Raman Spectroscopy of the Mixtures (x)1-Butyl-1-methylpyrrolidinium Chloride-($1 - x$)$TaCl_5$ in Solid and Molten States

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A series of novel ionic liquids consisting of 1-butyl-1-methylpyrrolidinium chloride ($Pyr_{14}Cl$) and $TaCl_5$ were obtained in a wide range of molar compositions for electrochemical application. Raman spectroscopy was used to investigate the complex formation of tantalum(V) in the mixtures of (x)$Pyr_{14}Cl$−($1 - x$)$TaCl_5$ ($x = 0.80-0.30$) over the temperature range 20−160 °C. Depending on the molar composition, different species of tantalum (V) were identified. In the *basic* and *neutral* mixtures of (x)$Pyr_{14}Cl$−($1 - x$)$TaCl_5$ ($x = 0.80-0.50$), tantalum(V) exists in the form of octahedral $[TaCl_6]^-$ in both solid and molten states. In *acidic* ionic liquids ($x = 0.45-0.30$), $[Ta_2Cl_{10}]$ units are the main species of tantalum(V) identified in the solid state. As the temperature rose, the gradual degradation of $[Ta_2Cl_{10}]$ units was observed in the solid state, accompanied by the formation of $[TaCl_6]^-$ and $[Ta_2Cl_{11}]^-$ anions. In the molten state, in the range between 130 and 160 °C, the latter two species exist in equilibrium and are the dominant species of tantalum(V). The formation of oxochloride species of tantalum(V) was investigated in mixtures of $Pyr_{14}Cl-TaCl_5-Na_2O$ ($x = 0.65$) at various O/Ta mole ratios, and the formation of the oligomeric species with Ta−O−Ta bridging bonds was determined.

Introduction

In recent years, there has been an increasing interest in the electrochemical deposition of refractory metals, particularly tantalum, from ionic liquids as alternative media to high-temperature molten salt electrolytes. The initial formation of different complexes of tantalum(V) or electrochemically active species in ionic melts defines the mechanism of electrochemical deposition. Studies on electrochemical deposition of tantalum(V) from ionic liquids have been reported,[1−7] but there is a lack of systematic spectroscopic investigation of the ionic liquids used as electrolytes.

Our spectroscopic studies were initiated by intensive investigation of the electrochemical behavior of tantalum(V) in different ionic liquids on the basis of pyrrolidinium ring cations with such anions as Cl^-, BF_4^-, and $CF_3SO_2^-$. Understanding the electrochemical processes can be clearer when they are supported by knowledge of the structure and composition of the complex species of tantalum(V) within the ionic liquids. Their formation is affected by the anionic and cationic compositions of ionic liquids, by oxygen impurities, and by the temperature.

In our studies, we have used 1-butyl-1-methylpyrrolidinium chloride ($Pyr_{14}Cl$) as a salt with a simple Cl^- anion which potentially may form the ionic liquids that resemble the ionic melts that may be produced by heating inorganic salts, such as alkali chloride, to high temperature. As pure $Pyr_{14}Cl$ (mp 203 °C) decomposes after melting, it cannot be used as a solvent for electrochemical application. Despite this fact, $Pyr_{14}Cl$ is suitable for the synthesis of novel ionic liquids with $TaCl_5$. In our previous studies,[6,8] the formation of an ionic liquid based on 1-butyl-1-methylpyrrolidinium chloride and $TaCl_5$ at a molar ratio for $Pyr_{14}Cl/TaCl_5$ of 0.65/0.35, which melted above 70 °C, was reported. It has a wide window of electrochemical stability (more than 6 V) and demonstrates promising properties as an electrolyte for the electrochemical deposition of tantalum at 140−150 °C. The mixtures of $Pyr_{14}Cl$ and $TaCl_5$ also form liquids at component molar ratios close to 0.65/0.35; namely, 0.60/0.40 and 0.67/0.33.

We have extended the range of compositions of ionic liquids studied and have succeeded in obtaining a series of novel ionic liquids consisting of $Pyr_{14}Cl$ and $TaCl_5$ with molar fractions of $Pyr_{14}Cl$ in the range 0.80−0.30. The thermal behavior of the mixtures (x)$Pyr_{14}Cl$−($1 - x$)$TaCl_5$ ($x = 0.80-0.30$) was investigated using differential scanning calorimetry (DSC),[9] and it was found that the (x)$Pyr_{14}Cl$−($1 - x$)$TaCl_5$ mixtures form stoichiometric 3:2 and 2:3 crystalline phases melting at 70 and 130 °C, respectively. The electrochemical behavior of the mixtures (x)$Pyr_{14}Cl$−($1 - x$)$TaCl_5$ ($x = 0.80-0.30$) was investigated,[10] and both the basic and acidic ionic liquids exhibited electrical conductivity and a wide window of electrochemical stability. FTIR and FTIR-emission spectroscopic studies of (x)$Pyr_{14}Cl$−($1 - x$)$TaCl_5$ mixtures ($x = 0.80-0.30$) were performed,[10] providing information about the changes in the vibrational features of pyrrolidinium ring cations depending on the molar composition and the formation of oxochloride complexes of tantalum(V), but they were not informative with respect to the structure and composition of tantalum(V) chloride species.

The present paper is a Raman spectroscopic study on the identification of chloride complexes of tantalum(V) in the novel ionic liquids (x)$Pyr_{14}Cl$−($1 - x$)$TaCl_5$ over a wide range of compositions ($x = 0.80-0.30$) and temperatures (20−160 °C) with respect to their potential use as electrolytes. The formation of oxochloride complexes of tantalum(V) also was investigated in $Pyr_{14}Cl-TaCl_5-Na_2O$ mixtures at various O/Ta mole ratios because of their crucial influence on the mechanism of electrochemical deposition of tantalum(V).

