

Buffered chlorogallate(III) ionic liquids and electrodeposition of gallium films

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Buffering of Lewis acidic chlorometallate ionic liquids is a useful tool to modify their properties for electrochemical and catalytic applications. Lewis acidic chlorogallate(III) ionic liquids containing the 1-octyl-3-methylimidazolium cation, buffered with sodium chloride, were studied using ⁷¹Ga NMR spectroscopy and cyclic voltammetry. All the studied Lewis acidic compositions (0.50 < χ_{GaCl_3} ≤ 0.75) could be buffered to mild or moderate acidity, but not to neutrality. Electrodeposition of gallium from such buffered systems was possible, yielding deposits of improved morphology over the unbuffered ionic liquids, due to the constant melt composition maintained by the buffer. These findings were in a stark contrast with older studies on chloroaluminate(III) ionic liquids buffered with sodium chloride.

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Introduction

Group 13 metal(III) chlorides (aluminium,¹ gallium² or indium³) react with various organic chlorides to form chlorometallate(III) ionic liquids. Anionic speciation in such systems depends both on the metal and on the reagent ratio, expressed as the nominal mol fraction of metal chloride, χ_{MCl_3} . Due to the alternation effect, properties do not change monotonically down the Group 13.⁴

Chloroaluminate(III) ionic liquids were the first group of ionic liquids to attract the broad attention of the scientific community.⁵ Being good solvents for a range of inorganic materials and organometallic complexes, they have found many applications in electrochemistry^{6,7} and catalysis^{8–10} (as Lewis acidic catalysts, co-catalysts and solvents in a number of reactions, particularly for Friedel–Crafts catalysis).

Speciation of chloroaluminates(III) is rather complex, and has been studied using ²⁷Al NMR spectroscopy,¹¹ vibrational spectroscopy,^{12,13} FAB mass spectrometry,¹⁴ potentiometry,¹⁵ and vapour pressure measurements.¹⁶ Depending on the composition (χ_{AlCl_3}), chloroaluminates(III) were proven to contain three sequential equilibrated anions from the following list: Cl[−], [AlCl₄][−], [Al₂Cl₇][−], [Al₃Cl₁₀][−] and [Al₄Cl₁₃][−].¹⁶ Consequently, they may be Lewis basic due to the presence of free chloride (χ_{AlCl_3} < 0.5), neutral (χ_{AlCl_3} = 0.5) or acidic due to the presence of polynuclear anions (χ_{AlCl_3} > 0.5),¹⁷ with negligible

influence of the cation.¹⁸ It was shown that Lewis acidity of the chlorometallate(III) ionic liquids is quantifiable using the Gutmann Acceptor Number,¹⁹ and the Lewis acidity of the χ_{AlCl_3} = 0.67 composition may be almost as high as that of trifluorosulfonic acid.²⁰ Also, the electrochemical window of chloroaluminates(III) is strongly composition-dependent: the widest for the neutral systems (4 V), and much narrower for the basic (2.8 V) and acidic régimes (2.4 V).²¹ The exact neutral composition is difficult to achieve, since any chemical or electrochemical processes that consume or generate acidic or basic species will displace the ionic liquid from neutrality.²² However, it was discovered that chloroaluminate(III) ionic liquids could be buffered using Group 1 metal chlorides, MCl,²¹ or strong organic bases (e.g. pyridine).²³ For example, when Lewis acidic chloroaluminate(III) systems were buffered to neutral with NaCl, any deviation from neutrality due to added or electrogenerated acidic/basic agents was hindered.²¹ At the same time, the buffered Lewis acidic chloroaluminates(III) possess chemical behaviour termed ‘latent acidity’²⁴ – when a weak base L is added, an adduct with aluminium(III) chloride is formed, and the solid MCl precipitates, according to eqn (1).

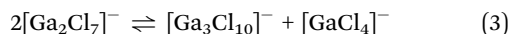
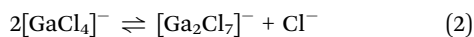


The latent acidity of such systems is also quantifiable by the Gutmann Acceptor Number,¹⁹ being dependent on the buffer used,²⁵ and always exhibiting a lower Lewis acidity than the unbuffered composition. Buffered systems were used successfully as solvents and co-catalysts for the oligomerisation of 1-alkenes, where moderate Lewis acidity is an advantage.²³

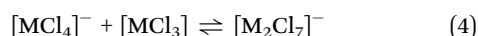
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Many successful applications of chloroaluminates(III) encouraged the search for other chlorometallate ionic liquids. Chlorogallate(III) systems,² firstly reported in 1987, were studied electrochemically, and by DSC studies,²⁶ Raman spectroscopy²⁷ and FAB mass spectrometry.²⁸ More recent research, aside from sparse physicochemical studies,²⁹ involved Raman scattering combined with pycnometric studies,³⁰ and ⁷¹Ga NMR spectroscopy combined with EXAFS.³¹ Based on these publications, chlorogallates(III) appear to have speciation analogous to that of chloroaluminates(III), with the main equilibria in the system given in eqn (2) and (3).



In contrast to the chloroaluminates(III), chlorogallate(III) systems form homogenous room-temperature ionic liquids for compositions between $\chi_{\text{GaCl}_3} = 0.67$ and $\chi_{\text{GaCl}_3} = 0.75$. It is known that the formation of $[\text{Ga}_2\text{Cl}_7]^-$ is thermodynamically more favourable than the formation of $[\text{Al}_2\text{Cl}_7]^-$; enthalpies of the reaction shown in eqn (4) are $-164.8 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Ga(III)}$ and only $-140.6 \text{ kJ mol}^{-1}$ for $\text{M} = \text{Al(III)}$.²⁰



Although such data are not available in the literature for trimeric and larger species, the existence of homogenous ionic liquids for $\chi_{\text{GaCl}_3} > 0.67$ indicates that the formation of $[\text{M}_3\text{Cl}_{10}]^-$ species is much more favoured for the gallium(III) systems than for the aluminium(III) systems.

Compared to chloroaluminates(III), chlorogallates(III) may provide equal or even stronger Lewis acidity²⁰ and have a higher moisture stability, but their applications are relatively poorly explored. In catalysis, neutral compositions were used for palladium-catalysed hydroethoxycarbonylation³² and acetal formation,³³ Brønsted superacidic system catalysed arene carbonylation,³⁴ and the Lewis acidic compositions were used for oligomerisation of alkenes to lubricant base oils.³⁵ Recently, an ionic liquid-based synthesis of a new related inorganic compound, $[\text{Bi}_3\text{GaS}_5]_2[\text{Ga}_3\text{Cl}_{10}]_2[\text{GaCl}_4]_2\text{S}_8$, was reported.³⁶

Electrodeposition of gallium from chlorogallate(III) and from chlorometallate systems has been described.³⁷ Flamini *et al.* studied the electrodeposition of gallium from aqueous solutions, where dihydrogen evolution was observed which can result in rough and non-uniform deposits.³⁸ Electrochemistry of a gallium(III) chloride solution in high-temperature molten salts was also investigated, and the redox properties were studied.^{39–41} Smolenskii reported briefly the electrodeposition of gallium on tungsten from 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide.⁴² Electrochemistry of gallium(III) chloride in air-stable ionic liquids, using *in situ* STM on the Au(111) electrode were carried out by Endres and co-workers,⁴³ and nanodeposition of gallium on Au(111) was reported by Freyland *et al.*⁴⁴

Aiming at further studies of electrodeposition of gallium metal, we have studied buffering of the chlorogallate(III) ionic liquids.⁴⁵ We report here a detailed study focussed on the

buffering of room temperature chlorogallate(III) ionic liquids, comparing with the behaviour of the analogous chloroaluminate(III) systems.

