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Measurement of the diffusion coefficients of $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$ in aqueous solution using microelectrode double potential step chronoamperometry

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ABSTRACT

Microelectrode double potential step chronoamperometry is reported which allows the measurement of the diffusion coefficients of $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$ in aqueous solutions containing various concentrations of the supporting electrolyte, KCl, KNO_3 or K_2SO_4. In the case of K_2SO_4, ion-pairing of hexaammineruthenium cations is inferred where for KCl and KNO_3 no such effects were noted. The triply charged ion was found to have a significantly lower diffusion coefficient than the doubly charged ion with a ratio of ~0.71 in the KCl and KNO_3 media.

1. Introduction

Hexaammineruthenium III/II (HexRu(III)|HexRu(II)) couple is a much used electrochemical redox couple [1–4]. In aqueous solutions it exhibits reversible redox behaviour, and has been widely used for comparisons between models and experiment in theoretical studies of mass transport [5]. Many literature papers have reported the diffusion coefficient for $[Ru(NH_3)_6]^{3+}$ [1,2,5], although very few have done so for $[Ru(NH_3)_6]^{2+}$ [6,7].

Normally, according to the classic Stokes–Einstein (S–E) equation, the diffusion coefficients for the two species of a redox couple should be the same, if there is no great change in their sizes under a stable environment. This is widely observed. It was reported that for the ferrocene|ferrocenium ($Fc|Fc^+$) couple in acetonitrile solutions supported by either tetra-*n*-butylammonium-perchlorate (TBAP) or tetra-*n*-butylammoniumhexafluoro-phosphate ($TBAPF_6$), the diffusion coefficient ratio of the reductive and oxidative species was found to be between 0.96 and 1.00 by different research groups [8–10]. Georges and Desmettre also estimated this ratio in water solutions using the Stokes–Einstein relationship and suggested a value of 1.00, although the solubility of Fc in water is as low as 5×10^{-5} M [11]. Wang and co-workers studied a series of species including *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylene-diamine (TMPD), 2,3,5,6-tetra-bromo-1,4-benzo-quinone (TBBQ), 2,3,5,6-tetra-chloro-1,4-benzo-quinone (TCBQ), pheno-thiazine (PTZ) and their oxidised species in acetonitrile. They suggested that all the couples studied had a diffusion coefficient ratio close to unity. In addition, they also found that in an aqueous solution of TMPD with 0.2 M KCl, the ratio was about 0.96 [12]. Ikeuchi et al. measured the $Ru(acac)_3|[Ru(acac)_3]^+$ couple in acetonitrile solutions with TBAP and $TBAPF_6$ separately, and found that the ratios were 0.99 and 1.01 respectively [13].

However, it has also been reported that in some cases the diffusion coefficients of the two compounds of a redox couple can differ a lot. Many studies were carried out employing Room-Temperature Ionic Liquids (RTILs), in which charged species may interact strongly with the counter ion of the solvent via Coulombic forces and so diffuse slower. For example, Rogers et al. reported diffusion coefficient ratios of 0.13–0.76 for the $Fc|Fc^+$ couple and 0.33–0.77 for the $Cc^+|Cc$ couple in various ionic liquids [14] where Fc^+ diffuses more slowly than Fc. Evans et al. studied the behaviour of TMPD in a range of ionic liquids at 323 K and found that the diffusion coefficient ratio of $TMPD^{+\cdot}|TMPD$ was between 0.54 and 0.57, and the ratio of $TMPD^{2+}|TMPD^{+\cdot}$ was around 0.33 [15]. Similarly, the two ratios for *N*,*N*-dimethyl-*p*-phenylene-diamine (DMPD), $D_{DMPD^{+\cdot}|DMPD}$ and $D_{DMPD^{2+}|DMPD^{+\cdot}}$, in the ionic liquid $[C_4mim][BF_4]$ was found to vary between 0.55 and 0.64 [16]. Wang et al. studied the reduction of benzo-quinone in the ionic liquid $[C_2mim][NTf_2]$, and the diffusion coefficient ratios of $BQ^{-\cdot}|BQ$ and $BQ^{2-}|BQ^{-\cdot}$ couples were 0.39 and 0.85 [17]. An extreme example was reported by Buzzeo et al. that in ionic liquids, the diffusion coefficient ratio of $O_2^{-\cdot}|O_2$ could be as small as 0.03 [18]. Redox couples may also have different diffusional behaviours in conventional organic solvents. Klymenko et al. suggested that the $TMPD^{+\cdot}|TMPD$ couple had a ratio of 0.78 in a ethanol solution with 0.1 M TBAP [19]. Ji

