ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 8, pp. 1720–1727. © Pleiades Publishing, Ltd., 2009. Original Russian Text © M.S. Gruzdev, L.M. Ramenskaya, U.V. Chervonova, R.S. Kumeev, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 8, pp. 1360–1368.

Preparation of 1-Butyl-3-methylimidazolium Salts and Study of Their Phase Behavior and Intramolecular Intractions

M. S. Gruzdev, L. M. Ramenskaya, U. V. Chervonova, and R. S. Kumeev

Institute of the Chemistry of Solutions, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia e-mail: gms@isc-ras.ru

Received February 5, 2009

Abstract—Seven organic salts of 1-butyl-3-methylimidazolium with anions Br^- , BF_4^- , NO_3^- , SO_4^{2-} , HSO_4^- , SCN^- , PO_4^{3-} were prepared. Structure of these compounds is elucidated and purity is confirmed. The products are characterized by melting point, thin layer chromatography, data of elemental analysis, cromatomass-, NMR and IR spectroscopy. All these compounds are ionic liquids, five are low temperature ones. Principal thermal characteristics are found that allow accounting for the phase behavior of the prepared compounds at their application. Existence of intramolecular and intermolecular interactions between the heterocyclic anion and inorganic cation in by means of the formation of hydrogen bond is established.

DOI: 10.1134/S1070363209080246

Among the priority directions of the modern "green chemistry" an important one is application of ionic liquids [1], the salts of heterocyclic bases with acid anions, as the most promising medium for some reactions. It is expected that application of ionic liquids can lead to change in rate, conversion, yield and selectivity, of catalitic processes in particular [2]. The ionic liquids are also used in biocatalysis, for producing membranes with improved transfer of substrate, as electrolyte in electrochemistry and stationary phase in chromatography, in certain modes of mass-spectrometry, for determination of vapors of volatile substances by gravimetric method [3–6]. Now the methods of treatment of plant biomass [7] and new methods for utilization of nuclear wastes are in development. In this connection, preparation of ionic

liquids with predefined properties, optimization of current methods for the preparation of the known ionic liquids, and the study of their properties is urgent.

There are different opinions now on the problem of intramoleclar interaction, in particular, of hydrogen bonding of counter ions in ionic liquids [7,8], and this is a theme of active investigations because it is closely connected with some physical properties of ionic liquids such as viscosity, conductivity, density and crystalline structure.

The aim of this work is preparation and study of phase behavior of ionic liquids, the salts of 1-butyl-3methylimidazolium with different anions, and elucidation of hydrogen bonding of the heterocyclic cation with various ionorganic anions.



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Phase behavior of the synthesized compounds. The values of thermodynamic parameters obtained by the investigations with differential scanning calorimetry (DSC) and thermogravimetry (TG) in the cycles of heating of the prepared compounds are listed in Table 1. Further we use formula [BuMeIm] to denote 1-butyl-3-methylimidazolium cation.

Bis-1-butyl-3-methylimidazolium sulfate [BuMeIm]₂. SO₄ can be classed with high-temperature ionic liquids (mp = 158.71°C). At first and second heating of [BuMeIm]₂SO₄ occurs two crystal–crystal phase transitions (107.9°C and 136.3°C) followed by complete melting at 158.7°C. These phase transitions most probable occur by the disruption of the cation–

Composition	Glass transition		Crystallization, exothermic effect		Melting, endothermic effect		Decomposition	
	T _g , ℃	$\Delta C_{\rm p}$, J g ⁻¹ K ⁻¹	<i>T</i> _c , °C	ΔH , J g ⁻¹	mp, °C	ΔH , J g ⁻¹	$T_{\rm dec}$, °C	Δm , wt %
BMImBr	-58.2	0.4	30.4	69.2	76.4	66.2	287	-2.74
[BMIm]BF ₄			-91.99	2.85	-66.30	0.16	296	-7.58
					6.15	0.36		
[BMIm]NO ₃			-20.28	44.36	2.06	9.51	113.52	-1.65
[BMIm] ₂ SO ₄					107.9	0.67	229.92	-4.43
					136.31	0.456		
					158.71	26.47		
[BMIm]HSO ₄	-65.5	0.035			4.3	1.67	291	-2.05
					24.8	0.69		
					31.52	36.70		
BMImSCN	-58.83	0.032			-28.63	1.41	-	—
[BMIm] ₃ PO ₄	-71.3	0.610					—	_

