3. Ionic liquids and their modification with lithium salts – synthesis and studies

Jonu šķidrumi un to modificēšana ar litija sāļiem – sintēze un pētījumi

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3.1. Introduction

The lithium iron phosphate (LiFePO$_4$) battery, which uses LiFePO$_4$ as a cathode material, and a graphitic carbon electrode as the anode, finds a number of roles in vehicle use and backup power because of low-cost, low-toxicity, well-defined performance, long-term stability, etc. Ionic liquids are electrolytes suitable for lithium batteries due to their high thermal stability and environment to dissolve the lithium salts. Ionic liquids form salts with inorganic acids, and it was reasonable to investigate phosphate salts for LiFePO$_4$ cells. Typical conductivity values for ionic liquids range from 10^{-5} to 10^{-1} S·cm^{-1} at a room temperature, which is equivalent to the strong acid water solutions.

3.2. N, N' – Dialkylimidazolium dimethyl phosphates – promising liquid media for different processes *(A. Zicmanis, S. Briča)*

3.2.1. Introduction to ionic liquids

Development of smart technologies demands applications of advanced materials with properties allowing overrun of possibilities known till today. Ionic liquids (ILs) are among the materials of this kind. An IL (ethylammonium nitrate) was mentioned for the first time in the famous paper by Paul Walden in 1914 [1] as an interesting fact in author's systematic research of non-aqueous electrolytes, and this year is considered as the discovery of ionic liquids. The first publication was followed by wider investigations only years later, in the 1940s, when American authors proposed ILs as non-aqueous new solvents for use as battery electrolytes [2, 3]. The applications of ILs in electrochemistry continued for many years and remain topical today. However, the greatest boom in the research of ILs commenced in the middle of 1980s, when ILs were used as media in organic synthesis in place of traditional organic solvents – molecular liquids. Therefore, during the following thirty years chemistry of ILs has widely developed. Achievements and problems of synthesis, characterization and use of ILs are well recognized and described in numerous reviews [2–13], and new possibilities of ILs continue to be discovered and demonstrated.

Innumerable amounts of cations and anions may form ILs, and every combination of both these ions assign specific properties to their combination – the resulting IL. A group of ILs with 1,3-dialkylimidazolium cation and dimethyl phosphate anion create especially interesting ion pairs. These ILs are more thermally stable and resistant to the action of acids, bases, oxidizing and reducing reagents, etc. than the majority of ILs. Therefore, they may be used more extensively in chemical and technological processes. Promising properties of the mentioned imidazolium dimethyl phosphates (IA-DMPs) have encouraged us to seek further development of their applications in organic synthesis, modifications of membranes, extraction processes, etc., and the most important information about these materials with a high potential will be presented below.

Ammonium dialkyl phosphates that may be considered as remote relatives of IA-DMPs for the first time were mentioned in 1951 [14]. They were followed by alkylation products of pyridine with trialkyl phosphates that were described as salts with very low melting points in 1989 [15]. Later on, other authors have filed patents on the synthesis of imidazolium-based dialkyl phosphate ionic liquids [15, 16]. A comprehensive and detailed study of IA-DMPs was performed by Wasserscheid's group [17]. A variety of these ionic liquids have been synthesized and characterized in this work, paying particular attention to properties of practical relevance.

3.2.2. Overview of imidazolium dimethyl phosphates ant their manufacturing

Today, there are two main ways for manufacturing the IA-DMP. The first, which has been known for more than thirty years, requires alkylation of 1-substituted imidazoles by trialkyl phosphates, mainly by trimethyl phosphate (route A, Fig. 3.1) [17–25]. This is the method for preparation of different 1-alkyl-3-methylimidazolium dimethyl phosphates (**2**).
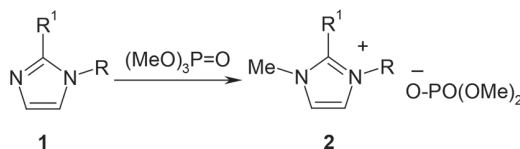

Figure 3.1. **The most popular way for synthesis of ionic liquids with 1,3-dialkylimidazolium cation and dimethyl phosphate anion (route A)**

Several organic solvents (toluene, ethyl acetate, acetonitrile, and others) are proposed for their synthesis. Various temperatures and reaction times up to 72 hours are successfully used. Reactions of 1-substituted imidazoles with trimethyl phosphate in boiling acetonitrile during 24 hours under nitrogen or argon are successfully applied for IA-DMP syntheses also in our laboratory (route A). The method allows obtaining practically colorless high quality ILs. A representative example of the method according to the route A is presented below.

1,2,3-Trimethylimidazolium dimethyl phosphate (2a) [26]. Trimethyl phosphate (8.41 g; 0.06 mol) was added drop by drop to the 1,2-dimethylimidazole (**1a**; 4.81 g; 0.05 mol), vigorously stirring in a round-bottom flask under argon. The mixture was stirred for 1 h at room temperature, then temperature was raised to 80 °C. 10 mL of acetonitrile was added after 30 minutes, and the content of the flask was stirred at 80 °C for 48 hours. The hot solution was poured into a conical flask and left at a room temperature for 24 hours. The precipitate formed was filtered, washed with ethyl acetate on the filter and dried in vacuum (0.5 mbar) during 6 hours after that. The IL (**2a**; 12.66 g; 91 %) was obtained as a white crystalline substance with m.p. 124-126 °C. ^{1}H NMR spectrum: (300 MHz, DMSO-d$_6$, δ): 7.59 (2H, s, NCH=CHN); 3.75 (6H, s, CH$_3$N-C(CH$_3$)=NCH$_3$); 3.23 (6H, d, P(OCH$_3$)$_2$); 2.55 (3H, s, NC(CH$_3$)N) ppm.

