Phase Behaviour and FTIR Spectra of Ionic Liquids: The Mixtures of 1-Butyl-1-methylpyrrolidinium Chloride and $TaCl_5$

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Z. Naturforsch. **63a,** 66 – 72 (2008); received July 19, 2007

Presented at the EUCHEM Conference on Molten Salts and Ionic Liquids, Hammamet, Tunisia, September 16 – 22, 2006.

A series of ionic liquids consisting of 1-butyl-1-methylpyrrolidinium chloride ($Pyr_{14}Cl$) and $TaCl_5$ at molar ratios of $Pyr_{14}Cl$ in the range of 0.85 – 0.20 was synthesized. They exhibit potential application as electrolytes for the electrochemical deposition of tantalum. The thermal behaviour of the $Pyr_{14}Cl$-$TaCl_5$ mixtures was investigated, using differential scanning calorimetry (DSC) to estimate the range of thermal stability and to determine the optimal compositions for electrochemical trials. The $Pyr_{14}Cl$-$TaCl_5$ mixtures formed stoichiometric 3 : 2 and 2 : 3 crystalline phases with melting points of 70 °C and 130 °C, respectively, characterized by entropies of fusion of 13.6 $J K^{-1} mol^{-1}$ and 10.1 $J K^{-1} mol^{-1}$. The mixtures with molar fractions of $Pyr_{14}Cl$ equal to 0.60 and 0.40 were clear and transparent liquids and had the lowest viscosity; they were the most suitable for electrochemical applications.

FTIR spectra of the $Pyr_{14}Cl$-$TaCl_5$ mixtures allowed to get insight into inter-ionic interactions and the nature of formation of these ionic liquids as a function of the molar ratio of the components.

Key words: Ionic Liquids; Pyrrolidinium; Tantalum; Thermal Behaviour; FTIR Spectroscopy.

1. Introduction

Low-temperature ionic melts, or ionic liquids, are attractive media for the electrochemical deposition of metals, particularly tantalum, which cannot be obtained from aqueous solutions.

The salts based on the pyrrolidinium cation exhibit conductivity values up to $1.0 \cdot 10^{-6}$ S cm^{-1} in the solid state and $2 \cdot 10^{-3}$ S cm^{-1} in the molten one [1], and have potential as media for electrochemical applications, particularly for lithium batteries. Thermal behaviour as well as other physical properties of ionic liquids based on 1-alkyl-1-methylpyrrolidinium with different anions [such as BF_4^-, trifluoromethanesulfonyl anion, (trifluoromethanesulfonyl) imide anion] and with the addition of LiX salts were extensively studied [2 – 7].

In our previous studies [8, 9] we have reported that 1-butyl-1-methylpyrrolidinium chloride ($Pyr_{14}Cl$) and $TaCl_5$ form an ionic liquid at a $Pyr_{14}Cl : TaCl_5$ molar ratio equal to 65 : 35 above 70 °C. It exhibits a wide window of electrochemical stability (more than 6 V) and shows promising properties as an electrolyte for the electrochemical deposition of tantalum at 140 – 150 °C. It was found that $Pyr_{14}Cl$ and $TaCl_5$ mixtures also form liquids at molar ratios of the components close to 65 : 35, namely 60 : 40 and 67 : 33.

Motivated by the search for optimal compositions for the electrochemical application, a series of ionic liquids consisting of 1-butyl-1-methylpyrrolidinium chloride and $TaCl_5$ with $Pyr_{14}Cl$ molar ratios in the range 0.85 – 0.20 was synthesized. Their thermal behaviour was investigated using differential scanning calorimetry (DSC) to estimate the thermal stability of the mixtures and their applicability for the electrochemical deposition of tantalum. Simultaneously, FTIR spectra of the quenched samples were recorded to determine the structure and composition of tantalum(V) species in the ionic liquids and the nature of their interactions with different functional groups of the organic component.