Table 1. Thermodynamic parameters of synthesized compounds

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Fig. 1. DSC curves of 1-butyl-3-methylimidazolium hydrosulfate in the cycles of heating and cooling.

anion interaction by hydrogen bonding. In the cycle of cooling, the crystallization occurs only at 86.3°C. This substance has also high enough decomposition temperature ($T_{\text{decomp.}} = 229.92$ °C) and can be used as a medium for carrying out high temperature syntheses in the range 160–220°C.

1-Butyl-3-methylimidazolium bromide being lowtemperature ionic liquid (mp = 76.4°C) can be used at the temperature up to 240°C ($T_{decomp.} = 241$ °C). This compound is a solid glassy substance at room temperature. At heating the crystallization of the sample occurs at the temperature ~30°C. The melting point characterizing the salt transition into a stable melt is ~76°C [11]. Noteworthy that at cooling the melt its transition into the crystalline state does not occur but proceeds direct transition to the glassy state. Just due to such phase behavior 1-butyl-3-methylimidazolium bromide synthesized by us is a thermally stable substance. Even more, the substance in glassy state is less hygroscopic as compared with the same substance in crystalline phase.

1-Butyl-3-methylimidazolium hydrosulfate resembles bromide by its thermal behavior. A difference in their phase behavior is that at the first cooling of the hydrosulfate from room temperature to the temperature below zero occurs its crystallization at -43.6° C followed by transition to glassy state (Fig. 1). Such behavior is specific for [BuMeIm]HSO₄, while at the first cooling of other ionic liquids from room temperature to low temperatures the crystallization does not occur but there is only the phase transition to glassy state. This feature can be ascribed to the existence of strong hydrogen bonds inside the molecules due to interaction of organic cation with inorganic anion. This interaction is registered clearly by means of IR spectroscopy as will be shown below. At further heating the substance suffers two phase crystal–crystal transitions, finally with melting at 31.5° C. At the second cooling the substance transfers from the melt to glassy state directly at -62.5° C, and then undergoes crystallization at 9.8° C and complete melting at 28.6° C. Noteworthy that at the second cooling of [BuMeIm]HSO₄ only the transition to glassy state was registered at -67.7° C.

Among the prepared compounds, 1-butyl-3methylimidazolium tetrafluoroborate and nitrate also belong to the group of low-temperature ionic liquids. Due to their low crystallization temperature (-91.99 and -20.28°C, respectively), they even at room temperature are in the state of stable melt. Noteworthy that we failed to register crystallization and melting tris-1-butyl-3-methylimidazolium points for orthophosphate that has vertification temperature in -71.32°C, below that of bromide (-58.2°C) and hydrophophosphate $(-65.5^{\circ}C)$. By the data of DSC, tris-1-butyl-3-methylimidazolium orthophosphate exists at low temperature (below zero) in glassy state while at room temperature in isotropic state (melt), therewith the processes of crystallization-melting have not been registered. Such existence of a compound in liquid state is ideal for its practical application.

