Understanding Solvent-Solute Interactions In Ionic Liquids: Studies of the Ferricenium/Ferrocene Redox Couple

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The use of ionic liquids as green reaction media in industrially relevant processes has increased dramatically in the last years (1). Many of these reactions are metal-mediated processes and, because metal complexes are expected to behave differently in ionic liquids than in conventional solvents, fundamental questions about solvent-solute interactions in ionic liquids have arisen.

Electrochemical techniques such a cyclic voltammetry, chronoamperometry and rotating disk electrode voltammetry add to the understanding of mass transport and solvent-solute interactions. We have applied these techniques to study the electrochemical behaviour of the ferricenium/ferrocene ($[Fc]^+/[Fc]$) redox couple in different ionic liquids (*e.g.*, $[C_4mim]X$, C_4mim = 1-butyl-3-methylimidazolium; X = $[CF_3SO_3]^-$, $[N(SO_2CF_3)_2]^-$ or $[PF_6]^-$).

Cyclic voltammetric experiments performed at both platinum and glassy carbon (GC) electrodes, showed that the $[Fc]^+/[Fc]$ couple was electrochemical reversible in all cases. Values of the half-peak potentials, $E_{1/2}$, peak-to-peak separation, ΔE_p, and peak currents ratios, $|i_p^c / i_p^a|$ are given in Table 1. In addition, controlled-potential electrolysis of ferrocene to the monocation was found to be chemically reversible.

The diffusion coefficients, D, of both the oxidized and the reduced species were determined from data obtained by cyclic, normal pulse and rotating disk electrode voltammetries (Table 2). The solvodynamic radii of the diffusing species, r_s, in each ionic liquid were estimated using a corrected version of the Stokes-Einstein equation [1],

$$r_s = k_B T / 2 \pi \eta D \qquad [1]$$

where k_B is the Boltzmann's constant, T is the absolute temperature, η is the viscosity of the medium, and D is the diffusion coefficient of the analyte. All the mass transport data of the ferrocene and ferricenium solutions are summarised in Table 2.

Interestingly, a dependency of the solvodynamic radii of ferrocene upon the anion of the ionic liquid was observed. Thus, whereas the calculated solvodynamic radii of ferrocene in $[C_4mim][PF_6]$ and $[C_4mim][NTf_2]$ (3.0 ± 0.4 and 4.3 ± 0.3 Å, respectively) corresponded to the crystallographic radius of ferrocene (3.5 Å), the solvodynamic radius of ferrocene in $[C_4mim][OTf]$ was significantly larger (13 ± 2 Å). This is in closer agreement with the crystallographic radius of a molecule of ferrocene (3.5 Å) plus two $[OTf]^-$ anions (6.4 Å).

In order to better understand the nature of the diffusing species in $[C_4mim][OTf]$, structural (*e.g.*, EXAFS) and molecular modelling studies have been carried out and will be presented. The electrochemical behaviour of the $[Fc]^+/[Fc]$ couple in a wider range of ionic liquids will also be analysed.

Table 1. Cyclic voltammetric data for [Fc] and $[Fc]^+$ in $[C_4mim]X$ ionic liquids.

	Working electrode	$E_{1/2}$ [(a)] */ mV*	ΔE_p */ mV*	$\lvert i_p^c / i_p^a \rvert$
		[Fc]		
$[PF_6]^-$	Pt	-0.032 ±0.001	0.050 ±0.004	0.97 ±0.02
	GC	-0.034 ±0.001	0.058 ±0.004	1.03 ±0.02
$[OTf]^-$	Pt	-0.011 ±0.001	0.069 ±0.005	0.95 ±0.02
	GC	-0.010 ±0.001	0.072 ±0.006	0.97 ±0.02
$[Tf_2N]^-$	Pt	-0.025 ±0.001	0.058 ±0.004	0.98 ±0.02
		$[Fc]^+$		
$[PF_6]^-$	Pt	-0.020 ±0.001	0.058 ±0.005	1.11 ±0.03
	GC	-0.021 ±0.001	0.053 ±0.003	1.05 ±0.02

[(a)] Half-peak potential *versus* Ag(I)/Ag

Table 2. Mass transport data of the [Fc] and $[Fc]^+$ in $[C_4mim]X$ ionic liquids.

	Viscosity [(a)] */ cp*	$D \times 10^7$ / $cm^2\ s^{-1}$	r_s / Å
		[Fc]	
$[PF_6]^-$	272	0.79±0.09	3.0±0.4
$[NTf_2]^-$	50.2	3.0±0.2	4.3±0.3
$[OTf]^-$	79.2	0.61±0.09	13±2
		$[Fc]^+$	
$[PF_6]^-$	272	0.31±0.04	7.7±1.0

[(a)] Viscosity measured for the neat ionic liquids.

REFERENCES

(1) P. Wasserscheid and W. Keim, Angew. Chem. Int. Ed., **39**, 3772 (2000).