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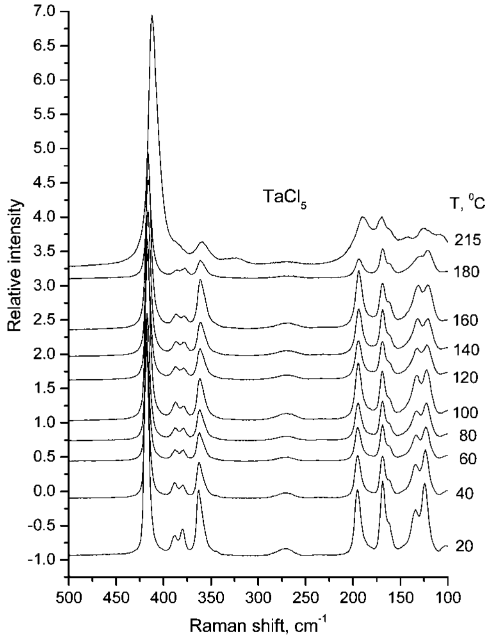


Figure 1. Raman spectra of $TaCl_5$ in the temperature range 20−215 °C recorded with a 532 nm laser (1 s exposure, D1) (D-optical density of the filter).

Experimental Section

Chemicals. 1-Butyl-1-methylpyrrolidinium chloride ($Pyr_{14}Cl$) (Merck, high purity, mp 203 °C) is a white powder that decomposes after melting. It was dried for 48 hours under high vacuum (up to 0.003 mbar) at 80−95 °C in flasks placed in an oil bath with stirring. The water content of the $Pyr_{14}Cl$ after drying, as determined by the Karl Fischer method, was typically 7−8 ppm.

Na_2O was prepared by heating a mixture of sodium oxide and sodium peroxide (Aldrich, 80% Na_2O, containing <20% Na_2O_2) at 600−650 °C in an alumina crucible under high vacuum until gas evolution ceased.[11] After the samples were crushed in a glove box, this procedure was repeated once more.

$TaCl_5$ (mp 211 °C) purchased from Aldrich Chemical Company (99.999%, ampoule packed) was used as received.

Sample Preparation. The mixtures $(x)Pyr_{14}Cl-(1-x)TaCl_5$ form liquids in the range $x = 0.80-0.30$ under heating at different temperatures. The salts were prepared by combining $Pyr_{14}Cl$ with a corresponding amount of $TaCl_5$. The compositions for spectroscopic measurements at various molar ratios of $Pyr_{14}Cl$ and $TaCl_5$ (each totally 0.250 g) were mixed in the glove box (MBraun Star, O_2 and H_2O content below 1 ppm), placed in Pyrex tubes, and melted in an inert atmosphere of argon (99.999%) in an oil bath with stirring until the liquids formed.

The mixtures $(x)Pyr_{14}Cl-(1-x)TaCl_5$ at $Pyr_{14}Cl/TaCl_5$ molar ratios of 0.60/0.40 and 0.40/0.60 are the most easily formed transparent liquids: the first one is a light-yellow liquid formed at ~80 °C, and the second one is colorless and formed at ~130 °C. In the range of compositions $x = 0.53-0.48$, liquids are difficult to form and are not transparent or homogeneous. At high concentrations of $TaCl_5$ ($x = 0.40-0.30$), a small precipitation of white powder was observed on the walls of the tubes during the heating due to the partial volatility of $TaCl_5$. After melting, the samples were quenched.

Spectroscopic Measurements. Raman spectra were recorded using a Raman spectrometer Labram Aramis Vis (Horiba Jobin Yvon) with BX41 microscope. The excitation source was a diode-pumped solid state laser, 532 nm, with nominal output power of ~50 mW. The Raman spectra were obtained in the frequency range of 4000−100 cm^{-1}. The 1 s exposure time gave Raman spectra of good quality in the range of 1000−100 cm^{-1}, whereas in the range of 4000−1000 cm^{-1}, longer exposure times (2−5 s) were necessary to obtain satisfactory spectra.

TABLE 1: Raman Spectral Data for $TaCl_5$ (cm^{-1})[a]

$TaCl_5$[b]		$TaCl_5$[c]		$TaCl_5$[d]			
solid	melt	25 °C	220 °C	20 °C	100 °C	160 °C	215 °C
126	126	125m	127w	124s	122	120	126w
136	143	134m		134m	132	131	143vw
163sh		161sh		162sh	161	161	161sh
171	172	168s	172m	169s	169	169	169m
197	191	196s	193m	196s	194	194	190m
241	240	232w					
274	282	269m	271w	271vw	269	268	
363	362	362s	363w	362s	361	361	360w
381		379m		380m	377	377	
390		388m	389w	389m	389	389	388vw
418	411	419vs	414vs	417vs	417	417	412s

[a] vw, very week; w, week; m, medium; s, strong; vs, very strong; sh, shoulder. [b] See ref 12. [c] See ref 13. [d] This work.

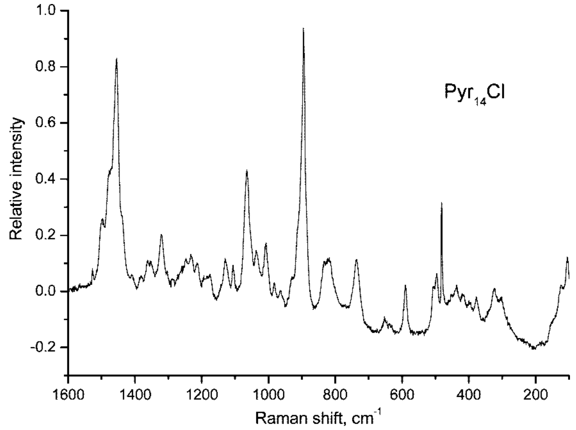


Figure 2. Raman spectrum of $Pyr_{14}Cl$ at 20 °C recorded with a 532 nm laser (5 s exposure, D0).

