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Immobilization of Imidazolium Cation Based Ionic Liquids on Thin Polymer Films

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Abstract—Methods of gravimetry, optical microscopy, FTIR spectroscopy, and conductometry were applied to the study of the adsorption of the following ionic liquids: 1-butyl-3-methylimidazolium chloride, bis-trifluoromethylsulfonylimide, and trifluoroacetate on thin-layer films of polymers of different nature including polypropylene, polyethylene terephthalate, polytetrafluoroethylene, poly(vinyl chloride), and hydrated cellulose. It was established that the hydrated cellulose film can serve as polymer matrices for the ion-conducting 1-butyl-3-methylimidazolium halide salts. The hydrated cellulose additive in the ionic liquids promotes their immobilization on the poly(vinyl chloride) film.

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Recently time ionic liquids attracted a growing interest to the application in various branches of science and technology. Due to the thermal stability, non-combustibility, low volatility, high conductivity, wide temperature range of liquid state, and other specific properties, they are widely used as alternative solvents in organic synthesis, extraction, chromatography, catalytic and electrolytic processes, and in several other areas [1].

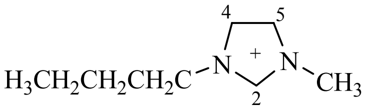
Ionic liquids consist of a bulky organic or inorganic cation (ammonium, phosphonium, imidazolium, pyridinium, etc.) and organic or inorganic anion (chloride, bromide, tetrafluoroborate, hexafluorophosphate, acetate, etc.). The cation and anion in a ionic liquid are bound by electrostatic and donor–acceptor (hydrogen bonding) interactions, thus forming extended bridged structure of hydrogen bonds. Proton donors in the ionic liquids, e.g., those based on the imidazole (Scheme 1), are the hydrocarbon groups of the heterocycle or alkyl radical, the proton acceptors are the atoms of the anion (Cl, O, etc.) [2–4]. The anion in the ionic liquid can interact through the hydrogen bonds not only with its own cation, but also with donor groups of the molecules of other substances. For instance, this is why 1-butyl-3-methylimidazolium chloride dissolves well inorganic salts [5, 6] and natural polymers [7–9], and is miscible with low molecular weight synthetic polymers [10].

Since the ionic liquids are composed mainly of free carriers of a charge, the non-conductive polymers filled with ionic liquids gain ionic conductivity. On the other hand, a decrease in the dielectric properties of polymers used as insulators impairs their performance. Therefore, the modification of polymer films with ionic liquids to supply them with conductive properties is of interest by virtue of the commercial availability of their components and the simplicity of the method.

Currently, the ion-conducting polymer electrolytes can be obtained by the *in sity* polymerization of the starting monomers in the ionic liquid as a solvent [11–13], as well as by the traditional method of direct mixing of the polymer with the ionic liquid [14–16]. The maximum conductivity of the film-forming gel electrolyte, obtained on the basis of the ionic liquid from ethylmethylimidazolium bromide and 2-hydroxyethyl methacrylate monomer, was 2.3×10^{-2} Cm cm^{-1} (300 K) [13].

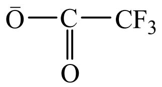
In this study we explored a possibility of immobilization of low-temperature ionic liquids on polymer matrices. The latter were selected among the commercial films made of synthetic and natural polymers with low conductivity (insulators), containing various substituents and functional groups. As ionic liquids the most common low-temperature salts with the 1-butyl-3-methylimidazolium cation and the anions of different nature, [bmim][X], were chosen. Structural formulas of the objects of the study are shown below.