Experimental

Materials and equipment

1-Chlorooctane (99%), $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.999%), sodium chloride (99.999%; anhydrous beads), and gallium(III) chloride (99.999%; anhydrous beads; ampoules sealed under argon) were purchased from Sigma-Aldrich and used without further purification. 1-Methylimidazole (Sigma-Aldrich) was redistilled immediately prior to use from solid sodium hydroxide. Dry ethanenitrile was obtained from the MBraun MB-SPS solvent purification system. 1-Butyl-3-methylimidazolium nitrate, $[\text{C}_4\text{mim}][\text{NO}_3]$, was prepared by a standard literature method.⁴⁶

An MBraun Labmaster DP glovebox was used for moisture-free synthesis and storage of the chlorogallate(III) ionic liquids ($<0.1 \text{ ppm H}_2\text{O}$, O_2). ¹H NMR spectra were acquired using Bruker DRX 300 spectrometer, whereas the ⁷¹Ga NMR ones were collected with a Bruker DRX 500 spectrometer. All spectra were collected at 27 °C. Cyclic voltammograms were recorded with a PC-controlled Autolab Type III Potentiostat. Sodium analysis of each buffered chlorogallate(III) ionic liquid was performed on a Perkin-Elmer Analyst 400 atomic absorption spectrometer operated in the atomic emission mode.

The scanning electron microscopy (SEM) studies on the electrodeposits were carried out using a JEOL 6500F Field Emission Scanning Electron Microscope, and the energy dispersive X-Ray analysis (EDX) was carried out using Oxford Instruments INCA systems.

Synthesis of 1-octyl-3-methylimidazolium chloride, $[\text{C}_8\text{mim}]\text{Cl}$

Dry ethanenitrile (100 cm^3) was poured into a two-necked round-bottomed flask (equipped with a stirring bar), fitted with a reflux condenser attached to a dinitrogen line. 1-Methylimidazole (1.000 eq., 53.40 g, 0.6504 mol) was added under a positive pressure of dinitrogen, which was then bubbled through the solution for 30 min. Subsequently, a pressure-equalising dropping funnel (250 cm^3) was mounted on the side neck of the round-bottomed flask through which 1-chlorooctane (1.350 eq., 130.7 g, 0.8791 mol) was added dropwise over 130 min to the vigorously stirred solution at room temperature. An excess of 1-chlorooctane was used to guarantee the consumption of 1-methylimidazole. Subsequently, the flask was wrapped in aluminium foil, and the reaction mixture was stirred at room temperature for 24 h. The reaction temperature was then increased to 60 °C, and the reaction was allowed to proceed for 9 d, until ¹H NMR spectra failed to detect 1-methylimidazole.

The reaction mixture was allowed to cool to room temperature, and washed with diethyl ether ($10 \times 100 \text{ cm}^3$) to remove the excess of 1-chlorooctane; the diethyl ether was then removed under reduced pressure using a rotary evaporator (1 h, 50 °C). Subsequently, the ionic liquid was dried under high vacuum (7 d, 65 °C) to yield a pale yellow, viscous liquid (95.9%, 144 g) and stored in the glovebox. This synthesis

method is slightly different from existing in literature⁴⁷ as it eliminates any contamination from unreacted 1-methylimidazole and thereby reduces its influence on electrochemical processes. ¹H NMR (CDCl₃, 300 MHz, 27 °C): δ/ppm = 10.52 (s, 1H, N-CH-N); 7.84 (s, 1H, CH₃-N-CH-CH); 7.60 (s, 1H, CH₃-N-CH-CH); 4.34 (t, 2H, *J* = 7.5 Hz, N-CH₂); 4.15 (s, 3H, N-CH₃); 1.92 (t, *J* = 6.9 Hz, 2H, N-CH₂-CH₂); 1.25 (m, 10H, (CH₂)₅-CH₃), 0.87 (t, *J* = 6.3 Hz, 3H, (CH₂)₅-CH₃).

Synthesis and buffering of [C₈mim]Cl–GaCl₃ ionic liquids

A range of compositions ($0.33 \leq \chi_{\text{GaCl}_3} \leq 0.75$) (see Table 1) of chlorogallate(III) ionic liquids based on the 1-octyl-3-methylimidazolium cation was prepared on a 4 g scale.

In the glovebox, an appropriate amount of [C₈mim]Cl was weighed into a sample vial (10 cm³) equipped with a stirring bar. Leaving the vial on the balance (± 0.0002 g), an appropriate amount of gallium(III) chloride was added slowly and carefully to achieve the desired composition. An exothermic reaction always occurred. When the addition was completed, the sample vial was closed with a cap, and the mixture was stirred vigorously for 1 h; homogenous, transparent ionic liquids were obtained in all cases. Samples were stored in the glovebox prior to study.

The buffered ionic liquids were prepared by adding a small molar excess of dry sodium chloride, in very small portions, to the vigorously stirred chlorogallate(III) ionic liquid. After each addition, if no undissolved sodium chloride was visible, more was added, and the stirring was continued until saturation was achieved, whence the mixtures were stirred vigorously (24 h, 60 °C). Neutralisation was ensured by noting the reduction of the voltammetric reduction current of [Ga₂Cl₇][−]. The presence of undissolved sodium chloride was considered as evidence for saturation. The ionic liquids were filtered through fine-fritted syringe filter to remove the excess of sodium chloride, and the clear liquid was analysed for sodium.

Table 1 Weights of reactants for the synthesis of [C₈mim]Cl–GaCl₃ ionic liquids, and the mass of the added NaCl

χ_{GaCl_3}	Mass/g		
	[C ₈ mim]Cl	GaCl ₃	NaCl
0.3300	2.9074	1.0926	0.3804
0.4500	2.4627	1.5373	0.5523
0.4600	2.4243	1.5757	0.5668
0.4700	2.3858	1.6142	0.5712
0.4800	2.3470	1.6530	0.5836
0.4900	2.3081	1.6919	0.5900
0.5000	2.2689	1.7311	0.6126
0.5100	2.2295	1.7705	0.6121
0.5200	2.1899	1.8101	0.6223
0.5300	2.1501	1.8499	0.6304
0.5500	2.1101	1.8899	0.6465
0.5800	1.9509	2.0491	0.7009
0.6000	1.8653	2.1347	0.7212
0.6300	1.7429	2.2571	0.7625
0.6700	1.5692	2.4308	0.8303
0.7000	1.4416	2.5584	0.8738
0.7200	1.3533	2.6467	0.9040
0.7500	1.2162	2.7838	0.9520

⁷¹Ga NMR spectroscopy

Gallium naturally occurs as two isotopes, ⁶⁹Ga and ⁷¹Ga (relative abundance ⁶⁹Ga – 60.1%, ⁷¹Ga – 39.9%), both with a nuclear spin equal to 3/2. The ⁷¹Ga isotope was chosen for the NMR spectroscopy experiments due to the higher relative intensity of the signal (0.024, as opposed to 0.007 for ⁶⁹Ga).⁴⁸

Neat ionic liquids were placed in borosilicate NMR tubes (5 mm diameter), with an external reference (saturated Ga(NO₃)₃ solutions in D₂O, 27 °C) in a sealed capillary tube. All experiments were performed using a Bruker DRX 500 spectrometer (152.53 MHz, 27 °C).

