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Thermal properties of 1-alkyl-3-methylpyridinium halide-based ionic liquids

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Abstract

This study was carried for the compare of thermal properties that determinate in various conditions and methods, including of the differential scanning calorimetry (DSC), thermogravimetry (DTG) and the Boëtius heated stage. Were synthesized of series 1-alkyl-3-methylpyridinium chloride- and bromide-based ionic liquids having alkylic chain lengths ranging from C_2 to C_{10}, and defined their thermal characteristics: glass transitions, melting and decomposition. Detailed thermal properties of ionic liquids, which obtained in this work, can be useful in a variety chemical engineering processes that are related with their application.

Keywords: ionic liquids; pyridinium salts; DSC; TGA; melting point; decomposition.

1. Introduction

Ionic liquids (ILs) defined as organic salts with melting points up to 100 °C and consisting of organic cation and organic or inorganic anion, in recent years found wide application in various fields of science and technology. Their unique properties such as high thermal stability, ability of regeneration, low flammability, low vapor pressure, electric conductivity make them promising for use in processes of separation and extraction [1 – 2], catalysis [3 – 4], electrochemistry [5], analytics [6], and use ILs as a solvents for many different reactions [7 – 8]. In the last two decades researchers focused attention on ILs as the solvents in biomass processing [9 – 11], especially for dissolution of cellulose [12 – 22] and other natural polymers [23], and preparation from this solutions new biodegradable materials, including films, membranes, and fibers [24]. Thus ILs represents a new class of direct solvents for natural polymers.

Cellulose can be dissolved with the ILs containing such cations as imidazolium, ammonium and pyridinium, and the following anions: bromide, chloride, acetate, etc [25].

Pyridinium cation-based ionic liquids have proved to be effective solvents for cellulose [13 – 15]. The first patent of the use of pyridinium chloride-based salts for cellulose dissolution was published by Graenacher [16]. However, at present one can find only few works devoted to investigation of pyridinium ILs dissolving power and other physical and chemical properties.

Dissolving power of pyridinium ILs depends on their chemical structure, especially on the type of anion, the length, number and the position of alkylic substituent in the pyridinium rings. It was revealed that 1-alkyl-3-methylpyridinium salts had the greatest dissolving power [14]. It is also known that with increasing of the alkylic chain length the dissolving power toward the cellulose is decreased.

It is necessary to select conditions of natural polymers dissolving within the temperature range in which the pyridinium-based ILs exist in liquid phase, melting and decomposition points of these compounds become important characteristics for processing of biopolymers by means of dissolving. Literature concerning these data is not numerous and the results described in these works are conflicting, their differences in the value may be more than 10 °C [13, 18, 20].

It is known that the thermal properties of many substances may be highly dependents from the method and the measurement conditions. However, detailed information on these properties is very important in the chemical engineering processes.

In order to find out the detailed thermal characteristics of the series of 1-alkyl-3-methylpyridinium halide-based ionic liquids ($[C_nMPy]X$) were synthesized. These compounds had different alkylic chain length from C_2 to C_{10} as well as allylic substituent and bromide- and chloride-anions. Thermal investigations of these ILs were conducted using different methods.

2. Materials and Methods

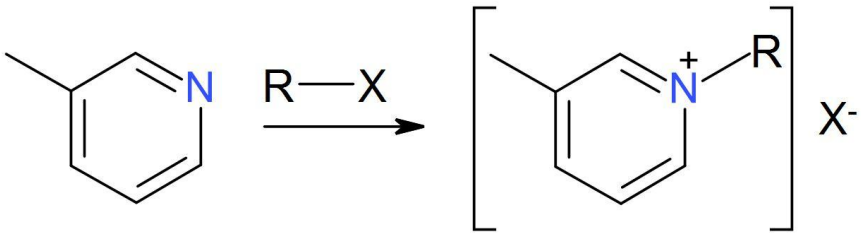
2.1. Reagents

The following chemicals were used in our work: allyl chloride (Fluka, 98 %), acetonitrile (Lab-scan analytical science, 99.9 %), 1-bromoethane (Aldrich, 98 %), 1-brombutan (Aldrich, 99 %), diethyl ether (Aldrich), 3-picoline (Aldrich, 99 %), toluene (Aldrich), 1-chloroethane (Aldrich, ≥ 99.7 %), 1-chloropropane (Aldrich, 98 %), 1-chlorobutane (Aldrich, 99 %), 1-chloropentane (Fluka, ≥ 99 %), 1-chlorohexane (Fluka, > 99 %), 1-chloroheptane (Aldrich, 99 %), 1-chlorooctane (Aldrich, 99 %), 1-chlorononane (Aldrich, 98 %), 1-chlorodecane (Aldrich, 98 %).

