of activation.

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