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et al. studied benzo-quinone in a propylene carbonate (PC) solution and found the ratios were 0.48 and 0.60 for $BQ^{-\cdot}|BQ$ and $BQ^{2-}|BQ^{-\cdot}$ respectively [20]. For benzo-quinone in acetonitrile solutions, a $BQ^{-\cdot}|BQ$ ratio of 0.70 was measured by Unwin and his group [21]. Belding et al. found that for para-quaterphenyl (PQ) THF solutions, the two ratios for $PQ^{-\cdot}|PQ$ and $PQ^{2-}|PQ^{-\cdot}$ were 0.45 and 0.59 [22]. Similar situations were also found in aqueous systems. Fisher and Compton measured the $[Fe(CN)_6]^{4-}|[Fe(CN)_6]^{3-}$ couple in a water solution with 0.1 M KCl, the diffusion coefficient ratio was found to be 0.85 [24]. Also, Baticle et al. found that the ratio for the $Fe^{2+}|Fe^{3+}$ couple was 1.24 in a H_2SO_4 solution [23]. One possible reason was that charged species may form ion-pairs with supporting electrolyte, which was widely cited in related researches [19,25–28]. Counter ions of electrolyte may associate with charged redox species, and the total size of these species becomes larger. Therefore, according to the Stokes–Einstein equation, the diffusion coefficients for them may also decrease.

The redox couple of $[Ru(NH_3)_6]^{3+}|[Ru(NH_3)_6]^{2+}$ is a frequently used couple in electrochemical studies due to its chemical and electrochemical reversibility [1–4]. However, currently there is little reporting about the ratio of its diffusion coefficients or about the possibility of either species forming ion-pairs with electrolyte. Hence, it is important to measure the diffusion coefficients of the two ions and study their interaction with different amount of supporting electrolytes. The present paper reports a diffusion coefficients for the hexaammineruthenium, finding as expected a dependence of $D_{\mathrm{HexRu(III)}}$ and $D_{\mathrm{HexRu(II)}}$ on the concentration of supporting electrolyte. Moreover, different common supporting electrolytes were studied revealing ion-pairing effects in the presence of K_2SO_4.

2. Experimental

2.1. Chemical reagents

Hexaammineruthenium(III) chloride ($[Ru(NH_3)_6]Cl_3$, Aldrich, 98%), potassium chloride (KCl, Aldrich, >99%), potassium nitrate (KNO_3, Aldrich, >99%), potassium sulphate (K_2SO_4, AnalaR, 99.5%), ferrocene ($Fe(C_5H_5)_2$, Aldrich, 98%), tetra-*n*-butylammonium-perchlorate (TBAP, Fluka, >99%), acetonitrile (MeCN, Fischer scientific, dried and distilled, >99%), and nitrogen (N_2, BOC, high purity oxygen free) were used directly, without further purification.

2.2. Instrumental

A computer-controlled μ-Autolab potentiostat (Eco-Chemie, Netherlands) was used to operate all the electrochemical experiments. The working electrode was a 25 μm radius platinum (Pt) microdisk electrode made of a 99.99% pure platinum wire (Goodfellow Cambridge Ltd., Cambridge), which was polished before each experiment using 1.0, 0.3 and 0.01 μm alumina–water slurry on soft lapping pads (Buehler, Illinois). A gold foil was introduced as a counter electrode, and the reference electrode was a Ag|AgCl electrode. The radius of the working electrode was calibrated by measuring the steady-state limiting current of a 2 mM ferrocene solution in acetonitrile with 0.1 M TBAP as supporting electrolyte at 293 K. A literature diffusion coefficient of $2.3 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$ was used to determine the radius (r_d) by the equation below:

$$i_{\mathrm{lim}} = 4nFr_dDc \qquad (1)$$

where i_{lim} is the steady-state limiting current, n is the number of electrons, F is the Faraday constant, D is the diffusion coefficient, and c is the initial concentration.