The cation–anion interaction. One target at the study of physicochemical properties of the prepared compounds is to confirm the structure of these compounds by the methods of IR and NMR spectroscopy. Below is shown general structural formula of the studied compounds:



 $X = Br^{-}, BF_{4}^{-}, NO_{3}^{-}, SO_{4}^{2-}, HSO_{4}^{-}, SCN^{-}, PO_{4}^{3-}.$

For each salt we obtained characteristic IR absorption bands of respective anion, but this does not allow elucidation of its location relative to the heterocycle. Nevertheless, we succeeded in registering a strong interaction between the organic cation and inorgatic anion. In the IR spectrum of 1-butyl-3-methylimidazolium tetrafluoroborate the bands of vibration of aromatic system 3217–3064 cm⁻¹ and aliphatic groups 3021–2801 cm⁻¹ [12] (Fig. 2) are strictly separated. The water absorption band 3435 cm⁻¹

in the spectrum of BuMeImBr is shifted to the value 3449 cm^{-1} and is not of clear character that is understandable because of the low content of water in the sample (0.24 wt %, Table 2). The shift of aromatic C-H vibration bands for H^2 , H^4 , H^5 of imidazolium cation in the region of $3100-3200 \text{ cm}^{-1}$ (Table 2) reflects the existence of C-H…F hydrogen bonds. Something similar occurred in the IR spectrum of 1butyl-3-methylimidazolium tetrafluoroborate synthesized by another procedure [12]. Dupont assumed the interaction of anion and cation through B-F...H-C hydrogen bond that has been latter confirmed by the data of two-dimensional ¹H NMR spectroscopy. In [12] was also shown appearance of strong bands at 3640 and 3562 cm⁻¹. Unfortunately, Dupont restricted himself to the statement of a fact of cation-anion interaction on account of formation of intramolecular bonds explaining the mechanism of its formation by analogy with [13, 14] and leaving without answer the appearance of the obvious bands of the formed dimers and trimers via intermolecular hydrogen bond [15–17]. The band at 3640 cm⁻¹ supposedly points to formation of inter-molecular hydrogen bond between fluorine atom and hydrogen atoms H⁴, H⁵ of imidazole ring. Another new band of lower intensity at 3562 cm⁻¹ indicates the presence of hydrogen bond between anion and the imidazole ring hydrogen atom H^2 . The possibility of appearance of cross-linked structures due to binding of cations and anions through hydrogen bonds is shown also in [18], by the examples of 1butyl-3-methyl-imidazolium tetrafluoroborate and hexafluorophosphate.

Introduction of less polar groups such as the anion (HSO_4^-) on the contrary leads to appearance of a broad but weak band (2497 cm⁻¹) in the IR spectrum of 1butyl-3-methylimidazolium hydrosulfate (Fig. 1). This is due to the formation of a dimer of two HSO₄ ions (H–O–S–O···H–O–S–O···), like that found for KHSO₄ [18, 20]. The HSO_4^- dimer in its turn interacts with the imidazole protons with the formation of a hydrogen bond. Similar picture was observed for dimethylimidazolium hydrosulfate [21] and was understood as H…O hydrogen bonding of imidazole ring and HSO₄⁻ ions. This conclusion confirms hydrophilic character of the compound and explains its phase transitions in the first cycle of heating and cooling. Similar picture is observed in the IR spectra of 1-butyl-3-methylimidazolium nitrate. In the region of 2386 cm⁻¹ appears a sharp strong band that supposedly reflects H...O interaction of imidazole ring and NO_3^- ions (Fig. 3).



Fig. 2. IR spectra of 1-butyl-3-methylimidazolium tetrafluoroborate and hydrosulfate.

To confirm the conclusions about the hydrogen bonding of the organic cation with anion we carried out NMR investigation of all seven prepared compounds. From the data of ¹³C NMR spectra collected in Table 3 it is not possible to the interaction of cation and anion on the intermolecular level. However, it can be concluded unambiguously that the structure of the spectrum of carbon skeleton remains unchanged with different anions. This evidences indirectly that in the interaction are involved the hydrogen atoms of imidazole ring rather than of aliphatic groups of the cation. From the analysis of ¹H NMR spectrum of the studied compounds follows that the interaction of anion with cation results in the shifts of the signals of the imidazole ring protons and in variations of spin-spin coupling constant J of the protons H^4 and H^5 (Table 4). The interactions like that were also detected in 1-butyl-3-methylimidazolium hexafluorophosphate [18, 22]. Note that rather strong