Catoin (bmim$^+$)



1-butyl-3-methylimidazolium

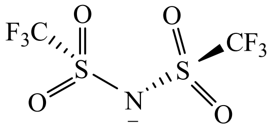
Anion (X$^-$)



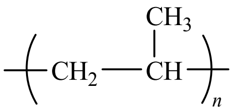
trifluoroacetate ($CF_3CO_2^-$)

Cl^-

chloride



bis(trifluoromethylsulfanyl)imide (Tf_2N^-)

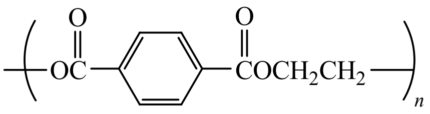


$-(CH_2-CH(CH_3))_n-$

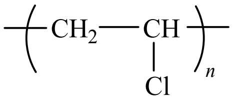
polypropylene **I**

$-(CF_2-CF_2)_n-$

polytetrafluoroethylene **II**

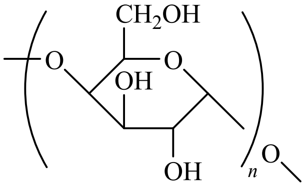


polyethyleneterephthalate **III**



$-(CH_2-CH(Cl))_n-$

poly(vinyl chloride) **IV**



hydrated cellulose **V**

Table 1 lists the relative change in the weight of synthetic polymer films $\alpha = (m_\tau - m)/m$ in ionic liquids. As seen, after prolonged treatment the weight of the film **II** of 355 μm thickness remains virtually unchanged, the value of α of the films **I** and **III** are of different sign and do not exceed 1–2%, the weight of the film **IV** decreases slightly. The negative swelling of polymer (a decrease in the initial weight) may occur as a result of leaching of soluble impurities [17].

Figure 1 shows the adsorption curves of ionic liquids by film **II** of 10 μm thickness (fluoroplastic sealing material tape, FSM). The maximum degree of adsorption is proportional to the molecular weight of the ionic liquid, and depending on the anion changes in a series of $[Tf_2N]^- > [CF_3CO_2]^- > [Cl]^-$, at the same time, polytetrafluoroethylene adsorbs ~4.5×10^{-5} M of ionic liquids per 1 g, regardless of the nature of the anion. The polymer does not hold the imbibed ionic liquid and it can be easily removed at the contact with filter paper. The weight gain of the polytetrafluoroethylene thin film is caused obviously by the capillary filling of the material open pores. The ionic liquid not connected with the film material is desorbed easily by contact with cellulose, which can interact with the ionic liquid [18].

Gravimetric measurements carried out with the hydrated cellulose–[bmim][X] system showed that the weight of the source film increases with the increase in processing time while the linear dimensions of the

Table 1. Relative mass change (α)[a] of the synthetic polymer films in ionic liquids [bmim][X]

Polymer	Time, h	$[Cl]^-$	$[CF_3CO_2]^-$	$[Tf_2N]^-$
I	7	0.0025	0.0026	0.0053
	24	–0.0051	–0.0077	–0.0026
	52	–0.0127	–0.0077	–0.0157
	97.5	0	0.02000	0.0184
II (355)	24.5	0.0001	0.0001	0
	47.5	0.0001	0	0
	71.5	0.0001	0.0001	0.0002
	95.5	0	0	0
III	7	–0.0018	0.0035	0.0018
	24	–0.0018	–0.0053	0.0071
	52	–0.0018	–0.0140	–0.0107
	97.5	0.0035	–0.0036	0.0053
IV	24	–0.0007	–0.0070	–0.0060
	48	–0.0021	–0.0898	–0.0094
	71	–0.0024	–0.0113	–0.0024

[a] $\alpha = (m_\tau - m)/m$, where m and m_τ are weights of the film before and after treatment.

