Heterogeneous electron transfer at Au/SAM junctions in a room-temperature ionic liquid under pressure†

Tina D. Dolidze,[ab] Dimitri E. Khoshtariya,*[ab] Peter Illner[a] and Rudi van Eldik*[a]

Received (in Cambridge, UK) 2nd January 2008, Accepted 1st February 2008
First published as an Advance Article on the web 25th February 2008
DOI: 10.1039/b719787j

Proven electrochemical approaches were applied to study heterogeneous electron transfer (ET) between selected redox couples and gold electrodes modified with alkanethiol self-assembled monolayers (SAMs), using the room-temperature ionic liquid (RTIL) [bmim][NTf$_2$] as reaction medium; ferrocene as freely diffusing redox probe in the RTIL was tested for ET through both thin (butanethiol) and thick (dodecanethiol) assemblages at pressures up to 150 MPa; well behaved kinetic patterns and reproducibility of data were demonstrated for ET within the unique Au/SAM/RTIL arrays.

Metal electrodes modified by alkanethiol self-assembled monolayer films (SAMs) [ω-(CH$_2$)$_n$–SH)] of different thickness (where "ω" indicates the SAM terminal group and normally n = 2–18) have proven to be perfect nanoscale devices for multiple technological applications,[1] as well as for rigorous testing of fundamental electron transfer theories.[2,3] Employment of the high-pressure electrochemical strategy in general,[4] and to the above-mentioned advanced composite systems in particular, opened new dimensions for in-depth understanding of intrinsic charge transfer mechanisms in aqueous, non-aqueous and biomolecular environments.[3,4] In another breakthrough development the new type of media, room temperature ionic liquids (RTILs), have been suggested as an advantageous alternative to aqua/organic solvents, due to a number of favourable physicochemical properties (*viz*. negligible vapour pressure, low toxicity, high chemical and electrochemical stability, high conductivity) and the ability to dissolve a wide range of organic and inorganic compounds.[5] Apart of numerous papers on physical parameters of RTILs, a number of remarkable accounts on mechanistic studies of homogeneous[6] and electrode[7] rate processes that proceed in these liquids have appeared.

Our recent ambient and high pressure kinetic studies of heterogeneous electron transfer (ET) employed the RTIL, [bmim][NTf$_2$], as reaction medium (whose viscosity was subjected to dramatic modification under high pressure).[8] These studies enabled us to reveal factors that control electron transfer dynamics at bare metal electrodes and the underlying molecular interactions.[8] Although lateral investigations have shown that SAMs are stable in related imidazolium based ionic liquids at ambient pressure,[9] as far as we know there are no reports available on SAM-implicated electrochemical ET occurring in RTILs, either at ambient or under high pressure conditions. In the present communication, for the first time, were report on voltammetric kinetic studies of heterogeneous ET, in [bmim][NTf$_2$] as solvent, at gold electrodes modified by alkanethiol SAMs [ω-(CH$_2$)$_n$–SH)] with different terminal groups (–CH$_3$ and –OH$^-$), and variable thickness (n = 3, 11) at ambient conditions and under pressure up to 150 MPa.

Dicyclopentadienyliron, [Fe(cp)$_2$]$^{+/0}$, tris(2,2-bipyridine)iron(II), [Fe(bipy)$_3$]$^{3+/2+}$, complexes, and [Fe(III) meso-tetra(*N*-methyl-4-pyridyl)porphyrin] were used as redox couples. In the case of thinner SAMs (n = 3), experimental voltammograms displayed reversible (at low scan rates) and quasi-reversible (at high scan rates) patterns; accordingly the Nicholson method[10,11] was employed to determine the experimental heterogeneous standard rate constants, k^0_{EXP}. Special care was taken to avoid the interference with effects of uncompensated resistance. In the case of thicker SAMs (n = 11), voltammograms exhibited an irreversible pattern. In the latter case, convolution analysis[10,11–14] has been applied to eliminate the effect of diffusion on the measured current, and values of standard rate constants were then calculated according to the method of Imbeaux and Savèant.[14] Details about the instrumentation, high-pressure electrochemical cell, preparation of SAM modified gold electrodes, and calculation of rate constants and related parameters can be found in ref. 3*c*,*d* and ESI.†