Table 2. Vibration bands of π -system of the obtained compounds

Compound	Vibration band Ph1, v, cm ⁻¹	Vibration band Ph2, v, cm ⁻¹	Vibration band H ₂ O, v, cm ⁻¹	
BMImBr	3065.66	3139.74	3435.98	
$BMImBF_4$	3124.39	3158.79	3449.51	
BMImNO ₃	3100.25	3148.24	3490.41	
[BMIm] ₂ SO ₄	3032.13	3138.24	3371.35	
BMImHSO ₄	3109.34	3152.69	3449.51	
BMImSCN	3070.95	3150.92	3453.53	
[BMIm] ₃ PO ₄	3115.63	3157.96	3391.35	
		1		

Compound	C^{10}	C ⁹	C^8	C ⁶	C ⁷	C ⁵	C^4	C^2
[BMIm]Br	13.43	19.49	32.01	36.48	50.02	122.96	124.20	136.55
[BMIm]BF ₄	13.27	19.42	31.95	36.23	49.92	122.86	124.15	136.49
[BMIm]NO ₃	13.23	19.38	31.90	36.18	49.88	122.80	124.06	136.43
[BMIm] ₂ SO ₄	13.46	19.46	31.96	36.52	49.96	122.93	124.17	136.47
[BMIm]HSO ₄	13.31	19.46	31.56	36.36	49.93	122.88	124.16	136.52
[BMIm]SCN ^a	13.49	19.57	32.06	35.5	50.07	122.95	124.2	136.53
[BMIm] ₃ PO ₄	13.32	19.38	31.84	36.32	49.90	122.84	124.13	136.26

Table 3. ¹³C NMR chemical shifts of the synthesized compounds

^a For SCN 17.63.

Table 4. ¹H NMR signals of imidazole ring protons of the prepared liquids

Compound	$C^{2}(H)$	$C^{4}(H)-C^{5}(H)$	$J(\mathrm{H_4H_5})$
[BMIm]Br	8.72	7.44	10.99
[BMIm]BF ₄	8.71	7.53	7.32
[BMIm]NO ₃	8.58	7.35	9.77
[BMIm] ₂ SO ₄	8.78	7.48	10.98
[BMIm]HSO ₄	8.53	7.34	9.77
[BMIm]SCN	8.73	7.47	10.99
[BMIm] ₃ PO ₄	8.41	7.14	8.55

spin-spin interaction of the protons in the organic cation (H^4, H^5) occurs for the salts that at room temperature are in melted state (liquid). On this basis we assume that the glassy state dominating in most of the prepared compounds is defined by the interaction of organic cation with inorganic anion with involvement of the hydrogen bond between these cation and anion. The strength of such interaction is defined by the nature of the acid anion.



Fig. 3. IR spectrum of 1-butyl-3-methylimidazolium nitrate.

EXPERIMENTAL

The IR spectra of compounds were registered on an Avatar 360 FT-IR ESP instrument in the region of 350-4500 cm⁻¹ from KBr pellets and between KRC plates. The NMR spectra on the nuclei ¹H (200.13 MHz) and ¹³C (50.32 MHz) were registered on a Bruker AC-200 spectrometer, with deuterated water as a solvent, external reference cyclohexanol. The elemental analysis of crystalline compounds was carried out on a FlashEA 1112 analyzer, that allows determination of carbon, hydrogen, sulfur and nitrogen in the samples by oxidation. The chromatograms and mass-spectra were registered on a Saturn 2000R chromato-mass spectrometer, carrier gas helium. Content of water was measured by amperometric titration by Fisher method. The thermogravimetric analysis (TG) was carried out on a NETZCH TG 209 F1 analyzer in the argon flow 20 ml min⁻¹, the heating rate 10 deg min⁻¹. The differential scanning calorimetry (DSC) was carried out on a NETZCH DSC 204 F1 instrument, the capsule material Al, sample weight ~ 20 mg, heating under N₂ atmosphere from -110 to 100°C, heating rate 10 deg/min. The capsule was prepared along the standard procedure just prior to each measurement. Thin layer chromatography was performed on Silufol UV 254 plates, Czech Republic. The plates were developed in a chamber filled with iodine vapor or under a UV lamp ($\lambda = 254$ nm).

