

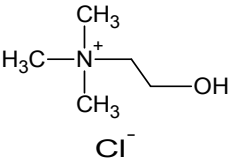
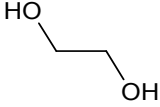
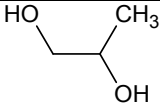
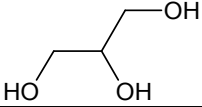
Voltammetric and spectroscopic study of ferrocene and hexacyanoferrate and the suitability of their redox couples as internal standards in ionic liquids

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Supporting information

Ionic liquids and deep eutectic solvents used

name	abbreviation	ionic liquids	
		cation	anion
1-ethyl-3-methyl-imidazolium acetate	[C ₂ mim][ac]		
1-ethyl-3-methyl-imidazolium tetrafluoroborate	[C ₂ mim][BF ₄]		
1-hexyl-3-methyl-imidazolium chloride	[C ₆ mim][Cl]		Cl ⁻
1-butyl-3-methyl-imidazolium dicyanamide	[C ₄ mim][DCN]		
1-ethyl-3-methyl-imidazolium diethylphosphate	[C ₂ mim][DEP]		
1-ethyl-3-methyl-imidazolium ethylsulfate	[C ₂ mim][EtSO ₄]		
1-butyl-3-methyl-imidazolium hydrogensulfate	[C ₄ mim][HSO ₄]	R = ethyl ≡ [C ₂ mim] R = butyl ≡ [C ₄ mim] R = hexyl ≡ [C ₆ mim]	
1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)-imide	[C ₂ mim][NTf ₂]		
1-ethyl-3-methyl-imidazolium triflate	[C ₂ mim][OTf]		
1-butyl-3-methyl-imidazolium hexafluorophosphate	[C ₄ mim][PF ₆]		
1-ethyl-3-methyl-imidazolium thiocyanate	[C ₂ mim][SCN]		S ⁻ -C≡N
ethylammonium nitrate	[EtA][NO ₃]		

name	Deep Eutectic Solvents	
	quaternary ammonium salt	hydrogen-bond donor
Ethaline		
Propaline		
Glyceline		

Electrochemical parameters modelled with DigiElch for the formal potential ΔE vs Ag-wire, charge transfer coefficient α , rate constant k_s , diffusion coefficient D and standard deviation of the fit S , and calculated values for the peak potential separation ΔE_p and peak current ratio I_{pa}/I_{pc} for samples of 10 mM ferrocene in various ILs, on a Pt, GC and Au working electrode and water content in wt% for each solution after dissolving process determined by Karl-Fisher titration.

Ionic liquid		$\Delta E / V$ (DigiElch)	$\Delta E_p / mV$ (from 5 to 100 mV s ⁻¹)	α	I_{pa}/I_{pc} (from 5 to 100 mV s ⁻¹)	$k_s / cm\ s^{-1} \cdot 10^{-4}$	$D / cm^2\ s^{-1} \cdot 10^{-8}$ (DigiElch)	$S / \%$	$H_2O\ content / wt\%$
[C ₂ mim][BF ₄]	Pt	0.4615(4)	68-74	0.78(3)	0.98-1.00	15.8(9)	17.1(1)	2.38	1.2
	GC	0.4616(4)	68-70	0.82(3)	0.98-1.00	15.5(9)	15.6(3)	2.19	
	Au	0.4576(9)	68-70	0.79(4)	1.00-1.01	15(1)	31.5(9)	4.14	
[C ₄ mim][DCN]	Pt	0.6718(6)	72-82	0.47(4)	1.04-1.02	12.9(9)	26.7(3)	2.13	0.92
	GC	0.6542(7)	72-76	0.50(4)	1.03-1.02	14(1)	25.8(3)	1.81	
	Au	0.6438(5)	74-78	0.44(2)	1.27-1.03	12.8(5)	33.2(2)	1.76	
[C ₂ mim][EtSO ₄]	Pt	0.0404(2)	72-102	0.51(2)	0.99-1.00	8.2(2)	20.1(1)	1.50	1.89
	GC	0.0423(3)	74-104	0.50(2)	1.01-1.00	8.5(3)	19.3(1)	1.69	
	Au	0.0442(4)	70-80	0.58(4)	1.01-0.97	13.5(9)	24.4(2)	2.78	
[C ₄ mim][HSO ₄]	Pt	0.531(2)	76-138	0.59(3)	0.94-0.95	0.43(2)	0.087(1)	3.56	0.40
	GC	0.5377(6)	76-142	0.58(3)	1.02-0.97	0.51(3)	0.156(2)	3.98	
[C ₂ mim][NTf ₂]	Pt	0.1793(8)	74-84	0.53(2)	1.00-1.01	11.4(4)	23.6(4)	1.76	0.14
	GC	0.1748(8)	70-76	0.50(6)	0.99-1.00	14.7(7)	23.2(3)	1.87	
	Au	0.1687(4)	78-76	0.74(3)	0.99-1.01	13.6(7)	33.5(4)	2.94	
[C ₂ mim][OTf]	Pt	0.3700(4)	70-88	0.51(2)	0.99-1.01	13.2(4)	40.1(2)	1.91	0.82
	GC	0.3645(3)	70-82	0.51(2)	1.04-1.00	13.4(5)	37.1(2)	2.07	
	Au	0.3522(2)	70-76	0.49(2)	1.07-1.02	16.7(9)	41.1(2)	1.65	
[C ₄ mim][PF ₆]	Pt	0.170(1)	82-132	0.53(3)	0.99-1.01	3.6(3)	14.3(2)	2.57	0.37
	GC	0.1840(4)	82-152	0.49(1)	0.99-1.00	3.6(1)	12.2(1)	2.39	
	Au	0.2003(6)	70-84	0.69(4)	0.98-1.00	14(1)	16.6(4)	3.05	
[EtA][NO ₃]	Pt	0.0972(3)	70-74	0.52(4)	1.00-1.01	11.1(9)	32.6(4)	2.92	2.49
	GC	0.0954(3)	68-72	0.51(3)	1.01-1.04	14.4(5)	26.4(3)	1.91	
	Au	0.096(1)	68-70	0.85(6)	1.01-1.00	13(2)	35.4(9)	2.76	

