Chemical and Electrochemical Behavior of Gallium in the Room-Temperature Ionic Liquid of the Composition $[C_6H_{11}N_2][N(SO_2CF_3)_2]$

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Abstract—The behavior of gallium trichloride in the room-temperature ionic liquid of the composition $[C_6H_{11}N_2][N(SO_2CF_3)_2]$ 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 $[C_6H_{11}N_2]$. [N(SO₂CF₃)₂] (EtMeIm–Tf₂N) 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 (~1.3 × 10^{-2} S cm⁻¹), and a wide range of electrochemical inertness (~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-ethylimidazolinium 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-methylimidazolinium bis[(tri-fluoromethyl)sulfonyl]amide (EtMeIm $-Tf_2N$).

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 $[C_6H_{11}N_2][N(SO_2CF_3)_2]$ (EtMeIm–Tf₂N) 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 GaCl₃ 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–Tf₂N–GaCl₃ solution with the straight solvent.

Electrochemical studies were carried out in a quartz



Fig. 1. Cyclic voltammogram of the $C_6H_{11}N_2$ –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; $C_6H_{11}N_2/N(SO_2CF_3)_2 = 1$.



Fig. 2. Cyclic voltammogram of the $[C_6H_{11}N_2-N(SO_2 \cdot CF_3)_2]$ -GaCl₃ melt. GaCl₃ concentration 0.95 mol %; all other conditions, as in Fig. 1.



Fig. 3. Anodic polarization of the $[C_6H_{11}N_2-N(SO_2CF_3)_2]-GaCl_3$ melt. Potential scanning rate 0.025 V s⁻¹; all other conditions, as in Fig. 2.

cell with a ground quartz cup equipped with tubes for introducing the electrodes. The cell was hermetically isolated by passing the electrodes through vacuum rubber plugs preliminarily fitted over the tubes. Also, the cell had two tubes for connection to an additional gas purification system. The cell was placed into a stainless-steel beaker hermetically mounted into the glove box bottom, which was the external part of the temperature-control system.

The electrolyte under study was placed into a container made of SU-2000 glassy carbon which simultaneously served as counterelectrode. As working electrode served a face electrode made of VRN metallic tungsten. It had an area of 0.1237 cm². As reference electrode served VRN metallic tungsten. The inert gas inside the cell was additionally freed from oxygen-containing impurities by circulation for several hours through the zirconium-packed gas-purification system using a ZALIMP PP-10-5A peristaltic pump.

We used a PI-50-1 standard potentiostat equipped with a PR-8 programmer and recorded the electrochemical responses from the system using an S9-8 digital storage oscillograph linked to a PC by a communication line. The scanning rate of the potential was varied from 0.040 to 10 V s⁻¹. The experiments were run at 298–308 K.

The IR spectra of gallium trichloride solutions in the EtMeIm–Tf₂N ionic liquid were recorded on a Specord M-80 spectrophotometer at 4000–200 cm⁻¹ at room temperature. The resolution of the spectrophotometer was no less than 1 cm⁻¹. The IR spectra were recorded in cells with CsI windows. The liquid layer was 0.1 mm thick.

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 can be 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

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showed that the quasiequilibrium potentials of metallic gallium vs. tungsten reference electrode are also approximately equal to -0.75 V.

Our results showed that gallium is reduced in the room-temperature ionic liquid of the composition EtMeIm–Tf₂N–0.95 mol % GaCl₃ at -1.7 V, and its quasiequilibrium potential is equal to -0.75 V.

Spectrophotometric Studies

The IR absorption spectra of the EtMeIm $-Tf_2N$ room-temperature ionic liquid with and without gallium trichloride additions are shown in Figs. 5 and 6, respectively, and the absorption band maxima are listed in the table.

The vibrational spectra of EtMeIm ($C_6H_{11}N_2$) and Tf_2N [N(SO₂CF₃)₂] and their structural models were discussed in detail in [10–13]. Figure 7 presents schematically the structures of these ions. Comparison of the experimental results reported in these works with our data (see table) shows good agreement of the vibration frequencies. The mutual influence of the EtMeIm⁺ and Tf_2N^- fragments on the fundamental



Fig. 4. Potential-time dependence recorded after brief polarization of the working electrode in the $[C_6H_{11}N_2-N(SO_2CF_3)_2]$ -GaCl₃ melt. Polarization potential -2.7 V; polarization time 180 s; all other conditions, as in Fig. 2.



