



Cations/Anions Effects of Imidazolium-based Ionic Liquids on the Diffusion Properties of Iron- and Ruthenium-bipyridine /phenanthroline Complexes



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ABSTRACT

The diffusion coefficients of both iron(II)-bipyridine ($[\text{Fe}(\text{bpy})_3]^{2+}$), ruthenium(II)-bipyridine ($[\text{Ru}(\text{bpy})_3]^{2+}$) are reported in five of different imidazolium-based ionic liquids (ILs) and iron(II)-phenanthroline ($[\text{Fe}(\text{phen})_3]^{2+}$), ruthenium(II)-phenanthroline ($[\text{Ru}(\text{phen})_3]^{2+}$) in one of imidazolium-based ionic liquid, using cyclic voltammetry and chronoamperometry at microdisc electrodes. Activation energies of diffusion, E_D , are calculated for each system. Diffusion coefficient ratios between oxidation and reduction species for both complexes were found to be close to 1. Plots of diffusion coefficients versus inverse viscosity deviate from expected linearity, especially for ILs with different kind of anions, suggesting that anions of the ILs contribute to the values of diffusion coefficients. E_D for both complexes in ILs are found slightly larger compared to the activation energies of viscous flow (E_η) for the corresponding IL, indicating that the viscosity is not the only factor determining the diffusion of the complexes. Furthermore, the hydrodynamic radius of complexes in ILs were estimated based on the diffusion coefficient values. They are found to be independent of temperature and ILs viscosity.

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1. Introduction

Ionic liquids (ILs) are investigated extensively in recent years under both, theoretical and experimental aspects. In particular, some ILs show wide electrochemical windows, low-pressure volatilization, high thermal stability and good conductivity. Therefore, ILs can be used in electrochemistry without adding supporting electrolytes [1]. From these favorable properties, redox flow batteries, electro-deposition, fuel cells and photo-electrochemical cells may be constructed using the redox reactions of transition metal species in ILs [2–4]. Recent publications report that the high viscosity of ILs leads to unusual results in mass and charge-transfer dynamics. The diffusion coefficients of the redox species and the heterogeneous electron transfer rate constants are usually smaller in ILs compared to conventional organic solvents [5–9].

A detailed study of diffusion coefficients leads to a better understanding of electrochemical systems related to mass transfer. Therefore, the diffusion coefficients for several sizes of molecules have been reported, starting from a small sized molecule like dioxygen (O_2), ferrocene (Fc), to organic molecules such as tetrathiafulvalene (TTF), tetramethyl-*p*-phenylenediamine (TMPPD) and several other nitroaromatic compounds, like 4-nitrotoluene (4NT), 2-nitro-mesitylene (2NMT) and 2,4,6-tri-*tert*-butyl-nitrobenzene (BNB). In commonly low viscous solvents, classical values for diffusion coefficients are on the range order of 10^{-5} – 10^{-6} $\text{cm}^2 \text{s}^{-1}$.

The dissimilarities in the diffusion coefficients between reactant and electrogenerated species are often revealed for one-electron reduction, such as O_2 to $\text{O}_2^{\bullet-}$ ($D_{\text{O}_2} \gg D_{\text{O}_2^{\bullet-}}$). $D_{\text{O}_2} = 1.48 \times 10^{-6}$ and $D_{\text{O}_2^{\bullet-}} = 4.66 \times 10^{-8}$ $\text{cm}^2 \text{s}^{-1}$ is found in hexyltriethylammonium bis(trifluoromethylsulfonyl)imide ($[\text{N}_{6222}][\text{NTf}_2]$) at 293 K [10]. For nitro compounds $D_{4\text{NT}} = 3.6 \times 10^{-7}$ and $D_{4\text{NT}^{\bullet-}} = 0.77 \times 10^{-7}$ $\text{cm}^2 \text{s}^{-1}$, $D_{2\text{NMT}} = 5.4 \times 10^{-7}$ and $D_{2\text{NMT}^{\bullet-}} = 1.7 \times 10^{-7}$ $\text{cm}^2 \text{s}^{-1}$, $D_{\text{BNB}} = 2.03 \times 10^{-7}$ and $D_{\text{BNB}^{\bullet-}} = 1.0 \times 10^{-7}$ $\text{cm}^2 \text{s}^{-1}$ are found in $[\text{bmim}][\text{NTf}_2]$ at 303 K [11]. Concerning to the mass transport, the diffusion coefficients of the oxidized and reduced states of redox couple, characterized by the ratio $\gamma = D_{\text{red}}/D_{\text{ox}}$, could be very different in ILs [12]. In case of $D_{\text{O}_2^{\bullet-}}/D_{\text{O}_2}$, $\gamma = 0.03$ and for some others system