2.2. Methods

2.2.1. Synthesis of 1-alkyl-3-methylpyridinium halide-based ILs

1-Alkyl-3-methylpyridinium halide salts were prepared by the alkylation reaction of 3-picoline with required alkyl halide (R — X) using standard procedure [17] according to the following scheme:



The used method was modified to increase the product yield: alkyl halide (0.2000 mol) was added into two-neck round-bottom flask with the solution of 3-substituted pyridine (0.1665 mol) in toluene (20 ml). The solution was then stirred

using a magnetic stirrer under a nitrogen atmosphere for 1 h at room temperature. After that the reaction mixture has been stirred at 110 - 130 °C for 24 - 48 hours to reflux condenser plant without access to nitrogen. After the reaction completion the obtained product delaminated; the dense layer of ionic liquid was decanted from the toluene layer. The product was washed with toluene. Recrystallization was carried out by dissolution in acetonitrile followed by precipitation in excess of diethyl ether. Volatile organic compounds have been removed for 6 – 8 h using the rotary evaporator (Rotavapor R-215, Büchi), at pressure gradual decrease from atmospheric one to 20 – 120 mbar, and temperature rise from 60 °C to 90 °C – 140 °C.

Twelve ionic liquids were synthesized. It is chloride-based ILs containing different alkylic substituents in the cation: 1-ethyl-3-methylpyridinium ([C_2MPy]Cl), 1-propyl-3-methylpyridinium ([C_3MPy]Cl), 1-butyl-3-methylpyridinium ([C_4MPy]Cl), 1-pentyl-3-methylpyridinium ([C_5MPy]Cl), 1-hexyl-3-methylpyridinium ([C_6MPy]Cl), 1-heptyl-3-methylpyridinium ([C_7MPy]Cl), 1-octyl-3-methylpyridinium ([C_8MPy]Cl), 1-nonyl-3-methylpyridinium ([C_9MPy]Cl), 1-decyl-3-methylpyridinium ([C_{10}MPy]Cl), 1-allyl-3-methylpyridinium ([AMPy]Cl); and bromide-based ILs with two cation: 1-ethyl-3-methylpyridinium ([C_2MPy]Br), and 1-butyl-3-methylpyridinium ([C_4MPy]Br).

2.2.2. Characterization of ILs

The obtained salts were identified using nuclear magnetic resonance with respect to ^{1}H nuclei (spectrometer Bruker Avance II Plus 700 MHz), Fourier transform infrared spectroscopy (Nicolet 6700 FT-IR), and liquid chromatography-mass spectrometry (spectrometer GCMSQP2010 Plus, Shimadzu). Water content was determined by thermogravimetric analysis (S**TA**R^{e} TGA/DSC 1 system, Mettler Toledo). As an example ^{1}H NMR spectrum of 1-ethyl-3-methylpyridinium chloride is given in Fig. 1. The absence of peaks corresponding to initial reagents and external impurities indicated the correct choice of synthesis and purification methods. The water content of the ILs was determine by TGA using argon as the protective gas, it is did not exceed 0.1 wt%.

2.2.3. Thermal study of ILs

Differential scanning calorimetry (NETZSCH-Gerätebau GmbH Thermal Analysis DSC 204), thermogravimetry methods (F. Paulik J. Paulik L. Erdey system) and Boëtius heated stage (VEB Wägetechnik Rapido) with an optical microscope of visual device RHMK 05 (with increasing in 16×) were used for thermal analysis.

The conditions of the experiment are shown in Table 1.

3. Results and Discussion

3.1. Glass transition and melting of ILs

Solid-liquid phase transitions of the investigated ILs (Table 2) were defined using the DSC-method. Melting points were not identified for all ILs samples because of the absence of distinct peaks in some cases.

After glass transition substances began to melt, as it followed from appearance of a broad endothermic peak at DSC curve, for instance, for melting of the salt [C_4MPy]Cl (Fig. 2a).

It should be noted that the glass transition were not revealed for all ILs. As appeared the DSC-method was not useful to find out melting points of some ILs, mainly with an odd number of carbon atoms in the alkylic chain. Most of the melting peaks obtained by DSC were not clearly defined. It was impossible to determine the melting point of [C_4MPy]Br by means of DSC, but that IL was a greenish-brown viscous liquid at room temperature, and therefore it could be related to room temperature ionic liquid (RTIL) species. In contrast, the salt [C_2MPy]Br, due to the high value of its melting point, was not considered as an ionic liquid.

In general, there was noticed the tendency to reducing the melting point values of 1-alkyl-3-methylpyridinium chloride-based ILs with the lengthening of the alkylic chain. This trend could be explained by the decrease in packing density of ion pairs of IL under increase in number of the alkylic chain carbon atoms [15, 19]. The existing data concerning melting points of imidazolium-based ILs [26 – 31] and ammonium-based ILs [32 – 33] demonstrated the same tendency.