Electrochemical experiments

Voltammetric experiments were carried out using 4 g of ionic liquid in a three-electrode arrangement with platinum (1.6 mm diameter) as the working electrode, a bright platinum coil as the counter electrode, and all potentials measured with respect to a Ag⁺/Ag reference (a silver wire immersed in 0.01 M AgNO₃ solution in [C₄mim][NO₃], and separated from the bulk solution *via* a glass frit). Voltammograms were reproducible by the use of this reference electrode and no ionic leakage detected as demonstrated by multiple experiments. The IR-drop was uncompensated. The platinum (Pt – BASi, US) electrode was polished using an alumina slurry (Kemet, UK) of decreasing particle sizes (6.0–0.1 μm) on soft lapping pads, washed with distilled water, sonicated for 10 min, and dried with compressed air prior to each experiment. Electrodeposition experiments were carried out on glassy carbon substrates of surface area 1 cm² (Alfa Aesar). All experiments were conducted inside the glovebox.

Results and discussion

Synthesis

The precursor of the chlorogallate(III) ionic liquid, [C₈mim]Cl, was prepared by a standard methodology, and was pure by ¹H NMR spectroscopy and elemental analysis. The absence of free amine was assured by using an excess of chloroalkane for synthesis. Water content, as determined by cyclic voltammetry, was less than 10 ppm. For all compositions of the chlorogallate(III) systems ($0.33 \leq \chi_{\text{GaCl}_3} \leq 0.75$), transparent, pale yellow to yellow, very fluid room temperature ionic liquids were obtained.

Buffering

Buffering of the chlorogallate(III) ionic liquids was ensured by preparing saturated solutions of sodium chloride for a range of compositions ($0.33 \leq \chi_{\text{GaCl}_3} \leq 0.75$); saturation was guaranteed when undissolved sodium chloride could be observed in a given solution.

Recently, Welton and co-workers⁴⁹ re-emphasised that salts dissolved in ionic liquids form randomly dispersed mixtures of anions and cations, which should not be treated in terms of traditional solute–solvent relationships (as for molecular solvent), but rather as new materials incorporating multiple types of cations and anions. This is in agreement with the

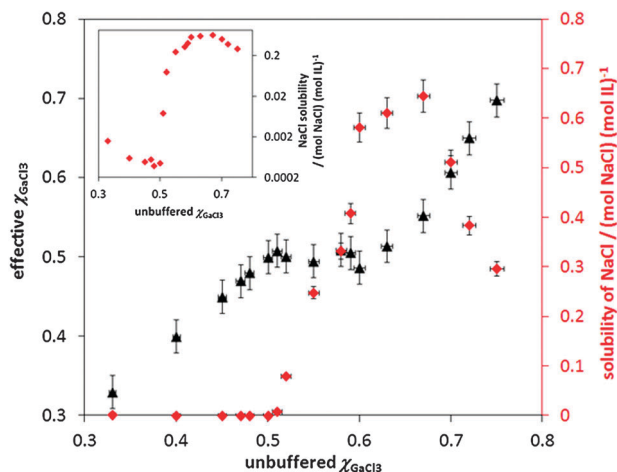


Fig. 1 Solubility of sodium chloride in various compositions of the $[C_8mim]Cl-GaCl_3$ system, \blacklozenge , and the achieved effective compositions, \blacktriangle , plotted as a function of the unbuffered (starting) composition at 80 °C. The insert shows the same solubility data, but with the y-axis (solubility) plotted on a logarithmic scale, which allows for the observation of solubility the trend observed for the basic compositions at 80 °C.

original studies on the buffered chloroaluminate(III) system by Wilkes and co-workers,^{21,50} who treated such buffered ionic liquids as ternary systems, e.g. $[C_2mim]Cl-AlCl_3-NaCl$, where reactive dissolution leads to formation of complex anions, and effectively new ionic liquid phases. Therefore, in this work, the solubility of sodium chloride in the $[C_8mim]Cl-GaCl_3$ system is expressed in terms of mole equivalents of NaCl in moles equivalents of $[C_8mim]Cl-GaCl_3$ composition (see Fig. 1 and Table 2), to enhance better understanding of the underpinning reactive dissolution.

Upon addition of a small molar excess (Na : Ga) of sodium chloride to a basic or neutral chlorogallate(III) ionic liquid, no visible dissolution was observed (Fig. 1 and Table 2).

Table 2 Solubility of sodium chloride^a in different compositions of chlorogallate ionic liquid

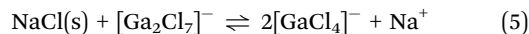
χ_{GaCl_3}	Solubility of NaCl/ (mol NaCl)(mol IL) ⁻¹	X_{GaCl_3}	Electrochemical window/V
0.3300	1.60×10^{-3}	0.3296	2.4
0.4000	6.01×10^{-4}	0.3999	2.4
0.4500	4.86×10^{-4}	0.4499	2.43
0.4700	5.59×10^{-4}	0.4699	2.41
0.4800	3.83×10^{-4}	0.4799	2.41
0.5000	4.55×10^{-4}	0.4999	3.7
0.5100	7.64×10^{-3}	0.5081	—
0.5200	7.98×10^{-2}	0.5008	—
0.5500	0.25	0.4947	—
0.5800	0.33	0.5089	—
0.6000	0.58	0.4867	—
0.6300	0.61	0.5139	—
0.6700	0.65	0.5524	—
0.7000	0.51	0.6069	—
0.7200	0.38	0.6501	—
0.7500	0.30	0.6981	—

^a Sodium chloride solubility was determined from the sodium concentrations in the buffered solutions, by atomic absorption spectroscopy in emission mode, using the method of Wilkes and coworkers.²¹

For $0.50 < \chi_{GaCl_3} \leq 0.60$, the solubility of sodium chloride increased rapidly, to produce effective compositions of values close to neutral, by analogy with chloroaluminate(III) systems in the same composition range.²¹ Although the solubility of sodium chloride increased further for $\chi_{GaCl_3} = 0.67$, the effective χ_{GaCl_3} (X) did not decrease to neutrality, but reached $X \cong 0.55$. Finally, for $\chi_{GaCl_3} = 0.75$, the solubility of sodium chloride decreased compared to $\chi_{GaCl_3} = 0.67$, and the X remained strongly acidic, as shown in Fig. 1 and Table 2.

One limitation of the study of the chloroaluminate(III) system was the impossibility to obtain a clear liquid upon buffering beyond $\chi_{AlCl_3} = 0.60$.²¹ In contrast, the analogous chlorogallate(III) system formed clear homogenous liquids up to $\chi_{GaCl_3} = 0.75$, permitting a much more extensive study of the acidic régime. Of interest, according to the detailed phase diagram of the $[C_2mim]Cl-AlCl_3$ system published by Øye *et al.*,¹⁶ $\chi_{AlCl_3} = 0.60$ is the most acidic composition where only $[AlCl_4]^-$ and $[Al_2Cl_7]^-$ are present, with no measurable amounts of $[Al_3Cl_{10}]^-$ yet in the system.

Analysing the solubility pattern in terms of the buffering reaction presented in eqn (5), two factors must be considered: the ability of the chlorogallate(III) ionic liquid to disrupt the sodium chloride crystal lattice to produce sodium and chloride ions, and the Lewis acidity of the heptachlorodigallate(III) anion.



The increase in the solubility of NaCl from $\chi_{GaCl_3} = 0.50$ to $\chi_{GaCl_3} \leq 0.60$ can be easily understood in terms of the increasing amounts of $[Ga_2Cl_7]^-$, available for the reaction given in eqn (5). The subsequent solubility decrease may be related to the formation of the decachlorotrigallate(III) anion, which would have a much lower ability to disrupt/solvate the sodium chloride lattice.

