Immiscible electrolyte systems based on asymmetric hydrophobic room temperature ionic liquids

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The effect on the melting point of the introduction of asymmetry in tetraalkylammonium halide salts has been investigated leading to the synthesis of new, hydrophobic (room temperature) ionic liquids suitable for liquid/liquid electrochemistry; one of these, tri(hexyl)decylammonium tetrakis(pentafluorophenyl)-borate, displays the largest electrochemical window observed to date for a biphasic room temperature ionic liquid system.

Ionic liquids (ILs) are substances composed exclusively of ions which form phases that are liquid below 100 °C. A subset of these materials are liquid at, or below, room temperature and these are termed room temperature ionic liquids (RTILs).[1] Research into ILs has grown substantially over the past decade due to their potential use as "green" solvents,[2] in part because of their very low vapour pressures, arising from their ionic nature.[3] It should be possible, by judicious choice of the anions and cations that compose an RTIL to "tune" the physical properties such as melting point, water miscibility, electrochemical potential window, conductivity and viscosity by selection and modification of the anion and cation of the IL.[4]

One area for RTIL research is the replacement of organic solvents in aqueous/organic biphasic systems.[5] This has applications in separation processes,[6] biphase catalysis[7] and electrochemistry at the interface between two immiscible electrolyte solutions (ITIES).[8,9] The latter approach allows for the study of solvation properties of ions in biphasic systems by investigating the Gibbs energy of transfer of ions across the interface between the immiscible phases.[10,11] This area has also resulted in the development of the BASIL process for the removal of acidic species developed during a reaction, and was the first example of an industrial use of ionic liquids.[12]

There has been a large amount of previous work on RTILs in biphasic systems, based on imidazolium, ammonium, phosphonium and isoquinolinium cations with anions such as hexafluorophosphate (PF_6), triflate (OTf), dodecylsulfate (DODS), tetrafluoroborate (BF_4), halide (X), bis(perfluoro-*n*-alkyl)sulfonylimide (TFSI) and tetrakis[3,5-bis(trifluoromethyl)]borate ($TPB(CF_3)_8$).[8,10,13] However each of these salts possesses limitations in its application to ITIES studies, such as a relatively high solubility of water, which in turn leads to small liquid/liquid electrochemical windows, *ca.* 0.4 V, or melting points above room temperature (RT).

We therefore sought to generate high purity, hydrophobic ionic liquids suitable for biphasic electrochemical applications. A library of ammonium salts has been prepared from the quaternisation of a series of trialkylamines with a long-chained alkyl halide in which systematic variation of the chain lengths of both components was undertaken.†

The entries listed in Table 1 show that the majority of the materials prepared do indeed possess melting points below 100 °C. Furthermore, as anticipated, varying the chain lengths of both the amine and of the alkyl halide can have a significant impact on the melting point of the resulting ammonium halide salts. While the triethylamine derived salts show relatively little variation in mp, for both tributylamine and trihexylamine, when the chain length of the quaternising alkyl bromide is C_{10} or C_{14}, a large reduction of the mp results. However, increasing the alkyl chain length to C_{18} did not result in a further decrease in melting point of the salts. This suggests that, for this system, there is an optimum combination of amine and alkyl halide to generate RTILs. The two most interesting salts listed are the bromide salts of the tri(hexyl)decylammonium (H3DA) and tri(hexyl)tetradecylammonium (H3TDA) cations, which possess glass transition temperatures of −18 and −23 °C, respectively.

We therefore sought to generate a series of hydrophobic RTILs by exchanging the halide ion for other anions. However, salts possessing melting points below RT are difficult to purify as they cannot be recrystallised except through low temperature crystallisation and filtration. This approach is difficult, time consuming and results in low yields. For these reasons the iodide salt of H3DA with the higher melting point of 68 °C, was chosen for subsequent ion-exchange studies. These were carried out by stirring the tetraalkylammonium halide with a slight excess of an alkali metal salt of the appropriate anion in a mixture of dichloromethane and water followed by extraction of the organic layer with water to remove any halide or metal

Table 1 Melting points (°C) of ammonium halide ionic liquids and salts (Hx = hexyl and Oct = octyl)

	IC_8H_{17}	$BrC_{10}H_{21}$	$BrC_{14}H_{29}$	$BrC_{18}H_{37}$
Et_3NR^+X	94–97	110–115	93–98	86–90
$Bu_3NR^+X^-$	72–76	22[a]	21[a]	64–67
$Hx_3NR^+X^-$	67–73	−18[b]	−23[b]	42–45
$Oct_3NR^+X^-$	95–98[c]	101–05[d]	51–54	43[a]

[a] Determined from onset of melt in DSC. [b] Determined from the glass transition in DSC. [c] Mp for corresponding bromide salt. [d] Mp for corresponding iodide salt.