Fig. 1 shows the voltammetric response for the ferrocene couple recorded for gold electrodes coated with CH$_3$-terminated alkanethiol monolayers [CH$_3$–(CH$_2$)$_n$–SH] of different thickness (n = 3, 11; v = 0.1 V s^{-1}). The dramatic change in the kinetic behavior is consistent with a much larger insulating effect of the dodecanethiol SAM compared to the butanethiol one (see refs. 2, 3 and 12). The examples of voltammograms obtained for two other redox couples can be found in ESI.† Values of the respective experimental (corrected for Ohmic drop) standard rate constants of electron transfer together with matching diffusion coefficients are collected in Table 1. The ferrocene couple acting at CH$_3$-terminated SAMs displayed the best voltammetric behavior (along with durable stability and remarkable data reproducibility) with both the dodecanethiol and butanethiol SAM assemblages compared to systems with other redox couples.

This observation was somewhat surprising because due to smaller dimensions and the more hydrophobic character of the ferrocene couple compared to the other two couples, one could expect complications caused by eventual penetration of these species into the SAM interior and further approach of the

---

[a] *Inorganic Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Egerlandstr. 1, 91058 Erlangen, Germany. E-mail: vaneldik@chemie.uni-erlangen.de*
[b] *Institute of Molecular Biology and Biophysics, and Institute of Inorganic Chemistry and Electrochemistry, Gotua 12, 0160 Tbilisi, Georgia. E-mail: dimitri.k@joker.ge*

† Electronic supplementary information (ESI) available: Experimental procedures and extra illustrations. See DOI: 10.1039/b719787j

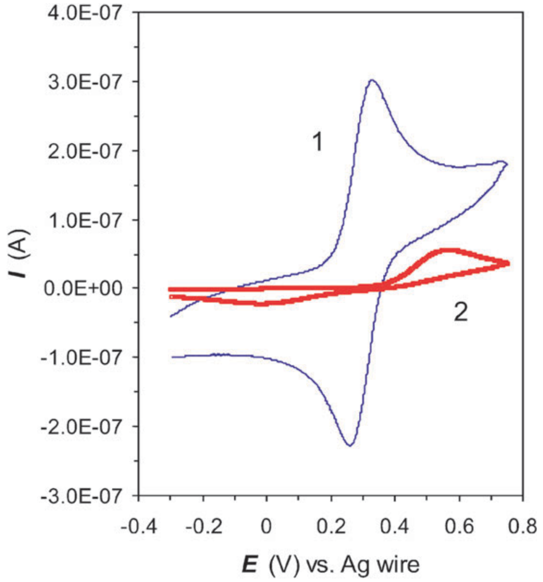
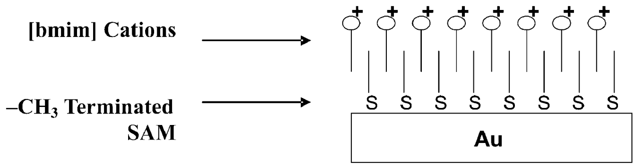


Fig. 1 Cyclic voltammograms of $[Fe(cp)_2]^{+/0}$ couple recorded in [bmim][NTf_2]] at gold electrodes (S = 0.02 cm^2) coated with: (1) 1-butanethiol ([CH_3–$(CH_2)_3$–SH]) and (2) n-dodecanethiol [CH_3–$(CH_2)_{11}$–SH] monolayers ($C_{Fc} = 2 \times 10^{-4}$ M, $v = 0.1$ V s^{-1}, $P = 0.1$ MPa).

electrode surface.[1,12,13] These processes may take place either through the fluctuational appearance of channels of appropriate dimensions within the sound SAM domains, or through pinhole-like defects,[1,12,13] and show up *via* specific CV signals as well as essential non-reproducibility of electrochemical response within a given experimental cycle and/or independent experimental series. Obviously, in RTIL solvents, some type of mechanism operates that prevents penetration of redox species into SAMs. We assume that due to the hydrophobic interaction, CH_3-terminated SAMs form with [bmim] cations interfacial bilayer structures with interpenetrating aliphatic chains, Scheme 1. These types of bilayers were suggested earlier for systems containing additional lipid components and shown to have significantly improved resistance against the permeability of redox spaces compared to monolayer SAMs (see ref. 13 and literature cited therein). On the basis of the above-mentioned details, we decided to apply the high-pressure kinetic strategy to the two types of Au/SAM assemblages in RTILs involving ferrocene as a redox probe to further test the pressure-resistive stability of these systems. Note, the well-behaved high-pressure performance has been demonstrated earlier for Au/SAM/cytochrome c assemblies in aqueous media.[3c,d]