Raman spectra in the temperature range 20−220 °C were recorded using an assembly designed specifically for the project. It consists of a small natural stone furnace with a compartment for the samples and a thermocouple. The objective of the Raman spectrometer is protected by an optical quartz plate (thickness 0.5 mm).

The samples for Raman measurements were placed in Duran tubes (outer Ø, 3 mm; inner Ø, 1.5 mm) in the glove box, and the tubes were sealed. The samples sealed in Duran tubes were premelted to obtain compact substances.

Results and Discussion

$TaCl_5$ and $Pyr_{14}Cl$. Raman spectra of $TaCl_5$ in the range 20−215 °C are presented in Figure 1. The Raman spectrum of solid $TaCl_5$ was found to be in good agreement with published data.[12,13] The crystal structure of $TaCl_5$ was determined by X-ray structural analysis[14,15] to consist of dimers (Ta_2Cl_{10}) with chlorine atoms forming two octahedra that share a common edge. The Raman spectra of solid and molten $TaCl_5$[12,13] were interpreted as structural Ta_2Cl_{10} units of D_{2h} symmetry with an endothermic monomerization reaction $Ta_2Cl_{10} \leftrightarrow 2\,TaCl_5$ taking place in molten $TaCl_5$ above 300 °C.[13] In Figure 1, a gradual broadening and loss of details in the vibrational features caused

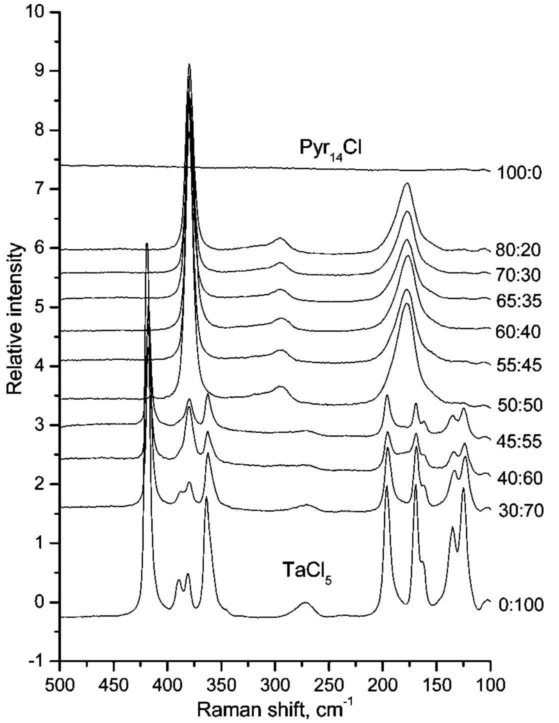


Figure 3. Raman spectra of the solidified (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ mixtures at 20 °C.

by the higher temperatures are observed as the temperature is increased up to 180 °C. Above the melting point, at 215 °C, a Raman spectrum changes and is the same as that for molten TaCl$_5$.[13] The Raman spectrum at 180 °C exhibits the vibrational features between the solid and molten states, demonstrating the reorganization of the TaCl$_5$ crystal structure before melting, meaning Ta$_2$Cl$_{10}$ units are the dominant species in both the premelt and molten states. Raman spectral data for TaCl$_5$ are collected in Table 1.

A Raman spectrum of Pyr$_{14}$Cl is presented in Figure 2. Despite the good resolution of the vibrational features of Pyr$_{14}$Cl, the intensities of the bands are very low as compared to the intensities of the bands of tantalum(V) species in the range 100−1000 cm^{-1}. That is the reason why we do not discuss the Raman spectral behavior of Pyr$_{14}^+$ cations as a function of the temperature or within the mixtures (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ in the present paper.

(x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ Mixtures. The Raman spectra of the solid (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ samples in the range of compositions x = 0.80−0.30 are shown in Figure 3, and the experimental frequencies are collected in Table 2.

The Raman studies were performed in the frequency range of the internal vibrations of tantalum(V) chloride and oxochloride species, 1000−100 cm^{-1}. The spectra of the mixtures (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ (Figure 3) are presented in the frequency range 500−100 cm^{-1} because practically no bands appear between 1000 and 500 cm^{-1}.

The Raman spectrum of Pyr$_{14}$Cl presented in Figure 3 exhibits no bands: their intensities are negligible as compared to those of the tantalum(V) species and are consequently not detectible in the Raman spectra of the (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ mixtures. Therefore, all the bands observed in the range 500−100 cm^{-1} are assigned to the Ta−Cl vibrations of different tantalum(V) species.

The spectra of the basic and neutral (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ mixtures in the range x = 0.80−0.50 exhibit bands at 178 cm^{-1} (s), 294 cm^{-1} (w, br), and 380 cm^{-1} (s). Two strong bands at 178 and 380 cm^{-1} are characteristic bands for octahedral complexes TaCl$_6^-$ (O$_h$) that were identified for different alkali chloride melts containing TaCl$_5$ by means of vibrational spectroscopy.[16] Evidence for the formation of TaCl$_6^-$ octahedra in solid and molten ATaCl$_6$ (A = Na, K, Cs) was also obtained.[13,17] The Raman spectral data for tantalum(V) species are collected in Table 3.

As long as excess of Cl$^-$ anions are present in the mixtures, TaCl$_5$ will be transformed into TaCl$_6^-$ according to the scheme:

$$\text{basic mixture}: 3\mathrm{Cl}^- + 2\mathrm{TaCl}_5 \rightarrow \mathrm{Cl}^- + 2\mathrm{TaCl}_6^- \quad (x = 0.60) \tag{1}$$

In a neutral mixture (x = 0.50), no free Cl$^-$ anions are available:

$$\text{neutral mixture}: \mathrm{Cl}^- + \mathrm{TaCl}_5 \rightarrow \mathrm{TaCl}_6^- \quad (x = 0.50) \tag{2}$$

As observed during sample preparation and according to the data of thermal analysis, ionic liquids in the range of compositions x = 0.53−0.48 are not real liquids; they are neither transparent nor homogeneous.

