Synthesis and Physico-Chemical Properties of Ionic Liquids Based on 1-Butyl-3-alkylimidazolium with Inorganic Anions

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Abstract—Ionic liquids with 1-butyl-3-alkylimidazolium (alkyl = C_4H_9, C_8H_{17}, or $C_{10}H_{21}$) cation and Br^-, BF_4^-, or PF_6^- anions have been obtained. Composition and structure of the compounds have been confirmed by elemental analysis and IR spectroscopy data. Electrical conductivity of solutions of the synthesized compounds in acetonitrile has been studied, and association constant as well as equivalent electrical conductivity at infinite dilution have been calculated. Thermal stability of the prepared ionic liquids in air at 25–500°C has been studied.

**Keywords:** ionic liquid, thermal stability, electrical conductivity, association

Ionic liquids are salts with low melting point (usually <100°C); they commonly consist of a bulky organic cation and inorganic or organic anion. Ionic liquids conform with recent ecology requirements, exhibiting low toxicity, inflammability, low vapor pressure, and high thermal stability; this practically rule out the possibility of ionic liquids ingress in the environment and allows their use in "green" chemistry processes. Ionic liquids have been widely applied as extracting agents [1], solvents [2], in synthesis of electroconductive polymers [3], transmission electron microscopy [4], and other areas. When mixed with molecular solvents, ionic liquids have been used as

catalytic media [2] and electrolytes for batteries and supercapacitors [5].

Most attention has been paid to synthesis, study of properties, and application issues of 1-alkyl-3-methylimidazolium ionic liquids with various inorganic or organic anions [6–9]. In this work, we prepared ionic liquids **1**–**8** consisting of 1-butyl-3-alkylimidazolium cation and inorganic anions (Br^-, BF_4^-, PF_6^-) and studied their physico-chemical properties (Scheme 1).

1-Butyl-3-alkylimidazolium bromides **3** and **6** were obtained via the interaction of 1-butylimidazole with the corresponding alkyl bromide and converted into

Scheme 1.

R = *n*-C_4H_9 (**1**, **2**), *n*-C_8H_{17} (**3–5**), *n*-$C_{10}H_{21}$ (**6–8**).
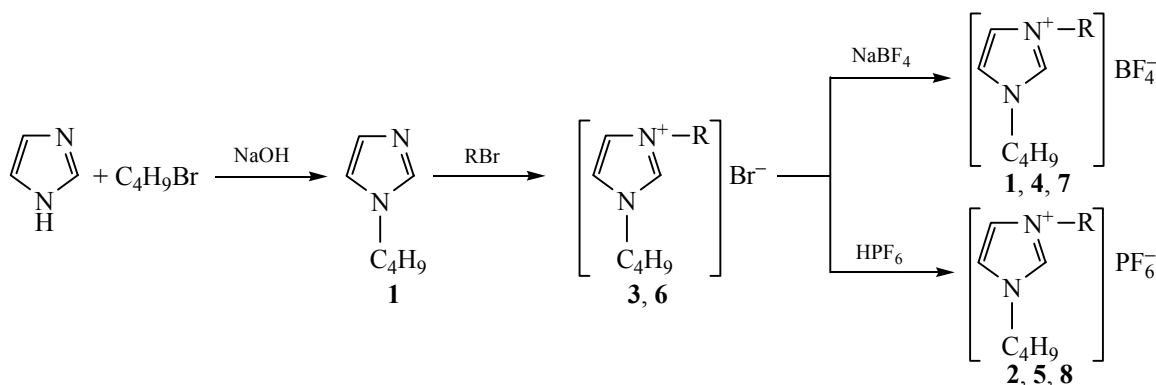
Table 1. Yield, physico-chemical parameters, and spectral features of 1-butyl-3-alkylimidazolium salts **1**–**8**