To confirm the buffering effect of the sodium chloride addition, *i.e.* the expected change in the anionic speciation corresponding to the effective χ_{GaCl_3} values, selected compositions of the $[C_8mim]Cl-GaCl_3$ system (buffered and unbuffered) were studied using ^{71}Ga NMR spectroscopy (Fig. 2).

For the unbuffered compositions, Fig. 2(c)–(h), the chemical shifts of the ^{71}Ga NMR signals did not vary significantly, but the peak widths changed dramatically with χ_{GaCl_3} , which is in agreement with the prior studies of the chlorometallate(III) ionic liquids.³¹ These changes were related to the three main factors: viscosity of the medium, symmetry of the species, and rapid exchange between anionic species. The sharpest peak was found for the neutral sample, where a highly symmetrical $[GaCl_4]^-$ is the only anion.³¹ The chemical shift (~ 273 ppm) was in accordance to the chemical shift found for this anion in other solvents (e.g. 240 to 275 ppm in water).⁴⁸ Viscosity, and hence the linewidth of the ^{71}Ga NMR signals, increased with increasing basicity, due to increasing amounts of the chloride anion in the samples. On the other hand, a rapid broadening (and eventual disappearance) of the signal on the acidic side could not be accounted solely for the viscosity changes, but it resulted predominantly from $[GaCl_4]^-$ remaining in dynamic equilibria with chlorogallate(III) species of lower symmetry, like $[Ga_2Cl_7]^-$ and $[Ga_3Cl_{10}]^-$, as shown in eqn (3).

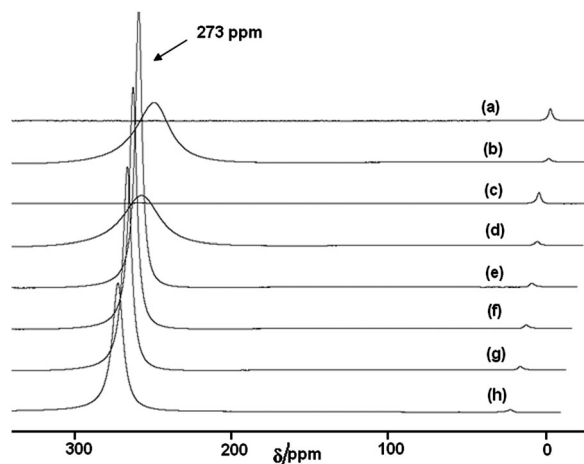


Fig. 2 ^{71}Ga NMR stacked spectra (117.6 MHz, neat liquid, 27 °C) of the $[\text{C}_8\text{mim}]\text{Cl}-\text{GaCl}_3$ system. Chemical shift, δ/ppm , is presented as a function of the samples composition, χ_{GaCl_3} : (a) 0.67 (buffered), (b) 0.55 (buffered), (c) 0.55, (d) 0.51, (e) 0.50, (f) 0.49, (g) 0.48 and (h) 0.47.

^{71}Ga NMR spectra of buffered samples are shown in Fig. 2(a) and (b). For the buffered $\chi_{\text{GaCl}_3} = 0.67$ composition, Fig. 2(a), the effective χ_{GaCl_3} value was calculated to be around $X = 0.55$ (acidic), and a 'flat' spectrum was obtained, as expected for strongly acidic chlorogallate(III) ionic liquid. For the buffered $\chi_{\text{GaCl}_3} = 0.55$ composition, Fig. 2(b), with the effective χ_{GaCl_3} value calculated to be $X = 0.4947$, a sharp ^{71}Ga NMR signal, characteristic of such a nearly-neutral composition, was expected. Nevertheless, the obtained broad signal was more similar to that of the slightly acidic $\chi_{\text{GaCl}_3} = 0.51$ composition, Fig. 2(d), than to the sharp peak found in the neutral sample, Fig. 2(e). Worth mentioning, an identical spectrum has been obtained for a $\chi_{\text{GaCl}_3} = 0.55$ sample that has been stirred with NaCl for a period of one week. This discrepancy between the calculated $\chi_{\text{GaCl}_3, \text{eff}}$ value and the ^{71}Ga NMR spectrum, obviously indicating the presence of a small amount of $[\text{Ga}_2\text{Cl}_7]^-$ indicates, that in the ternary $[\text{C}_8\text{mim}]\text{Cl}-\text{GaCl}_3-\text{NaCl}$ system, the equilibrium in the eqn (2) is shifted slightly to the right. In other words, unlike for the binary $[\text{C}_8\text{mim}]\text{Cl}-\text{GaCl}_3$ system, in the 'nearly neutral' $X = 0.495$ composition, there are significant amounts of Cl^- and $[\text{Ga}_2\text{Cl}_7]^-$ anions present.

Apparently, sodium chloride has a buffering effect on the acidic chlorogallate(III) ionic liquids. The buffering does not lead to neutral ionic liquids, but to compositions of lower acidity. Consequently, electrodeposition of gallium metal from such buffered systems should be possible. To test this hypothesis, three chlorogallate(III) systems were selected for the electrodeposition studies: unbuffered $\chi_{\text{GaCl}_3} = 0.50$, as well as buffered and unbuffered $\chi_{\text{GaCl}_3} = 0.67$. ^{71}Ga NMR spectra of these samples are compared in Fig. 3.

Cyclic voltammetry

The electrochemical window is the potential difference between the oxidation and reduction potentials of an electrolyte used in a voltammetric experiment, where the cut-off limiting current is arbitrarily chosen.^{6,51} In the present work, the cut-off limiting

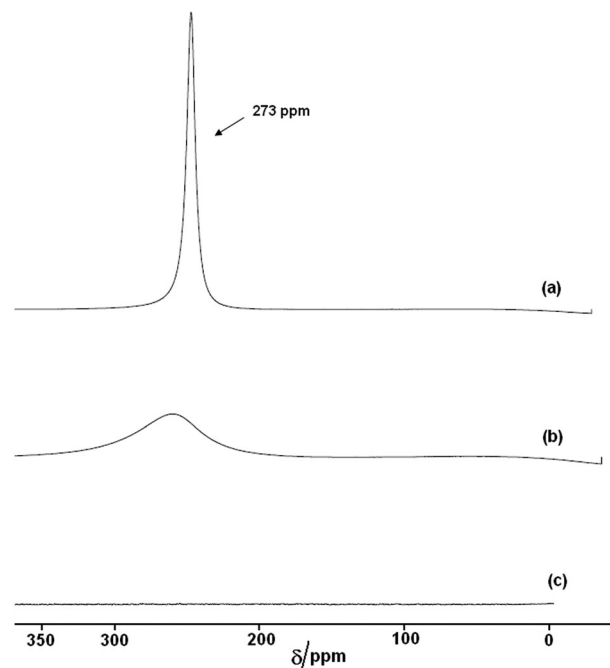


Fig. 3 ^{71}Ga NMR stacked spectra (117.6 MHz, neat liquid, 27 °C) of chlorogallate(III) systems: (a) unbuffered, $\chi_{\text{GaCl}_3} = 0.50$, (b) buffered, $\chi_{\text{GaCl}_3} = 0.67$ and (c) unbuffered, $\chi_{\text{GaCl}_3} = 0.67$.