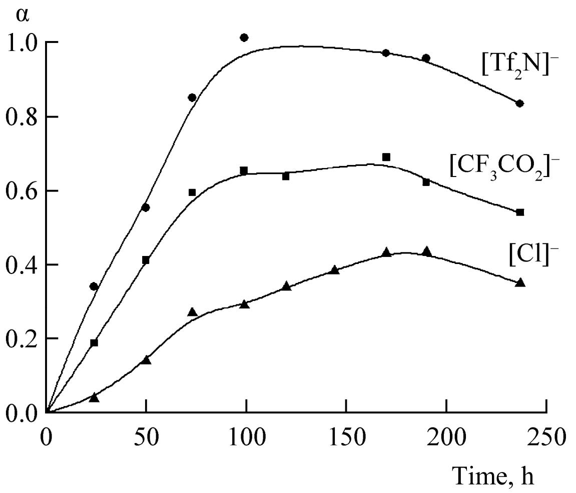


Fig. 1. Kinetic curves of adsorption of ionic liquids [bmim][X] by film **II** (10 μm), 25°C.

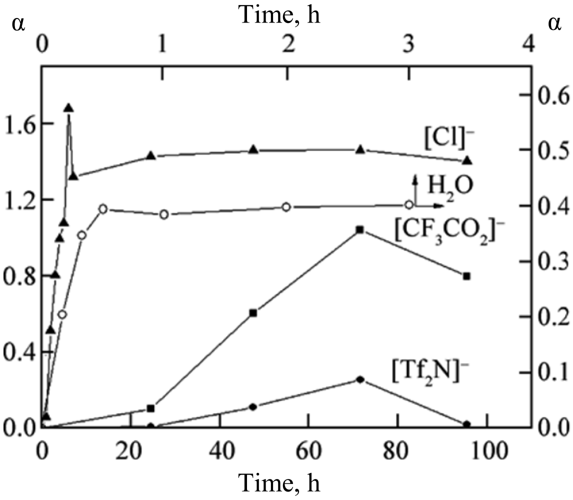


Fig. 2. Adsorption isotherms of ionic liquids [bmim][X] by film **V**, 25°C.

samples do not change, that is, the hydrated cellulose film (cellophane) limitedly swells in imidazole ionic liquid [17]. Adsorption curves of hydrated cellulose films in the ionic liquids and H_2O (the cellulose based materials are rather hygroscopic, and the used ionic liquids contain equilibrium water) are shown in Fig. 2. In contrast to water, at the immersion of the film in the ionic liquid its weight increases slowly as a function of the immersion duration. As seen from Fig. 2, the degree of swelling in water does not exceed 40%, and taking into account the moisture content in the ionic liquid it is obvious that in the system of hydrated cellulose–[bmim][X] the cellulose films adsorbs mainly the ionic liquid.

Figure 2 shows that after reaching maximum the value of α decreases, which is typical for the process of swelling of polymers, when it releases a part of the adsorbed liquid due to restructuring its own structure and relaxation processes occurring therewith [17]. As a result, the previously adsorbed ionic liquid [bmim]·$[Tf_2N]$ leaves the polymer almost completely. Ionic liquids with anions $[Cl]^-$ and $[CF_3CO_2]^-$ in contrast to $[bmim][Tf_2N]$, are held by the hydrated cellulose (weight of the film at a constant temperature and humidity remains almost unchanged). Thus, analysis of the curves in Fig. 2 shows that the value of the equilibrium swelling degree of the hydrated cellulose film depends on the nature of the ionic liquid anion varying in the series $[Cl]^- > [CF_3CO_2]^- >> [Tf_2N]^-$. The swelling as well as dissolution of cellulose are due to the formation of hydrogen bonds between the ionic liquid anion and the hydrogen of the hydroxy group of cellulose [19].

The ionic liquids adsorbed by films practically could not be detected with a microscope, but were well registered by means of infrared spectroscopy. Figure 3 shows the IR reflectance spectra of hydrated cellulose films before and after treatment with a ionic liquid, as well as the spectra of these films after contact with filter paper (within three days). All spectra in the range 2500–4000 cm^{-1} have the same scale along the ordinate and are comparable with each other. In the IR spectra of the hydrated cellulose films after treatment with the ionic liquids (*1a*–*3a*) the bands appear in the frequency range from 2800 to 3200 cm^{-1}, which are absent in the spectrum of the initial film (spectrum 0). They are due to vibrations of the C–H bonds of the aromatic ring (3000–3200 cm^{-1}) and aliphatic substituents (2800–3000 cm^{-1}) of the imidazolium cation [2–4]. The presence of these bands in the spectra of the films after desorption (*1b*–*3b*) suggests that the ionic liquids, especially with the ion $[Cl]^-$ (*3b*), are firmly held by the polymer matrix. The weight of the ionic liquid remaining in the film reaches 10% and 50% of the initially adsorbed $[bmim][CF_3CO_2]$ and [bmim][Cl], respectively.