| Comp. no.	Yield, %	Found, %			Formula	Calculated, %			IR spectrum, ν, cm^{-1}
		C	H	N		C	H	N	
1	77	49.2	8.12	10.42	$C_{11}H_{21}BF_4N_2$	49.25	7.84	10.45	3110 (C–H$_{Ar}$); 2964, 2938, 2877 (C–H); 1566, 1480 (C–C$_{Ar}$); 1400, 1380 [δ(C–H)], 1059 (BF$_4$)
2	86	40.26	6.69	8.52	$C_{11}H_{21}F_6N_2P$	40.49	6.44	8.59	3119 (C–H$_{Ar}$); 2965, 2930, 2878 (C–H); 1613, 1566, 1469 (C–C$_{Ar}$); 1408, 1384, 1336 [δ(C–H)], 839 (PF$_6$)
3	71	56.52	9.48	8.79	$C_{15}H_{29}BrN_2$	56.78	9.15	8.83	3069 (C–H$_{Ar}$); 2958, 2929, 2857 (C–H); 1580, 1564, 1465 (C–C$_{Ar}$); 1407, 1390 [δ(C–H)]
4	80	55.23	9.24	8.58	$C_{15}H_{29}BF_4N_2$	55.56	8.95	8.64	3115 (C–H$_{Ar}$); 2959, 2929, 2859 (C–H); 1566, 1467 (C–C$_{Ar}$); 1379 [δ(C–H)], 1060 (BF$_4$)
5	83	46.94	7.81	7.29	$C_{15}H_{29}F_6N_2P$	47.12	7.59	7.33	3116 (C–H$_{Ar}$); 2960, 2931, 2859 (C–H); 1565, 1467 (C–C$_{Ar}$); 1385 [δ(C–H)], 840 (PF$_6$)
6	68	58.89	9.79	8.08	$C_{17}H_{33}BrN_2$	59.13	9.57	8.12	3063 (C–H$_{Ar}$); 2958, 2926, 2855 (C–H); 1564, 1465 (C–C$_{Ar}$); 1377 [δ(C–H)]
7	76	57.73	9.69	7.92	$C_{17}H_{33}BF_4N_2$	57.95	9.38	7.95	3088 (C–H$_{Ar}$); 2959, 2927, 2857 (C–H); 1566, 1467 (C–C$_{Ar}$); 1380 [δ(C–H)], 1058 (BF$_4$)
8	79	49.62	8.43	6.80	$C_{17}H_{33}F_6N_2P$	49.76	8.05	6.83	3117 (C–H$_{Ar}$); 2959, 2927, 2856 (C–H); 1565, 1467 (C–C$_{Ar}$); 1378 [δ(C–H)], 840 (PF$_6$)

the tetrafluoroborates (**1**, **4**, **7**) and hexafluorophosphates (**2**, **5**, **8**) under the action of NaBF$_4$ and HPF$_6$, respectively.

The prepared hexafluorophosphates and tetrafluoroborates of 1-butyl-3-alkylimidazolium were light brown liquids, insoluble in water, and readily soluble in polar organic solvents (ethanol, acetone, acetonitrile, etc.). Their composition and structure were confirmed by the data of elemental analysis and IR spectroscopy. Yield, physico-chemical parameters, and spectral features of the prepared compounds are summarized in Table 1.

Ionic liquids can partially or completely dissociate in the solution (i.e., exist in the form of ions or neutral molecules). The behavior of the ionic liquids in the solution was studied by conductometry of their solutions in acetonitrile. Basing on the obtained data, we plotted the equivalent electrical conductivity (λ) as a function of concentration (Fig. 1) and calculated the values of ionic association constant (K_a), limiting molar electrical conductivity (λ_0), and Gibbs energy of association (ΔG). Those parameters were obtained from the experimental conductometry data on the activity coefficient and electrical conductivity using the second approximation of Debye–Huckel theory and the Lee–Wheaton equation [10–12].

Special attention was paid to the choice of the highest concentration for the corresponding data to be used in the calculations. For the highest average ionic concentration of an electrolyte [12], Eq. (1) could be written.
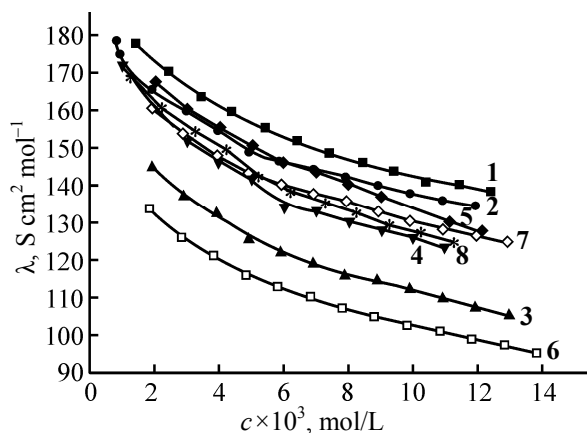
Fig. 1. Equivalent electrical conductivity of solutions of ionic liquids **1**–**8** in acetonitrile at 25°C as a function of concentration.