current was chosen to be 0.1 mA. The anodic and cathodic potential limits observed in pure ionic liquids are due to the oxidation and reduction of their anionic and cationic components, respectively.^{1,52} Linear sweep DC cyclic voltammetry is the simplest and the most commonly used technique to determine the electrochemical window.⁵¹

The electrochemical responses of the unbuffered chlorogallate(III) systems (basic, neutral and acidic), obtained at a platinum electrode, are illustrated in Fig. 4. The potentials were scanned initially towards the negative direction down to -2 V from the open circuit potential and then reversed towards the anodic direction up to $+2$ V. Fig. 4(a) shows the cyclic voltammogram for $\chi_{\text{GaCl}_3} = 0.47$, where two anions, Cl^- and $[\text{GaCl}_4]^-$, are present.³¹ Under these basic conditions, the cathodic background process is the reduction of the 1-octyl-3-methylimidazolium cation.^{53,54} In this system, chloride oxidation is the anodic limit.²¹

For the neutral ($\chi_{\text{GaCl}_3} = 0.50$) composition, $[\text{GaCl}_4]^-$ is the predominant anion, and the concentrations of Cl^- and $[\text{Ga}_2\text{Cl}_7]^-$ are undetectably low.³¹ In such a neutral environment, reduction of the cation remained as the primary cathodic process – see Fig. 4(b). However, with no free chloride present, the anodic limit here was shifted towards the more difficult oxidation of $[\text{GaCl}_4]^-$. The electrochemical window for the neutral system, shown in Fig. 4(b) is 3.7 V, which is in agreement with findings of Gale and co-workers (3.6 V),² who justified this wide electrochemical window for an exactly neutral $[\text{C}_4\text{mim}]\text{Cl}-\text{GaCl}_3$ system in terms of absence of either Cl^- to shorten the anodic limit, or $[\text{Ga}_2\text{Cl}_7]^-$ to shorten the cathodic limit.

Fig. 4(c) shows the cyclic voltammetric response at the platinum electrode from an acidic composition ($\chi_{\text{GaCl}_3} = 0.55$),

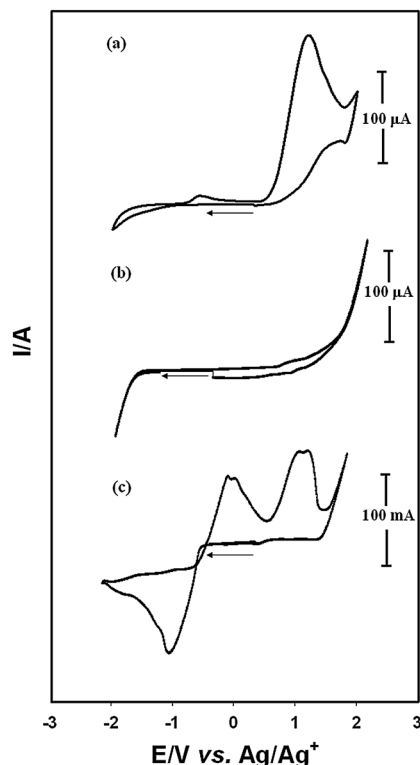


Fig. 4 Cyclic voltammetry of unbuffered $[\text{C}_8\text{mim}]\text{Cl}-\text{GaCl}_3$ systems at a platinum electrode, 50 mV s^{-1} , 20°C ; (a) $\chi_{\text{GaCl}_3} = 0.47$; (b) $\chi_{\text{GaCl}_3} = 0.50$ and (c) $\chi_{\text{GaCl}_3} = 0.55$.

where $[\text{GaCl}_4]^-$ and $[\text{Ga}_2\text{Cl}_7]^-$ are expected to be the predominant anions.^{26–31} In this case, the cathodic limit (-0.5 V) corresponds to the reduction of $[\text{Ga}_2\text{Cl}_7]^-$ to deposit gallium upon the electrode at a more positive potential than that necessary to reduce the imidazolium cation. The anodic processes are the oxidation of $\text{Ga}(0)$ to $\text{Ga}(\text{I})$ at *ca.* -0.37 V , and $\text{Ga}(\text{I})$ to $\text{Ga}(\text{III})$ at *ca.* 1.1 V .⁴⁰

While dichlorine was generated at the anodic limits in all compositions,⁵⁵ it was produced at different potentials and in various amounts, as it was sourced from different electrochemical oxidations.

It has been demonstrated that the electrochemical windows of chlorogallate(III) systems vary with composition, by analogy to the behaviour observed for chloroaluminate(III) ionic liquids,²¹ with the widest window identified for the neutral composition. Following this analogy, chlorogallates(III) were expected to behave similarly to chloroaluminates(III) when buffered with anhydrous sodium chloride.

Buffering with sodium chloride left the electrochemical windows of $0.33 \leq \chi_{\text{GaCl}_3} \leq 0.50$ compositions unaffected (see Table 2), as its solubility is too small to change the ionic liquid composition significantly.

For the acidic compositions, a significant dissolution of sodium chloride was followed by the observable change in the electrochemical window. Interestingly, the buffered acidic compositions of chlorogallate(III) ionic liquids were not completely neutralised, *i.e.* the expected wide electrochemical window of the exactly neutral composition was not achieved.

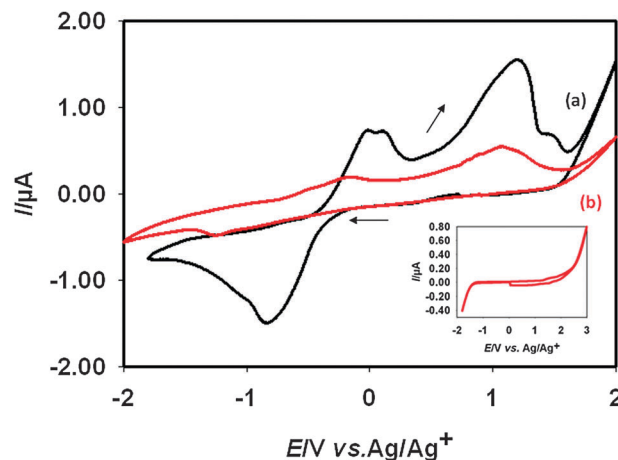


Fig. 5 Cyclic voltammetry of unbuffered and buffered $[\text{C}_8\text{mim}]\text{Cl}-\text{GaCl}_3$ systems at a platinum electrode, 50 mV s^{-1} , 20°C ; (a) unbuffered $\chi_{\text{GaCl}_3} = 0.51$; (b) buffered $\chi_{\text{GaCl}_3} = 0.51$.

The redox peaks associated with the reduction of $\text{Ga}(\text{III})$ to $\text{Ga}(0)$ and with its oxidation back to $\text{Ga}(\text{I})$ and then to $\text{Ga}(\text{III})$ were still present. This suggests that the buffering reaction of $[\text{Ga}_2\text{Cl}_7]^-$ with the excess of NaCl , given with eqn (5), does not lead to complete regeneration of the neutral $[\text{GaCl}_4]^-$ but, in contrast to the chloroaluminate(III) systems, NaCl buffers chlorogallates(III) to milder acidity.

Fig. 5 shows the cyclic voltammetry of the $\chi_{\text{GaCl}_3} = 0.51$ composition before buffering, Fig. 5(a), and after buffering, Fig. 5(b). In the buffered system, although the peak intensities are reduced drastically, the gallium reduction around -0.5 V is not eliminated in the cathodic region and the subsequent oxidation peaks for $\text{Ga}(\text{I})$ and $\text{Ga}(\text{III})$ in the anodic region are also present clearly, showing that the system is not buffered to absolute neutrality, as shown in the inset, but to a lower acidity.