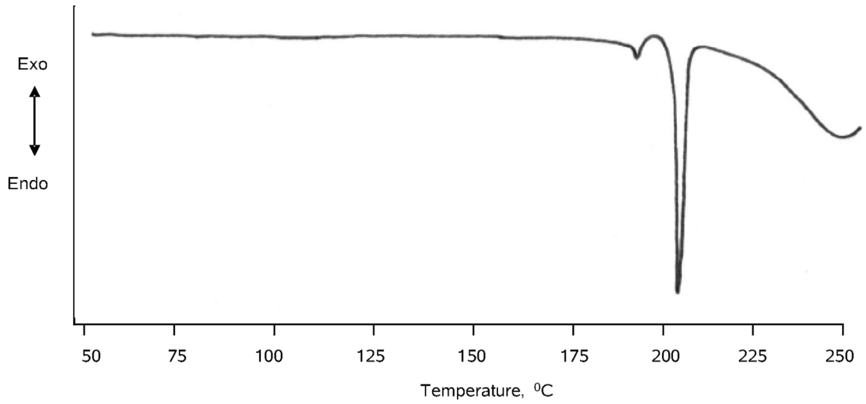

Fig. 1. DSC heating trace of $Pyr_{14}Cl$ (scan rate 3 °C/min).

2. Experimental

2.1. Chemicals

$Pyr_{14}Cl$ (Merck, high purity) is a white powder with m. p. 203 °C decomposing at 210 °C. It was preliminary dried under high vacuum (up to 0.003 mbar) at 80 – 100 °C for 48 h. The water content in $Pyr_{14}Cl$ after drying, estimated by the Karl Fischer method, was typically 7 – 8 ppm. $TaCl_5$ (m. p. 211 °C) from Aldrich Chemical Company (99.999%, ampoule-packed) was used without preliminary purification.

2.2. Samples Preparation

The mixtures of $Pyr_{14}Cl$ and $TaCl_5$ form liquids when the molar ratio of $Pyr_{14}Cl$ is within the range 0.85 – 0.20. The samples for thermal measurements with various $Pyr_{14}Cl$ and $TaCl_5$ molar ratios (0.250 g of each composition) were prepared by mixing the components in a glove box MBRAUN Star, with an O_2 and H_2O content below 1 ppm, placing them in Pyrex tubes and melting them in an inert argon atmosphere (99.999%) with stirring in an oil bath. This process took 30 min to 2 – 3 h, depending on the composition. To obtain compositions with 45 – 55 mol% $TaCl_5$ was very difficult, and they were not entirely transparent or homogeneous. Heating of these mixtures with intensive stirring for 2 – 3 h was ineffective, and increasing the temperature above 180 °C led to the decomposition of the organic component, $Pyr_{14}Cl$, with evolution of CH_3Cl. The same decomposition process was observed for many mixtures heated above 180 °C. Visual observations showed that compositions of $Pyr_{14}Cl$ and $TaCl_5$ with molar ratios equal to 60 : 40 and 40 : 60 are the most easily formed transparent liquids: the first one is a light-yellow liquid, melting at ~ 80 °C, and the second one is a colourless liquid, melting at ~ 130 °C. At high $TaCl_5$ contents (60 – 80 mol%) a light precipitation of a white powder was observed on the walls of the tubes due to the partial volatility of $TaCl_5$.

2.3. Thermal Measurements

Thermal measurements were performed using a differential scanning calorimeter DSC821^e Mettler Toledo. Standard samples of indium were used for the calibration of temperature and power measurements over the temperature range 30 – 180 °C. The samples for DSC measurements (about 10 mg) were placed in standard aluminium pans (40 µl), hermetically sealed in a glove box with an argon atmosphere (99.999%) and heated from 30 to 180 °C at a scan rate of 3 °C/min.

2.4. Spectroscopic Measurements

FTIR internal reflection spectra (Golden Gate ATR-unit with KRS5-lens) of the same samples as for DSC measurements (quenched samples) were recorded using a Bruker FTIR spectrometer Equinox 55 with a MCT nitrogen-cooled detector in the range 200 – 4000 cm^{-1} at room temperature.