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Table 2 Physical properties of tri(hexyl)decylammonium (H3DA) and tri(hexyl)tetradecylammonium (H3TDA) salts

Salt[a]	T_g/°C[b]	T_m/°C[c]	S/µS cm^{-1}[d]	η/Pa s[de]	Solubility in H_2O/ mmol l^{-1}[f]
[H3DA][ClO_4]	—	68	—	—	—
[H3DA][BF_4]	—	59	—	—	—
[H3TDA][BF_4]	—	57	—	—	—
[H3DA][OTf]	−41	—	—	1.70	0.18
[H3TDA][OTf]	−41	—	—	—	0.18
[H3DA][DODS]	—	19	4	1.22	—
[H3TDA][DODS]	—	22	4	1.28	—
[H3DA][TFSI4]	−10	—	26	1.05	0.05
[H3DA][(TPB(CF_3)$_8$)]	9	37	—	—	<0.02
[H3DA][TPBF20]	−9	—	<1	4.57	<0.02
[H3DA][TFSI]	<−70	—	125	0.28	0.11
[H3TDA][TFSI]	<−70	—	113	0.30	0.10

[a] For anion abbreviations see text. [b] Determined from glass transition in DSC. [c] Determined from onset of melt in DSC. [d] Values quoted at 27 °C. [e] Viscosity, determined by rheometry. [f] Determined using ^{19}F NMR spectroscopy by integrating against a known amount of 1,1,1-trifluoroethanol.

salts. Any residual metal salt was removed using a celite/silica/activated carbon column as described by Seddon *et al.*[14] In this way a variety of different ions were introduced, ranging from small, symmetric anions, such as BF_4, up to much larger ions, such as bis(nonafluorobutyl)sulfonylimide (TFSI4) and tetrakis(pentafluorophenyl)borate (TPBF20); their physical properties are listed in Table 2.

All of the salts listed in Table 2 were found to be ILs with a number being RTILs. The physical properties vary considerably, from T_g values of less than −70 °C for [H3DA][TFSI] up to a melting point of 68 °C for [H3DA][ClO_4]. The RTILs also show a range of conductivities between 4 and 125 µS cm^{-1}. These values are low when compared to conventionally-used imidazolium-based ILs but are similar to those found for ammonium salt systems. Similarly, the viscosities are higher than those measured for corresponding imidazolium RTILs but comparable to some ammonium salt systems. As would be expected the conductivity decreases as the viscosity increases.

We were interested in using these RTILs to form a biphasic system with water. For this reason the solubility of water in each of the RTILs was investigated using ^{19}F NMR spectroscopy by shaking the RTIL with D_2O then comparing the integrals of the RTIL dissolved in water with that of a known concentration of added trifluoroethanol. Using this method it suggests that these RTILs have very low miscibilities with water, with the largest solubility being approximately 0.18 mmol l^{-1}. Comparison with other RTILs is often difficult, as these data are not always reported, but our values are much lower than those measured for some imidazolium RTILs.[15]

Having established that the water-solubility of the RTILs is low, electrochemical studies at the interface between these new hydrophobic room temperature ionic liquids and water were undertaken. Both [H3DA][TFSI] and [H3DA][TPBF20] were studied in contact with an aqueous solution of lithium chloride.

The [H3DA][TFSI]/aqueous electrolyte system possesses a liquid/liquid electrochemical window of approximately 0.4 V, which is comparable to the largest found for other RTILs in the literature.[6] However, Fig. 1 shows that the electrochemical window for [H3DA][TPBF20] is approximately 0.7 V, which is by far the largest reported at room temperature to date. The voltammogram labelled "**b**" shows the RTIL [H3DA][TPBF20] in contact with an aqueous solution of tetramethylammonium chloride ([TMA][Cl]) (4 mmol l^{-1}) and lithium chloride (20 mmol l^{-1}). The reversible feature seen at *ca.* 0.25 V is due to the transfer of the TMA cation between the aqueous phase and the RTIL.

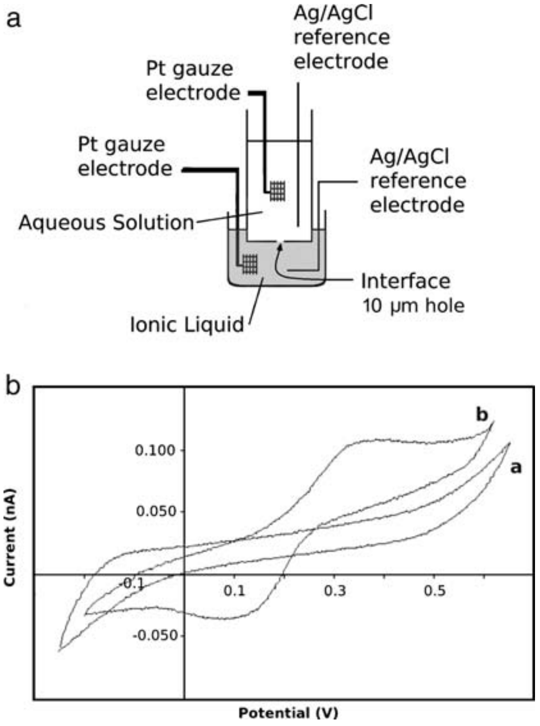

Fig. 1 (a) Electrochemical setup for ITIES studies; (b) cyclic voltammograms of the aqueous/[H3DA][TPBF20] interface showing the blank potential window obtained with a 20 mmol l^{-1} LiCl solution **a** and tetramethylammonium (TMA) transfer from the aqueous 4 mmol [TMA][Cl] and 20 mmol l^{-1} LiCl solution into the RTIL **b**.

