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Synthesis and Dissolving Power of 1-Alkyl-3-methylpyridinium-Based Ionic Liquids

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Abstract—1-Alkyl-3-methylpyridinium-based ionic liquids with substituents from C_2 to C_{10} and anions Cl^- and Br^- were synthesized, and their dissolving power toward the cellulose was investigated. The results of quantum-chemical calculations of molecules of ionic liquids are presented.

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Ionic liquids defined as organic salts with melting points up to 100°C and consisting of cation and anion, in recent years found wide application in various fields of science and technology. Their unique properties of thermal stability, ability of regeneration, and low vapor pressure make them promising for use in processing of natural polymers, primarily cellulose [1–7], and in the production of new biodegradable materials, including films, membranes, and fibers. An important feature of this new class of solvents is the possibility of varying the cation–anion pairs, which allows assembling the ionic liquids with the required properties.

A significant number of the solvents dissolving cellulose is known now belonging to the class of ionic liquid, salts based on the nitrogen-containing cations like ammonium, pyridinium, and imidazolium, with anions Cl^-, Br^-, $RCOO^-$, SCN^-, $(MeO)_2(R)PO_2^-$ etc. [8–10]. The best studied ionic liquids are based on the imidazolium cation. The pyridinium-containing ionic liquids were studied comparatively poorly, although the first report of dissolving cellulose in them relates to 1934 [10]. In [8] the data on the maximum concentration of dissolved cellulose were presented achieved with the use of the chloride-based ionic liquid on the 1-butyl-3-methylimidazolium, 1-butyl-3-methylpyridinium, and benzyldimethyl(tetradecyl)ammonum clorides. The quaternary pyridinium salt was the most effective, providing 39% solution of cellulose (DP 286), for comparison, with imidazolium salt 18% solution was obtained and with the ammonium salts 5% concentration was achieved.

However, such an important issue as the relationship between the structure of ionic liquid (the nature of the cation and anion, the number and size of the substituents), is yet little studied, although some trends have already been identified. For example, the efficiency of the solvent is strongly dependent on the nature of the anion: the dissolving power of 1-alkyl-3-methylimidazolium-based ionic liquids decreases in the series of $CH_3COO^- > Cl^- \gg Br^- \approx SCN^-$ [7]. Equally important is the number and position of substituents in the ring. For example, pyridinium salts with one substituent in the ring have lower dissolving power than those with two alkyl chains [10–12]. According to [13], a series of solvents with decreased dissolving power that includes allylpyridinium chlorides and acetates corresponds to the following positions of methyl substituent: 3–4–2.

At replacing the allyl group in the position 1 by propyl or butyl, only the salt with 1,3-position of two substituents is capable to dissolve cellulose. Thus, among of the most effective solvents for cellulose may be pyridinium ionic liquids with two alkyl chains in the positions 1 and 3. It can be assumed that the size of the substituents also affects the dissolving power of ionic liquids, as was shown for the imidazolium-containing solvents [7].

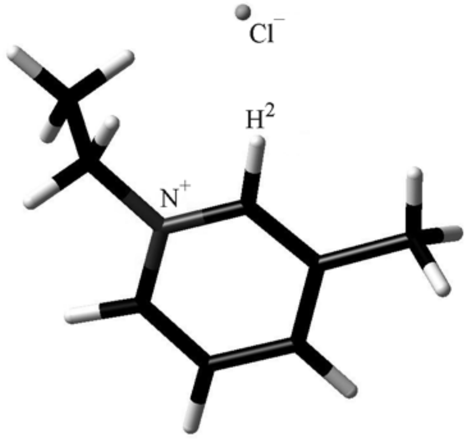

Fig. 1. Optimized structure of 1-ethyl-3-methylpyridinium chloride ion pair.

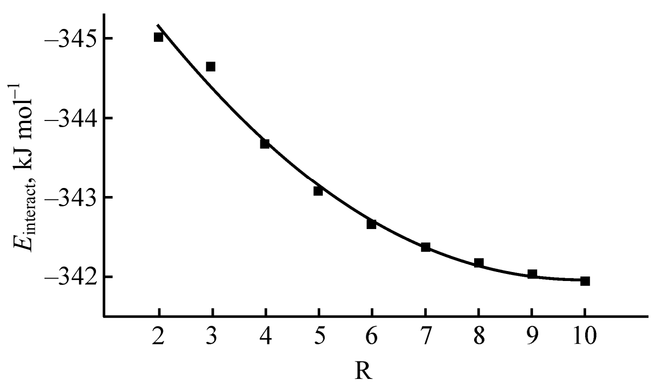

Fig. 2. Dependence of the interaction energy of the ion pair on the length of the alkyl chain (R) in 1-alkyl-3-methylpyridinium chlorides-based ionic liquids.

