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Interaction of Ionic Liquids Based on 1-Butyl-3-methylimidazolium Cation with Hydrated Cellulose According to the Data of Infrared Spectroscopy

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Abstrtact—Methods of Fourier-transform infrared spectroscopy and gravimetry were used to study hydrated cellulose films doped with ionic liquids based on the 1-butyl-3-methylimidazolium cation with either chloride, or trifluoroacetate, or bis(trifluoromethylsulfonyl)imid anions. The ionic liquid is retained in the polymer matrix mainly due to the formation of hydrogen bonds between the ionic liquid anion and protons of the hydroxy groups of cellulose, the strength of hydrogen bonding decreasing in the series of $[Cl]^- > [CF_3CO_2]^- >> [N(Tf)_2]^-$.

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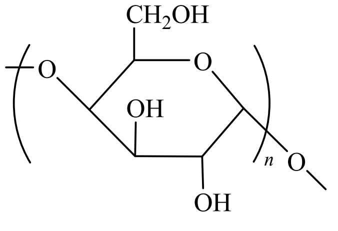
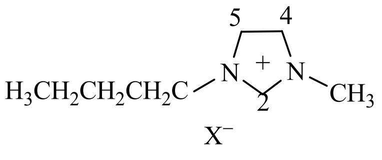
Ionic liquids are salts with organic cations (ammonium, phosphonium, imidazolium, pyridinium, etc.) and are in the liquid (molten) state at temperatures below 100°C. Their chemical and physical properties may differ significantly from each other depending on the possible combinations of the cation and anion. Ionic liquids with imidazolium cation ($[im]^+$) are widely used in the extraction and organic synthesis as alternative solvents due to their unique properties: a wide temperature range of liquid state, low volatility, thermal stability, possibility of recycling and reuse, etc. [1]. They have a high polarity and are capable of dissolving many organic and inorganic compounds.

Since recently imidazolium ionic liquids are suggested as “green” solvents for natural polymers, including cellulose [2–6]. They are extremely promising, for example, in the manufacture of regenerated cellulose instead of conventional organic solvents [7]. On the other hand, combining macromolecules with ionic liquids used as additives opens great possibilities for creating ion-conductive polymer materials for electrochemical applications [8].

Despite the promise of use, there are not sufficient data on the nature of the ionic liquid interaction with cellulose. Studies on the dissolution showed that the best solvents for cellulose are the salts of 1-butyl-3-methylimidazolium with chloride and acetate anions. Therefore it was suggested that the solvation of cellulose is due to the formation of hydrogen bonds between proton-donor hydroxy groups of the polymer and proton-acceptor sites of the ionic liquid anion [2]. Further studies performed with the use of ^{13}C and $^{35/37}Cl$ NMR spectroscopy on the model sugar systems confirmed this assumption [9, 10]. The hypothesis of intermolecular hydrogen bonding was also confirmed by computational methods [6, 11].



Hydrated cellulose



$[bmim]^+ X^-$

Table 1. Kinetics of swelling of the hydrate cellulose films in ionic liquids **I–III** (H_2O wt %) and in water at 25°C

τ, h	α^a			
	I (23)	**II** (10)	**III** (0.8)	H_2O
1	0.058	0	0	0.384
2	0.512	0	0	0.397
3	0.804	0	0	0.402
24	1.427	0.105	0.009	0.389
47	1.460	0.606	0.111	–
71	1.462	1.042	0.256	–
95	1.403	0.800	0.022	–

[a] $\alpha = m_\tau – m_0/m_0$, where m_0 and m_τ are sample initial weight and at time τ, respectively.

In this work we used IR spectroscopy to study interaction of the hydrated cellulose with ionic liquids based on 1-butyl-3-methylimidazolium cation $[\text{bmim}]^+$ X^- where X was either chloride $[Cl]^-$ (**I**), or trifluoroacetate $[CF_3CO_2]^-$ (**II**), or bis(trifluoromethylsulfonyl)imidate anions $(CF_3SO_2)_2N]^-$ denoted as $[N(Tf)_2]^-$ (**III**). The infrared spectroscopy is a reliable and accessible method for studying intra- and intermolecular interactions in the ionic liquids.