Whereas, in chloroaluminate systems, it was impossible to maintain a liquid buffered system for acidic compositions

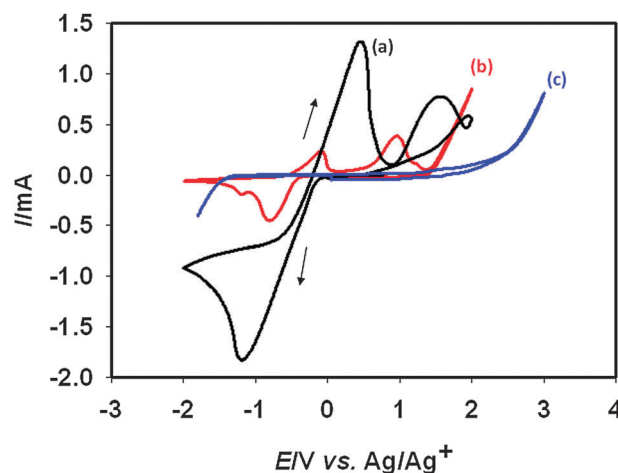


Fig. 6 Cyclic voltammetry of unbuffered and buffered $[\text{C}_8\text{mim}]\text{Cl}-\text{GaCl}_3$ systems on platinum electrode, 50 mV s^{-1} , 20°C ; (a) unbuffered $\chi_{\text{GaCl}_3} = 0.67$; (b) buffered $\chi_{\text{GaCl}_3} = 0.67$ and (c) unbuffered $\chi_{\text{GaCl}_3} = 0.50$.

higher than $\chi_{\text{AlCl}_3} = 0.60$,²¹ the highly acidic chlorogallate system *viz.* $\chi_{\text{GaCl}_3} = 0.67$ composition could be buffered to milder acidity; Fig. 6 shows the cyclic voltammetry of the $\chi_{\text{GaCl}_3} = 0.67$ composition before buffering, Fig. 6(a), and after buffering, Fig. 6(b), compared with the unbuffered, neutral ($\chi_{\text{GaCl}_3} = 0.50$) chlorogallate(III) system, Fig. 6(c).

The electrochemical behaviour of the unbuffered $\chi_{\text{GaCl}_3} = 0.67$ system, Fig. 6(a), clearly demonstrated the deposition and

stripping of gallium(0). However, the cyclic voltammogram was not typical for metal deposition/stripping. A classical deposition/stripping pattern, observed for example when aluminium wire in chlorogallate(III) was used as the reference electrode,³⁷ involves a sharp reduction of Ga(III) to Ga(0), followed by immediate sharp oxidations. In Fig. 6(a), a broad reduction wave, Ga(III) to Ga(0), and two broad oxidation waves, Ga(0) to Ga(I), followed by Ga(I) to Ga(III), are observed. The second anodic wave, for Ga(I) to Ga(III), was complex, as the oxidation kinetics were faster.

After buffering, Fig. 6(b), a drastic reduction (but not elimination) in the current for the peaks corresponding to the deposition and stripping of gallium(0) was observed. The cyclic voltammogram was similar to that of the unbuffered $\chi_{\text{GaCl}_3} = 0.55$ composition, but not to that of the neutral chlorogallate(III) ionic liquid, Fig. 6(c). Changes in temperature, or prolonged stirring with sodium chloride (even several weeks), had no effect on this behaviour of the buffered acidic system.

In the cyclic voltammetry of the buffered $\chi_{\text{GaCl}_3} = 0.67$ composition, Fig. 6(b), the gallium reduction/deposition is strongly shifted into the cathodic direction, by 0.5 V from that observed in the unbuffered system, Fig. 6(a), but the complete elimination of electro-reduction of gallium was not observed. Fig. 7(b) shows the electrochemical behaviour of the buffered $\chi_{\text{GaCl}_3} = 0.67$ system compared with the electrochemical behaviour of unbuffered $\chi_{\text{GaCl}_3} = 0.55$ system, Fig. 7(a). A similar pattern of redox peaks in the cyclic voltammetry was observed,

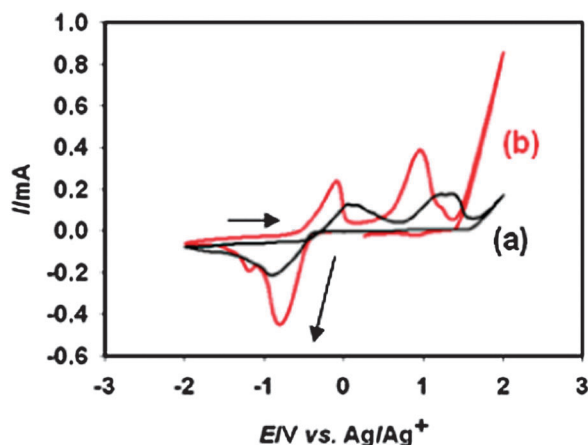


Fig. 7 Cyclic voltammetry of unbuffered and buffered $[\text{C}_8\text{mim}]\text{Cl}-\text{GaCl}_3$ systems on platinum electrode, 50 mV s^{-1} , 20°C ; (a) unbuffered $\chi_{\text{GaCl}_3} = 0.55$, (b) buffered $\chi_{\text{GaCl}_3} = 0.67$.

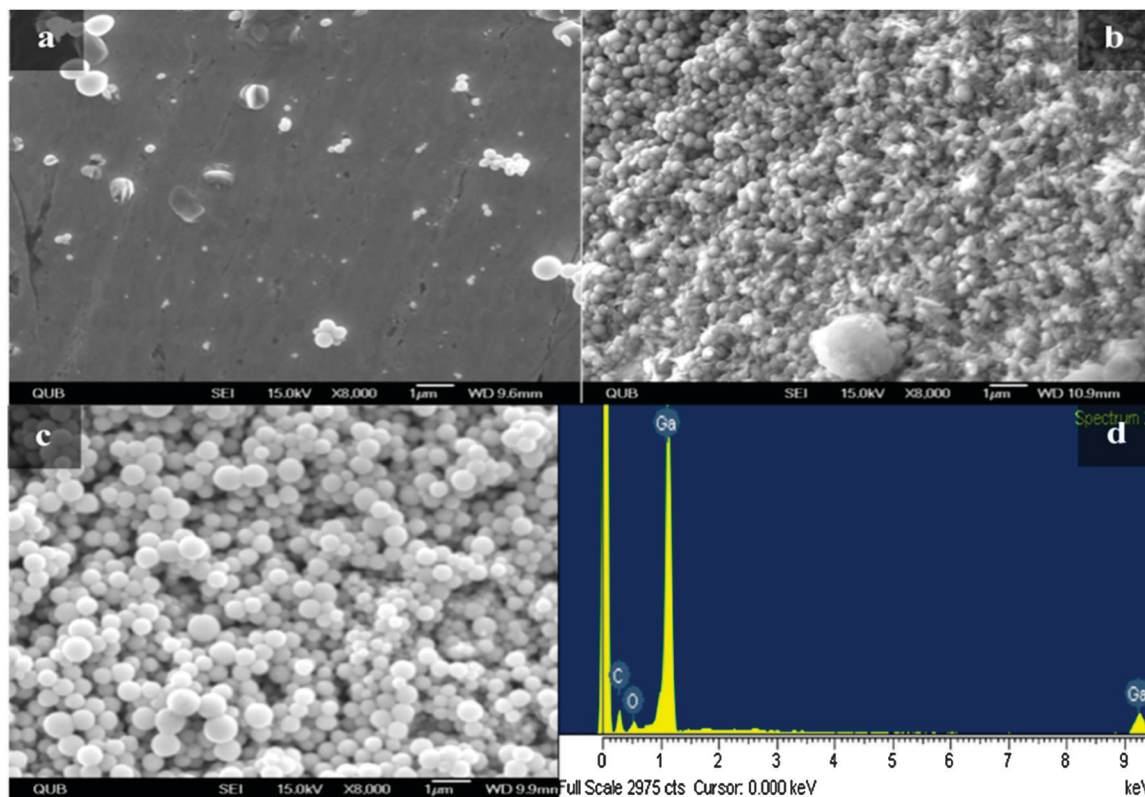


Fig. 8 Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) analysis of the gallium deposits, obtained on glassy carbon substrate from chlorogallate(III) systems; (a) unbuffered $\chi_{\text{GaCl}_3} = 0.50$; (b) unbuffered $\chi_{\text{GaCl}_3} = 0.67$; (c) buffered $\chi_{\text{GaCl}_3} = 0.67$ and (d) EDX spectrum of the deposits.

