Chemical and Electrochemical Behavior of Gallium in the Room-Temperature Ionic Liquid of the Composition $[\text{C}_6\text{H}_{11}\text{N}_2][\text{N}($SO$_2$CF$_3$)$_2]$  

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Abstract—The behavior of gallium trichloride in the room-temperature ionic liquid of the composition $[\text{C}_6\text{H}_{11}\text{N}_2][\text{N}($SO$_2$CF$_3$)$_2]$ at 298–308 K in an inert gas atmosphere was studied by linear and cyclic voltammetry and spectrophotometry. The reduction and oxidation potentials of gallium were determined. Assumptions concerning the composition of the gallium complex species were made.  

Weapons plutonium contains up to 5% of gallium which is an undesirable impurity in energy reactor fuel. Therefore, conversion of weapons plutonium into MOX fuel implies exhaustive removal of gallium [1].  

Room-temperature ionic liquids are promising media for preparation, separation, and decontamination of a number of elements and compounds. The reason is that a low temperature lifts many limitations due to, above all, corrosivity of melts.  

In this work, we used as solvent the $[\text{C}_6\text{H}_{11}\text{N}_2][\text{N}($SO$_2$CF$_3$)$_2]$ (EtMeIm–Tf$_2$N) ionic liquid offering all the advantages characteristic of this class of compounds. In particular, it is thermally stable to 670 K, melts at 270 K, and exhibits certain hydrophobicity, enhanced (for its class) conductivity ($\sim 1.3 \times 10^{-2}$ S cm$^{-1}$), and a wide range of electrochemical inertness ($\sim 5$ V) [2–7].  

There are published data on the electrochemical behavior of gallium compounds in room-temperature ionic liquids, e.g., in 1-butylpyridinium chloride and 1-methyl-3-ethylimidazolium chloride [7–9]. However, the results of these studies do not suggest unambiguously the reduction mechanism for gallium.  

In this study, we comprehensively studied the behavior of gallium compounds in a room-temperature ionic liquid, 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (EtMeIm–Tf$_2$N).  

EXPERIMENTAL  

The chemical and electrochemical behavior of gallium in the room-temperature ionic liquid (RTIL) was studied by linear and cyclic voltammetry and IR spectroscopy, as well as by registration of changes in the potential of the working electrode after its brief polarization.  

All the manipulations, including assembling the electrochemical and spectrophotometric cells, were carried out in a dry glove box in an argon atmosphere. Argon was continuously freed from oxygen-containing impurities by forced circulation through a column packed with zirconium metal chips heated to 1000 K. Argon circulation was effected by a membrane pump placed directly inside the glove box.  

As solvent served the room-temperature ionic liquid $[\text{C}_6\text{H}_{11}\text{N}_2][\text{N}($SO$_2$CF$_3$)$_2]$ (EtMeIm–Tf$_2$N) which was synthesized, purified, and supplied by the Los Alamos National Laboratory (the United States). Prior to use, it was treated additionally for 12 h at the residual pressure of $10^{-3}$ atm.  

Gallium trichloride was prepared by chlorination of the metal (99.99%) in a flow of chlorine prepared by electrolysis of lead chloride. Chlorination was carried out at 480 K in a Pyrex reactor. The GaCl$_3$ vapor was transported by a chlorine flow to the water-cooled section of the reactor, and excess chlorine left the reactor via a hydroseal filled with concentrated sulfuric acid. The product was stored in sealed ampules. Gallium trichloride solutions of required concentration were prepared by mixing the preliminarily prepared equimolar EtMeIm–Tf$_2$N–GaCl$_3$ solution with the straight solvent.  

Electrochemical studies were carried out in a quartz
Fig. 1. Cyclic voltammogram of the C₆H₁₁N₂–N(SO₂CF₃)₂ melt. Temperature 308 K; tungsten as working electrode, metallic tungsten as reference electrode, and glassy carbon as counterelectrode; potential scanning rate 0.1 V s⁻¹; C₆H₁₁N₂/N(SO₂CF₃)₂ = 1.

Fig. 2. Cyclic voltammogram of the [C₆H₁₁N₂–N(SO₂CF₃)₂]–GaCl₃ melt. GaCl₃ concentration 0.95 mol %; all other conditions, as in Fig. 1.

Fig. 3. Anodic polarization of the [C₆H₁₁N₂–N(SO₂CF₃)₂]–GaCl₃ melt. Potential scanning rate 0.025 V s⁻¹; all other conditions, as in Fig. 2.

RESULTS AND DISCUSSION

Voltammetric Studies

Figure 1 shows the cyclic voltammogram of the EtMeIm–TF₂N room-temperature ionic liquid at 308 K. At potentials from −3.0 to 3.0 V vs. tungsten reference electrode, there were no visible peaks, which suggests a wide range of electrochemical inertness and makes this electrolyte promising as solvent. Upon introducing gallium trichloride into solution (Fig. 2), new peaks of current appeared at −1.7 V in the cathodic branch of the curve and at 0.2 V in the anodic branch, which is due to gallium reduction and oxidation. Anodic polarization of the gallium-containing melt (Fig. 3) at potentials from −0.5 to 1.5 V gives no visible peaks, which suggests that gallium in the melt occurs in the trivalent state only.

The potential–time dependences recorded after brief polarization of the working electrode showed (Fig. 4) that, at cathodic polarizations more negative than −1.7 V, a plateau appeared at a potential of −0.75 V. At the same time, special experiments...