The Raman spectra of the basic ionic liquids at x = 0.70 and 0.65 were recorded over the temperature range of 20−160 °C, but only the informative spectra are presented in Figure 4 at x = 0.65 (at x = 0.70, the Raman spectra were similar). Above 160 °C, the partial decomposition of ionic liquids was observed according to the following routes:

$$\text{1-butyl-1-methylpyrrolidinium chloride} \rightarrow \text{1-butylpyrrolidine} + \mathrm{CH_3Cl} \tag{3}$$

$$\text{1-butyl-1-methylpyrrolidinium chloride} \rightarrow \text{1-methylpyrrolidine} + \mathrm{C_4H_9Cl} \tag{4}$$

The gradual heating of the samples does not cause the changes in the vibrational features of TaCl$_6^-$ octahedra that were identified in the solid basic (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ mixtures. Above 80 °C, the usual broadening of the bands is observed accompanying the melting process. Octahedral TaCl$_6^-$ complexes remain the main species of tantalum(V) in the basic (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ molten mixtures. New, very week bands appear in the Raman spectra at ~340 and 157 cm^{-1} (sh). One may suggest that they originate from the negligible impurities of oxochloride complexes of tantalum(V) in the excess of Pyr$_{14}$Cl that is the main source of moisture in the system. The presence of even trace amounts of moisture leads to the formation of oxochloride species of tantalum(V) at elevated temperatures.

In a very narrow range of neutral and slightly acidic compositions between x = 0.50–0.45, the dramatic structural changes occur, shifting from the isolated octahedral TaCl$_6^-$ to Ta$_2$Cl$_{10}$ dimers. Data from the DSC have also demonstrated the rapid changes of the thermal behavior in this concentration range.[9] At x = 0.45 (Figure 3), one can still observe the bands of TaCl$_6^-$ species (in negligible amounts) in addition to the bands of the dominating fragments of the quasi-crystal structure of TaCl$_5$.

In the strongly acidic range of x = 0.40−0.30, Pyr$_{14}$Cl is introduced into the fragments of the quasi-crystal structure of TaCl$_5$, and ionic liquids are easily formed above 130 °C due to the suitable mutual space orientation of the Pyr$_{14}^+$ cations and TaCl$_5$. In the Raman spectra for these compositions shown in Figure 3, one can observe the vibrational features of the Ta$_2$Cl$_{10}$

TABLE 2: Raman Spectral Data for the $(x)Pyr_{14}Cl-(1-x)TaCl_5$ Solid Mixtures (20 °C)[a]

compositions			assignment/frequency (cm^{-1})														
complexes	$Pyr_{14}Cl/TaCl_5$					ν_5 (F_{2g})			ν_2 (E_g)			ν_1 (A_{1g})					
	100	0							no bands								
	80	20				178 s			294 w, br			380 s					
$TaCl_6^-$	70	30				178 s			294 w, br			380 s					
O_h	65	35				178 s			294 w, br			380 s					
	60	40				178 s			294 w, br			380 s					
	55	45				178 s			294 w, br			380 s					
	50	50				178s			294 w, br			380 s				416 vw	
	45	55	125 m	135 m	162 w		169 m	196 m		271 vw			362 m	380 m	389 sh		418 s
	40	60	124 m	134 m	162 sh		169 m	195 m		271 vw			362 m	380 s	389 sh		417 s
Ta_2Cl_{10}, D_{2h}	30	70	124 m	133 m	162 sh		169 m	196 m		271 vw			362 m	380 w	387 w		419 s
dimers	0	100	125 s	135 s	162 sh		170 s	196 s		271 w	345 vw		364 s	381 m	389 m		419 vs

[a] vw, very week; w, week; m, medium; s, strong; vs, very strong; sh, shoulder; br, broad.

TABLE 3: Raman Spectral Data for Different Tantalum(V) Species (cm^{-1})[a]

$KTaCl_6$[b]		$NaTaCl_6$	$KTaCl_6$	$CsTaCl_6$[c]	LiCl/KCl	NaCl/CsCl +5 mole % $TaCl_5$ [d]	CsCl	species/assignment
25 °C	420 °C	350 °C	450 °C	600 °C	450 °C	600 °C	620 °C	$TaCl_6^-$
184 m	183 m	172 m	182 m	179 m	185	181	175	ν_5 (F_{2g})
187 m								
302 vw, br								ν_2 (E_g)
386 s	390 s	389 s	387 s	379 s	387	381	378	ν_1(A_{1g})

[a] vw, very week; m, medium; s, strong; br, broad. [b] 13. [c] 16. [d] 15.

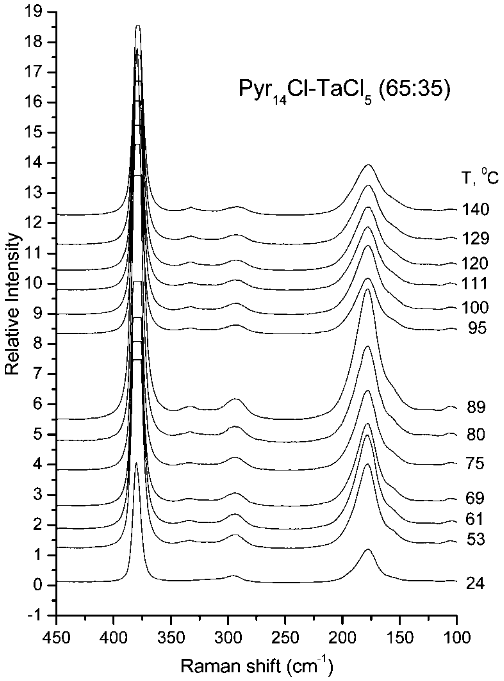


Figure 4. Raman spectra of the $(x)Pyr_{14}Cl-(1-x)TaCl_5$ mixtures at $x = 0.65$ in the temperature range 20−140 °C.