According to gravimetry, films **I**, **III**, and **IV** do not adsorb ionic liquids, nevertheless the IR spectra of these films contain the vibration frequencies characteristic of the imidazolium aromatic CH groups from the ionic liquid. Figure 4 by the example of film **III** shows changes in the spectra of the studied synthetic polymer films processed in the ionic liquids. As seen, the adsorbed ionic liquid is completely removed after immersion desorption. But if these films are impre-

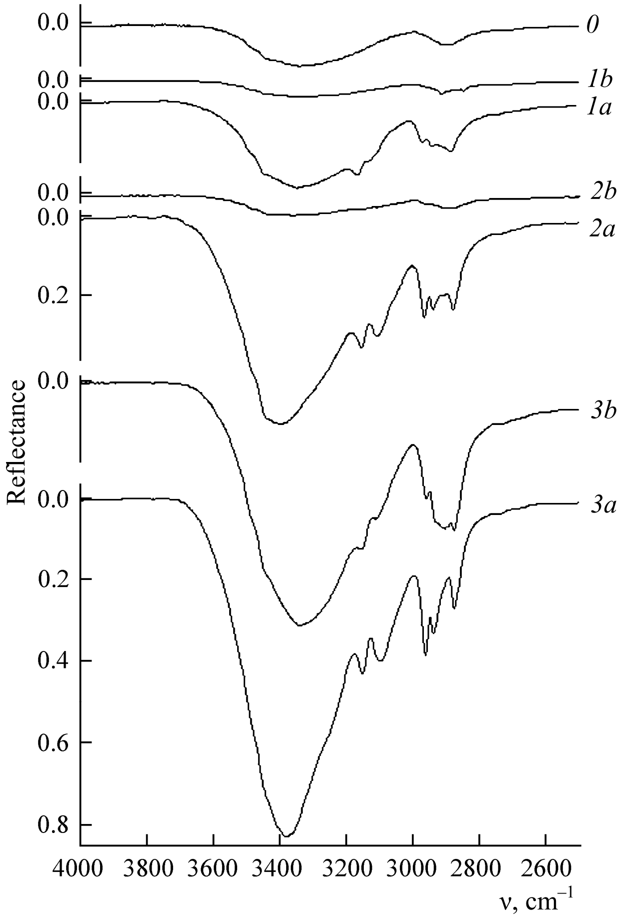


Fig. 3. FT–IR reflectance spectra of the film **V** before (*0*) and after (*1–3*) reaching equilibrium adsorption of ionic liquid [bmim][X], X: Tf_2N (*1*), CF_3CO_2 (*2*) and Cl (*3*), (a) before and (b) after desorption.