1-Butyl-3-methylimidazolium bromide (I). Two basic methods of synthesis of 1-butyl-3-methylimidazolium bromide as a source reagent for the following preparation of representatives of ionic liquids have been published. The first is to carry out the quarternization reaction at elevated temperature (110–130°C) for 3–4 hours, sometimes with the use of solvent [9]. As a result, the target product yield reaches 95–98%. The main disadvantage of this approach is formation of a number of impurities that affect the physical and chemical properties and application of the product. The second way is based on the prolonged (72 h) stirring at low temperature (50°C) in an inert medium in a solvent, which leads to an increase in the synthesis duration and thus increases the costs of its production. The yield of the product reaches 80–90% [10]. We developed a modified method for the synthesis of 1butyl-3-methylimidazolium bromide, which is featured by controlled temperature (not above 75°C) and controlled feeding of the second reagent, butyl bromide. This approach allows to prepare the product in a relatively short time interval and does not increase the cost of subsequent stages of purification. The main advantage of our approach is to reduce the moisture content in the final product, which makes it convenient for further application and for the use in physical and chemical research without prior drying.

For this purpose, according to the developed scheme, to 33.75 g of 1-methylimidazole at 70°C with stirring was added butyl bromide (60.96 g), so that the temperature did not rise above 70°C. After adding the entire butyl bromide, the mixture was maintained at stirring for 4 h at a temperature of about 70°C. The product (BMImBr) is a light-yellow liquid that crystallizes into a white solid mass. Yield 90 g (98.5%). IR spectrum of BMImBr, v, cm^{-1} : 3100– 3000 s (aromatic C-H vibrations), 2970-2760 (CH₂ aliphatic); 1600–1480 (C–N); 1070–1000 (1,3substituted system), 622 [amide (III) band). Mass spectrum, m/e: calculated M 219, found 219 $[M]^+$, 125 $[M - Me]^+$, 97 $[M - CH_2 - CH_2 - Me]^+$, 82 [M - C(H)NC(H) - C(H)NC(H)CH₂–CH₂–CH₂–Me]⁺. ¹H NMR spectrum (D₂O), δ , ppm: 0.8 t (3H, CH₃), 1.21 m (2H, CH₃-CH₂-(CH₂)₂-N); 1.73 m (2H, N–CH₂–CH₂); 3.81 s (2H, N–CH₂), 4.07 t (3H, N-CH₃); 7.43 d (2H, N-CH-CH-N); 8.72 s (1H, N–C(N)–N). ¹³C NMR spectrum (D₂O), δ_C , ppm, reference cyclohexanol: 13.43, 19.49, 32.01, 36.48, 50.02, 122.96, 124.20, 136.55. Water content 0.64 wt %. Found, %: C 42.16, H 7.50; N 13.38; Br 37.96. C₈H₁₅BrN₂. Calculated, %: C 43.58, H 7.47; N 12.70; Br 36.24.

1-Butyl-3-methylimidazolium tetrafluoroborate (II). 29.1 g of fresh silver(I) oxide was stirred with 100 ml of water in a Teflon beaker to formation of a homogeneous mass. Then from a plastic burette was added within 30 minutes 32.8 ml of tetrafluoroboric acid (Aldrich, 48%). Stir ring was continued for 2 h, and then the colorless clear solution of salt $AgBF_4$ was filtered from unreacted silver oxide. To a weighted