The main limitation of the synthesis according to route A is the availability of the necessary raw materials – the corresponding 1-alkylimidazoles. Therefore, another method for obtaining IA-DMPs was recently developed in our laboratory – alkylation of 1,3-dialkylimidazolium chlorides by trimethyl phosphate (route B, Fig. 3.2) [25, 26].
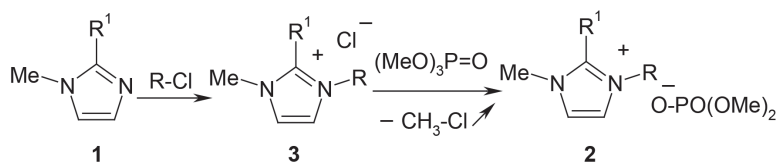

Figure 3.2. **The alternative way for synthesis of ionic liquids with 1,3-dialkyl-imidazolium cation and dimethyl phosphate anion (route B)**

In fact, route B represents an alkylation reaction of chloride anion. The driving force of the synthesis is the possibility to remove one of the reaction products (gaseous chloromethane) from the reaction area. The reaction demands elevated temperatures (80–110 °C) but takes quite a short time – only 2–4 hours. It is worth noting that raw materials for the aforementioned transformation – the corresponding 1,3-dialkylimi-dazolium chlorides – can be easily prepared according to the well-established protocol for the synthesis of ILs. We improved the old, well-investigated method with a slight modification – we performed the alkylation reaction in a tightly closed screw-top steel pressure tube. No inert gas is needed in this case for maintaining the quality of the product, and 1-chloroalkanes with low boiling temperatures can be used as alkylating reagents. 1-Methyl- and 1,2-dimethylimidazoles (**1**) were alkylated by 1-chloroalkanes in the mentioned steel pressure tube in our laboratory at 80 °C for the duration of 72 hours; the twofold molar excess of the alkylating reagent was applied. Expected imidazolium chlorides (**3**) formed in high yields, and the excess of the reagent was removed by

extracting the reaction mixture by ethyl acetate at the end. The obtained ILs with the chloride anion (**3**) were ready for further transformations after careful drying in high vacuum (0.5 mbar, 60 °C, 6 h) and analysis.

The second stage of the process according to route B – the exchange of the chloride ion for dimethyl phosphate anion (alkylation of chloride ion by trimethyl phosphate) was accomplished at temperatures 80–110 °C (Fig. 3.2), accompanied by the gas (CH_3-Cl) release and providing the shift of the reaction equilibrium to the right. The negative $AgNO_3$ test together with the end of the evolution of gas allows fixing the end of the reaction. A complete conversion of the chloride ion can be ensured by using twofold molar excess of the alkylating reagent – trimethyl phosphate. There is no problem to dispose of the unreacted trimethyl phosphate; a simple extraction of the reaction mixture by ethyl acetate followed by drying of the obtained product in high vacuum (0.5 mbar, 70 °C, 8 h) is sufficient. A representative example of the method according to route B is shown below.

1-Butyl-2,3-dimethylimidazolium chloride (3b) [26] (the <u>first stage</u> of route B). 1,2-Dimethylimidazole (**1b**; 9.61 g; 0.10 mol), 1-chlorobutane (12.03 g; 0.13 mol), magnetic stirrer, and ethyl acetate (6 mL) were placed in a sealed screw-top home-made steel pressure tube. The airproof tube was placed in a glycerol bath, and the reaction mixture was stirred at 80 °C for 72 hours. Then the reaction mixture was poured in a round-bottom flask after cooling to room temperature and placed in the freezer for 24 hours. The obtained crystalline mass was filtered, washed with ethyl acetate (4 × 25 mL) on the filter, then dried under vacuum of rotary evaporator at 40°C and after that under high vacuum (0.5 mbar) at 60 °C for 6 hours. The IL (**3b**; 23.34 g; 89%) was obtained as a white crystalline substance with m.p. 93–94 °C. ^{1}H NMR spectrum (300 MHz, DMSO-d_6, δ): 7.63 (2H, s, NC$\underline{H}$=C$\underline{H}$N); 4.11 (2H, t, NC$\underline{H}_2$-CH$_2$- CH$_2$- CH$_3$); 3.74 (3H, s, C$\underline{H}_3$NCCH$_3$); 2.58 (3H, s, CH$_3$NCC$\underline{H}_3$); 1.68 (2H, m, NCH$_2$-C$\underline{H}_2$- CH$_2$- CH$_3$); 1.29 (2H, m, NCH$_2$-CH$_2$- C$\underline{H}_2$-CH$_3$); 0.92 (3H, t, NCH$_2$-CH$_2$- CH$_2$- C$\underline{H}_3$) ppm.