which complements the results from sodium chloride solubility studies (Table 2).

In order to compare the morphology of gallium deposited from various compositions, electrodeposition experiments on glassy carbon substrates were carried out by holding the potential at -0.5 V vs. Ag/Ag⁺ for a period of 15 min at 20 °C (Fig. 8). Deposition experiments were repeated under similar conditions in triplicate and the results were reproducible.

Depositions from buffered, Fig. 8(c), and from unbuffered $\chi_{\text{GaCl}_3} = 0.67$ chlorogallate(III) ionic liquids, Fig. 8(b), were studied, and compared with the deposition from an unbuffered $\chi_{\text{GaCl}_3} = 0.50$ composition, Fig. 8(a). The deposit from the unbuffered $\chi_{\text{GaCl}_3} = 0.67$ composition was visibly denser than that from the unbuffered system (*N.B.* for chloroaluminates(III), no aluminium metal electrodeposition was observed from the buffered $\chi_{\text{AlCl}_3} = 0.55$ composition, here or elsewhere).²¹ The uniform morphology of the deposit obtained from the buffered system can be attributed to the constant anionic speciation of the ionic liquid, maintained by the buffer.

The deposits were identified as gallium metal using EDX analysis, Fig. 8(d). Elemental gallium was observed as an enhanced peak, along with traces of oxygen and carbon. The peak for oxygen was present due to the thin film of oxide formed on the surface of the gallium, while the traces of carbon originated from the glassy carbon substrate.

Combination of the results from the electrodeposition experiments (Fig. 8) and the ⁷¹Ga NMR spectroscopy study (Fig. 2) gave a new insight to electrochemical properties of chlorogallate(III) ionic liquids. For both chlorometallate(III) systems, sodium chloride is only marginally soluble in $\chi_{\text{MCl}_3} \leq 0.50$ ionic liquids, as there is no reaction which would drive passing of the salt into the ionic liquid. When $[\text{M}_2\text{Cl}_7]^-$ appears in the system ($\chi_{\text{MCl}_3} > 0.50$), the reaction given by eqn (5) drives the increased solubility, and yields buffered systems. Since the stability of $[\text{Ga}_2\text{Cl}_7]^-$ is higher than that of $[\text{Al}_2\text{Cl}_7]^-$, the equilibrium of this reaction is shifted more to the left for the former system, hence lowering the solubility of sodium chloride, resulting in incomplete buffering. Finally, for $\chi_{\text{MCl}_3} > 0.60$, when polynuclear species appear, the situation becomes less trivial, with solidification of chloroaluminate(III) systems, and an unexpected decrease in the solubility of sodium chloride in the chlorogallate(III) ionic liquids. Of importance, this finding is in contrast to the prevailing assumptions present in the literature, where it is common to perceive the electrochemical properties of chloroaluminate(III) and chlorogallate(III) systems as analogous.³¹

Conclusions

Buffering of a range of compositions of a chlorogallate(III) system, $[\text{C}_8\text{mim}]\text{Cl}-\text{GaCl}_3$, with sodium chloride, was investigated. It was demonstrated by ⁷¹Ga NMR spectroscopy and cyclic voltammetry that $0.50 < \chi_{\text{GaCl}_3} \leq 0.60$ compositions, although nominally containing enough sodium chloride to buffer them to neutrality, in reality display mild acidity. Furthermore, strongly acidic samples ($\chi_{\text{GaCl}_3} = 0.67$ and 0.75) can be buffered to moderate acidity.

From these buffered systems, it was possible to electrodeposit metallic gallium, which was subsequently studied using SEM and EDX. The morphology of the deposit from the buffered system was more uniform than that obtained from the unbuffered one, due to stable anionic speciation of the former system, maintained by the buffer.

These findings are in stark contrast with the behaviour of chloroaluminate(III) ionic liquids,^{21,50} which can be buffered to neutrality with sodium chloride, but only up to $\chi_{\text{AlCl}_3} = 0.60$ composition, and display only latent acidity when buffered (*i.e.* it is not possible to electrodeposit aluminium from such systems).²¹

Notes and references

- 1 J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263–1264.
- 2 S. P. Wicelinski, R. J. Gale and J. S. Wilkes, *J. Electrochem. Soc.*, 1987, **134**, 262–263.
- 3 M. K. Carpenter and M. W. Verbrugge, *J. Mater. Res.*, 1994, **9**, 2584–2588.
- 4 A. Earnshaw and N. N. Greenwood, *Chemistry of the Elements*, Butterworth-Heinemann, Oxford, 2nd edn, 1997.
- 5 C. L. Hussey, *Adv. Molten Salt Chem.*, 1983, **5**, 185–229.
- 6 H. Ohno, *Electrochemical Aspects of Ionic Liquids*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2nd edn, 2011.
- 7 F. Endres, *ChemPhysChem*, 2002, **3**, 145–154.
- 8 *Ionic Liquids in Synthesis*, ed. P. Wasserschied and T. Welton, Wiley Interscience, Weinheim, 2nd edn, 2007.
- 9 H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal., A*, 2010, **373**, 1–56.
- 10 J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.
- 11 (a) J. L. Gray and G. E. Maciel, *J. Am. Chem. Soc.*, 1981, **103**, 7147–7151; (b) S. Takahashi, M.-L. Saboungi, R. J. Klingler, M. J. Chen and J. W. Rathke, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3591–3595; (c) K. Ichikawa and T. Matsumoto, *J. Magn. Reson.*, 1985, **63**, 445–453.
- 12 (a) R. J. Gale, B. Gilbert and R. A. Osteryoung, *Inorg. Chem.*, 1978, **17**, 2728–2729; (b) S. Takahashi, L. A. Curtiss, D. Gosztola, N. Koura and M.-L. Saboungi, *Inorg. Chem.*, 1995, **34**, 2990–2993.
- 13 C. J. Dymek, J. S. Wilkes, M.-A. Einarsrud and H. A. Øye, *Polyhedron*, 1988, **7**, 1139–1145.
- 14 A. K. Abdul-Sada, A. M. Greenway, K. R. Seddon and T. Welton, *Org. Mass Spectrom.*, 1993, **28**, 759–765.
- 15 C. L. Hussey, T. B. Scheffler, J. S. Wilkes and A. A. Fannin, Jr., *J. Electrochem. Soc.*, 1985, **133**, 1389–1391.
- 16 H. A. Øye, M. Jagatoyen, T. Okseffjøl and J. S. Wilkes, *Molten Salt Chemistry and Technology*, in *Materials Science Forum*, ed. M. Chemla and D. Devilliers, Trans. Techn. Publ. Aldermannsdorf, Switzerland, 1991, vol. 73–75, pp. 183–189.
- 17 T. Tsuda and C. L. Hussey, *Electrochemistry of Room-Temperature Ionic Liquids and Melts*, in *Modern Aspects of Electrochemistry*, ed. R. E. White, Springer, Dordrecht, 2009, vol. 45, pp. 63–174.