The aim of this work is finding a possible relationship between the structure of ionic liquids based on the cation of 1-alkyl-3-methylpyridinium and their dissolving power toward cellulose. The problem can be solved by comparing the results of quantum-chemical calculations and experimental study of their physicochemical properties. To do this, we synthesized a series of ionic liquids based on 1-alkyl-3-methylpyridinium.

Quantum-chemical calculations of the geometric parameters and electron density distribution on atoms in the ionic liquids based on 1-alkyl-3-methylpyridinium was performed by the HF/6-31++G(6d,7f) method with the Gaussian 03 package. An example of the optimized geometry of the ion-pair model of 1-ethyl-3-methylpyridinium chloride is shown in Fig. 1.

Analysis of the results of calculations shows that with increasing length of the alkyl chain of the substituent at the nitrogen atom in a series of C_2–C_{10} the absolute value of the interaction energy (E_{interact}) in the ion pairs decreases (Fig. 2). At the same time, there is a tendency to an increase in the distance between the hydrogen atom in 2 position of the pyridinium ring and the anion with the increase in the number of carbon atoms in the *N*-alkyl chain (Table 1). For the same cation, the distance $H^2\cdots Br$ is longer than $H^2\cdots Cl$. The distances $H^2\cdots Cl$ in ionic liquid with *N*-allyl and *N*-ethyl substituents are comparable. The results of calculation show that with the lengthening of the *N*-alkyl chain the cation and anion become less associated, therefore, the packing density of the solvent decreases.

Twelve ionic liquids with various anions and diverse alkyl substituents at the nitrogen atoms in the cation were synthesized (Table 2). As an example, Figs. 3 and 4 show the ^{1}H NMR and IR spectra of 1-ethyl-3-methylpyridinium chloride. No peaks of the starting materials and external contaminants were detected indicating the acceptability of the chosen method of synthesis and purification. The water content in the synthesized ionic liquid does not exceed 0.6–0.7 wt %.

The results of the thermal analysis show that the lengthening of the *N*-alkyl chain reduces the melting temperature of the compounds (Fig. 5). The ionic liquids with the number of carbon atoms in the substituent at the nitrogen atom from C_4 to C_{10} melt at the temperature below 90°C.

Table 1. The distance between the ring proton H^2 and anion X, and the charge on the anion (by Mulliken) in ionic liquids based on 1-alkyl-3-methylpyridinium

R	X	$H^2\cdots X$, Å	*q*, *e*
C_2H_5	Cl	2.23021	–0.778
C_3H_7	Cl	2.24275	–0.774
C_4H_9	Cl	2.24370	–0.773
C_5H_{11}	Cl	2.24396	–0.772
C_6H_{13}	Cl	2.24410	–0.773
C_7H_{15}	Cl	2.24416	–0.773
C_8H_{17}	Cl	2.24401	–0.773
C_9H_{19}	Cl	2.24425	–0.772
$C_{10}H_{21}$	Cl	2.24413	–0.772
$CH_2{=}CHCH_2$	Cl	2.22811	–0.767
C_2H_5	Br	2.32403	–0.741
C_4H_9	Br	2.34980	–0.730

Table 2. The maximum achieved concentration of cellulose (*D*) in chloride- and bromide-containing solvents

Ionic liquid	*T*, °C	*D*, wt %
1-Ethyl-3-methylpyridinium chloride	140	26
1-Propyl-3-methylpyridinium chloride	110	22
	120	22.5
1-Butyl-3-methylpyridinium chloride	120	23
1-Pentyl-3-methylpyridinium chloride	110	21
	120	21
1-Hexyl-3-methylpyridinium chloride	110	19
	120	19
1-Heptyl-3-methylpyridinium chloride	110	14.5
	120	15
1-Octyl-3-methylpyridinium chloride	110	6.5
	120	8
1-Nonyl-3-methylpyridinium chloride	110	4
	120	5.5
1-Decyl-3-methylpyridinium chloride	110	6
	120	7.5
1-Allyl-3-methylpyridinium chloride	130	24
1-Ethyl-3-methylpyridinium bromide	165	6.5
1-Butyl-3-methylpyridinium bromide	110	3.5
	165	7

The study of the solubility of cellulose in the synthesized ionic liquid showed that for the same cation the 1-alkyl-3-methylpyridinium bromides show lower dissolving ability than chlorides, the latter provide more concentrated solutions of cellulose (Table 2). This is consistent with the results of studies of 1-alkyl-3-methylimidazolium halides [7]. The rise of the temperature from 110 to 165°C leads to twofold increase in the maximum concentration of cellulose in solutions of bromide-containing ionic liquid.