$$c_{max}^i = 9.1 \times 10^{-15} (\varepsilon T)^3. \tag{1}$$

The calculations were performed using the conductometry data for the concentration range of 10^{-4}–10^{-2} mol/L. The data were processed as described elsewhere [13]; the results are collected in Table 2.

In is to be seen in Fig. 1 that equivalent electrical conductivity of acetonitrile solutions of the ionic liquid decreased monotonously with the increase in the concentration of the ionic liquid in the solution. Such dependence is typical of aqueous solutions of strong electrolytes. Of the studied compounds, the lowest electrical conductivity was found for 1-butyl-3-decylimidazolinium bromide **6**, and the highest electrical conductivity was observed for 1,3-dibutylimidazolinium tetrafluoroborate **1**. The increase in the

Table 2. Limiting molar electrical conductivity λ_0, association constant K_a, and Gibbs energy of association ΔG for compounds **1**–**8**

| Comp. no.	M	λ_0, S cm^2 mol^{-1}	K_a, L/mol	ΔG, kJ/mol
1	267.9	200.10±0.89	51.42±2.50	–9.767
2	326.0	192.43±1.27	54.43±4.97	–9.908
3	317.1	174.59±1.82	89.69±7.37	–11.146
4	323.9	196.54±2.13	100.23±8.84	–11.421
5	382.1	189.20±1.13	52.82±2.82	–9.838
6	345.1	159.66±1.57	83.68±6.59	–10.974
7	351.9	186.02±1.82	58.37±3.39	–9.976
8	410.1	190.64±1.59	68.21±4.10	–10.467

cation size (from 1,3-dibutyl- to 1-butyl-3-decylimidazolium), the anion being the same, resulted in the decrease in the equivalent electrical conductivity, due to the lower mobility of the cation in the solution. The trend could be followed in the data for compounds **2**, **5**, and **8**, although the electrical conductivity of 1,3-dibutylimidazolium and 1-butyl-3-octylimidazolium hexafluorophosphates was close. Electrical conductivity of the solutions of the ionic liquids with the same cations increased in the anions series Br$^-$ < BF$_4^-$ < PF$_6^-$. That could be explained by the fact that the larger anions had smaller solvate shell, and that increased the anion mobility in the solution.

Analysis of the data in Table 2 showed that the values of association constants for ionic liquids with hexafluorophosphate and bromide anions were equal within the accuracy limits. On the contrary, the constants for the tetrafluoroborates were significantly different: for example, the association constants for 1-butyl-3-octylimidazolinium and 1,3-dibutylimidazolinium tetrafluoroborates differed by two times. The association constants were different for the ionic liquids with the same cation as well. That led to the conclusion that the association constant was affected by the size and nature of both the anion and the cation of the ionic liquid. The Gibbs energy of association of the studied ionic liquids ranged from –9.7 to –11.4 kJ/mol. From the values of the constants and the Gibbs energy of association it followed that the most associated ionic liquids were 1-butyl-3-octylimidazolium tetrafluoroborate and bromide.

The influence of temperature on the equivalent electrical conductivity of the solutions of the studied ionic liquids in acetonitrile is shown in Fig. 2. The heating induced the proportional increase in the equivalent electrical conductivity. The effect could be explained by the higher mobility of the ions due to the partial disruption of the solvate shell and the increase in the total energy of the system upon heating.

The behavior of the acetonitrile solutions of the prepared ionic liquids coincided with the data of [9] on properties of solutions of imidazolium and pyridinium ionic liquids dissolved in methanol.