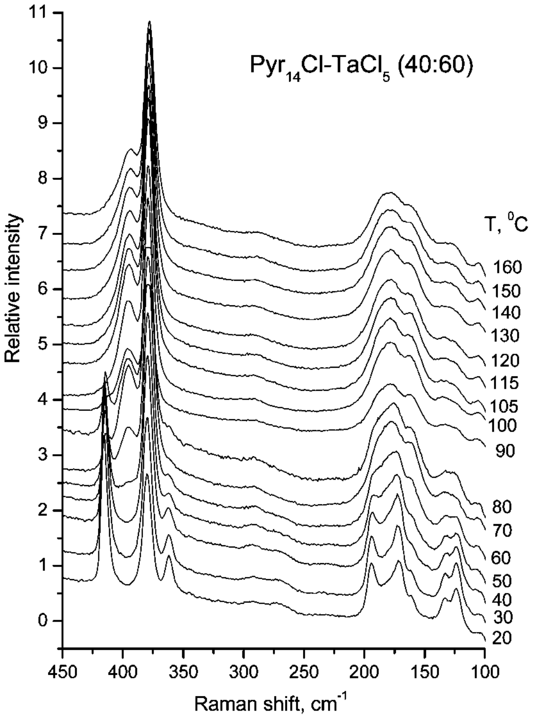


Figure 5. Raman spectra of the $(x)Pyr_{14}Cl-(1-x)TaCl_5$ mixtures ($x = 0.40$) in the temperature range 20−160 °C.

structural units that may be easily identified on the basis of the spectrum of $TaCl_5$ and the results presented above.

The Raman spectra of the mixture $(x)Pyr_{14}Cl-(1-x)TaCl_5$ at $x = 0.40$ in the temperature range of 20−160 °C are shown in Figure 5. It is important to notice that gradual changes occur within the observed spectra before the melting of this mixture at 130 °C and demonstrate the significant structural changes occurring in the solid state. The most pronounced changes are observed in the frequency range of 430−340 cm^{-1}. The intensity of the strongest peak at 415 cm^{-1} decreases until it disappears totally at 90 °C. The same occurs with the peak at 362 cm^{-1}. Simultaneously, the intensity of the band at 379 cm^{-1} increases, and a new band at 396 cm^{-1} appears.

Because of a lack of free Cl^- anions in the ionic liquid at $x = 0.40$, one can suppose the transformation of the fragments

TABLE 4: Areas and Peak Positions of Different Bands of Tantalum(V) Species in the $(x)Pyr_{14}Cl-(1-x)TaCl_5$ Mixtures at $x = 0.40$ in the Temperature Range 20−160 °C (Calculated by Resolving into Gaussian Functions)

T, °C	$TaCl_6^-$		$Ta_2Cl_{11}^-$		Ta_2Cl_{10}	
	area	peak	area	peak	area	peak
20	18.3	379.9			18.8	415.3
30	23.0	379.8			21.1	415.1
40	27.0	379.4			16.7	414.6
50	32.2	379.2			12.6	414.3
60	37.7	378.7	20.3	395.9	8.7	414.3
80	38.8	378.7	25.5	395.7	6.6	414.2
90	26.9	378.7	18.6	395.6	2.2	412.5
100	41.0	378.5	31.0	395.8		
105	41.2	378.5	32.0	395.8		
115	44.0	378.2	33.1	395.4		
120	42.9	378.1	31.3	395.2		
130	42.5	377.9	31.8	395.0		
140	40.9	377.7	32.3	394.6		
150	38.0	377.5	30.8	394.2		
160	32.8	377.4	29.6	393.5		

of quasi-crystal structure, from $[Ta_2Cl_{10}]$ to $Ta_2Cl_{11}^-$ and $TaCl_6^-$ anions according to eq 5:

$$\left.\begin{array}{l} TaCl_5 + Cl^- \rightarrow TaCl_6^- \\ 2TaCl_5 \rightarrow Ta_2Cl_{10} \\ TaCl_6^- + TaCl_5 \rightarrow Ta_2Cl_{11}^- \\ Ta_2Cl_{10} + Cl^- \rightarrow Ta_2Cl_{11}^- \end{array}\right\} \quad (5)$$

In this case, the band at 415 cm^{-1} is assigned to the symmetric Ta−Cl stretching vibration of Ta_2Cl_{10} units, and the band at 379 cm^{-1}, to the stretching Ta−Cl vibration in $TaCl_6^-$ anions. A new band appears at 396 cm^{-1}: it is reasonable to attribute it to the Ta−Cl stretching vibration in $Ta_2Cl_{11}^-$ anions consisting of two octahedra that share a common corner. The position of the band at 396 cm^{-1}, between the Ta−Cl stretching vibrations in Ta_2Cl_{10} units (415 cm^{-1}) and isolated $TaCl_6^-$ anions (379 cm^{-1}), is in accordance with this assignment.

The Raman spectra presented in Figure 5 were evaluated by computer-resolving the bands into sums of Gaussian functions in the range 430−370 cm^{-1}. The following bands were obtained: 379 cm^{-1}, $TaCl_6^-$; 396 cm^{-1}, $Ta_2Cl_{11}^-$; and 415 cm^{-1}, Ta_2Cl_{10} (Table 4). All three bands shift by ~2.5 cm^{-1} between 20 and 160 °C. The calculated distribution of different tantalum(V) species as a function of the temperature is presented in Figure 6. According to these data, at room temperature, one-half of the tantalum(V) exists as $TaCl_6^-$, and one-half as Ta_2Cl_{10}. At 60 °C, the $Ta_2Cl_{11}^-$ species appears in an amount of ~30%, accompanied by a simultaneous decrease in the number of Ta_2Cl_{10} units. When Ta_2Cl_{10} units disappear completely between 90 and 100 °C, the ratio between $TaCl_6^-$ and $Ta_2Cl_{11}^-$ anions remains constant at 57−43% (±0.3%). Some deviations from eq 5 regarding the direction of the formation of excess of $TaCl_6^-$ may be due to the partial volatility of $TaCl_5$, which results in a decrease in the concentration of $TaCl_5$ in the mixture.