Scheme 1 Possible structure of interfacial bilayer for a Au/SAM/RTIL junction composed of CH_3–$(CH_2)_n$–SH and [bmim][NTf_2] constituents.

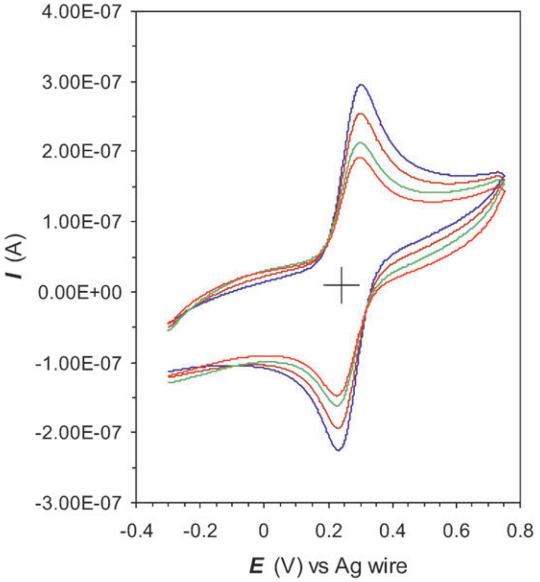


Fig. 2 Cyclic voltammograms of $[Fe(cp)_2]^{+/0}$ couple ($C_{Fc} = 2 \times 10^{-4}$ M) recorded in [bmim][NTf_2] at Au electrode (S = 0.02 cm$^{2\cdot}$) modified with butanethiol [CH_3–$(CH_2)_3$–SH] monolayer at different pressures (P = 5, 50, 100 and 150 MPa) (peak current decrease); scan rate $v = 0.1$ V s^{-1}.

Fig. 2 shows the voltammetric response of ferrocene at the 1-butanethiol modified gold electrode under variable pressure up to 150 MPa at a scan rate, $v = 0.1$ V s^{-1}. Values of k^0_{EXP} for the $[Fe(cp)_2]^{+/0}$ couple measured at the butanethiol and dodecanethiol modified gold electrode under variable pressure are presented in Table 2. We stress again the well-behaved voltammetric patterns, and high reproducibility of the extracted kinetic parameters throughout the ambient conditions, as well as throughout the high pressure cycles. The pressure-resistive stability/reproducibility is clearly visible from Fig. S2 and S3 (ESI†) where the voltammograms recorded at the start and end of the pressure cycles (at P = 5 MPa) are displayed.

Table 1 Values of rate constants (corrected for ohmic potential drop, IRe) for different redox couples at alkanethiol SAM [ω-$(CH_2)_n$–SH)] modified gold electrodes of different thickness (n = 3, 11) at T = 25 °C , P = 0.1 MPa. Values of diffusion coefficients for $[Fe(cp)_2]^{+/0}$ and $[Fe(bipy)_3]^{3+/2+}$ redox couples were taken from ref. 8 and for the porphyrin was estimated from the peak current of CV (Fig. S1, ESI†). The average error for rate constants from independent series was within ±8%

		$k^0_{EXP(cor)}$/cm s^{-1}	
Redox couple	$10^7 D_R$/cm^2 s^{-1}	ω ≡ OH$^-$	ω ≡ CH_3
$[Fe(cp)_2]^{+/0}$	2.84		2.66×10^{-2} (n = 3)
		4.62×10^{-3} (n = 11)	1.50×10^{-5} (n = 11)
$[Fe(bipy)_3]^{3+/2+}$	0.75	1.54×10^{-3} (n = 11)	—
[Fe porphyrin]$^{+/0}$	2.60	2.45×10^{-4} (n = 3)	—