Practical application of ionic liquids is often related to the use of high temperature. Ionic liquids have been recognized as the compounds with relatively high thermal stability. The information on thermal stability of ionic liquids allows prediction of their decomposition in various real-life processes.
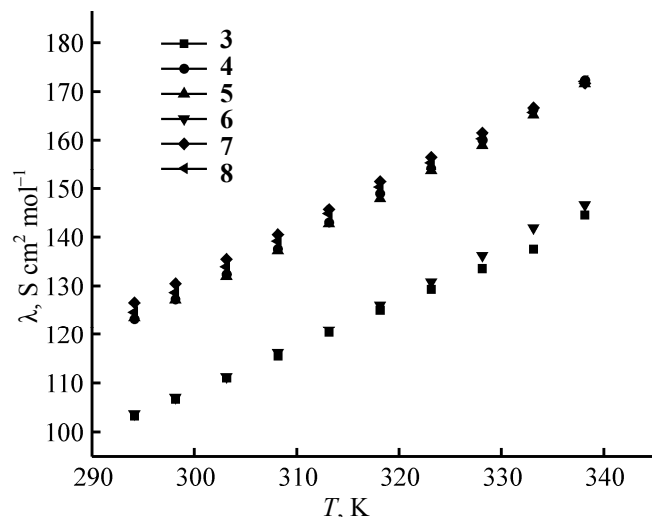
Fig. 2. Equivalent electrical conductivity of solutions of ionic liquids **1–8** (c = 0.01 mol/L) as a function of temperature.

Fig. 3. Mass loss curves for 1-butyl-3-alkylimidazolium tetrafluoroborates and hexafluorophosphates.

Thermal stability of ionic liquids can be different depending on the nature and symmetry of its ions. The salts with high-symmetry cations are generally more thermally stable than these with the non-symmetric cations. Thermal decomposition of the salts containing the similar anions is determined by the nature and structure of the cation [14]. Imidazolium-based ionic liquids are more thermally stable as compared with the ammonium-containing ones, since the latter undergo transalkylation and dealkylation reactions (retro-quaternization) at elevated temperature (up to 180°C). However, these reactions are affected by the anion nature. For example, temperature of 150°C is the highest operation temperature for quaternary ammonium chlorides. whereas the tetrafluoroborates are stable up to 300°C [15–16].

We studied thermal stability of the prepared ionic liquids at 25–500°C in air (Fig. 3). The studied 1-butyl-3-alkylimidazolium tetrafluoroborates and hexafluorophosphates were stable up to 280–310°C and slowly decomposed at 300–450°C. The decomposition process was complex and consisted of several stages, as indicated by the inflections at the mass loss curves. The tetrafluoroborates were less thermally stable than the hexafluorophosphates. Thermal stability of the studied tetrafluoroborates was practically equal (they were stable up to 290°C). Similarly, thermal stability of the hexafluorophosphates was independent of the length of the alkyl fragment in position 3 of the ring; those compounds were stable up to 310°C.
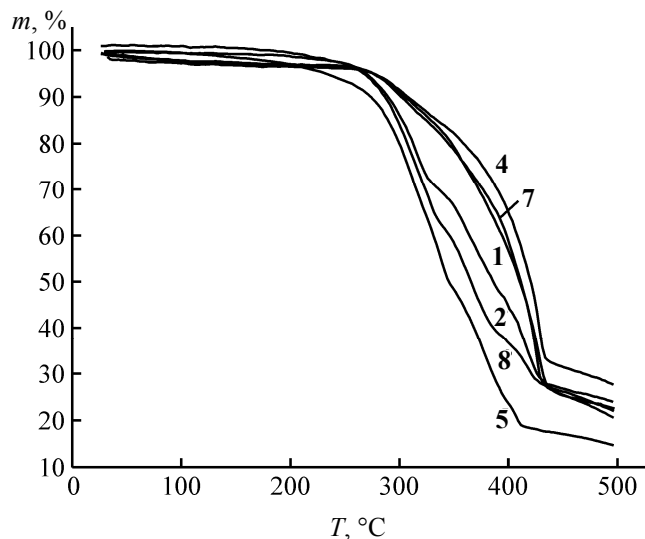
In comparison with 1-butyl-3-alkylimidazolinium hexafluorophosphates and tetrafluoroborates, the corresponding bromides were less thermally stable and rapidly decomposed in a single stage at 250–320°C, the mass loss being quantitative (Fig. 4).