With the increasing length of the N-substituent in the pyridinium chloride ionic liquids their dissolving power with respect to cellulose decreases. A similar trend was found for 1-alkylpyridinium [10–12, 15] and 1-alkyl-3-methylimidazolium [7] halides.

Thus, the results obtained suggest that ionic liquids based on pyridinium cations are the most effective solvents of cellulose. For comparison, under identical conditions the replacement of 1-butyl-3-methylpyridinium by 1-butyl-3-methylimidazolium leads to a decrease in the dissolving power from 23 to 17 wt %. This is confirmed by the data of [8, 13].

In the FTIR spectra of the cellulose regenerated from the ionic liquid appear two intense bands at 3440 cm^{-1} and 3484 cm^{-1}, corresponding to the intramolecular hydrogen bonds, which indicate a modification of cellulose II (Fig. 6).

Thus, according to the results of quantum-chemical calculations, with the increasing length of *N*-alkyl substituent of 1-alkyl-3-methylpyridinium the interaction energy between the cation and anion decreases, while the distance between them increases. Therewith, the melting points, as well as dissolving power of ionic liquids with respect to cellulose diminish. Replacing the chloride anion by bromide decreases the effective

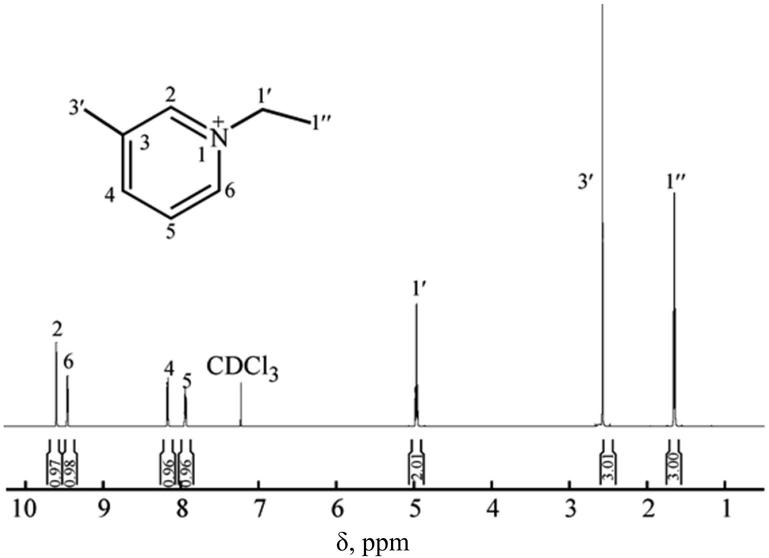

Fig. 3. The assignment of the peaks in the ^{1}H NMR spectrum ($CDCl_3$) of 1-ethyl-3-methylpyridinium chloride.

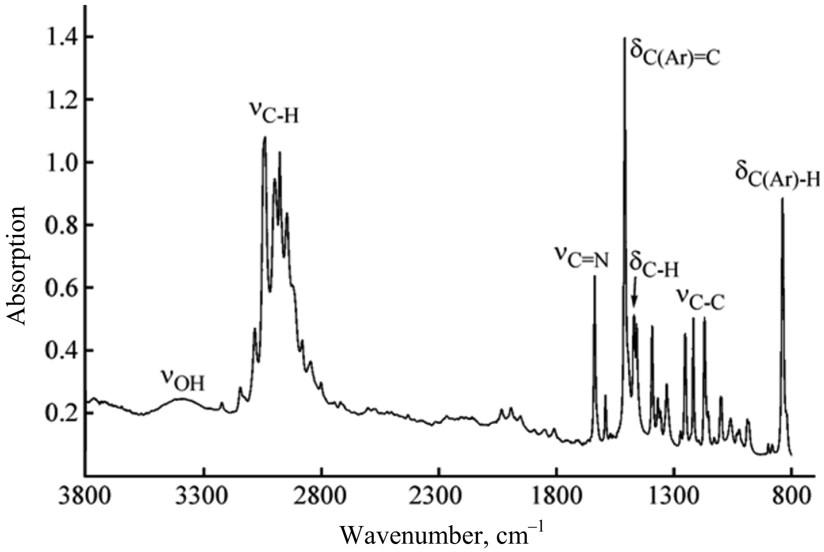

Fig. 4. The assignment of the IR bands of the Fourier spectrum of 1-ethyl-3-methylpyridinium chloride.

charge of the anion and reduces the dissolving power of the ionic liquid with respect to cellulose. Pyridinium-containing ionic liquids dissolve cellulose more efficiently than ionic liquids based on the imidazolium cation with the same substituents and anions.