Table 2 Pressure dependence of diffusion coefficients, solution resistances between reference and working electrodes (Re) (see ESI† for details), uncorrected and corrected (for Ohmic potential drop, IRe) rate constants for ferrocene ($C_{Fc} = 2.0 \times 10^{-4}$ M) at alkanethiol SAM [ω-$(CH_2)_n$–SH)] modified gold electrodes of different thickness (n = 3, 11) at T = 25 °C): v = 0.5 V s^{-1}. The average error for rate constants within the given pressure cycle was within ± 5%

P/MPa	$10^7 D_R$/cm^2 s^{-1} (ref. 8)	Re/kΩ	$10^2 k^0_{EXP(uncor)}$/cm s^{-1} (n = 3)	$10^2 k^0_{EXP(cor)}$/cm s^{-1} (n = 3)	$10^5 k^0_{EXP(cor)}$/cm s^{-1} (n = 11)
5	2.61	0.67	2.67	2.8	1.80
50	1.63	1.08	1.55	2.0	2.50
100	0.95	1.86	1.13	1.28	4.54
150	0.65	2.72	0.52	0.68	6.20

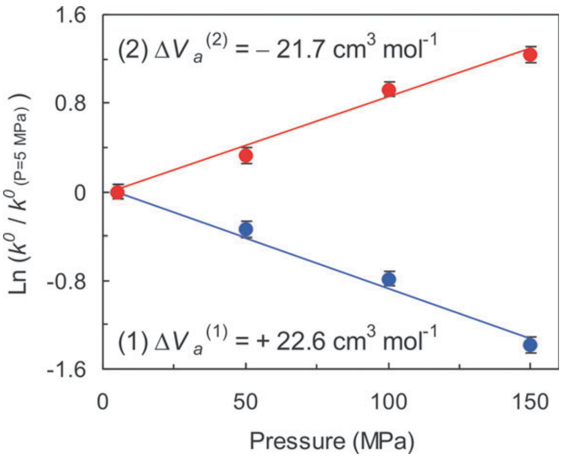


Fig. 3 Impact of high pressure on rate constants (normalized by standard values obtained at 5 MPa) for a $[Fe(cp)_2]^{+/0}$ couple at gold electrode modified by: (1) 1-butanethiol ($[CH_3–(CH_2)_3–SH]$) and (2) n-dodecanethiol $[CH_3–(CH_2)_{11}–SH]$ monolayer films in [bmim][NTf$_2$]] at 25 °C.

This is indicative of a general remarkable stability of these particular Au/SAM/$[Fe(cp)_2]^{+/0}$ assemblages (along with the other two less systematically studied systems in the present work) in a typical RTIL, [bmim][NTf$_2$], as reaction medium.

Importantly, the present electrochemical kinetic studies in [bmim][NTf$_2$] revealed spectacular effects of high pressure (fully reproducible within the pressure cycles) observed as a decrease in the heterogeneous standard rate constant in the case of thin SAMs (n = 3) and an increase in the case of thick SAMs (n = 11) with increasing pressure, Table 2, Fig. 3. The change of experimental heterogeneous standard rate constant with pressure can be ascribed to the intrinsic ET process provided that the impact of pressure on the pre-equilibrium stage of the reactants' inclusion into the reactive zone (located near the electrode) is negligible.[3c,d,4] The corresponding volume of activation can be obtained from eqn (1).[3c,d,4]

$$\Delta V_a = -RT\left[\frac{\partial(\ln k^0_{EXP})}{\partial P}\right]_T \qquad (1)$$

Our data result in large positive and negative values for the volume of activation, for the short-range and long-range ET (involving 1-butanethiol ($[CH_3–(CH_2)_3–SH]$) and n-dodecanethiol $[CH_3–(CH_2)_{11}–SH]$ monolayer films), respectively, in [bmim][NTf$_2$] at 25 °C, Fig. 3. According to our previous investigations[3] supported by lateral studies of other authors,[4] this result can be interpreted as a manifestation of the change-over between the solvent-controlled (adiabatic) and tunnelling-controlled (non-adiabatic) intrinsic ET mechanisms. An extended experimental report, along with detailed mechanistic interpretation on this phenomenon will be given elsewhere.[15]

Financial support for T. D. D. from DAAD and for D. E. K. from the Alexander von Humboldt Foundation and the Dr Hertha and Helmut Schmauser Foundation is gratefully acknowledged. This work was funded by the Deutsche Forschungsgemeinschaft as part of SFB 583 on "Redox-active Metal Complexes".