Fig. 5. IR absorption spectrum of the $[C_6H_{11}N_2] \cdot [N(SO_2CF_3)_2]$ ionic liquid. Temperature 298 K.

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Vibration frequencies, cm ⁻¹		Assignment
EtMeIm	Tf ₂ N	
3160		v(CH) (ring)
3124		v(CH) (ring)
2992		ν(CH)
1574		$v_{\rm s}({\rm ring})$
1465		$v_{s}(ring)$
1450		$v_{s}(ring)$
	1350	$v_{as}(SO_2)$
	1330	$v_{as}(SO_2)$
	1190	$v_{as}(CF_3)$
1140		$v_{s}(ring)$
	1060	$v_{as}^{\prime}(SNS)$
840		$\delta(CH)$ (ring)
790		δ (CH) (ring)
650		$v_{as}(ring)$
628		$v_{as}^{as}(ring)$
	618	$\delta_{as}(SO_2)$
	572	$\delta_{as}(SO_2)$
	514	$\delta_{as}^{us}(CF_3)$
	408	$\omega(SO_2)$
	359	$\tau(SO_2)$
	290	$\rho(CF_3)$

Absorption band maxima of the EtMeIm–Tf₂N ionic liquid



Fig. 6. IR spectrum of gallium trichloride in $[C_6H_{11}N_2]$ · $[N(SO_2CF_3)_2]$. Temperature 298 K. GaCl₃ concentration, mol %: (1) 15.7, (2) 20.8, and (3) 50.2.



Fig. 7. Structural model of the EtMeIm-Tf₂N ionic liquid.



Fig. 8. Difference spectrum obtained by subtracting the spectrum of the EtMeIm $-Tf_2N$ ionic liquid from that of the EtMeIm $-Tf_2N$ -GaCl₃ solution. Temperature 298 K.

vibration frequencies seems to be weak and results in insignificant departures from the known values. All the absorption band maxima in the table were assigned according to [10-13].

Introduction of gallium trichloride into the EtMeIm-Tf₂N ionic liquid affects the vibration frequencies lower than 500 cm^{-1} . This holds for the intensities and positions of the absorption bands at 408 and 359 cm⁻¹ belonging to the SO_2 group and that at 290 cm⁻¹ belonging to the CF₃ group (Fig. 6). Also, in the same region, a new absorption band appears at 375 cm^{-1} whose intensity depends on the gallium trichloride concentration in solution. This absorption band is located near the triple-degenerate vibration frequency v_3 of the GaCl₄ complex (T_d symmetry) whose vibrational spectra are well studied [14, 15]. By subtracting the spectrum of the EtMeIm-Tf₂N solvent from that of the EtMeIm-Tf₂N-GaCl₃ solution, we revealed a non-Lorenzian absorption band (Fig. 8). This band is split into two components, which suggests lowering of the site symmetry to $C_{3\nu}$. Since the changes in the vibrational spectrum concern primarily the libration modes of the SO₂ group only, it can be assumed that gallium trichloride, which is a Lewis acid and interacts with Tf_2N^- , forms a heteroligand gallium complex whose coordination sphere contains, along with three chlorine atoms, one of the oxygen atoms from the SO₂ group of the Tf_2N^- anion. Indeed, if the gallium cation formed a chemical bond with the nitrogen atom (bearing the largest negative charge), this would result in a strong delocalization of the S–N–S bond and, thereby, affect the force constants of the bond and vibration frequencies of the Tf₂N⁻ anion: v(SNS), δ (SNS), v(SO₂), and δ (SO₂) [13], which is not the case. Notably, when interacting with the Tf_2N^- anion, gallium trichloride does not markedly affect the stretching vibrations of the SO_2 group and only affects the libration modes of the SO₂ and CF_3 groups (Fig. 6).

Thus, the IR absorption spectra of the solutions of gallium trichloride in the EtMeIm–Tf₂N ionic liquid suggest that the Tf₂N⁻ ion is coordinated via one of the oxygen atoms of the SO₂ group, yielding GaOCl₃²⁻ heterocomplex with the C_{3v} site symmetry.

Our studies allowed certain suggestions concerning the ionic composition and structure of RTIL and the mechanism of the cathodic processes occurring during electrolysis of the EtMeIm–Tf₂N melt with gallium additions.

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