The evolution of the vibrational features within the frequency range of 250−100 cm^{-1} as a function of the temperature demonstrates the gradual loss of details and overlapping of the bands, which complicates their quantitative interpretation. One can mention that in the range of 20−50 °C, five bands are observed very clearly: 194, 173, 162 (sh), 132, and 124 cm^{-1}. In the temperature range of 60−80 °C, the transformation of the bands occurs. At 90 °C, only three broad and unclear bands remain: 179, 162, and 127 cm^{-1}. The predominant forms of tantalum(V) chloride species found at various molar ratios of $Pyr_{14}Cl$ and $TaCl_5$ and different temperatures are collected in Table 5.

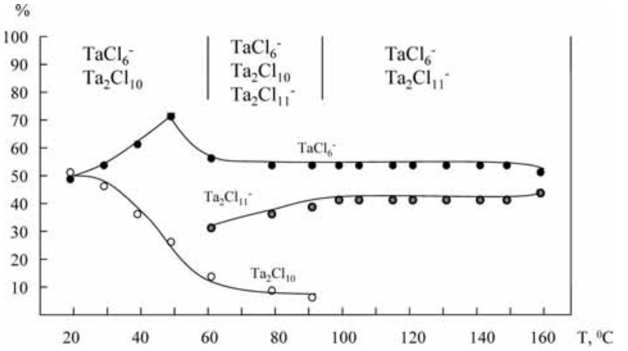
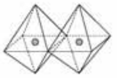
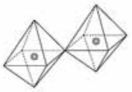
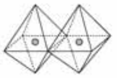
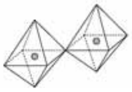


Figure 6. Distribution of different tantalum(V) species as a function of the temperature in the $(x)Pyr_{14}Cl-(1-x)TaCl_5$ mixture at $x = 0.40$.

TABLE 5: Predominant Forms of Tantalum(V) Chloride Species in the $(x)Pyr_{14}Cl-(1-x)TaCl_5$ Mixtures as a Function of Temperature (20−160 °C)

T, °C	Basic and neutral ionic liquids 0.80>x≥0.50	Acidic ionic liquids 0.45 > x> 0.30		
	$TaCl_6^-$ (O_h)	$TaCl_6^-$	$Ta_2Cl_{11}^-$	Ta_2Cl_{10}
20-50 °C				
60-90 °C				
100-160 °C				

$Pyr_{14}Cl-TaCl_5-Na_2O$ Mixtures. The formation of tantalum(V) oxochloride species is undesirable in media used for electrochemical tantalum deposition because they can change the routes of electrochemical reduction of tantalum(V) and lead to the appearance of tantalum oxides in deposits.

The influence of oxygen-containing impurities on the composition and structure of tantalum(V) complexes was investigated for the ionic liquid $(x)Pyr_{14}Cl-(1-x)TaCl_5$ ($x = 0.65$) at various concentrations of Na_2O. The $Pyr_{14}Cl-TaCl_5-Na_2O$ mixtures were synthesized at O/Ta mole ratios equal to 0.5, 1.0, and 2.0; the Raman spectra are presented in Figure 7. A Raman spectrum of the same ionic liquid $(x)Pyr_{14}Cl-(1-x)TaCl_5$ ($x = 0.65$) was also recorded after air was allowed into the cell.

The vibrations of tantalum(V) oxochloride complexes are expected in the frequency range between 1000 and 700 cm^{-1}. Terminal stretching vibration of the Ta=O bond in $TaOCl_5^-$ and $TaOCl_4^-$ was identified at ~925 and ~960 cm^{-1}, respectively.[18,19] Bridging oxygen bonds typically show vibrational bands in the frequency range between 850 and 700 cm^{-1}.[19–21] Tantalum(V) exhibits a considerable tendency to form bridging oxygen bonds between tantalum atoms, even at tantalum concentrations as low as 10−20 mol %.[8,19] The bands due to the bridging oxygen, Ta−O−Ta, in the range 700−850 cm^{-1} are usually very broad and of low intensity in Raman spectra, which makes their attribution very complicated.