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$\gamma = 0.21$, $\gamma = 0.32$, $\gamma = 0.50$ for D_{4NT^+}/D_{4NT} , D_{2NMT^+}/D_{2NMT} , D_{BNB^+}/D_{BNB} , respectively. It has been proven that additional charge of the electro-active species lowers the diffusion coefficients due to coulombic interactions between the electro-active species and the cations and/or anions of the ILs. Further, Zigah et al. [11] also showed that the bulky structure of organic molecules such as 2,4,6-tri-*tert*-butyl-nitrobenzene lowers the diffusion coefficients by a factor of two times for 2-nitro-mesitylene in the same of IL.

For larger molecules such as inorganic complexes, where the influence of the size and the charge density of the complexes are expected to be significantly larger, quantitative studies on diffusion properties are rare. Silvester et al. [13] reported redox properties of neutral rhenium-tetrazolato complex, namely *fac*-[Re(CO)₃(phen)L] (where L is 5-(4'-cyanophenyl)tetrazolate. However, there is little information on the diffusion of charged inorganic metal complexes and their kinetics of charge transfer processes. Tachikawa et al. reported on the diffusion coefficients of differently charged iron complexes such as [Fe(bpy)₃]²⁺, [Fe(Cp)₂]⁺ (Cp = cyclopentadienyl), [FeCl₄]⁻ and [Fe(CN)₆]³⁻ in [bmp][NTf₂]. They suggested that the redox potentials of the iron complexes are affected by the donor properties of the ligands. The diffusion of the iron complexes mainly depends on the size of complexes [14]. Miura et al. [15,16] reported that coulombic interaction between [Ru(bpy)₃]²⁺ complex and ILs has been found to effect the diffusion coefficients and the rate constant of the redox reaction. Furthermore, redox reactions between trivalent and divalent iron and ruthenium complexes are reported to be electrochemically reversible [17].

Beside the size of a complex, it is suggested that the size and the charged density of the cation/anion of ILs will also influence the value of the diffusion coefficients. Prior to this suggestion, Murray et al. have proposed a model for control of electron transfer rates called "ion atmosphere relaxation" [18]. The electron transport rate is controlled by the diffusive relaxation that comes from anions/cations atmosphere. Since electroactive species migrating through IL is analogous to the electron percolation, thus the diffusion coefficients might be influenced by anions/cations atmosphere as well. In this study, diffusion properties of [Fe(bpy)₃]²⁺ and [Ru(bpy)₃]²⁺ in several different ILs are investigated. Variation of diffusion coefficients of these complexes are expected and it is also suggested that values of diffusion coefficients will not only follows the viscosity of ILs.

Chronoamperometry (CA) and cyclic voltammetry (CV) are used as reliable electrochemical methods to determine diffusion coefficients. CA is widely used for systems with sluggish heterogeneous kinetics. Moreover, the analysis of chronoamperometric transient does not only supply the value of the diffusion coefficients, but also the concentration of the diffusing species [19]. However, choosing an optimal measuring time scale to avoid convection and charging current is the most significant problem in using CA methods. Compton et al. [20], pointed out that reliable values of diffusion coefficients may not be obtained by short transient time due to the large double layer capacitance of the ILs. Alternatively, CV at microelectrodes is used [21–23]. In this case the ohmic drop must be taken into account because of the higher resistance of ILs compared with organic solvents with added supporting electrolyte.