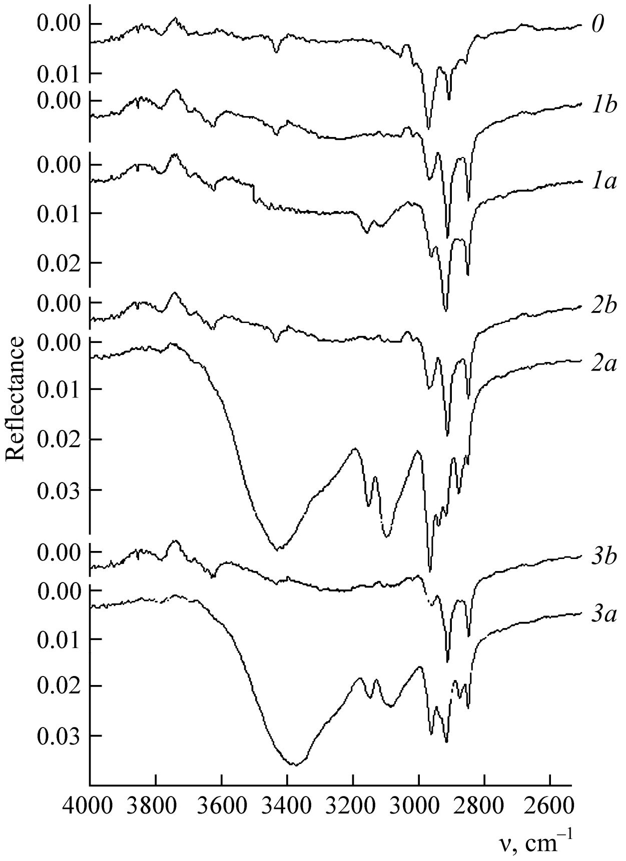


Fig. 4. FT-IR reflectance spectra of films **III** before (*0*) and after (*1–3*) reaching equilibrium adsorption of ionic liquid [bmim][X], X: Tf_2N (*1*), CF_3CO_2 (*2*) and Cl (*3*), (a) before and (b) after desorption.

gnated with the ionic liquids containing an admixture of hydrated cellulose (the hydrated cellulose partly dissolves in the ionic liquid at swelling), apart from the frequencies characteristic for the ionic liquids, the IR spectra contain the characteristic vibration frequencies of OH groups of the hydrated cellulose (3390 cm^{-1}), which in the films of poly(vinyl chloride) do not disappear completely after desorption (Fig. 5). According to IR spectroscopy, they contain 30–45% of the initial amount of adsorbed chloride or trifluoroacetate ionic liquid. It is obvious that the hydrated cellulose promotes the retention of the ionic liquids with the anions $[Cl]^-$ and $[CF_3CO_2]^-$ in poly(vinyl chloride) films. It follows from the IR spectroscopic data that the ionic liquids in trace amounts could penetrate the films of synthetic polymers (the amorphous phase or defects of crystalline phase). Using as a sorbent the 1-butyl-3-methylimidazolium chloride or trifluoroacetate containing some hydrated cellulose, we can obtain stable poly(vinyl chloride) film doped with the components of the sorbent.

Table 2 shows the results of electrochemical measurements, which indicate the change in the bulk specific conductivity of the film after processing with ionic liquids with respect to the same characteristic of the original film. We see that the adsorbed hydrophilic ionic liquid [bmim][Cl] and $[bmim][CF_3CO_2]$ increases the conductivity of the hydrated cellulose film by several orders of magnitude. After the treatment with the hydrophobic $[Tf_2N]^-$, the conductivity may decrease due to the leaching of the admixture from the film. The ionic liquids retained, according to IR spectra, in the synthetic polymer increase the conductivity of the poly(vinyl chloride) film, but insignificantly reduce the conductivity of the polyethylene terephthalate film. The dependences presented in Fig. 6 show that the conductivity of the

