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Short Communication

Separation of cations in buffered 1-methyl-3-ethylimidazolium chloride–aluminum chloride ionic liquids by ion chromatography

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ABSTRACT

Ion chromatography was used to separate sodium and 1-methyl-3-ethylimidazolium cations in the buffered 1-methyl-3-ethylimidazolium chloride–aluminum chloride room-temperature molten salt system. The calibration curves for the two species were linear over three decades and the accuracy of the method was ± 2.8% relative error.

INTRODUCTION

The addition of aluminum chloride to 1-methyl-3-ethylimidazolium chloride (MEIC) results in the formation of an ionic liquid (melt) at room temperature [1]. The liquids are described in terms of the apparent mole fraction, N, of aluminum chloride used to make them. Melts with $N<0.5$ are termed 'basic' because of the presence of the Lewis base, Cl^-. Melts with $N>0.5$ are termed 'acidic' because of the presence of the Lewis acid, $Al_2Cl_7^-$, and melts with $N=0.5$ are termed 'neutral' because the only anion present is the Lewis neutral $AlCl_4^-$.

These ionic liquids are of interest to our laboratory as battery electrolytes because of their wide electrochemical window, high specific conductance and good thermal properties [2,3]. Their application as battery electrolytes has been demonstrated [4,5]. The neutral composition has the widest electrochemical window (over 4 V), but is difficult to maintain because small changes in ion concentrations alter the electrochemistry, closing the electrochemical window by as much as 2 V. Recently, we have discovered that the addition of sodium chloride to acidic melts results in the formation of neutral buffered ionic liquids [6]. The resulting ionic liquid has the wide electrochemical window associated with the neutral composition and is still liquid at room temperature over a wide composition range. It is buffered against addition of the Lewis base, Cl^-, by the presence of Na^+ by the reaction

$$Na^+ + Cl^- \rightarrow NaCl(s)$$

and is buffered against the addition of the Lewis acid, $Al_2Cl_7^-$, by the presence of excess NaCl(s) by the reaction

$$NaCl(s) + Al_2Cl_7^- \rightarrow Na^+ + 2AlCl_4^-$$

A parameter of particular interest in battery applications is the transport number for the various ions in the electrolyte of choice. The transport number for an ion defines the fraction of current carried by that particular ion across a separator when charge is passed in an electrochemical cell. Previous experiments in the unbuffered MEIC–aluminum chloride system have shown that the bulk of the current, approximately 70%, is carried by MEI [7]. The addition of sodium chloride to this system should affect the transport numbers of the various species involved.

The aim of the present study was to develop a method by ion chromatography to monitor changes in the concentrations of Na^+ and MEI^+ in the neutral buffered ionic liquids. The method can then be used to help determine transport number for the new system.

EXPERIMENTAL

The ion chromatograph was a Dionex (Sunnyvale, CA, USA) Model 4500i, with an IonPac CS3G guard column, IonPac CS3 column, cation micromembrane suppressor and conductivity detector. Chromatographs were recorded and integrated on a Dionex 4400 integrator.

The starting materials and room-temperature molten salts were made as described previously [6,8]. Tetrabutylammonium hydroxide (40, w/w), 2,3-diaminopropionic acid monohydrochloride (DAP) (99%), hydrochloric acid (ACS reagent grade) and sodium chloride (99.999%) were obtained from Aldrich (Milwaukee, WI, USA). All dilutions were made with 18.3 M Ω cm water from a Barnstead (Boston, MA, USA) Nanopure II still. Ultrex nitric acid was obtained from J. T. Baker (Phillipsburg, NJ, USA). Disposable 10-ml B–D brand syringes and Gelman Acrodisc 0.45-μm PTFE syringe filters were obtained from Fisher Scientific (Denver, CO, USA).