ILs have also been studied as solvents for electrochemical processes, due to some possessing a large electrochemical window, which enables investigation of otherwise inaccessible processes.[16] Fig. 2 shows two cyclic voltammograms of the

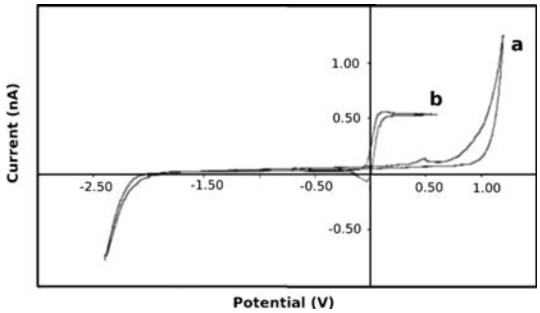

Fig. 2 Cyclic voltammograms of [H3DA][TFSI] **a** and [H3DA][TFSI] containing 30 mmol ferrocene **b** at a 10 mV s^{-1} scan rate using a 10 μm diameter Pt microelectrode referenced to Ag/AgCl.

RTIL tri(hexyl)decylammonium bis(trifluoromethyl)sulfonylimide ([H3DA][TFSI]). Voltammogram "**a**" shows a "blank" scan (*i.e.* no added solute) at 10 mV s^{-1} whereas voltammogram "**b**" is the response in the presence of ferrocene (30 mmol). The IL shows an electrochemical window of approximately 3 V and the oxidation of ferrocene can be seen very clearly and distinctly at 0 V wrt Ag/AgCl. The diffusion coefficient for ferrocene was calculated to be 8.2×10^{-8} cm^2 s^{-1}, which is three orders of magnitude lower than the value reported for conventional non-aqueous solvents, in accord with the expected Stokes–Einstein dependence since the viscosity of this RTIL is *ca.* 1000 times higher than typical non-aqueous liquids.[17]

In conclusion, using a systematic approach, a number of asymmetric tetraalkylammonium halide salts have been prepared for the development of ionic liquids. The two cations H3DA and H3TDA are useful candidates for the synthesis of ionic liquids. We have used these to generate a number of new ILs and RTILs with a wide range of physical properties. All of the ionic liquids that we have tested show low solubility of water, indicating that these could be useful for extraction processes involving aqueous solutions. In addition, the RTIL [H3DA][TPBF20], when used in a water–IL biphasic system, produces a polarisable interface over a range of 0.7 V, which is, as far as we are aware, the largest reported to date for biphasic ionic systems operating at room temperature.

Notes and references

† All products were characterised by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy and elemental analysis. For example [H3DA][TPBF20]: ^{1}H NMR ($CDCl_3$, reference TMS) δ 3.02 (t, $^3J_{HH}$ = 8.2 Hz, 8H, NCH_2N), 1.60 (s, 8H, CCH_2C), 1.31 (m, 32H, CCH_2C), 0.90 (t, $^3J_{HH}$ = 6.6 Hz, 12H, CCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, reference TMS) δ 59.23 (s, NCH_2C), 31.19 (s, CCH_2C), 29.50 (s, CCH_2C), 29.44 (s, CCH_2C), 29.11 (s, CCH_2C), 26.31 (s, CCH_2C), 25.99 (s, CCH_2C), 22.86 (s, CCH_2C), 22.47 (s, CCH_2C), 21.89 (s, CCH_2C), 14.27 (s, CCH_3), 13.84 (s, CCH_3). ^{19}F NMR ($CDCl_3$, reference $CFCl_3$) δ −132.8 (d, $^3J_{FF}$ = 10.7 Hz, 8F, CCFC), −163.05 (t, $^3J_{FF}$ = 20.6 Hz, 4F, CCFC), −166.97 (t, $^3J_{FF}$ = 18.3 Hz, 8F, CCFC). Anal. calc. for $C_{52}H_{60}BF_{20}N$: C 57.28, H 5.55, N 1.29; found C 57.54, H 5.64, N 1.23%. Melting points and glass transition temperatures were measured on a Perkin-Elmer Diamond DSC at scan rates of 5 and 50 °C min^{-1}, respectively. Viscosities were measured on a Bohlin Instruments CS-50 rheometer, at 27 °C with an applied pressure of 100 Pa. In electrochemical experiments an Ag/AgCl reference electrode was used (E° = +0.22216 V at 25 °C). In electrochemical experiments at the ITIES[9] Pt gauze was used for the counter electrodes and Ag/AgCl as reference electrodes. A PET film with a 10 μm hole generated by laser ablation was used to separate the phases and ensure a small surface area for the liquid/liquid interface.

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