The obtained data on the thermal stability revealed that the nature and structure of the anion was the factor determining thermal stability of the studied ionic liquids. The enhanced thermal stability has been earlier marked for ammonium tetrafluoroborates as well [15]. Ionic liquids containing halide anions are generally decomposed at lower temperature than the correspon-
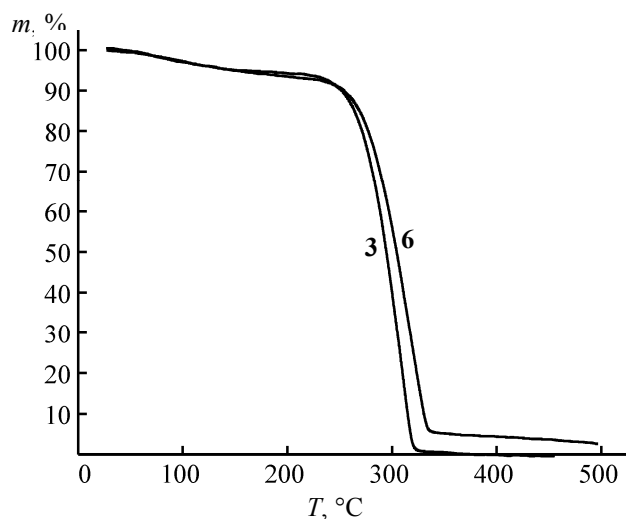
Fig. 4. Mass loss curves for 1-butyl-3-alkylimidazolium bromides **3** and **6**.

ding ionic liquids with bulky anions exhibiting low nucleophilicity [17]. Thermal decomposition of ionic liquids containing bulky leaving groups evidently occurs via the Hoffman E2-elimination and leads to the formation of the least substituted alkene [18]. Since the increase in temperature does not affect the decomposition onset, it can be concluded that thermal decomposition of ionic liquids is primarily determined by thermodynamic stability of the compound (activated complex) rather than its oxidation with air oxygen.

EXPERIMENTAL

IR spectra were recorded using an ALPHA spectrometer (thin film between KBr plates for liquids and KBr pellets for solids). Elemental analysis was performed using a Perkin Elmer CHNS/O PE 2400-II analyzer. Thermogravimetry data were obtained using a Netzsch STA 449 F3 instrument (air atmosphere, temperature range 25–500°C, heating rate 5 deg/min). Electrical conductivity of the solutions in acetonitrile was measured using a Seven Go Pro Mettler Toledo conductometer at 25±0.1°C. Acetonitrile was dried by boiling and distillation over P_4O_{10}.

1-Butylimidazole. 100 mL of acetone was added to a solution of 33.7 g (0.6 mol) of KOH in 33 mL of water, and then 13.6 g (0.2 mol) of imidazole was added at vigorous stirring. After 15 min, 23.2 mL (0.22 mol) of freshly distilled butyl bromide was added over 20 min, and the mixture was refluxed during 10 h. The obtained mixture was cooled down to ambient and kept in a fridge during a day. Acetone was distilled off the organic layer, and the residue was distilled in vacuum, mp 114–116°C (12 mmHg). Yield 17.8 mL (65%), colorless oily liquid, n_D^{20} 1.4825, d 0.945 g/cm^3.

1-Butyl-3-alkylimidazolium bromides. Equimolar amount of a freshly distilled alkyl bromide (1-bromobutane, 1-bromooctane, or 1-bromodecane) was added dropwise to 7 mL (0.05 mol) of 1-butylimidazole. The mixture was heated on a water bath at 70–80°C during 10–18 h. The formed crystals of the quaternary salt were filtered off, washed with anhydrous cold diethyl ether, recrystallized from acetone, and dried in vacuum. The salts were white crystalline solids, readily soluble in water.

1-Butyl-3-alkylimidazolium tetrafluoroborates. Equimolar amount of aqueous solution of sodium tetrafluoroborate was added dropwise at stirring to a solution of 0.01 mol of 1-butyl-3-alkylimidazolinium bromide in a minimal amount of water. The resulting mixture contained of aqueous NaCl solution (upper phase) and the ionic liquid (bottom phase). They were separated using a separating funnel. Ionic liquid was several times washed with water and dried in vacuum during 24 h.

1-Butyl-3-alkylimidazolinium hexafluorophosphates were prepared similarly from 0.01 mol of the bromide and equimolar amount of 60% aqueous solution of hexafluorophosphoric acid ($d = 1.75$ g/cm^3).

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