amount of 1-butyl-3-methylimidazolium bromide (48 g) in water (30 ml), with thorough stirring was added dropwise the AgBF₄ solution. The reaction mixture was vigorously stirred in the dark for 2 h. Then the resulting AgBr precipitate was filtered off and washed with water. The filtrate was concentrated on a rotory evaporator. The resulting mass of amber color was chromatographed on a column (silica gel, eluent chloroform-acetonitrile, 1:2). The product is a lightyellow liquid. Yield 43.2 g (87%). IR spectrum (BMImBF₄), v, cm⁻¹: 3162, 3122 s (aromatic C-H vibrations), 2964, 2877 s [(CH₂)_n-CH₃ vibrations], 1467 s (symmetric aromatic ring vibrations), 1171 s (symmetric vibrations of aromatic ring), 1054 br.s (BF₄ vibrations), 624 m [amide (III) band]. ¹H NMR spectrum (D₂O), δ, ppm: 0.97 t (3H, CH₃), 1.39 sextet (2H, CH₃-CH₂-(CH₂)N); 1.91 q (2H, N-CH₂-CH₂), 3.83 s (3H, N-CH₃), 4.24 t (2H, N-CH₂), 7.53 d (2H, N-CH-CH-N); 8.71 s (1H, N-C(H)-N). ¹³C NMR spectrum (D₂O), δ_C , ppm, reference cyclohexanol: 13.27, 19.42, 31.95, 36.23, 49.92, 122.86, 124.15, 136.49. Water content 0.24 wt %.

1-Butyl-3-methylimidazolium nitrate **(III)**. Weighted amount (16.31 g) of 1-butyl-3-methylimidazolium bromide was dissolved in 30 ml of water, and a solution of 12.65 g of silver nitrate in 20 ml of water was added dropwise. Stirring was continued for 2 h in the dark. The AgBr precipitate was filtered off, the resulting filtrate was evaporated on a rotary evaporator and then subjected to azeotropic distillation with ethyl alcohol. Then a few portions of dry acetone were added to remove unreacted AgNO₃. The product, dissolved in ethanol, was applied to the chromatographic column filled with activated carbon. The solvent was removed on a rotory vacuum evaporator. The product is a light-yellow viscous liquid. Yield 12.28 g (83%). IR spec-trum (BMImNO₃), v, cm⁻¹: 3147, 3101 s (aromatic C-H vibrations), 2962, 2875 s $[(CH_2)_n$ -CH₃ vibrations), 1465 s (symmetric vibrations of aromatic ring), 1169 s (symmetric vibrations of aromatic ring), 1344 br.s (NO₃ vibrations), 624 m [amide (III) band]. ¹H NMR spectrum (D₂O), δ , ppm: 0.78 t (3H, CH₃), 1.20 sextet (2H, CH₃-CH₂-(CH₂)N); 1.74 g (2H, N-CH₂-CH₂); 3.82 s (3H, N-CH₃), 4.09 t (2H, N-CH₂), 7.35 d (2H, N-CH-CH-N); 8.58 s (1H, N–C(H)–N). ¹³C NMR spectrum (D₂O), δ_{C} , ppm, reference cyclohexanol: 13.23, 19.38, 31.9, 36.18, 49.88, 122.80, 124.06, 136.46. Water content 8 wt %.

Bis-1-butyl-3-methylimidazolium sulfate (IV). To a solution of 1-butyl-3-methylimidazolium bromide (4.19 g) in water (30 ml), with careful stirring was