Conducted investigations showed that melting points identified by DSC were different from those obtained by use of a heated stage. These probably could be explained by the difference in applied heating techniques: in an atmosphere of inert nitrogen or air. Taking into consideration that these ILs were highly hygroscopic their samples could absorb air moisture during heating on the Boëtius stage, and that could affect the results. There were published data with different melting point values for dehydrated and water-containing ILs [26]. The values of melting points obtained under different atmospheric conditions might be useful for processes running either in nitrogen atmosphere or air.

3.2. Decomposition of ILs

Table 3 represents values of the salts decomposition temperature obtained by different methods. Complete decomposition of ILs occurred at temperature about 250 °C (fig. 2b). The decomposition temperature values slightly decreased with growth of the alkylic chain length. And again quaternary pyridinium salts, $[C_2MPy]Cl$ and $[C_3MPy]Cl$, appeared to be the exceptions, as well as they were in the melting point tendency. Change of the anion ambiguously affected the decomposition temperature, thus $[C_2MPy]Br$ decomposed at higher temperature than $[C_2MPy]Cl$ but the decomposition temperature of bromides and chlorides having the $[C_4MPy]^+$ cation were comparable.

4. Conclusions

A comparative study of the thermal properties of 1-alkyl-3-methylpyridinium-based IL was performed. This study included variety methods that allowed to get detailed of the thermal characteristics of series of quaternary pyridinium salts. 1-Alkyl-3-methylpyridinium chlorides with alkylic chain length C_2-C_{10} were in liquid state at temperatures ranging from 70 – 130 °C till their decomposition at 230 – 250 °C. Bromide of the same cation with substituent C_2 was liquid at 165 °C, it's decomposition occurred at 284 °C, and with substituent C_4 was liquid at room temperature (it's decomposition temperature was 251 °C). The melting points of quaternary pyridinium salts were higher than those of imidazolium quaternary salts. The values of melting points and decomposition temperatures of the salts decreased with lengthening of the alkylic chain. As well replacement of the alkylic substituent on the allyl one reduced the values of the salt melting point and decomposition temperature. Detailed thermal characteristics of the pyridinium salts, which obtained in this work, can be useful in a variety chemical engineering processes that are related with their application.

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Table 1. Conditions of thermal analysis of ionic liquids.

Method	Temperature range, °C	Heating rate, deg/min	Sample mass, mg	Atmosphere
TGA	20 ÷ 200	10	5.000 ÷ 6.000	Argon
DSC	–80 ÷ 350	10	7.800 ÷ 8.500	Nitrogen
DTG	20 ÷ 400	7.9	~ 90.000	Air
Boëtius heated stage	20 ÷ mp[a]	10	7.000 ÷ 10.000	Air

a - For the melting point is taken the state of total loss of sharp edges of the salts' crystals.

Table 2. ILs glass transition temperature and melting obtained by differential scanning calorimetry (DSC) and use of the Boëtius heated stage (Bo.), °C