1-Butyl-2,3-dimethylimidazolium dimethyl phosphate (2b) [26] (the <u>second stage</u> of the route B). 1-Butyl-2,3-dimethylimidazolium chloride (18.67 g; 10.0 mmol) and trimethyl phosphate (35.02 g; 25.0 mmol) were placed in a 50 mL round-bottomed flask equipped with a reflux condenser and CaCl$_2$ drying tube. The obtained mixture was stirred at the 110 °C for 24 h. Toluene (5 × 10 mL) was added to the crude product and the mixture was vigorously stirred and heated to reflux for 10 minutes. The toluene layer was then decanted while hot. The washing procedure was repeated further four times. Any remaining solvent was removed by rotary evaporation (10 mbar, 70 °C, 4 h). The pure product was dried under high vacuum (0.5 mbar, 70 °C, 8 h) and was subjected to AgNO$_3$ analysis to confirm the absence of a starting material. The ionic liquid with dimethyl phosphate anion (**2b**; 24, 13 g; 92%) was obtained as an oil that solidifies into a white crystalline substance with m.p. 92–93 °C during 24 h in a refrigerator. ^{1}H NMR spectrum (300 MHz, DMSO-d_6, δ): 7.64 (2H, d, NC$\underline{H}$=C$\underline{H}$N); 4.13 (2H, t, NC$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$); 3.74 (3H, s, C$\underline{H}_3$NCCH$_3$); 3.23 (6H, d, P(OC$\underline{H}_3$)$_2$); 2.58 (3H, s, CH$_3$NCC$\underline{H}_3$); 1.67 (2H, m, NCH$_2$-C$\underline{H}_2$-CH$_2$-CH$_3$); 1.29 (2H, m, NCH$_2$-CH$_2$-C$\underline{H}_2$-CH$_3$); 0.92 (3H, t, NCH$_2$-CH$_2$-CH$_2$- C$\underline{H}_3$) ppm.

1,3-Dialkylimidazolium dimethyl phosphates (**2**) prepared via both routes are colorless or slightly yellow oils. IA-DMPs with methyl group in their cations at C_2-atom crystallize after being kept in a refrigerator for several days, while non-substituted at C_2-atom substances remain in the form of thick oils. The yields of the second stage of the process – the alkylation of chloride ions – are high in all experiments (≥ 87 %) (Table 3.1).

Table 3.1. **Some popular 1,3-dialkylimidazolium dimethyl phosphates [26]**

No	Ionic liquid R	R^1	route*	yield, %	m. p., °C	purity, %**	water, %***	T$_{5\%dec}$, °C****
2a)	R = CH$_3$	CH$_3$	A	93	124–126	99.6	0.33	290
2b)	R = C$_4$H$_9$	CH$_3$	B	92	92–93	99.4	0.55	297
2c)	R = C$_8$H$_{17}$	CH$_3$	B	87	liquid	99.3	0.62	231
2d)	R = C$_{12}$H$_{25}$	CH$_3$	B	92	113–114	99.2	0.71	218
2e)	R = CH$_3$	H	A	93	liquid	99.5	0.44	302
2f)	R = C$_4$H$_9$	H	B	98	liquid	99.5	0.43	315
2g)	R = C$_8$H$_{17}$	H	B	93	liquid	99.4	0.45	286
2h)	R = C$_{12}$H$_{25}$	H	B	96	liquid	99.2	0.60	261
2i)	R = CH$_2$CH$_2$OH	H	B	97	liquid	99.4	0.46	284

where: *route of synthesis; **purity determined by potentiometric titration with perchloric acid in glacial acetic acid; ***water content (moisture) determined by Karl Fisher titration; **** decomposition temperatures (T$_{5\%dec}$) determined by TGA from onset to 5 wt % mass loss, heating at 10 °C min^{-1} under air.

The previously discussed route B can be considered as an attractive alternative to route A, when problems arise with the preparation of 1-substituted imidazoles. Both aforementioned synthetic routes together allow preparing almost every imaginable IA-DMP, and both are successfully tested in our laboratory.

Every application of IA-DMP demands the necessary characterization of these materials after the synthesis and/or before use. Spectroscopic, titrimetric, and thermo-gravimetric methods were normally used for characterization of all the obtained ILs. ^{1}H NMR spectroscopy was the most useful tool for the qualitative analysis (confirmation of structures) of ILs. ^{1}H NMR spectra contained all the resonance signals characteristic to imidazolium salts, and the NMR data were consistent with literature data. The complete exchange of chloride ions for IA-DMP (prepared according to route B) was confirmed not only by the above-mentioned negative AgNO$_3$ test, but also by NMR data. The integral intensities of the resonance signals of protons of both O-CH$_3$ groups (6H) with δ 3.23–3.26 ppm that fully corresponded to those of protons C$_4$-H and C$_5$-H (2H) in the imidazolium cation ring with δ 7.63–7.67 ppm (an example in Fig. 3.3).

Like many other ILs, the ILs containing DMP anion are highly hygroscopic substances, and they should be stored in tightly closed containers. The Karl Fisher titration method was used for the control of moisture content in the obtained ILs. The water content did not exceed 1.0% in all the analysed correctly prepared samples (Table 3.1), but it is recommended to check the moisture content in ILs before their use, particularly in the samples stored over a longer time.