3. Results and Discussion

3.1. DSC Measurements

A DSC thermogram of $Pyr_{14}Cl$ is presented in Figure 1. $Pyr_{14}Cl$ exhibits an endothermic peak at 193 °C and melts at 203 °C. The thermal behaviour of $Pyr_{14}Cl$ is associated with the existence of two phases, and

Table 1. Thermal properties of $Pyr_{14}Cl$-$TaCl_5$ mixtures at various molar ratios of the components (water content < 10 ppm).

Molar ratio $Pyr_{14}Cl : TaCl_5$	T (°C)	ΔS ($J\,K^{-1}mol^{-1}$)	T (°C)	ΔS ($J\,K^{-1}mol^{-1}$)	T (°C)	ΔS ($J\,K^{-1}mol^{-1}$)	T (°C)	ΔS ($J\,K^{-1}mol^{-1}$)
100 : 0					193.3	3.2	202.8	27.4
85 : 15	69.1	2.2	79.6	4.7				
80 : 20	70.7	3.7	80.6	5.8				
75 : 25	71.1	5.2	80.8	5.9				
70 : 30	70.5	5.7	80.3	6.4				
67 : 33	71.3	5.3	83.8	4.0				
65 : 35	72.6	8.1	78.9	1.0				
63 : 37	71.6	13.6						
60 : 40	71.7	11.0						
55 : 45	71.1	6.5						
53 : 47	69.4	3.6			126.1	0.1	130.9	0.1
52 : 48	69.5	2.0			126.1	0.1	131.7	0.7
51 : 49	65.7	1.0			127.7	0.2	131.3	0.5
50 : 50					126.2	0.6	131.1	0.1
48 : 52					126.8	0.1	131.5	1.2
40 : 60					126.1	4.9	131.1	10.1
30 : 70							130.5	11.6
20 : 80							130.5	9.4

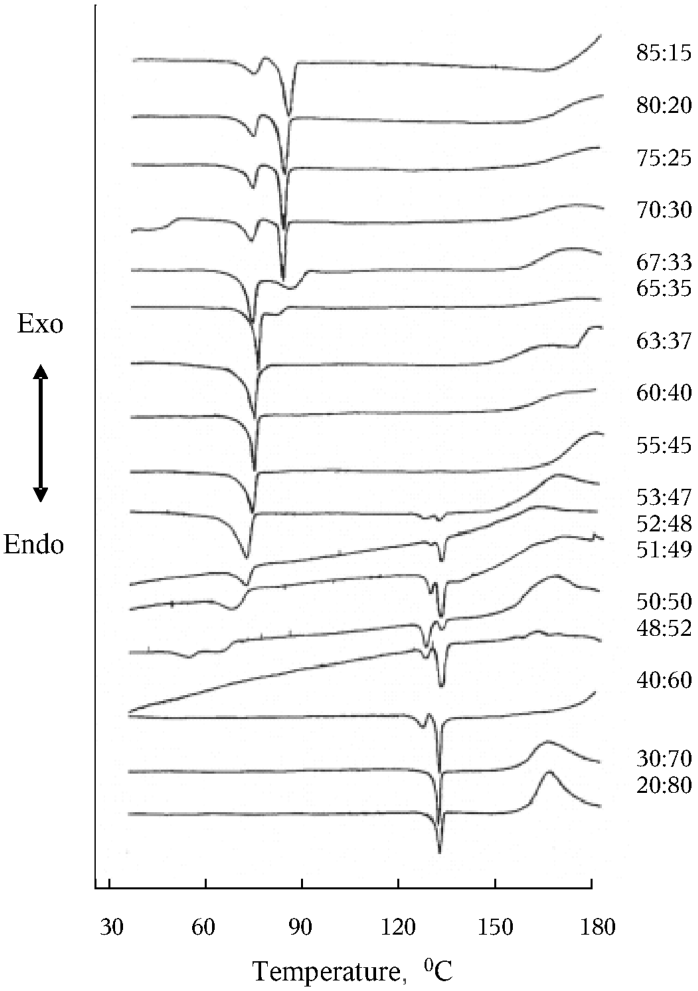

Fig. 2. DSC heating traces of $Pyr_{14}Cl$-$TaCl_5$ mixtures (scan rate 3 °C/min).