Two millimolar hexaammineruthenium(III) chloride solutions were made with ultrapure water with resistivity >18.2 $\mathrm{M\Omega\ cm^{-1}}$, with various supporting electrolytes species (KCl, KNO_3 and K_2SO_4) in a range of concentrations of 0.1, 0.3 and 0.5 M. All the solutions were degassed for 30 min with N_2 before each experiment, and the temperature was controlled at 298 K using a thermostatted Faraday Cage.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammograms were first recorded at a scan rate of 500 mV s^{-1}, at solutions containing 2 mM hexaammineruthenium(III) chloride, with different supporting species (KCl, KNO_3 and K_2SO_4) at various concentrations (0.1, 0.3 and 0.5 M) at a 25 μm radius platinum (Pt) microdisk electrode. The recorded voltammograms are presented as examples in Fig. 1 for a concentration of 0.1 M of the supporting electrolytes in each case. The cyclic voltammograms obtained from the solutions containing KCl and KNO_3 are undistinguishable within experimental error, therefore, both the formal potential and diffusion coefficients of the electroactive couple are almost equal. However, the curve recorded using K_2SO_4 as supporting electrolyte shows that both the reduction and oxidation peaks are significantly smaller compared to the cases using KCl and KNO_3, which is a possible indication of a decrease of diffusion coefficients of both species, $[Ru(NH_3)_6]^{3+}$ and $[Ru(NH_3)_6]^{2+}$. Also, a shift in the half wave potential of −0.05 V is observed for K_2SO_4 in comparison with the other supporting electrolytes. These features are an indication that the sulphate anions affect the behaviour of the electrochemical couple. Next a more detailed experimental procedure was employed in order to obtain accurately the diffusion coefficients for both compounds of the electroactive couple.

3.2. Potential step chronoamperometric experiments

Double potential step chronoamperometry at a 25 μm radius platinum (Pt) microdisk electrode was employed to quantitatively determine the diffusion coefficients for the hexaammineruthenium(III) cation as well as the hexaammineruthenium(II) cation. The sampling time was 0.005 s. The potential was stepped from 0 V vs. Ag|AgCl (where there was no faradaic current) to a potential of −0.4 V vs. Ag|AgCl, assuring that the potential step was to potentials where the reduction is diffusion controlled. The chronoamp-

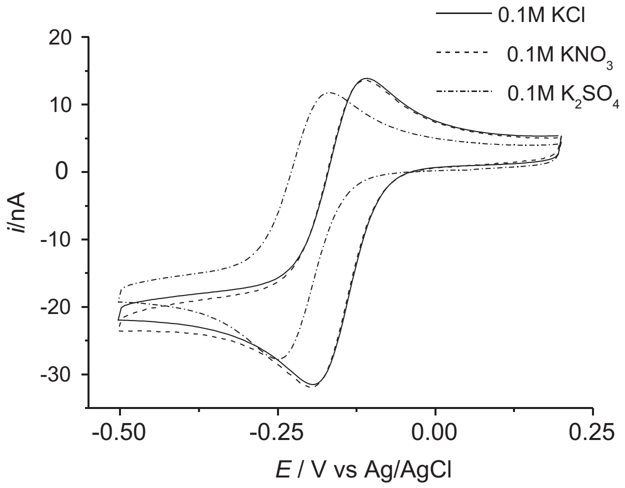

Fig. 1. The cyclic voltammograms for 2 mM hexaammineruthenium(III) chloride solutions supported by 0.1 M KCl (solid), KNO_3 (dash) and K_2SO_4 (dash dot) respectively. The potential was stepped from 0.2 to −0.5 and back to 0.2 V vs. Ag|AgCl.