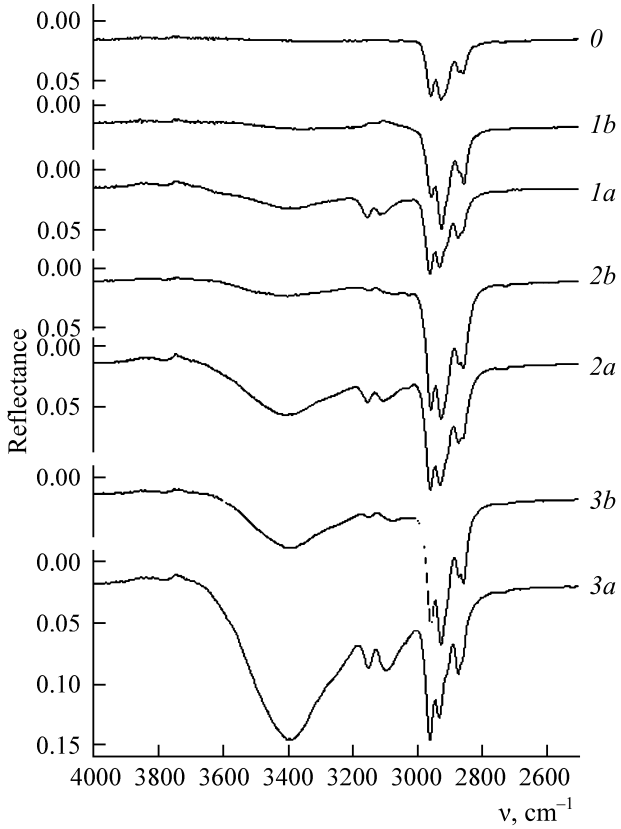


Fig. 5. FT-IR reflectance spectra of film **IV** before (*0*) and after (*1–3*) reaching adsorption equilibrium of ionic liquid [bmim][X] –**V**, X: Tf_2N (*1*), CF_3CO_2 (*2*) and Cl (*3*), (a) before and (b) after desorption.

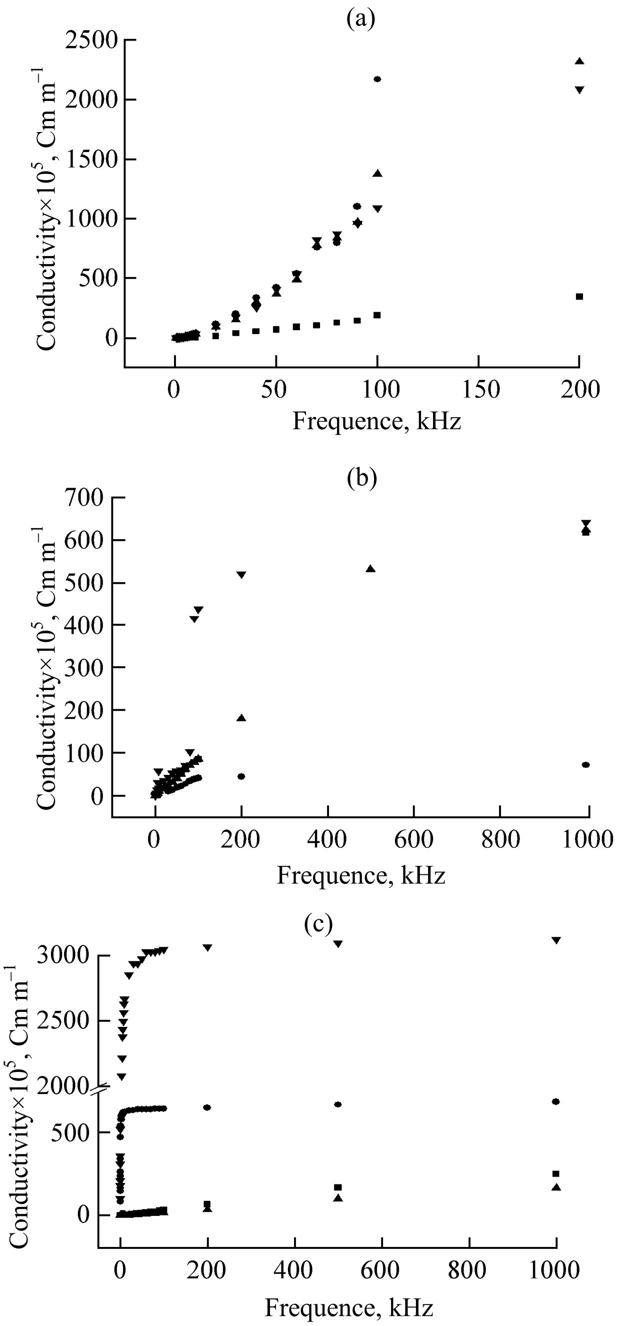


Fig. 6. Dependence of specific conductivity of the films (a) **IV**, (b) **III**, and (c) **V** on the frequency of alternating current before (squares) and after treatment in [bmim][X]–**V**; CF_3CO_2 (circles), Tf_2N (vertex up triangles) Cl (vertex down triangles) $U = 0.04$ V (a, c), 0.5 V (b), 25°C.