An important characteristic attesting to the quality of IA-DMP is their purity. Usually, it is tested by using chromatography. The HPLC/MS is usually used to determine the quality of prepared ILs. Only one signal can be observed in correctly made samples of IA-DMPs. The chromatogram of a frequently used IA-DMP – 1-butyl-3-methyl-imidazolium dimethyl phosphate [C$_4$C$_1$im] [DMP] is shown below for illustration (Fig. 3.4). Mass spectrum of the signal serves well to confirm the structure of IA-DMP (Fig. 3.5).
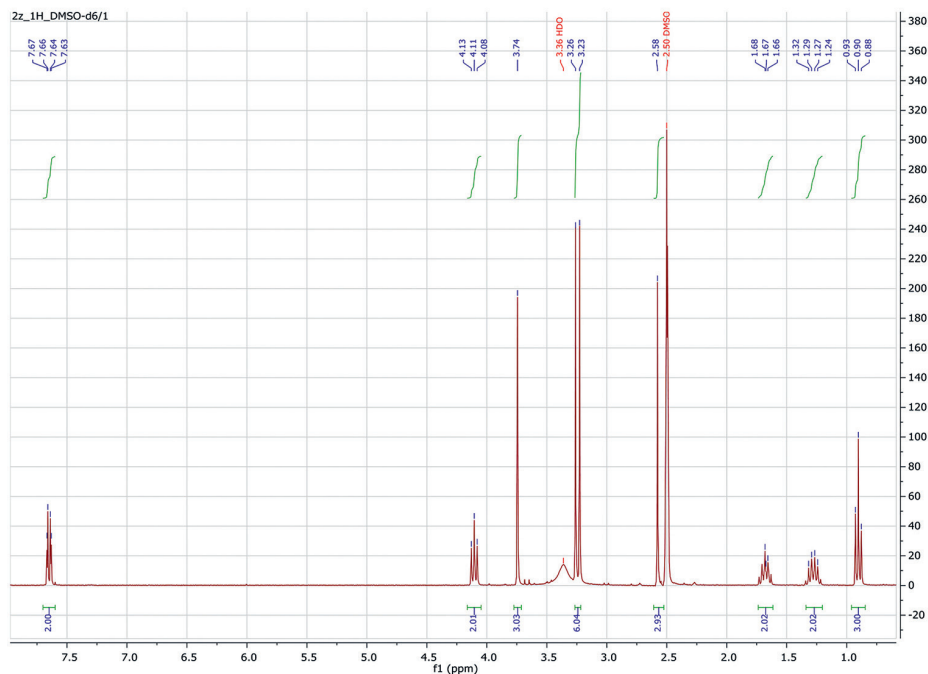
Figure 3.3. **¹H NMR spectrum of 1-butyl-2,3-dimethylimidazolium dimethyl phosphate ([C₄C₁im][DMP]) [26]**
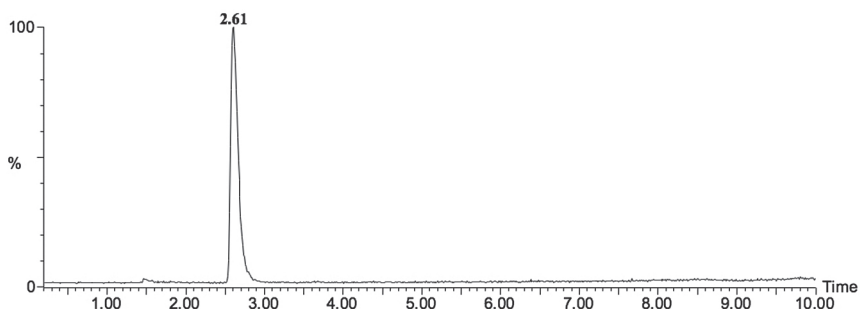
Figure 3.4. **HPLC for 1-butyl-3-methylimidazolium dimethyl phosphate ([C₄C₁im][DMP])**
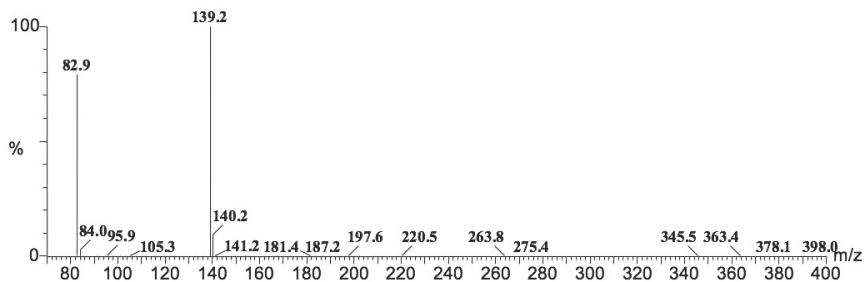