added a solution of $(NH_4)_2SO_4$ (2.51 g). The reaction mixture was stirred at room temperature for 7 days. Water was removed on a vacuum rotory evaporator. The product was washed with a mixture of acetone (100 ml) and ethanol (50 ml). The reaction mixture was several times dissolved in ethanol and subjected to azeotropic distillation on a rotory evaporator. The product obtained is a viscous yellow liquid. After adding dichloromethane, white crystals precipitated that were filtered off on a glass filter and washed with cold CH₂Cl₂. Yield 0.82 g (16.42%). IR spectrum ([BMIm]₂SO₄), v, cm⁻¹: 3147, 3032 s (aromatic C-H vibrations), 2971, 2889, s [(CH₂)_n-CH₃ vibrations), 2798 w [(CH₂)_n-CH₃ vibrations], 1398 s (symmetric vibrations of aromatic ring), 1170 s (symmetric vibrations of aromatic ring), 1009. br.s (SO₄ vibrations), 607 w [amide (III) band]. Mass spectrum, m/e: calculated M 348.54, found $[M^+ + Na^+]$ 371, $[M^+ +$ Ca²⁺] 390. ¹H NMR spectrum (D₂O), δ , ppm: 0.93 t (6H, CH₃), 1.4 sextet (4H, CH₃-CH₂-(CH₂)N); 1.92 q (4H, N-CH₂-CH₂); 3.98 s (6H, N-CH₃), 4.28 t (4H, N–CH₂), 7.48 d (4H, N–CH–CH–N); 8.78 s (2H, N–C (H)–N). ¹³C NMR spectrum (D₂O), δ_{C} , ppm, reference cyclohexanol: 13.46, 19.46, 31.96, 36.52, 49.96, 122.93, 124.17, 136.47. Water content 3 wt %. Found, %: C 55.01, H 9.45; N 8.43; O 17.94. C₁₆H₃₀N₄O₄S. Calculated, %: C 55.05; H 9.49; N 8.02; S 9.17; O 18.32.

1-Butyl-3-methylimidazolium hydrosulfate (V). To a solution of silver sulfate (4.08 g) in 40% H₂SO₄ (20 ml) was added 1-butyl-3-methylimidazolium bromide (4.05 g) dissolved in ethyl alcohol. The mixture was stirred for 2 h at 50°C. The precipitate was filtered off. To the filtrate was added acetonitrile, the mixture was filtered again, and acetonitrile was distilled off. The procedure was repeated several times. The product is a liquid of amber color, which crystallized at storage. The product was recrystallized from a mixture of acetonitrile and ethyl acetate, 1:5. Yield is about 7.75 g (75%). IR spectrum of (BMImNSO₄), v, cm⁻¹: 3150, 3108 s (aromatic C-H vibrations), 2962, 2875 with [(CH₂)_n-CH₃ vibrations], 2936 with $[(CH_2)_n$ -CH₃ vibrations], 1466 s (symmetric vibrations of aromatic ring), 1171 s (symmetric vibrations of aromatic ring), 1046 br.s (NSO₄ vibrations), 624 m [amide (III)]. Mass spectrum, m/e: calculated M 237, found 235 $[M]^+$. ¹H NMR spectrum (D₂O), δ , ppm: 0.75 t (3H, CH₃), 1.66 sextet [2H, CH₃-CH₂-(CH₂)N]; 1.68 g (2H, N-CH₂-CH₂], 3.73 s (3H, N-CH₃), 3.99 s (1H, NSO₄), 4.06 t (2H, N-CH₂),

7.3 d (2H, N–CH–CH–N); 8.53 s [1H, N–C(H)–N]. ¹³C NMR spectrum (D₂O), δ_{C} , ppm, reference cyclohexanol: 13.31, 19.46, 31.96, 36.3, 49.93, 122.88, 124.16, 136.52. Water content 1.5 wt %. Found, %: C 39.31; H 7.43; N 11.86; S 13.16; O 28.23 C₈H₁₆N₂O₄S. Calculated, %: C 40.43; H 7.39; N 11.79; S 13.47; O 26.92.