EXPERIMENTAL

We used the following chemical reagents and materials: allyl chloride (Fluka, 98%), acetonitrile (Lab-scan analytical science, 99.9%, Poland), 1-bromoethane (Aldrich, 98%), 1-bromobutane (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%), and 1-chlorodecane (Aldrich, 98%). To determine the dissolving ability of ionic liquids the Alicell Super pulp (Western Pulp, Inc., Canada) was used with the degree of polymerization 599 and water content 8%.

The halide salts of 1-alkyl-3-methylpyridinium were prepared by the alkylation of 3-picoline [14] with the corresponding alkyl halide. To a two-neck flask with a reflux condenser and a magnetic stirrer a solution of 3-substituted pyridine (0.1665 mol) in toluene (20 ml) was charged, and to it alkyl halide (0.2000 mol) was added. The solution was then stirred for 1 h at room temperature under nitrogen atmosphere. Then the

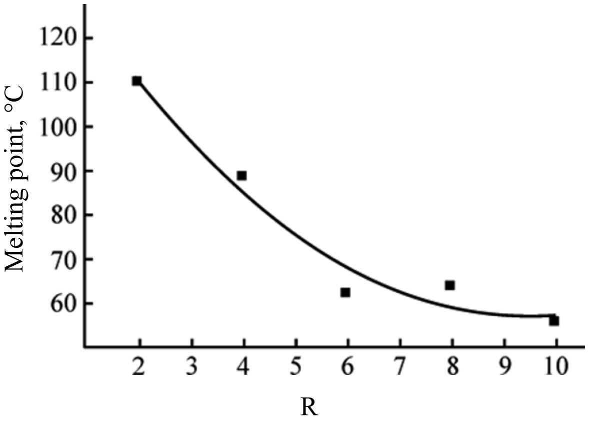

Fig. 5. The dependence of the melting point on the length of the alkyl chain (R) for 1-alkyl-3-methylpyridinium chlorides-based ionic liquids .

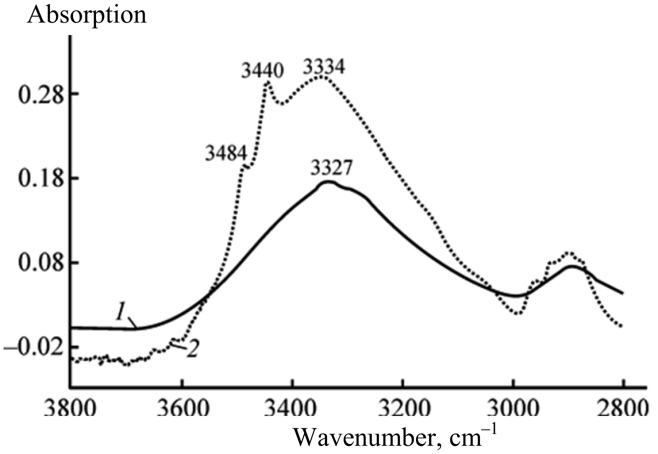

Fig. 6. IR spectrum in the region of 2800–3800 cm^{-1} of (*1*) the initial cellulose and (*2*) recovered from a 5% solution in 1-butyl-3-methylpyridinium chloride.

reaction mixture was stirred at a temperature of 110–130°C for 24–48 h with reflux without nitrogen flow. Upon completion, the reaction product obtained separated in layers, toluene was decanted from the dense layer of ionic liquid. The product was washed with toluene. Recrystallization was carried out by dissolution in acetonitrile followed by precipitation with excess diethyl ether. Volatile organic compounds were removed on a rotary evaporator (Rotavapor R-215, Büchi, Switzerland) for 6–8 h, the pressure gradually was reduced from atmospheric to 20–120 mbar, and the temperature was raised from 60°C to 90–140°C.

The obtained salts were identified by ^{1}H NMR spectroscopy (spectrometer Bruker Avance II Plus 700 MHz, USA), infrared spectroscopy (FT spectrometer Nicolet 6700 FT-IR, USA), and chromatography–mass spectrometry (spectrometer GCMS-QP2010 Plus, Shimadzu, Japan). Water content was determined by thermogravimetric analysis (system STAR^e TGA/DSC 1, Mettler Toledo, Germany).

The melting point of ionic liquids were determined by thermal analysis using differential scanning calorimetry (calorimeter NETZSCH-Gerätebau GmbH Thermal Analysis DSC 204, Germany).

Dissolving power of the synthesized ionic liquids was determined as follows. Cellulose was added to the solvent by portions after the complete dissolution of the previous portion. For dissolution the mixture was stirred continuously for at least 12 h with temperature control. The dissolved cellulose con-centration D was calculated by the formula:

$$D = [m_1/(m_1 + m_2)](100 - c_{\mathrm{w}}),$$

where D is the cellulose concentration in the ionic liquid, m_1 and m_2 are weights of cellulose and ionic liquid, respectively, g; c_{w} is the water content in the pulp, %.

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