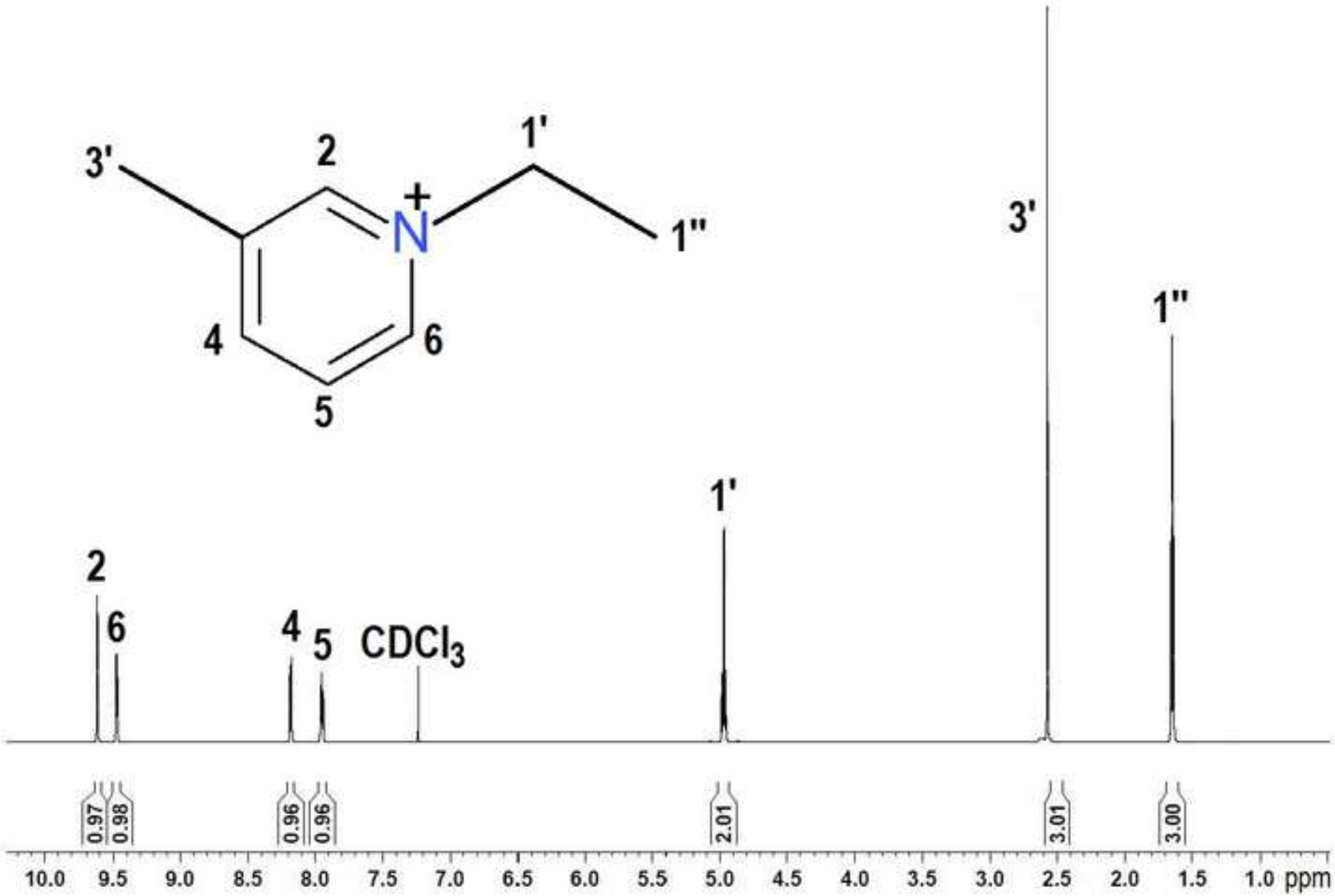
ILs	Glass transition (DSC)			Melting (DSC)			Melting (Bo.)
	onset	Tg	endpt	Tm	endpt	Ref	
$[C_2MPy]Cl$	25	29	33	*a*			130
$[C_3MPy]Cl$	9	18.5	28	*a*			92
$[C_4MPy]Cl$	17	35	53	93	113	95 [13], 111.35 [18]	97
$[C_5MPy]Cl$	16	21.5	27	*a*			92
$[C_6MPy]Cl$		*a*		62	84	81.95 [18]	77
$[C_7MPy]Cl$	8	16.5	25	*a*			72
$[C_8MPy]Cl$		*a*		69	83	67.1 [20], 80.05 [18]	74
$[C_9MPy]Cl$		*a*		*a*			64
$[C_{10}MPy]Cl$		*a*		55	82	79.35 [18]	64
[AMPy]Cl	18	27.5	37	*a*			108
$[C_2MPy]Br$		*a*		146	165		163
$[C_4MPy]Br$		*a*		*a*			RTIL

a – Not detected.

Table 3. Thermal characteristics of decomposition for ILs obtained by differential scanning calorimetry (DSC), thermogravimetry (DTG) and literature values (ref) obtained by thermogravimetric analysis (TGA), °C.

ILs	(DSC)		(DTG)		ref (TGA)
	onset	endpt	onset	endpt	
[C_2MPy]Cl	194	249			
[C_3MPy]Cl	200	245			
[C_4MPy]Cl	202	251	175	254	242 [26]
[C_5MPy]Cl	196	248			
[C_6MPy]Cl	196	244	187	245	238 [26]
[C_7MPy]Cl	193	244			
[C_8MPy]Cl	190	242			232 [26]
[C_9MPy]Cl	189	241	190	245	
[C_{10}MPy]Cl	183	241	192	245	227 [26]
[AMPy]Cl	170	229			
[C_2MPy]Br	190	284			
[C_4MPy]Br	190	251			199 –235 [34]

Figure 1. 1H NMR spectrum of [C2MPy]Cl (in CDCl3).



- 1-Alkyl-3-methylpyridinium halide-based ionic liquids were synthesized.
- A comparative study allowed to get detailed of the thermal characteristics of ILs.
- The melting points of pyridinium ILs decreased with lengthening of the alkyl chain.
- Detailed thermal characteristics can be useful in variety chemical processes.

Figure 2. Regions of DSC curve for [C4MPy]Cl: (a) glass transiti