the endothermic peak at 193 °C can be attributed to the phase transition in a solid state. Above its melting point, at ∼ 210 °C, $Pyr_{14}Cl$ decomposes and cannot be used for electrochemical applications. $TaCl_5$ melts at 211 °C and is volatile above its melting point.

In spite the fact that both initial components, $Pyr_{14}Cl$ and $TaCl_5$, have melting points above 200 °C and are not stable after melting, the salts synthesized at various molar ratios of the components are stable. DSG heating traces in Fig. 2 show the gradual transformation of the thermal behaviour of $Pyr_{14}Cl$-$TaCl_5$ mixtures as a function of the composition. Thermal properties of $Pyr_{14}Cl$-$TaCl_5$ mixtures at various molar ratios of the components are collected in Table 1.

In the range of 85 – 70 mol% $Pyr_{14}Cl$, two endothermic peaks are observed at 70 and 80 °C which can be associated with two coexisting phases. Starting at 67 mol% $Pyr_{14}Cl$ the peak at 80 °C is decreased, almost disappearing at 63 mol% $Pyr_{14}Cl$. The endothermic peak at 70 °C is the only one which remains at 60 mol% $Pyr_{14}Cl$. In this range of composition the DSC thermograms exhibit binary mixtures behaviour with an eutectic point at 60 mol% $Pyr_{14}Cl$ and a melting point of 70 °C. These liquids form very quickly and are the most transparent.

At high concentrations of $TaCl_5$ (60 – 80 mol% of $TaCl_5$) the mixtures melt above 130 °C with a corresponding endothermic peak. The mixture at 60 mol% $TaCl_5$ is a thermally stable, transparent, colourless liquid. At higher concentrations of $TaCl_5$ an exothermic peak appears in the DSC thermogram above 150 °C, and its intensity is increased with increasing $TaCl_5$ content. This can be caused by a chemical reaction between partially volatile $TaCl_5$ and the aluminium pan.

In the composition range of 53 – 48 mol% $Pyr_{14}Cl$ the thermal behaviour of the $Pyr_{14}Cl$-$TaCl_5$ mixtures is intermediate between two structural states described above and is characterized by the coexistence of thermal effects typical for each of them. Forming liquids in this range is very difficult and they are not homogeneous and transparent.

The mixtures with $Pyr_{14}Cl$ molar fractions equal to 0.60 and 0.40 are clear and transparent liquids with entropies of fusion of 13.6 $J\,K^{-1}\,mol^{-1}$ and 10.1 $J\,K^{-1}\,mol^{-1}$, respectively. According to Timmerman's criteria [10], $Pyr_{14}Cl$-$TaCl_5$ mixtures with entropies of fusion below 20 $J\,K^{-1}\,mol^{-1}$ can be defined as ionic plastic crystals.

The data from the thermal analysis allow to conclude that besides the $Pyr_{14}Cl$-$TaCl_5$ ionic liquid with the molar ratio of 65 : 35 which was found previously to be successful as the electrolyte for the electrochemical deposition of tantalum, another promising composition is at 60 mol% $TaCl_5$. The mixtures at higher $TaCl_5$ contents are not suitable for electrochemical application due to the partial volatility of $TaCl_5$.

Table 2. Experimental frequencies and tentative assignments of the bands observed in the FTIR spectrum of $Pyr_{14}Cl$.