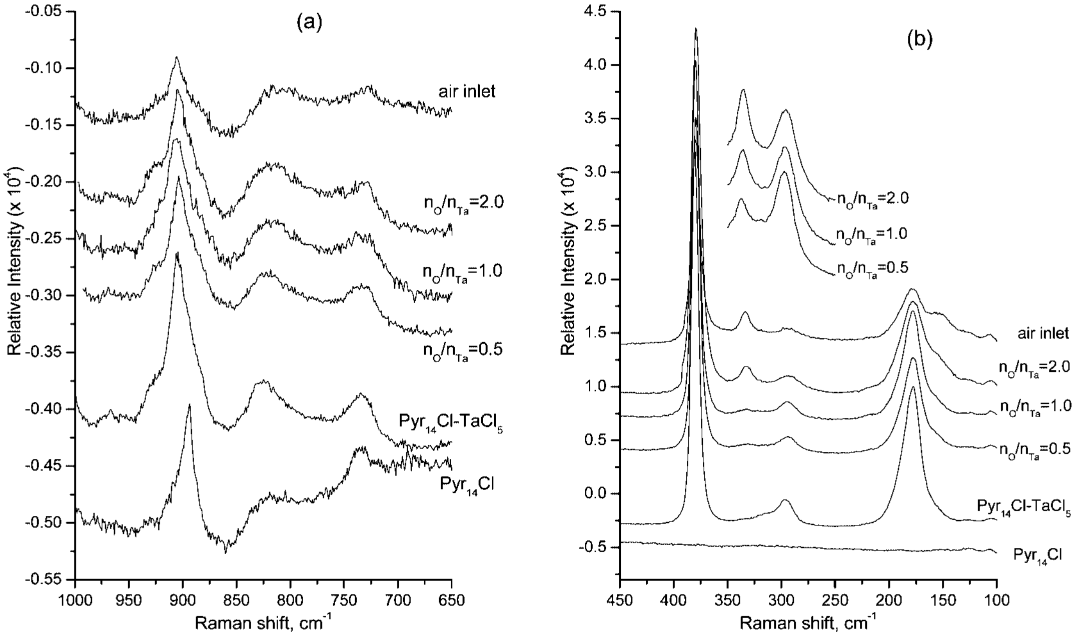


Figure 7. Raman spectra of the $(x)Pyr_{14}Cl-(1 - x)TaCl_5$ mixtures ($x = 0.65$) with the addition of Na_2O at O/Ta mole ratios equal to 0.5, 1.0, and 2.0 and after air was allowed into the cell: (a) -1000 to 650 cm^{-1}; (b) -450 to 100 cm^{-1}.

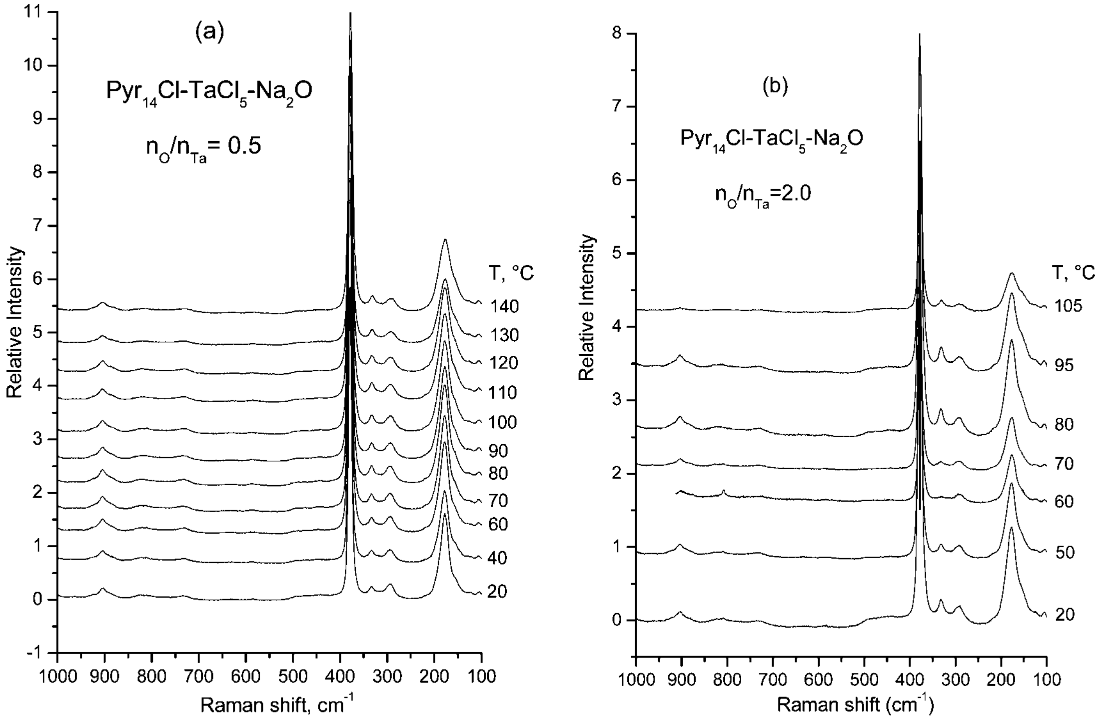


Figure 8. Raman spectra of the $(x)Pyr_{14}Cl-(1 - x)TaCl_5$ mixtures ($x = 0.65$) with the addition of Na_2O at O/Ta mole ratios equal to 0.5 (a) and 2.0 (b) as a function of the temperature.

Raman spectra of the solid samples demonstrate new bands at 333 and 153 cm^{-1}, which become the most pronounced at a O/Ta mole ratio equal to 2.0 and after air was allowed into the cell. Simultaneously, the intensities of the other three bands 380, 297, and 179 cm^{-1} decreased. In the frequency range of the tantalum−oxygen vibrations in different tantalum(V) oxochloride species, the Raman spectra at various O/Ta mole ratios exhibit bands at ~820 and ~730 cm^{-1}. These bands are also observed in the mixture $Pyr_{14}Cl-TaCl_5$ without the Na_2O additive, and it seems reasonable that they originate from $Pyr_{14}Cl$. Some redistribution of the intensity of the band at 905 cm^{-1} in the ionic liquids $Pyr_{14}Cl-TaCl_5-Na_2O$ (appearance of the shoulder at ~930 cm^{-1}) was observed in the mixture $Pyr_{14}Cl-TaCl_5$ and reflects the changes in the vibrational features of the pyrrolidinium ring as the large tantalum(V) species replace the Cl^- anions.