Simulated values with DigiElch for the formal potential ΔE vs 100 mM AgCl/Ag for the chloride based liquids and vs Ag for the other ILs, charge transfer coefficient α , rate constant k_s , diffusion coefficient D and standard deviation of the fit S , and calculated values for the peak potential separation ΔE_p and peak current ratio I_{pa}/I_{pc} for samples of 10 mM $K_3[Fe(CN)_6]$ in various ILs, on a Pt, GC and Au working electrode and water content in wt% for each solution after dissolving process determined by Karl-Fisher titration.

Ionic solvent		$\Delta E / V$ (DigiElch)	$\Delta E_p / mV$ (from 5 to 100 mV s ⁻¹)	α	I_{pa}/I_{pc} (from 5 to 100 mV s ⁻¹)	$k_s / cm\ s^{-1} \cdot 10^{-4}$	$D / cm^2\ s^{-1} \cdot 10^{-8}$ (DigiElch)	$S / \%$	H₂O content / wt%
Ethaline	Pt	0.0896(3)	70-80	0.63(2)	1.03-1.00	7.6(3)	10.16(5)	1.87	1.18
	GC	0.0928(2)	70-78	0.56(1)	1.01-0.99	5.0(1)	8.73(2)	1.76	
	Au	0.0953(7)	70-76	0.81(2)	1.01-0.95	5.4(3)	11.1(2)	4.35	
Propaline	Pt	0.0604(4)	72-88	0.52(2)	0.97-1.00	3.8(4)	4.32(3)	2.51	1.23
	GC	0.0632(3)	72-82	0.49(2)	1.00-1.01	5.0(2)	3.98(3)	2.26	
	Au	0.0670(6)	74-84	0.84(2)	0.99-0.94	3.9(2)	6.70(9)	3.00	
Glyceline	Pt	0.0964(3)	72-94	0.50(2)	1.03-1.00	1.80(6)	1.066(7)	2.31	0.72
	GC	0.0971(3)	70-90	0.49(2)	1.01-1.00	2.2(1)	1.035(7)	2.47	
	Au	0.0995(5)	70-84	0.43(4)	1.12-0.98	1.39(2)	1.39(2)	3.93	
[C ₂ mim][ac]	Pt	0.1144(3)	72-95	0.47(2)	0.98-0.97	4.3(2)	5.21(3)	1.75	3.19
	GC	0.1185(2)	70-80	0.47(3)	0.98-0.97	5.9(2)	5.17(3)	1.61	
	Au	0.1308(7)	76-114	0.68(2)	0.96-1.09	3.2(2)	10.6(2)	4.8	
[C ₂ mim][BF ₄]	Pt	-0.2085(5)	68-80	0.51(5)	1.00-0.97	8.0(4)	11.6(1)	2.53	0.56
	GC	-0.217(1)	72-82	0.52(8)	0.99-1.00	5.2(8)	11.1(3)	4.33	
	Au	-0.1964(9)	74-84	0.83(4)	0.89-1.05	7.5(9)	20.0(4)	6.60	
[C ₆ mim][Cl]	Pt	0.002(2)	108-240	0.57(2)	0.83-0.76	0.077(7)	0.037(1)	9.21	1.05
	GC	0.017(2)	110-270	0.52(2)	0.75-0.77	0.10(2)	0.072(3)	8.44	
	Au	0.021(2)	98-130	0.58(3)	0.90-0.89	0.19(2)	0.091(3)	8.12	
[C ₂ mim][DEP]	Pt	-0.0159(5)	82-130	0.66(1)	0.84-0.78	1.08(3)	1.73(2)	2.78	1.66
	GC	-0.0110(4)	74-116	0.59(2)	0.85-0.82	1.74(6)	1.62(1)	2.39	
	Au	-0.0148(6)	90-185	0.62(1)	0.86-0.55	0.65(2)	1.76(2)	3.44	
[C ₄ mim][HSO ₄]	Pt	0.48(1)	120-260	0.58(1)	0.56-0.41	0.074(3)	0.029(1)	5.20	0.53
	GC	0.479(1)	120-164	0.53(3)	0.70-0.54	0.21(1)	0.048(2)	6.05	
[C ₂ mim][SCN]*	Pt	0.3664(5)	114-138	0.53(1)	0.85-0.93	1.16(3)	6.48(6)	2.08	0.75
[EtA][NO ₃]	Pt	0.0012(3)	68-76	0.44(2)	0.98-0.96	9.5(4)	17.0(1)	1.71	1.23
	GC	0.0093(4)	68-76	0.46(2)	1.00-0.98	9.8(3)	16.9(2)	1.77	
	Au	0.0160(5)	68-76	0.66(3)	1.03-0.99	11.1(5)	21.7(1)	2.38	

*calculated values for $K_3[Fe(CN)_6]$ in [C₂mim][SCN] from a 1 mM solution with sweep rates from 5 to 20 mV s⁻¹