Frequency[a]	Tentative assignment
2999 sh	C-H stretching in CH_3
2964 vs	C-H stretching in CH_2
2939 s, sh	C-H stretching in CH_2
2876 s	C-H stretching in CH_2
1464 vs	CH_3 scissoring (connected with N-atom)
1381 w	CH_2 in C_4H_9
1349 w	CH_2 twisting
1316 w	CH_2 twisting
1316 w	CH_2 twisting
1131 w	CH_2 twisting
1061 m	ring mode
1032 w	CH_2 wagging in C_4H_9
1006 m	CH_2 wagging in C_4H_9
963	ring mode C-N stretching
929 m	ring mode
912 s	ring mode C-C stretching
892 m	ring mode (symmetric ring breathing)
832 w	CH_2 rocking
767 w	
748 w	
634 vw	ring mode
589 w	ring-deformation mode

[a] sh, shoulder; vs, very strong; s, strong; w, weak; v, very weak; m, medium.

3.2. FTIR Spectroscopy of $Pyr_{14}Cl$-$TaCl_5$ Mixtures

The FTIR spectrum of $Pyr_{14}Cl$ is presented in Fig. 3 and the experimental IR frequencies are collected in Table 2. The tentative assignments of the internal vibrations of $Pyr_{14}Cl$ are made based on the results reported for bis (pyrrolidinium) chloride-hexachloroantimonate(V) [11], 1-methyl-1-propylpyrrolidinium cation [1], di-methylpyrrolidinium iodide [12], and pyrrolidine and N-D pyrrolidine [13, 14]. The structure of $Pyr_{14}Cl$ results from the electrostatic interactions among anions and cations, the hydrogen bonding interaction among the chloride anions and the ring as well as the substituents' hydrogen atoms, and a weak interaction among the butyl chains which could have a parallel orientation.

The spectrum of $TaCl_5$ in the far-infrared range (Fig. 3) is characterized by a broad band with a maximum at 398 cm^{-1} and is in agreement with data reported in [15]. The crystal structure of $TaCl_5$ consists