films of synthetic polymers both before and after treatment with the ionic liquids increase with the growing frequency of alternating current (Figs. 6a and 6b), which is typical for polymers. The frequency dependence of the specific conductivity of hydrated cellulose film with adsorbed [bmim][Cl] and [bmim]·[CF_3CO_2] (Fig. 6c), in contrast to other examined systems of polymer film–ionic liquid, have a broad plateau (the area of assessment of conductive properties of the material) characteristic of an electrolyte [20]. The limiting (frequency independent) value of σ characterizes the ionic conductivity of composite polymer films, they are 0.65×10^{-5} and 3.0×10^{-2} Cm m^{-1} for systems of hydrated cellulose–$[bmim]^+[CF_3CO_2]^-$ and hydrated cellulose–$[bmim]^+[Cl]^-$, respectively.

Thus, this study established that polypropylene, polytetrafluoroethylene (fluoroplast), polyethylene terephthalate, and poly(vinyl chloride) do not adsorb ionic liquids with the cation 1-butyl-3-methylimidazolium in a significant amount, and insulator properties of the polymers remained unchanged. Polytetrafluoroethylene as a tape cannot be used as an insulating material in a ionic liquid medium. Hydrated cellulose contributes to fixing the 1-butyl-3-methylimidazolium chloride and trifluoroacetate on the poly(vinyl chloride) film. The films of hydrated cellulose can serve as carriers of hydrophilic 1-butyl-3-methylimida-

Table 2. Relative changes in bulk specific conductivity of polymer films (σ–σ)/σ after processing with [bmim][X], *f* = 2 kHz, 25°C

Anion	**I**	**III**	**IV**	**V**
$[Cl]^-$	–0.44	–0.03	5.77	6810
$[CF_3CO_2]^-$	–0.04	–0.02	0.05	2730
$[Tf_2N]^-$	–0.10	–0.07	5.50	–0.05

zolium halide and acetate salts. The immobilization of 1-butyl-3-methylimidazolium chloride leads to an increase in electrical conductivity of the original film by several orders of magnitude and imparts it the properties of solid polymer electrolytes.

EXPERIMENTAL

The polypropylene, polytetrafluoroethylene, polyethylene terephthalate, poly(vinyl chloride) and hydrated cellulose polymer films from various manufacturers were conditioned at the atmospheric humidity 70–75% and temperature 25°C. The obtained samples were characterized by the density (*d*), thickness (δ), melting point (mp), and glass transition temperature (t_g), bulk specific conductivity (σ), and IR transmission spectra. The ionic liquids 1-butyl-3-methylimidazolium trifluoroacetate [bmim][CF_3CO_2], bistrifluromethylsulfonyl imide [bmim][$(CF_3SO_2)_2N$] or [bmim][Tf_2N] from Merck, and chloride [bmim][Cl] from Across Organics contained at least 96–98% of the main substance and 0.09, 0.07, and 2.58 wt % of water, respectively. These salts were kept in air at a humidity of 70–75% and a temperature of 25°C, the equilibrium moisture content was 10, 0.8, and 23 wt %, respectively. During the experiment, all the salts were in the melt or supercooled melt state. Some physicochemical properties of polymer films and ionic liquids are given in Table 3.