Figure 3.5. **Mass spectrum for the peak at 2.61 min**

Both NMR spectroscopy and chromatography are quite robust analytical methods. Very much more accurate data about the true quality of IA-DMP can be obtained using titrimetric methods. Titration of ILs containing DMP anion with perchloric acid in glacial acetic acid according to the recently published method [19, 26] was used for the quantitative analysis of ILs made in our laboratory. The method presents excellent titration curves, and all the obtained and carefully dried ILs have shown high purity (the content of the main substance in the product) – above 99 % (Table 3.1). A titration curve of 1-butyl-3-methylimidazolium dimethyl phosphate is shown below, again for the purposes for illustration (Fig. 3.6).
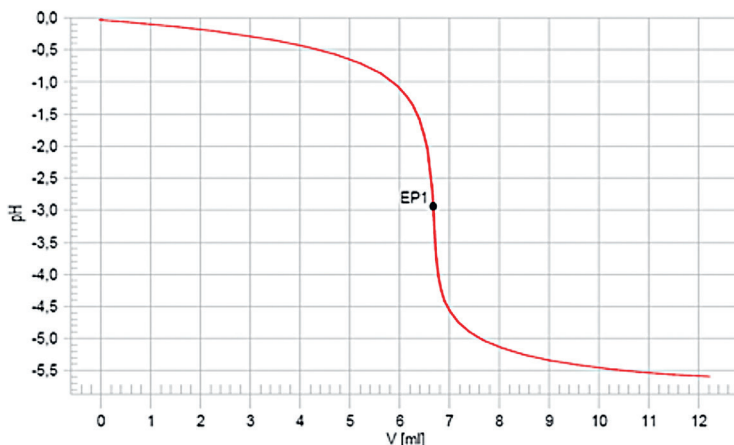
Figure 3.6. **Titration curve of 1-butyl-3-methylimidazolium dimethyl phosphate ([C₄C₁im] [DMP])**

The performance of the quantitative analysis of IA-DMP is quite simple – just the traditional potentiometric non-aqueous titration.

Quantitative analyses of ionic liquids 1,3-dialkylimidazolium dimethyl phosphates. A sample of an ionic liquid (**2** or **4**) (~100 mg) was dissolved in glacial acetic acid (50 mL) and titrated with the solution of perchloric acid in glacial acetic acid (0.05 mol/L) in the equipment of potentiometric titration. The purity (content of the main substance, %) of the sample was calculated from obtained titration curves and presented in Table 3.1.

An important characteristic of the quality of IA-DMP is their stability at elevated temperatures. The thermogravimetric analysis (TGA) is normally used for its determination. Our results have confirmed that IA-DMPs are highly stable ILs, disintegrating usually above 260 °C. Only IA-DMPs with long alkyl chains in their cations are a little bit less stable – their decomposition of 5 % was observed already at temperatures ≥ 218 °C. Hence, ILs with DMP anion are considerably more stable substances than similar ILs with carboxylate anions – even in cases, when their cation contains long alkyl groups (C_8–C_{16}) at nitrogen atom. These properties noticeably expands the available temperature interval for processes performed in these ILs and further expand their exploitation possibilities. A TGA curve of 1-butyl-3-methylimidazolium dimethyl phosphate (C_4C_1im] [DMP]) is presented below just for illustration of the thermal stability of IA-DMP (Fig. 3.7).
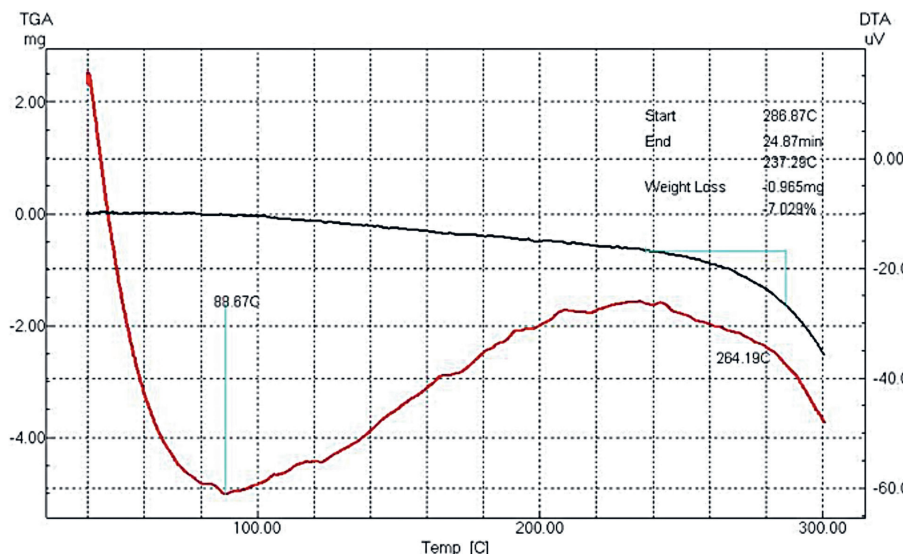
Figure 3.7. **Curve of thermogravimetric analysis of 1-butyl-3-methylimidazolium dimethyl phosphate (C$_4$C$_1$im] [DMP])**

3.2.3. Summary on imidazolium dimethyl phosphates

Like other ILs, IA-DMPs most frequently are used as reaction media or/and catalysts in organic synthesis. This field of application has lately been also quite extensively investigated at the University of Latvia [19–26]. The use of IA-DMP in other research areas (electrochemistry, extraction processes, formation of composite materials, etc.) at the University of Latvia has started slightly later, and currently is in progress. This will be discussed hereafter.