1-Butyl-3-methylimidazolium tiocyanate (VI). To a solution of NH₄CNS (5.79 g) in 10 ml of H₂O in small portions was added a solution of 1-butyl-3methylimidazolium bromide (16.65 g) in 20 ml of H₂O. The mixture was stirred for 7 days at room temperature. Then water was distilled off on a rotory evaporator. Ethyl alcohol was added several times in small portions, and azeotropic distillation followed. Then to the flask was added 50 ml of chloroform, and white crystalline precipitate formed was filtered off. The resulting product is a dark red solution. By TLC data, the product consists of two compounds: 1-butyl-3-methylimidazolium bromide and thiocyanate. The existence of thiocyanate ions was also confirmed by infrared spectroscopy. Isolation of 1-butyl-3-methylimidazolium tiocyanate was performed by column chromatography on aluminum oxide, eluent acetonitrile-carbon tetrachloride in the ratio 2:1. The target product contained in the second fraction. Yield about 1.3 g (51%). IR spectrum (BMImSCN), v, cm^{-1} : 3145, 3105 s (aromatic C-H vibrations), 2962, 2873 s [(CH₂)_n-CH₃ vibrations], 2932 w $[(CH_2)_n-CH_3 \text{ vibrations})$, 2055 br.s (SCN vibrations) 1464 s (symmetric vibrations of aromatic ring), 1167 s (symmetric vibrations of aromatic ring), 621 [m, amide (III) band]. Mass spectrum *m/e*: calculated *M* 197.33, found 207 $[M^+ + Na^+ + K^+]$. ¹H NMR spectrum (D₂O), δ , ppm: 0.85 t (3H, CH₃), 1.21 sextet (2H, CH₃-CH₂-(CH₂)N); 1.80 quintet (2H, N-CH₂-CH₂) 3.85 s (2H, N-CH₂), 4.6 t (2H, N–CH₃), 7.47 d (2H, N–CH–CH–N); 8.74 s (1H, N–C(H)–N). ¹³C NMR spectrum (D₂O), δ_C , ppm, reference cyclohexanol: 13.49, 17.63, 19.57, 32.06, 35.5, 50.07, 122.95, 124.2, 136.53. The appearance of a new signal (17.63 ppm) corresponds to the carbon nucleus in the SCN⁻ anion. Water content 1.5 wt %. Found, % C 53.18; H 6.744 N 20.17; S 11.34. C₉H₁₅N₃S. Calculated, %: C 54.79; H 7.66; N 21.29; S 16.25.

Tris-1-butyl-3-methylimidazoly orthophosphate (VII). A weighted amount of Ag_3PO_4 (8.16 g) was dissolved in 60 ml of H_3PO_4 and a solution of 1-butyl-3-methylimidazolium bromide (12.81 g) in water (30 ml) was added dropwise at permanent vigorous

stirring. The reaction was carried out in the dark for 4 h. The reaction mixture was filtered, water was distilled off from the filtrate on a vacuum rotory evaporator. As a result we obtained a viscous yellow liquid with pH 2–3. For the neutralization of H_3PO_4 the crude product was dissolved in ethanol and neutralized with a solution of KOH in alcohol. The reaction mixture was then filtered through a fine-porous glass filter. Alcoholic filtrate was applied to a chromatographic column filled with activated carbon. Solvent was then distilled off on a vacuum rotory evaporator. The product is a viscous yellow liquid. Yield about 8.73 g (87.3%). IR spectrum ($[BMIm]_3PO_4$), v, cm⁻¹: 3154, m 3148 (conjugated vibrations of heterocyclic ring), 2964, 2876 s [(CH₂)_n-CH₃ vibrations], 1465 s (symmetric vibrations of aromatic ring), 1172 s (symmetric vibrations of aromatic ring), 937, 879 (vibrations of PO₄ surrounded by three heterocyclic rings), 624 [amide (III) band]. ¹H NMR spectrum (D₂O), δ, ppm: 0.95 t (9H, CH₃), 1.36 sextet [6H, CH₃-CH₂-(CH₂)N]; 2.01 q (6H, N-CH₂-CH₂) 3.98 s (9H, N–CH₃), 4.27 t (6H, N–CH₂), 7.14 d (6H, N–CH– CH–N); 8.41 s [3H, N–C(H)–N]. ¹³C NMR spectrum (D_2O) , δ_C , ppm, reference cyclohexanol: 13.32, 19.38, 31.84, 36.32, 49.9, 122.84, 124.13, 136.26. Water content 0.5 wt %.

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