The interpretation of the spectra of the mixtures $Pyr_{14}Cl-TaCl_5-Na_2O$ is not simple because of the possible coexistence of various oligomeric complexes in equilibrium and due to the overlapping with the bands that were observed in this mixture without the Na_2O addition. Nevertheless, some suggestions can be made. First of all, at the high $TaCl_5$ content equal to 35 mol %, one could expect Ta−O−Ta bridging bonds in oligomeric species instead of the terminal Ta=O bonds. The

Raman spectra of the mixture (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ with the TaCl$_5$ content equal to 35 mol % confirm this suggestion: no band belonging to the terminal Ta═O vibrations in $TaOCl_5^-$ (∼925 cm^{-1}) or $TaOCl_4^-$ (∼960 cm^{-1}) complexes was observed as Na$_2$O was added. No evident bands were also observed in the range 700–850 cm^{-1} of Ta–O–Ta bridging bonds. It could be due to the negligible low intensity of these vibrations in the Raman spectra, as was observed in ref 19. Therefore, the Raman bands that increase in intensities when Na$_2$O is added can be explained by the formation of tantalum (V) complexes with bridging Ta−O−Ta bonds. The bands at 333 and 153 cm^{-1} in this case belong to the Ta−Cl vibrations in oxygen-containing oligomeric complexes.

The Raman spectra of the mixture (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$−Na$_2$O at $x = 0.65$ in the temperature range of 20−140 °C are shown in Figure 8. At a O/Ta mole ratio equal to 0.5, the Raman spectra demonstrated the usual changes as the temperature rose. At a O/Ta mole ratio equal to 2.0, the Raman spectra were obtained only up to 105 °C. The spectral behavior is complicated and difficult to interpret due to the incomparable intensities of the bands observed in the Raman spectra at different temperatures. Na$_2$O either did not completely dissolve in the ionic liquid, or the formation of the intermediate compounds occurs, most probably different tantalum oxides, which have a low solubility.

Conclusions

In the basic and neutral mixtures of (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ ($x = 0.80−0.50$), tantalum(V) exists in the form of octahedral $[TaCl_6]^-$ in both solid and molten states up to 160 °C.

In a very narrow range of neutral and slightly acidic compositions between $x = 0.50–0.45$, the dramatic structural changes occur, shifting from the isolated octahedral $TaCl_6^-$ to Ta$_2$Cl$_{10}$ dimers. In this range of composition, liquids are difficult to form and are not transparent or homogeneous.

In acidic ionic liquids ($x = 0.45−0.30$), [Ta$_2$Cl$_{10}$] units are the main species of tantalum(V) identified in the solid state.

In the acidic mixture at $x = 0.40$, the gradual degradation of [Ta$_2$Cl$_{10}$] units already started in the solid state, accompanied by the formation of $[TaCl_6]^-$ and $[Ta_2Cl_{11}]^-$ anions. In the molten state, in the range between 130 and 160 °C, the last two species exist in equilibrium and are the dominant species of tantalum(V).

When Na$_2$O was added to the (x)Pyr$_{14}$Cl−(1 − x)TaCl$_5$ mixture ($x = 0.65$) at various O/Ta mole ratios, oligomeric species with Ta−O−Ta bridging bonds were formed.

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References and Notes

(1) Barnard, P. A.; Hussey, C. L. *J. Electrochem. Soc.* **1990**, *137*, 913–918.

(2) Morimitsu, M.; Matsuo, T.; Matsunaga, M. *Proc. Electrochem. Soc.* **2000**, *99* (41), 117–121.

(3) Morimitsu, M.; Matsunaga, M. Patent. Jpn. Kokai Tokyo Koho; Coden: JKXXAF JP 2001279486 A220011010, 2001.

(4) Zein El Abedin, S.; Farag, H. K.; Moustafa, E. M.; Welz-Biermann, U.; Endres, F. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2333–2339.

(5) Welz-Biermann, U.; Endres, F.; Zein El Abedin, S. Merck Patent GmbH; Patent WO 2006/061081 A2, 2006.

(6) Babushkina, O. B.; Ekres, S.; Nauer, G. E. *7th International Symposium on Molten Salt Chemistry and Technology*, Toulouse, France, 2005; p 319−322.

(7) Babushkina, O. B.; Ekres, S.; Nauer, G. E. *Z. Naturforsch.* **2008**, *63a*, 73–80.

(8) Babushkina, O. B.; Nauer, G. E *Ukr. Khim. Zh. (in English)* **2005**, *72*, 70–73.

(9) Babushkina, O. B. *Z. Naturforsch.* **2008**, *63a*, 66–72.

(10) Babushkina, O. B.; Ekres, S.; Nauer, G. E. *57th ISE Annual Meeting*, Edinburgh, UK, 2006, S5-O-33.

(11) Horsley, G.W. *J. Iron Steel Inst.* **1956**, *1*, 43.

(12) Beattie, I. R.; Gilson, T. R.; Ozin, G. A. *J. Chem. Soc. A* **1968**, 2765–2771.

(13) Huglen, R.; Poulsen, F. W.; Mamantov, G.; Begun, G. M. *Inorg. Chem.* **1979**, *18*, 2551–2555.

(14) Zalkin, A.; Sands, D. A. *Acta Crystallogr.* **1958**, *11*, 615–619.

(15) Rolsten, R. F. *J. Am. Chem. Soc.* **1958**, *80*, 2952–2953.

(16) Voyiatzis, G. A.; Pavlatou, E. A.; Papatheodorou, G. N.; Bachtler, M.; Freyland, W. *International Symposium on Molten Salt Chemistry and Technology, Electrochem. Soc. 93-9*; 1993; p 252−263.

(17) Kipouros, G. J.; Flint, J. H.; Sadoway, D. R. *Inorg. Chem.* **1985**, *24*, 3881–3884.

(18) Fordyce, J. S.; Baum, R. L. *J. Phys. Chem.* **1965**, *69*, 4335–4337.

(19) Rosenkilde, C.; Voyiatzis, G. A.; Ostvold, T. *Acta Chem. Scand.* **1995**, *49*, 405–410.

(20) Sala-Pala, J.; Calves, J. Y.; Guerchais, J. E.; Brownstein, S.; Dewan, J. C.; Edwards, A. J. *Can. J. Chem.* **1978**, *56*, 1545–1558.

(21) Morozov, S.; Lipatova, N. P. *Russ. J. Inorg. Chem.* **1968**, *13*, 1101–1102.

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