3.3. Ionic liquids with lithium salts *(G. Vaivars, E. Sprūģis, J. Singatulovs)*

3.3.1. Application of ionic liquids with Li salts*

Lithium-ion batteries are promoting the commercialization of electric car and home usage of local electric storage. However, safety issues are of the utmost importance. The lithium iron phosphate (LiFePO$_4$) battery, which uses LiFePO$_4$ as a cathode material, and a graphitic carbon electrode as the anode is finding a number of roles in vehicle use and backup power because of low-cost, low-toxicity, well-defined performance, long-term stability, etc. Ionic liquids (IL) are suitable electrolytes for lithium batteries due to high thermal stability and environment to dissolve the lithium salts [27]. Ionic liquids form salts with inorganic acids and it was reasonable to investigate phosphate salts for LiFePO$_4$ cells. Typical conductivity values for ionic liquids range from 10^{-5} to 10^{-1} S·cm^{-1} at a room temperature [28], which is equivalent to the strong acid water solutions.

In the study, two ionic liquids were chosen for tests and synthesized: 1-butyl-3-methyl-imidazolium dimethylphosphate and 1, 3-dimethylimidazolium dimethylphosphate.

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The structure of lithium nitrate solutions in a protic ionic liquid due to interactions between lithium ion and other species is of higher importance, because the electric conductivity will depend on it [29]. Méndez-Morales, et al. [30] studied solvation of lithium salts. It was concluded that the lithium cations were solvated by embedding them in the polar nanodomains of the solution formed by the anions, where they coordinated with the latter in a solid-like fashion reminiscent of a pseudolattice structure. This coordination led to interaction and increase of viscosity, which would determine the charge transfer properties [29–32]. The increase of viscosity would decrease the lithium ion mobility and therefore lithium ion conductivity [33].

One of the limitations when working with ionic liquids is to obtain these components with a high and known purity [34]. The most problematic are those that have high affinities with ionic liquids, such as water with hydrophilic ionic liquids. The most striking example is the viscosity that dramatically decreases only with traces of water. It was observed that 1% of water changes viscosity by 30%. However, the water molecules will adsorb on electrode surface, and the impact on electric double layer formation might be reasonable. It will influence the electrochemical stability of the system and the electrode potential, which is important for lithium batteries. Literature on ionic liquids often shows non-reproducible values or important deviations between different sets of data for a number of properties, in particular viscosity and density. These discrepancies mainly result from (i) the purity of the samples, (ii) inappropriate measurement methods [35]. Typically, ionic liquids melt at temperatures below 100 C [36–38]. Their partial vapour pressure is close to zero, they are not flammable and therefore are suitable for application in different devices. The high hygroscopicity limits the usage of ILs. They also physically absorb CO_2 gas [39], which is a physical absorption and might be used to remove the gas from environment. The process is slow [39], but the volume of absorbed gas could be reasonable [39–43]. The nature of ionic liquid is important. However, the length of hydrocarbon chain was less important [43].

3.3.2. Experimental part to ionic liquids with lithium salts

The used ionic liquids were synthesized, as follows (Fig. 3.8): 1-methylimidazolium and trimethyl phosphate was mixed at a room temperature and molar ratio 1:1. The resulting mixture was intensively stirred and heated up to 80 C under argon. The mixture was stirred for 24 hours. The product was extracted using diethyl ether and dried at 0.5 Torr pressure for 4 hours at 80 C. 1-buthyl-3-methylimidazolium dimethyl phosphate was produced by replacing 1-methylimidazolium with 1-buthylimidazolium. 0.1 mol/kg (or 0.5 mol/kg) of lithium nitrate was dissolved in IL providing lithium ion conductivity.

Conductivity and electrochemical stability dependence of temperature were determined for pure ionic liquids and ionic liquid – lithium nitrate electrolytes. Detection methodology of conductivity dependence on temperature was designed. The factors affecting conductivity were identified with impedance spectroscopy. AUTOLAB potentiostat/galvanostat with a FRA was used for electrochemical and impedance measurements. The frequency range was from 3.5 to 20 kHz (signal amplitude 10 mV). The electrochemical stability window was obtained in a range from –3.5 to +3.5 V. A small glass vessel (2.5 mL) with stainless steel electrodes was used for measurements. The temperature control was realized using glycerol bath.

The thermal stability of ionic liquids was characterized using DTG-60 series from Shimadzu thermogravimetric equipment with aluminium crucibles (heating rate 10 deg/min).
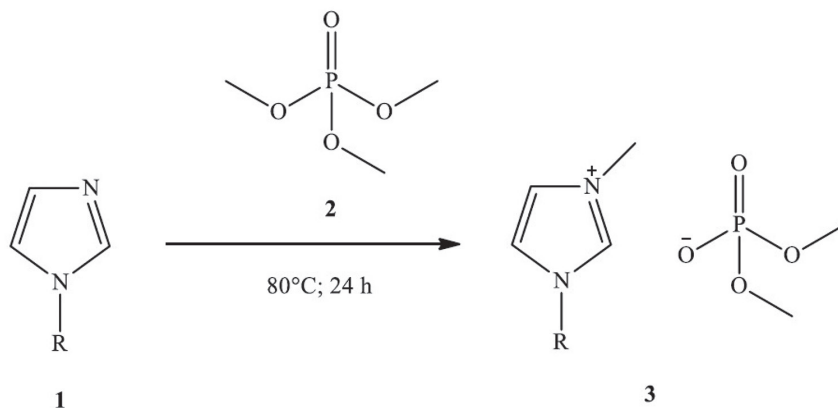
Figure 3.8. **Synthesis procedure for the used ionic liquids**