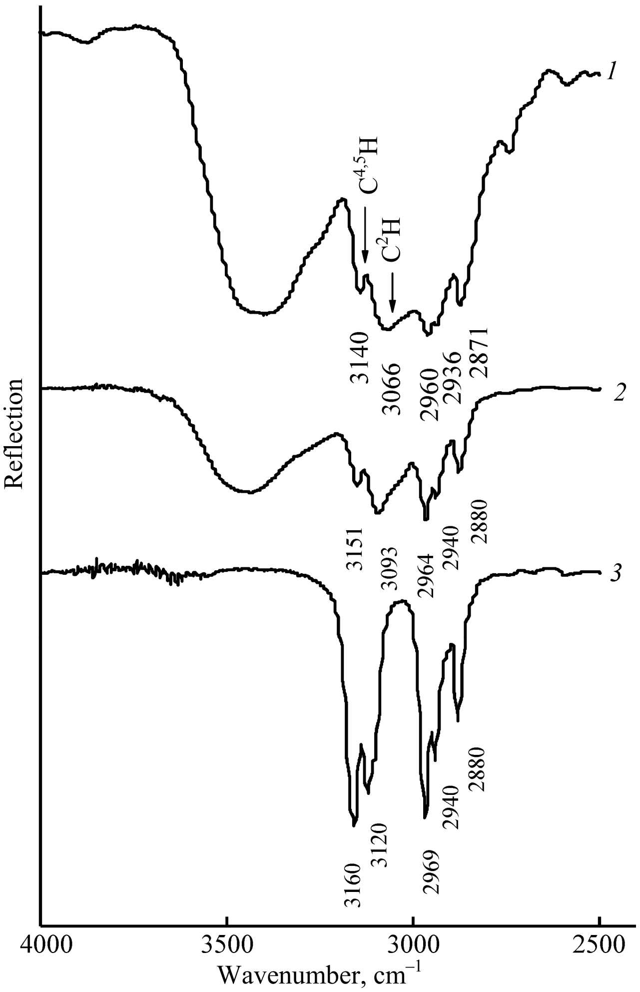


Fig. 1. Fourier-transform infrared reflectance spectra of ionic liquids **I** (*1*), **II** (*2*), and **III** (*3*).

Table 1 shows the values of the degree of swelling of samples of the hydrate cellulose films (α) vs. the immersion time (τ) in the ionic liquid and water, because all ionic liquids contain bound water in equilibrium. As seen, the hydrate cellulose films sorb and retain the ionic liquid with anions **I** and **II** better than with the anion **III**. The mass of the film increases rapidly in water and slowly in ionic liquid. The maximum degree of swelling in H_2O does not exceed 40%, while reaches 100.4% and 146.2% in the hydrophilic ionic liquids **I** and **II**, respectively. Given the equilibrium moisture content, the maximum weight gain by the film due to "water-free" ionic liquids **III**, **II** and **I** was 25.4%, 90.4%, and 112.5% respectively. That is, under these conditions cellulose swells due mainly to the adsorption of the ionic liquid. Thus, the gravimetric method shows that the 1-butyl-3-methyl-imidazolium chloride and trifluoroacetate are adsorbed well by hydrocellulose.

What is the nature of this interaction? It is well established now that the bonding between the cation $[\text{im}]^+$ and the anion X^- occurs due to the forces of electrostatic interactions and C–H···X hydrogen bonding, mainly through the hydrogen atoms at the carbon atoms C^2, C^4, and C^5 of the aromatic ring [12–14]. In the IR spectra (Fig. 1), the characteristic vibrations of aromatic C–H bonds are manifested as two bands with the frequency (ν) in the range from 3000 to 3200 cm^{-1}, three bands in the range of 2800–3000 cm^{-1} are attributed to the CH vibrations of the aliphatic (CH_3 and CH_2) groups of the butylmethylimidazolium cation [15]. The formation of a hydrogen bond C–H···X leads to an increase in the distance between the carbon and hydrogen atoms and a decrease in the vibration frequency (red shift). The stronger is the hydrogen bond, the greater is the red shift. The chlorine anion being a strong proton acceptor forms a strong hydrogen bond C–H···Cl with a pronounced low-frequency shift (Fig. 1).

Figure 2 shows the infrared spectra of ionic liquid adsorbed on hydrate cellulose. The spectra were obtained by subtracting the initial spectra of the films from the spectra of the films after treatment with ionic liquid. Table 2 lists the changes (Δν) of the characteristic vibration frequencies of C–H bonds of adsorbed ionic liquid relative to the frequencies in the spectra of initial ionic liquid. It is seen that $\nu(C^2H)_{\text{arom}}$

of ionic liquids with the ions **I** and **II** are higher by 12–29 cm^{-1}. This shift may be due to the formation of hydrogen bonds (X···H–O) of anion X^- with stronger proton-donor hydroxy groups of hydrate cellulose and water [16–18]. The spectra of ionic liquid with different water content showed that a blue shift caused by the water encased in the film is no more than 6–9 cm^{-1}. It appears that the shift $\Delta\nu(C^2H)_{arom} = 29\ cm^{-1}$ to higher frequencies is caused mainly by the Cl···H–O interaction of the ionic liquid anion Cl^- with the OH groups of hydrate cellulose.