Filling the polymer films with ionic liquids was carried out as follows. In a glass sample bottle with 5 ml of an ionic liquid (sorbate) was immersed a polymer film (sorbent) weighing (*m*) from 0.019 to 0.3 g (depending on the polymer density). The liquor ratio was ~500, the processing temperature (25±2)°C, the humidity (73±2)%. Before immersing, the film was degreased by rubbing with a cotton swab soaked in ethyl alcohol. At regular time intervals the film was taken from the bath, the excess ionic liquids was removed from the surface mechanically with a glass spatula and a cotton swab with ethanol, dried, weighed (m_0) on an analytical balance Sartorius ME215S, and then again immersed in the ionic liquid. The adsorption process was regarded as completed when the film weight at the next weighing remained unchanged within the experimental error, or permanently decreased. The accuracy (±2%) estimated as the standard deviation of four independent short-term immersion of polypropylene and polyethylene terephthalate samples in the ionic liquid followed by the common treatment. The proposed method of adsorption of thin polymer films in a small volume of a fluid was pre-tested using traditional solvents with the polyethylene terephthalate–$CHCl_3$ and polypropylene–CCl_4 systems, as well as with the system under the study of hydrated cellulose–[bmim][Cl]. As a result,

Table 3. Physicochemical properties of polymer films and ionic liquids [bmim][X]

Compound	*M* [22]	δ, μm	d^{25}, g cm^{-3}	mp, °C	t_g ,°C	$σ^{25}$, Sm m$^{-1\ a}$
I	$(7–30)\times10^4$	20	0.98	164	–9	2.2×10^{-5}
II	$(5–1000)\times10^4$	355	2.84	>320	44, 140	1.4×10^{-6}
		10	1.07	349	–58	8.9×10^{-5}
III	$(2–5)\times10^4$	22	1.44	257	44, 152	3.4×10^{-5}
IV	$(1–15)\times10^4$	220	2.27	>150	–59, 57	4.4×10^{-6}
V	30–100 g m^{-3}	30	1.43	75	–	4.5×10^{-5}
$[Cl]^-$	174.7	–	1.08	–	–42	2.6
$[CF_3CO_2]^-$	252.4	–	1.209^b	85	–50	3.9^b
$[Tf_2N]^-$	419.4	–	1.429^b	0.5	–88, –60	3.2^b

^{a} *U* = 0.5 V (**I-III**), 0.04 V (**IV, V**), *f* = 2 kHz. ^{b} 20°C [21].

we obtained the classical curves of the polymer adsorption (swelling) [17], for three independent samples with the hydrated cellulose. These curves satisfactorily coincided with each other, which indicate the adequacy of the methodology used. The ionic liquid desorption from the polymer film was performed by prolonged contact with the filter paper.

The FT–IR reflectance spectra of the films **I**, **III–V** were recorded on a VERTEX 80v spectrophotometer in the frequency range from 8000 to 350 cm^{-1}. Microscopy of the films was performed using an optical microscope Mikromed coupled with a web camera DCM-130, the zoom 40 and 100. FT–IR transmission spectra of ionic liquids were recorded on a spectrophotometer Avatar 360 FT-IR ESP from thin layers between two KRS-5 plates, the frequency range 4000–200 cm^{-1}.

The melting temperature and the glass transition temperature of the studied objects were determined on a differential scanning calorimeter NETZCH DSC 204 F1, the capsule material was Al, the sample weight ~20 mg, heating in an atmosphere of N_2 from –90 to 100°C, heating rate 10°C min^{-1}.

The conductivity measurements were performed at 25°C using an immittance meter E7-20 in a cell with two smooth Pt electrodes with the area $S = 1.32$ cm^2. Film resistance (R) was measured at the alternating current voltage (u) on the cell of 0.04 or 0.5 V in the frequency range (f) from 25 Hz to 1 MHz. The values of bulk specific resistance ($r = R \times S/d$, Ω m) and the specific bulk specific conductivity ($\sigma = 1/r$, Cm m^{-1}) were calculated. The values of σ of the ionic liquids were determined at 25°C as described in [23].

As far as the ionic liquid after treatment of a film was carefully removed from the film surface, all changes in physical and chemical properties of the polymer films were considered to be associated with the adsorbed ionic liquid.

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