3.3.3. Results and discussion about ionic liquid with Li salts

Ionic liquids are stable up to 200 C (Fig. 3.9, 1-buthyl-3-methylimidazolium dimethyl phosphate). The stability was controlled before and after impedance measurements. The thermal stability was just slightly influenced by adding lithium nitrate.
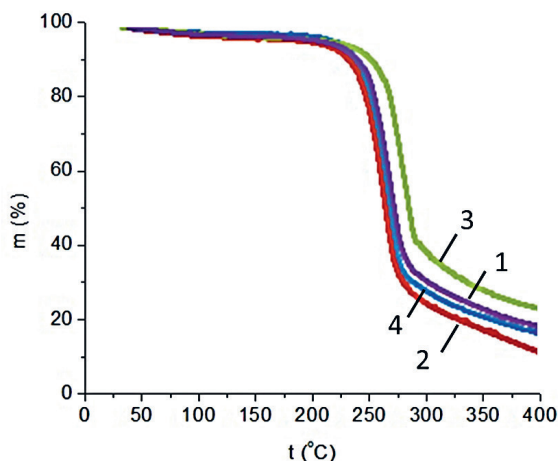

Figure 3.9. **Thermal stability of 1-buthyl-3-methylimidazolium dimethyl phosphate: 1) freshly prepared; 2) after impedance measurements; 3) with 0.1 mol/kg lithium nitrate added; 4) with 0.5 mol/kg lithium nitrate added**

The electrochemical stability window (+/– 3V) was established from voltamperic curves measured in a two-electrode system. It was sufficient for current research. After drying under argon, the IL contains some impurities of water and they are narrowing the electrochemical stability window (see Table 3.2). At higher temperatures, the electro-chemical stability window is also reduced.

Table 3.2. **IL and IL- lithium nitrate electrolyte electrochemical stability window at different temperatures**

T,°C	1,3-dimethylimidazolium dimethyl phosphate			1-buthyl-3-methylimidazolium dimethyl phosphate		
	+ 0,5 mol/kg LiNO$_3$	+ 0,1 mol/kg LiNO$_3$			+ 0,1 mol/kg LiNO$_3$	+ 0,5 mol/kg LiNO$_3$
25	6 V	6 V	6 V	7 V	7 V	7 V
50	6 V	6 V	6 V	7 V	7 V	7 V
100	5 V	5 V	5.5 V	6 V	6 V	6 V
150	5 V	5 V	5.5 V	4 V	4 V	5 V

The impedance of two-electrode cell containing IL was measured, stabilizing the cell before measurement for 20 minutes at each temperature. The cell was stabilized in order to achieve the same results for both heating and cooling cycle. The cell resistance R was obtained from the Nyqvist plot extrapolating to the higher frequencies. The cell constant K was obtained using standard KCl solution at a room temperature. Both parameters were used to calculate the electrolyte conductivity σ ($\sigma = K/R$). Arrhenius plot revealed non-linear behaviour from room temperature up to 150 C (Fig. 3.10), which is characteristic for ILs.
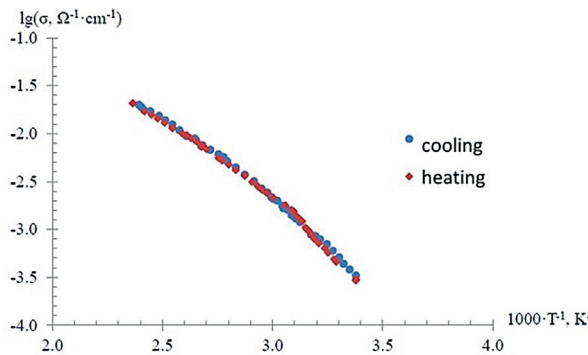

Figure 3.10. **Arrhenius plot of conductivity for 1-buthyl-3-methylimidazolium dimethyl phosphate (both heating and cooling cycles)**

After dissolving lithium nitrate, the temperature dependence of electrolyte was measured and plotted in Arrhenius coordinates. The plot (Fig. 3.11) revealed that the conductivity values practically not increases by adding lithium salt.

Analogous behaviour was observed also for the second investigated IL – 1,3- dimethylimidazolium dimethyl phosphate (Fig. 3.12). Most likely, the reason is the increase of viscosity by adding lithium salt and subsequent decrease of lithium ion mobility as it was discussed before. The conductivity most strongly was influenced by increasing the length of the hydrocarbon chain. The dimethyl group replacing by butyl decreased the conductivity by 0.5 units in Arrhenius coordinates.