The correlation of the data in Tables 1 and 2 shows that the sorption of salts of 1-butyl-3-methylimidazolium by hydrate cellulose is caused by the hydrogen bonds between the anion of ionic liquid and the polymer, and the hydrogen bonding strength decreases in the series $[Cl]^- > [CF_3CO_2]^- \gg [N(Tf)_2]^-$. The dissolution of cellulose occurring also through the mechanism of hydrogen bonding [9] decreases in the series $[CH_3CO_2]^- > [Cl]^- \gg [Br]^- \sim [SCN]^-$ [6]. The acetate ion contains two oxygen atoms interacting with the hydroxy groups of cellulose, so it is more active with respect to the polymer than the $[Cl]^-$ anion. Obviously, the coordination of the fluorinated acetate anion $[CF_3CO_2]^-$ with cellulose is sterically hindered. Oxygen atoms of the $[N(Tf)_2]^-$ anion are strongly shielded and do not form visible hydrogen bonds with the cellulose and the imidazolium cation.

Thus, in this work using gravimetry and FT-IR spectroscopy we showed that the ionic liquid based on the 1-butyl-3-methylimidazolium cation was retained in the polymer matrix of cellulose, mainly due to the formation of hydrogen bonds between the ionic liquid anions and protons of the cellulose hydroxy groups. The hydrogen bonding strength, depending on the nature of the anion, falls in the series: $[Cl]^- > [CF_3CO_2]^- \gg [N(Tf)_2]^-$.

EXPERIMENTAL

The cellulose used was the commercial cellophane film of the density 1.50–1.52 g cm^{-3}, the thickness of 30 microns, the equilibrium water content of ~12 wt % (relative humidity 70%). Salts **I** from Across Organics, **II** and **III** from Merck (main substance content at least 96–98%) were conditioned before use at the 70% humidity, the equilibrium water content was respectively 23, 10, and 0.8 wt %. All salts in the experiment were in the liquid state. Ionic liquids with a desired water content were prepared gravimetrically and titrated by the Fischer method.

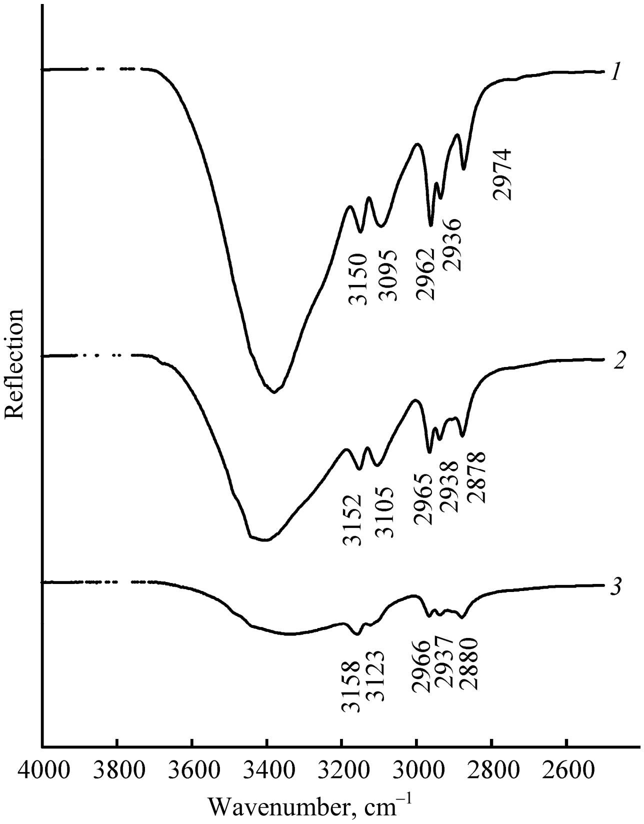


Fig. 2. Fourier-transform infrared reflectance spectra of ionic liquid adsorbed by hydrate cellulose film: **I** (*1*), **II** (*2*), **III** (*3*).

The film samples of the 0.02–0.3 g weight were filled with ionic liquids (module ~500) at 25°C in a closed vessel under conditions of constant humidity (70%). The method of swelling the films in a small volume of fluid was described and tested in [19]. The completeness of the removal of ionic liquid from the film surface before the measurement was monitored by IR spectra. The film weight before and after treatment was determined on an analytical balance Sartorius ME215S.

The Fourier-transform infrared reflection spectra of the films were obtained on a spectrophotometer Avatar

Table 2. Shifts of characteristic vibration frequencies ($\Delta\nu^a$) of the C–H bonds of ionic liquids **I–III**

X	$\Delta\nu(CH)_{arom}$, cm^{-1}		$\Delta\nu(CH)_{aliph}$, cm^{-1}		
	$C^{4,5}H$	C^2H	ν_s CH_3	ν_{as} CH_2	ν_{as} CH_3
I	–10	–29	–2	0	–3
II	–1	–12	2	2	–1
III	2	–3	3	3	0

[a] $\Delta\nu = \nu(C–H)_{ion.liq.} - \nu(C–H)_{hydr.cel.+ion.liq.}$

360 FT-IR ESP in the frequency range 4000–200 cm^{-1} with a resolution of 4 cm^{-1}. The IR spectra of the initial ionic liquids were taken from a thin layer between two KRS-5 plates.

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