- 18 R. A. Mantz, P. C. Trulove, R. T. Carlin, T. L. Theim and R. A. Osteryoung, *Inorg. Chem.*, 1997, **36**, 1227–1232.
- 19 (a) V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum Press, New York, 1978; (b) T. A. Zawodzinski, Jr. and R. A. Osteryoung, *Inorg. Chem.*, 1989, **28**, 1710–1715.
- 20 J. Estager, A. A. Oliferenko, K. R. Seddon and M. Swadźba-Kwaśny, *Dalton Trans.*, 2010, **39**, 11375–11382.
- 21 T. J. Melton, J. Joyce, J. T. Maloy, J. A. Boon and J. S. Wilkes, *J. Electrochem. Soc.*, 1990, **137**, 3865–3869.
- 22 M. Lipstajn and R. A. Osteryoung, *J. Electrochem. Soc.*, 1983, **130**, 1968–1969.
- 23 B. Ellis, W. Keim and P. Wasserscheid, *Chem. Commun.*, 1999, 337–338.
- 24 (a) I. C. Quarmby and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1994, **116**, 2649–2650; (b) R. A. Osteryoung, I. C. Quarmby, R. A. Mantz and L. M. Goldenberg, *Anal. Chem.*, 1994, **66**, 3558–3561.
- 25 P. Koronaios, D. King and R. A. Osteryoung, *Inorg. Chem.*, 1998, **37**, 2028–2032.
- 26 S. P. Wicelinski, R. J. Gale and J. S. Wilkes, *Thermochim. Acta*, 1988, **126**, 255–263.
- 27 P. Wicelinski, R. J. Gale, S. D. Williams and G. Mamantov, *Spectrochim. Acta, Part A*, 1989, **45**, 759–762.
- 28 S. P. Wicelinski, R. J. Gale, K. M. Pamidimukkala and R. A. Lane, *Anal. Chem.*, 1988, **60**, 2228–2232.
- 29 (a) J. Tong, Q.-S. Liu, W. Guan and J.-Z. Yang, *J. Phys. Chem. B*, 2007, **111**, 3197–3200; (b) W. G. Xu, X.-M. Lu, J.-S. Gui, Q.-G. Zhang and J.-Z. Yang, *Chin. J. Chem.*, 2006, **24**, 331–335; (c) W. Martino, J. Fernandez de la Mora, Y. Yoshida, G. Saito and J. Wilkes, *Green Chem.*, 2006, **8**, 390–397.
- 30 H. Z. Yang, Y. Jin, W.-G. Xu, Q.-G. Zhang and S.-L. Zang, *Fluid Phase Equilib.*, 2005, **227**, 41–46.
- 31 C. Hardacre, R. W. Murphy, K. R. Seddon, G. Srinivasan and M. Swadźba-Kwaśny, *Aust. J. Chem.*, 2010, **63**, 845–848.
- 32 G. Rangits and L. Kollar, *J. Mol. Catal. A: Chem.*, 2006, **246**, 59–64.
- 33 Y. J. Kim and R. S. Varma, *Tetrahedron Lett.*, 2005, **46**, 7447–7456.
- 34 E. J. Angueira and M. G. White, *J. Mol. Catal. A: Chem.*, 2007, **277**, 164–170.
- 35 M. P. Atkins, K. R. Seddon and M. Swadźba-Kwaśny, *Pure Appl. Chem.*, 2011, **83**, 1391–1406.
- 36 D. Freudenmann and C. Feldmann, *Dalton Trans.*, 2011, **40**, 452–456.
- 37 (a) M. K. Carpenter and M. W. Verbrugge, *J. Electrochem. Soc.*, 1990, **137**, 123–129; (b) M. W. Verbrugge and M. K. Carpenter, *AIChE J.*, 1990, **36**, 1097–1106; (c) Y. Yoshida, O. Akihiro, S. Gunzi, N. Seiichi, N. Eiji, T. Masaki, S. Makoto, T. Masahide and Y. Toshinobu, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1921–1928; (d) P.-Yu. Chen, Y.-F. Lin and I.-W. Sun, *J. Electrochem. Soc.*, 1999, **146**, 3290–3294.
- 38 (a) D. O. Flamini, S. B. Saidman and J. B. Bessone, *J. Appl. Electrochem.*, 2007, **37**, 467–471; (b) D. O. Flamini, S. B. Saidman and J. B. Bessone, *Thin Solid Films*, 2007, **515**, 7880–7885.
- 39 J. M. Shafir and J. A. Plambeck, *Can. J. Chem.*, 1970, **48**, 2131–2132.
- 40 S. P. Yatsenko, V. N. Danilin and L. N. Volkova, *Zh. Fiz. Khim.*, 1968, **42**, 874–877.
- 41 U. Anders and J. A. Plambeck, *Can. J. Chem.*, 1969, **47**, 3055–3060.
- 42 V. V. Smolenskii, A. L. Bove, A. A. Khokhryakov and A. G. Osipenko, *Radiochemistry*, 2003, **45**, 449–452.
- 43 L. H. S. Gasparotto, N. Borisenko, O. Höfft, R. Al-Salmana, W. Maus-Friedrichs, N. Bocchi, S. Zein El Abedin and F. Endres, *Electrochim. Acta*, 2009, **55**, 218–226.
- 44 G. B. Pan, O. Mann and W. Freyland, *J. Phys. Chem. C*, 2011, **115**, 7656–7659.
- 45 K. Seddon, G. Srinivasan and A. Wilson, *Electrodeposition of elemental zirconium from a mixture of a Lewis acid and an ionic liquid*, *World Pat.*, WO2010136814, 2010.
- 46 A. E. Bradley, C. Hardacre, M. Nieuwenhuyzen, W. R. Pitner, D. Sanders, K. R. Seddon and R. C. Thied, *Inorg. Chem.*, 2004, **43**, 2503–2514.
- 47 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156–164.
- 48 J. Mason, *Multinuclear NMR*, Plenum Press, New York, 1987.
- 49 M. Lui, L. Crowhurst, J. Hallett, P. Hunt, H. Niedermeyer and T. Welton, *Chem. Sci.*, 2011, **2**, 1491–1496.
- 50 A. M. Elias and J. S. Wilkes, *J. Chem. Eng. Data*, 1994, **39**, 79–82.
- 51 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, 1980.
- 52 M. Ue, A. Murakami and S. Nakamura, *J. Electrochem. Soc.*, 2002, **149**, A1572–A1577.
- 53 P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168–1178.
- 54 L. E. Barrosse-Antle, A. M. Bond, R. G. Compton and A. M. O'Mahony, *Chem.-Asian J.*, 2010, **5**, 202–230.
- 55 T. Schubert, S. Z. E. Abedin, A. P. Abbott, K. J. McKenzie, K. S. Ryder and F. Endres, *Electrodeposition of metals, in Electrodeposition from Ionic Liquids*, ed. F. Endres, A. P. Abbott and D. R. MacFarlane, Wiley-VCH, Weinheim, 2008, p. 105.