The IL temperature stability is higher than 200 °C. However, by adding lithium salt, the chemical interaction was observed at temperatures higher than 170 °C, which resulted in a reasonable decrease of conductivity (Fig. 3.13).
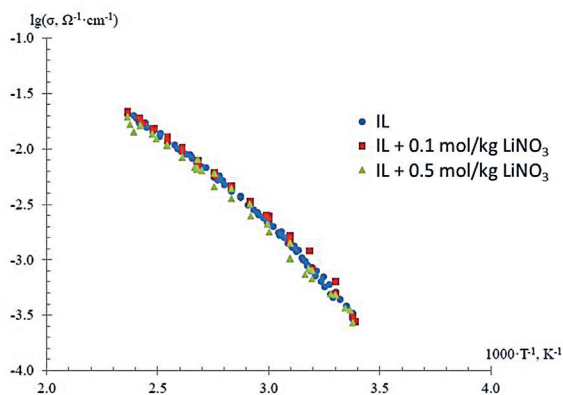
Figure 3.11. **Arrhenius plot of conductivity for 1-buthyl-3-methylimidazolium dimethyl phosphate with and without adding lithium nitrate**
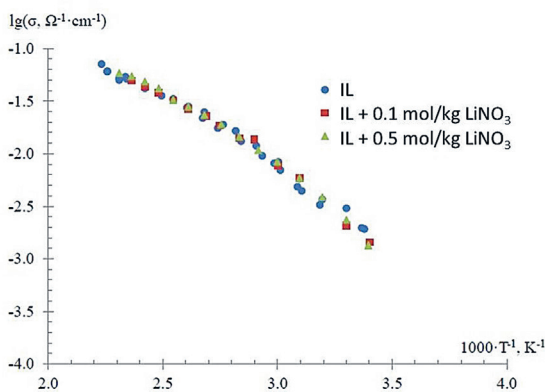

Figure 3.12. **Arrhenius plot of conductivity for 1,3-dimethylimidazolium dimethyl phosphate with and without adding lithium nitrate**
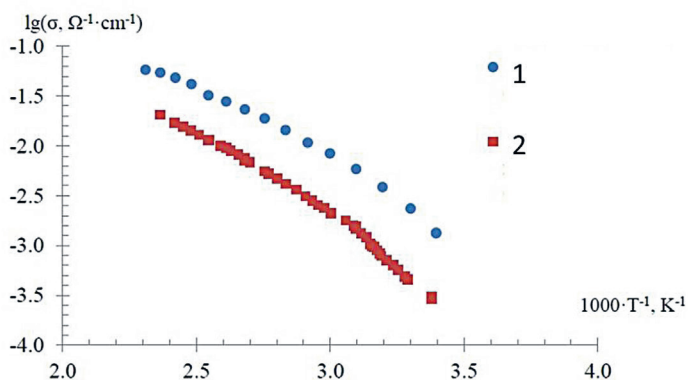

Figure 3.13. **Arrhenius plot of conductivity for 1, 3-dimethylimidazolium dimethyl phosphate (1) and 1-buthyl-3-methylimidazolium dimethyl phosphate (2)**

3.3.4. Conclusions to ion liquids with Li salts

This research confirmed that the ILs such as imidazolium dimethyl phosphates are an excellent environment to dissolve the lithium salts. It will change ion equilibrium, but it is not possible to reach higher conductivity values. Investigated electrolyte system was designed to be used in lithium-ion batteries with a lithium iron phosphate electrode. It was assumed that the saturation of electrolyte with the phosphate-based ions will stabilize the interface with the phosphate-based electrode. More stability tests for batteries are planned in a future.

3.4. References

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3.5. Kopsavilkums

Tāpat kā citi jonu šķidrumi (JŠ), arī imidazolija dimetilfosfāti (IA-DMP) visbiežāk tiek izmantoti kā reakcijas vide un/vai katalizatori organiskajā sintēzē. Tie iegūti, vai nu alkilējot 1-aizvietotos imidazolus ar trimetilfosfātu, vai hlorīda jona metatēzēs atbilstošajos imidazolija sāļos. Izveidotas minēto JŠ kvalitatīvās un kvantitatīvās analīzes metodes. Gan JŠ sintēze, gan to pielietojumi ir plaši pētīti arī Latvijas Universitātē dažādās jomās: elektroķīmija, organiskā sintēze, ekstrakcijas procesi, kompozītmateriālu veidošanās. Darbā dots pārskats par imidazolija dimetilfosfātu jonu šķidrumu sintēzes metodēm un struktūras pētījumiem. Jonu šķidrumus 1914. gadā atklājis Pauls Valdens, pēc tam tie tika aizmirsti līdz 1940. gadiem, kad amerikāņu pētnieki ierosināja izmantot JŠ kā nešķīstošu šķīdinātāju akumulatora elektrolītiem. Litija jonu akumulatori veicināja elektrisko automobiļu komercializāciju un mājsaimniecību pašu saražotās elektriskās enerģijas uzglabāšanu vēlākai izmantošanai. Tomēr drošības jautājumi ir vissvarīgākie. Litija dzelzs fosfāta (LiFePO$_4$) akumulators, kas kā katoda materiālu izmanto LiFePO$_4$ un kā anodu – oglekļa elektrodu, pēdējos gados ir atradis plašu pielietojumu transportlīdzekļos – mazs svars, liels enerģijas blīvums, zema cena, zema toksicitāte, laba veiktspēja, ilglaicīga stabilitāte utt. Jonu šķidrumi ir piemēroti elektrolīti litija baterijām savas augstās termiskās stabilitātes un vides draudzīguma dēļ. JŠ veido sāļus ar neorganiskām skābēm, tādēļ mūsu darbā pētīti JŠ fosfātu sāļi LiFePO$_4$ šūnām. Jonijas šķidrumu tipiskās vadītspējas vērtības istabas temperatūrā svārstās no 10^{-5} līdz 10^{-1} S $\cdot$ cm^{-1}, kas ir ekvivalenta stipriem skābes ūdens šķīdumiem.