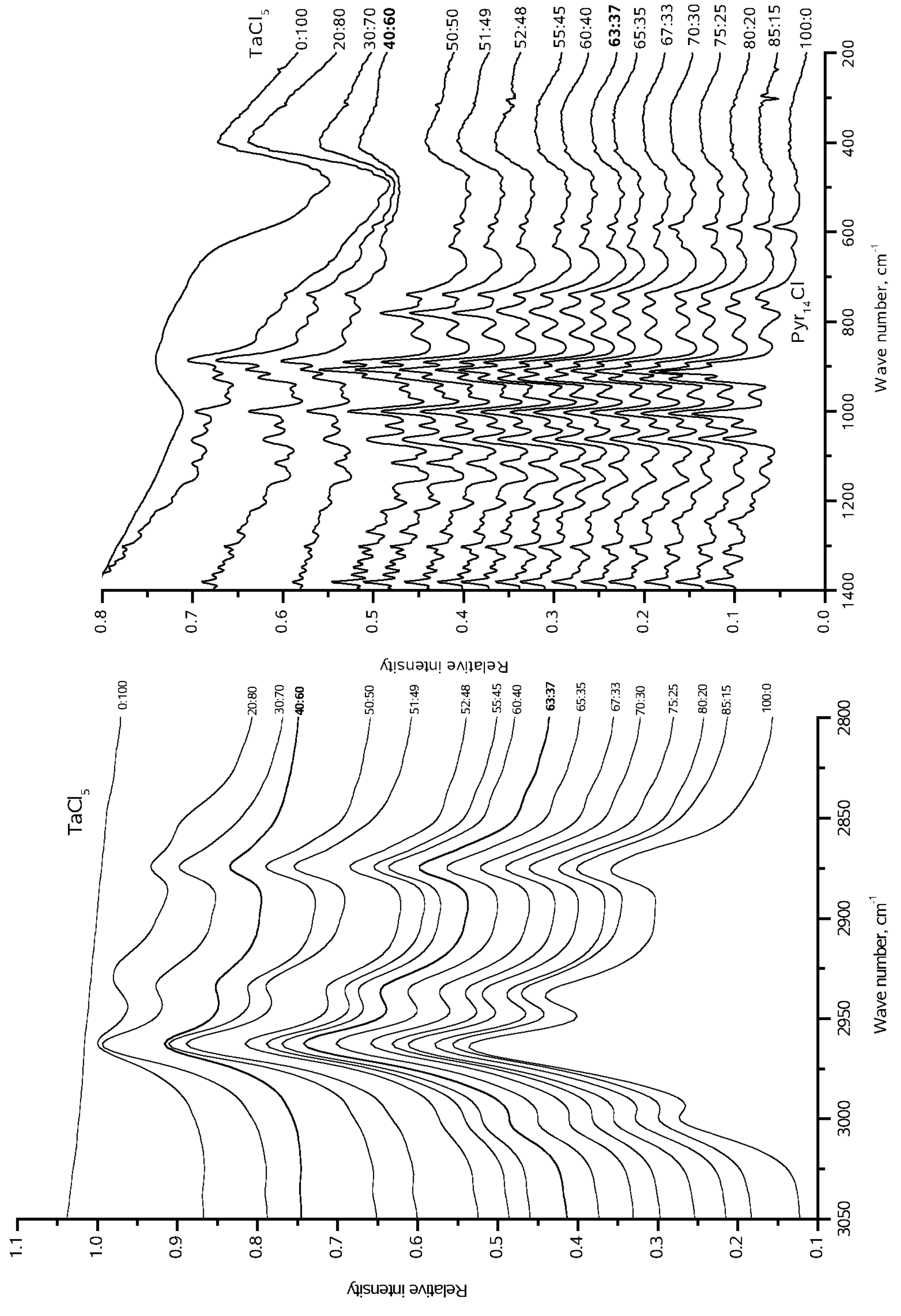

Fig. 3. FTIR spectra of the quenched Pyr$_{14}$Cl-TaCl$_5$ mixtures at various molar ratios of the components.

of dimers (Ta_2Cl_{10}) with chlorine atoms forming two octahedra sharing a common edge [16]. $TaCl_5$ was investigated in different alkali chlorides by means of vibrational spectroscopy, and the evidence for the formation of $[TaCl_6]^-$ of octahedral structure was reported [17 – 19].

FTIR spectra of $Pyr_{14}Cl$-$TaCl_5$ mixtures at various molar ratios of the components (Fig. 3) reflect the changes of the vibration features of the pyrrolidinium cations caused by transformation of the mutual space orientation of the pyrrolidinium cations, and inorganic anions like the Cl^- anions are gradually replaced by $[TaCl_6]^-$ anions.

The formation of the ionic liquid $Pyr_{14}Cl$-$TaCl_5$ at the molar ratio 63 : 37 occurs according to the reaction

$$2\,C_9H_{20}NCl + TaCl_5 \rightarrow 2\,(C_9H_{20}N)^+ + [TaCl_6]^- + Cl^-.$$

As the mole fraction of $TaCl_5$ in $Pyr_{14}Cl$-$TaCl_5$ increases from 0.15 to 0.50, the anionic composition changes, and theoretically, at the molar ratio $Pyr_{14}Cl$-$TaCl_5$ equal to 50 : 50, no free Cl^- anions are present in the ionic liquid. The main species present in the basic $Pyr_{14}Cl$-$TaCl_5$ mixtures are the octahedral $[TaCl_6]^-$ complexes but their content depends strongly on the composition of the ionic liquid.