In this work, the diffusion properties of the [Fe(bpy)₃](PF₆)₂ and [Ru(bpy)₃](PF₆)₂ complexes in ILs will be studied in detail, and any similarities/differences in the electrochemical behavior in different ILs will be explored. Cyclic voltammetry will be presented in one chosen IL ([bmim][NTf₂]) to describe the general electrochemical reaction. Then, the diffusion properties of the complexes in five different ILs with different cations and anions will be presented.

Finally, temperature-dependence of diffusion properties of each complex will be given and the applicability of the Stokes-Einstein equation for these large inorganic metal complexes in ILs will be addressed.

Five different imidazolium-based ionic liquids, containing as cations: 1-ethyl-3-methylimidazolium [emim], 1-butyl-3-methylimidazolium [bmim], and 1-hexyl-3-methylimidazolium [hmim], coupled with the anions: bis(trifluoromethylsulfonyl)imide [NTf₂], trifluoromethanesulfonate [OTf], and tetrafluoroborate [BF₄] are used in this study.

2. Experimental

2.1. Apparatus and cyclic voltammetry measurements

All electrochemical measurements are conducted under nitrogen atmosphere with a three-electrode cell using an Autolab PGSTAT302N potentiostat (Eco Chemie B.V., Utrecht, Netherlands) equipped with the General Purpose Electrochemical System (GPES) software version 4.9. This software is used for a variety of data analyses including the post-measurement background currents and ohmic drop corrections. The possible background currents was recorded for each IL without electro-active species and digitally subtract it from the scan collected for the solution of electro-active [Fe(bpy)₃]²⁺ and [Ru(bpy)₃]²⁺ in the ILs. The resistances of ionic liquids was determined by impedance measurements, typical Bode-plots were recorded in the range of frequency from 100–15000 Hz at temperature range of 293–343 K. The ohmic drop corrections were made by GPES program with inserting the value of the resistance of ionic liquids.

In order to measure in small sample volumes at different temperatures, the three-electrode cell was constructed with two lines of thermostated water inlet and outlet. These lines are connected to a Haake thermostat type G, with an accuracy of ±0.5 K. Voltammograms are recorded using a 1 ± 0.04 mm diameter glassy carbon-disc (GC) as working electrode, a platinum (Pt) ring-wired counter electrode, and a centered tungsten (W) wire was chosen as pseudo-reference electrode. Prior to each measurement, the active area of the GC electrode was mechanically polished stepwise using diamond paste (IDA Industrie-Diamant-Aachen, Germany) of decreasing particle size 15, 6, 3, 1 and 0.25 μm on polishing pads, sequentially rinsed with distilled water and then dried. Cyclic voltammograms were recorded at scan rates 20, 40, 60, 80, 100, 200, and 300 mV s⁻¹. During the measurements, nitrogen gas was used instead of argon due to solubility issues of unexpected influence of argon gas on the voltammetry and rate of diffusion [24].

2.2. Chronoamperometric Experiments

The same three-electrode cell with the same type of electrodes is used for the chronoamperometry measurements. Chronoamperometric transients were achieved by stepping the potential from a point of zero current (with 50 s pre-equilibration) to a chosen potential after the oxidative peak. The current was measured for 10 s with a sample time of 0.01 s. In order to diminish the thermal convection currents, thermostat-controlling had to start at least one hour prior to measurement to ensure a constant cell temperature. Experimental data were fitted using the software package Origin 8.0 (Microcal Software Inc.) The equations proposed by Shoup and Szabo [25] as shown in eq. 1–3 were imported into the nonlinear curve fitting function, and the computer program performs 100 iterations on the data, which are sufficient to give D and c within an error of 0.6%.

$$I = 4nFDc\text{erf}(\tau) \quad (1)$$

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