Notes and references

1 (*a*) H. O. Finklea, *Self-Assembled Monolayers on Electrodes*, Encyclopedia of Analytical Chemistry, ed. R. A. Meyers, Wiley, Chichester, 1996, pp. 1–29; (*b*) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103–1170.

2 (*a*) C. E. D. Chidsey, *Science*, 1991, **251**, 919–922; (*b*) H. D. Sikes, J. F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey and S. W. Feldberg, *Science*, 2001, **29**, 1519–1523.

3 (*a*) D. E. Khoshtariya, T. D. Dolidze, L. D. Zusman and D. H. Waldeck, *J. Phys. Chem. A*, 2001, **105**, 1818–1829; (*b*) D. E. Khoshtariya, J. Wei, H. Liu, H. Yue and D. H. Waldeck, *J. Am. Chem. Soc.*, 2003, **125**, 7704–7714; (*c*) D. E. Khoshtariya, T. D. Dolidze, S. Seyfert, D. Sarauli, G. Lee and R. van Eldik, *Chem.–Eur. J.*, 2006, **12**, 7041–7056; (*d*) D. E. Khoshtariya, T. D. Dolidze, D. Sarauli and R. van Eldik, *Angew. Chem., Int. Ed.*, 2006, **45**, 277–281; (*e*) T. D. Dolidze, S. Rondinini, A. Vertova, D. H. Waldeck and D. E. Khoshtariya, *Biopolymers*, 2007, **87**, 68–73.

4 (*a*) Y. Fu, A. S. Cole and T. W. Swaddle, *J. Am. Chem. Soc.*, 1999, **21**, 10410–10415; (*b*) M. Matsumoto and T. W. Swaddle, *Inorg. Chem.*, 2004, **43**, 2724–2735; (*c*) T. W. Swaddle, *Chem. Rev.*, 2005, **105**, 2573–2608.

5 (*a*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2084; (*b*) S. T. Handy, *Chem.–Eur. J.*, 2003, **9**, 2938–2944; (*c*) M. C. Buzzeo, R. G. Evans and R. G. Compton, *ChemPhysChem*, 2004, **5**, 1106–1120.

6 (*a*) A. Skrzypczak and P. Neta, *J. Phys. Chem. A*, 2003, **107**, 7800–7803; (*b*) P. Illner, A. Zahl, R. Puchta, N. van Eikema Hommes, P. Wasserscheid and R. van Eldik, *J. Organomet. Chem.*, 2005, **690**, 3567–3576; (*c*) P. Illner, S. Kern, S. Begel and R. van Eldik, *Chem. Commun.*, 2007, 4803–4805.

7 (*a*) J. Zhang and A. J. Bond, *Analyst*, 2005, **130**, 1132–1147; (*b*) G. R. Evans and R. G. Compton, *ChemPhysChem*, 2006, **7**, 488–496; (*c*) M. Matsumiya, M. Terazono and K. Tokuraku, *Electrochim. Acta*, 2006, **51**, 1178–1183.

8 T. D. Dolidze, D. E. Khoshtariya, P. Illner, L. Kulisiewicz, A. Delgado and R. van Eldik, *J. Phys. Chem. B*, 2008, DOI: 10.1021/jp077734j.

9 J. Li, Y. Shen, Y. Zhang and Y. Liu, *Chem. Commun.*, 2005, 360–362.

10 A. J. Bard and L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, John Wiley & Sons, New York, 2nd edn, 2001.

11 R. S. Nicholson, *Anal. Chem.*, 1965, **37**, 1351–1355.

12 C. Miller, P. Cuendet and M. Grätzel, *J. Phys. Chem.*, 1991, **96**, 877–886.

13 C. Cannes, F. Kanoufi and A. J. Bard, *J. Electroanal. Chem.*, 2003, **547**, 83–91.

14 J. C. Imbeaux and J. M. Savèant, *J. Electroanal. Chem.*, 1973, **44**, 169–187.

15 D. E. Khoshtariya, T. D. Dolidze and R. van Eldik, in preparation.