Acidic melts were made in the range $N = 0.50$–0.60. They were then buffered to neutrality with a 10% excess of sodium chloride and allowed to equilibrate for 24 h prior to use. All glassware was stored under 1:3 ultrex nitric acid–deionized water for a minimum of 48 h before use. The melt samples were filtered through a 0.45-μm PTFE syringe filter prior to weighing. The melts were then weighed (2.0–2.5 g samples) into a 25-ml volumetric flask in a dry box, removed from the box, cooled in a dry ice–acetone bath, slowly hydrolyzed with deionized water and diluted to volume. Na^+ and MEI^+ were quantitated with a calibration curve. A standard stock solution of MEI^+ was prepared from MEIC. A standard stock solution of Na^+ was prepared from 99.999% sodium chloride.

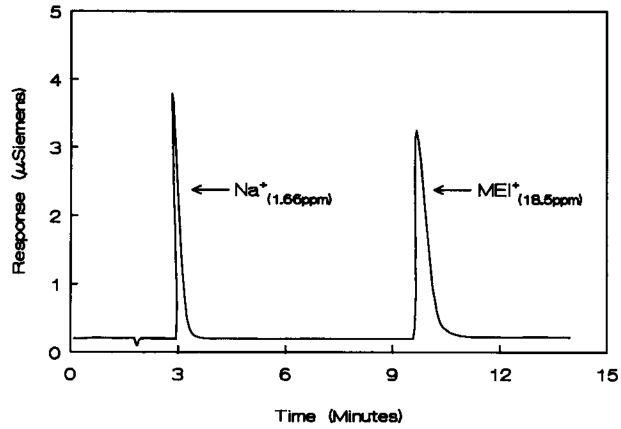

Fig. 1. Separation of Na^+ and MEI^+ by ion chromatography.

RESULTS AND DISCUSSION

The optimum mobile phase composition for the separation of the two ions was found to be a solution of 25 m*M* hydrocloric acid and 0.35 m*M* DAP in deionized water delivered isocratically at 1.0 ml/min. With this mobile phase and the column described, the cations from the melt could be separated in a 12-min run. The MEI^+ elutes at retention time 10.2 min. Fig. 1 shows the separation of the two ions. The regenerant for the chemical suppressor was 50 m*M* tetrabutylammonium hydroxide delivered at a rate of 3.0 ml/min to the suppressor column. The resulting capacity factors for the ions are $k'_{Na+} = 0.65$ $k'_{MEI+} = 4.10$.

The calibration curves for the two ions are linear over three decades. Standards and sample dilutions were chosen so as to fall near the center of the calibration curves (0.2–2 ppm for Na^+ and 10–40 ppm for MEI^+). Samples included buffered melts over the composition range 0.52–0.60 apparent mole fraction, *N*, of aluminum chloride. The Na^+ and MEI^+ peaks were quantitated and the weight percentage of sodium chloride and MEIC calculated. The results are summarized in Table I. The accuracy

TABLE I

ANALYTICAL DATA FOR MEIC AND NaCl DETERMINATION

N	MEIC			NaCl		
	Theoretical (%)	Experimental[a] (%)	Relative error (%)	Theoretical (%)	Experimental[a] (%)	Relative error (%)
52	49.40	50.77	+2.80	1.70	1.77	+2.30
54	46.06	46.36	+0.65	3.08	3.01	−2.27
56	44.26	44.68	+0.95	4.73	4.66	−1.50
58	41.75	41.62	−0.31	6.18	6.09	−1.46
60	38.14	39.14	+0.13	7.73	7.78	+0.65

[a] Average of three trials.

of the method (worst case + 2.8%) for determination of Na^+ and MEI^+ is sufficient to distinguish between melts over the composition range studied and therefore could be used to monitor changes in the concentrations of these ions during a transport number experiment.

Ion chromatography provides a convenient method for the quantitation of Na^+ and MEI^+ from the buffered aluminum chloride–MEIC ionic liquid. Other group 1A metal ions could also be separated and quantitated using this method. The solvent strength and flow may require further optimization depending on the ions of interest. Divalent cations would not elute under the given conditions and time frame of the experiment described.

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