The most pronounced changes of the vibration features of the $Pyr_{14}Cl$-$TaCl_5$ ionic liquids are observed in the range 890 – 970 cm^{-1} for the breathing vibrations of the pyrrolidinium ring and at 589 cm^{-1} for the ring deformation mode. The relative intensities of the bands at 892, 912, 929 cm^{-1} bands are changed significantly. The most pronounced effect is observed for the 929 cm^{-1} band which is registered as a shoulder at the molar ratio 50 : 50. At the same time the position of the bands of this triplet stay constant, excluding the small shifts resulting from the redistribution of the relative intensities of the bands. The vibration of pure $Pyr_{14}Cl$ at 963 cm^{-1} splits in two bands, 965 and 950 cm^{-1}. The breathing vibrations of pyrrolidinium cations are the most sensitive to the influence of increased fractions of $[TaCl_6]^-$ anions. FTIR spectra also exhibit numerous small changes in the wagging and twisting modes.

The evolution of the Ta-Cl vibrations in different chloride species is not so pronounced, and as the content of $TaCl_5$ decreases, one can observe the broadening of the band at $\sim$ 400 cm^{-1} with a simultaneous decrease in its intensity.

$Pyr_{14}Cl$ melts at 203 °C and is not stable after melting. The introduction of $TaCl_5$ in small amounts (15 mol%) leads to the stabilization of the $Pyr_{14}Cl$ structure due to the formation of $[TaCl_6]^-$ complexes which refill the vacancies between the $Pyr_{14}{}^+$ cations, increasing the influence of the electrostatic component for the stability of the structural units.

As the content of $TaCl_5$ increases and $TaCl_5$ is introduced step by step into the structure of $Pyr_{14}Cl$ in the form of $[TaCl_6]^-$ anions, the weak H-H interaction between butyl chains can also be interrupted and replaced by the formation of the stronger Cl-H bonds between $[TaCl_6]^-$ octahedra and H atoms. In this case the bonds can be formed both with H atoms of methyl and butyl groups and with H atoms of CH_2 groups from the pyrrolidinium ring.

In the case of high $TaCl_5$ content (above 60 mol%), the molecules of $Pyr_{14}Cl$ are introduced in the crystal structure of $TaCl_5$ where the dominant species are Ta_2Cl_{10} dimers. One can suggest the structure of the acidic ionic liquids partially consisting of $[TaCl_6]^-$ octahedra and the fragments of the quasi-crystal structure of $TaCl_5$ which are incorporated by $Pyr_{14}{}^+$ cations.

FTIR spectra of $Pyr_{14}Cl$-$TaCl_5$ mixtures are in good agreement with the thermal data, showing the gradual delicate changes of the vibrational features in the range 85 – 50 mol% $Pyr_{14}Cl$, where the $[TaCl_6]^-$ octahedra are the structural units of tantalum(V), and significant changes above 60 mol% $TaCl_5$, where the fragments of the quasi-crystal structure of $TaCl_5$ become the dominant ones.

4. Conclusions

$Pyr_{14}Cl$-$TaCl_5$ salts obtained at the molar fraction of $Pyr_{14}Cl$ in the range 0.85 – 0.20 form stoichiometric 3 : 2 and 2 : 3 crystalline phases with melting points of 70 °C and 130 °C, respectively. These mixtures are clear and transparent liquids with the lowest viscosity, making them the most suitable for electrochemical applications.

FTIR spectra of $Pyr_{14}Cl$-$TaCl_5$ mixtures reflect the gradual evolution of the vibrational features of the pyrrolidinium cations. The interaction of $[TaCl_6]^-$ ions is connected with the reorientation motion of the pyrrolidinium ring. The breathing vibrations of pyrrolidinium cations are the most sensitive to the influence of the increased fraction of $[TaCl_6]^-$ anions. The best mutual space orientation of the cations and anions is achieved at molar fractions of $Pyr_{14}Cl$ equal to 0.60 and 0.40, with the formation of two crystalline phases.

The $Pyr_{14}Cl$-$TaCl_5$ ionic liquids have important advantages comparing with high-temperature molten alkali chloride electrolytes: the operating temperatures are below 170 °C, and they have negligible vapour pressures.

Acknowledgement

The financial support within the K plus Programme provided by the Austrian Government via Technology Impulse GmbH and by the Government of Lower Austria is gratefully acknowledged.

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