PHYSICAL AND CHEMICAL PROPERTIES OF IONIC LIQUIDS BASED ON THE DIALKYLIMIDAZOLIUM CATION

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Abstract. Thermogravimetric curves and IR and UV–VIS spectra were measured for 1-butyl-3-methylimidazolium based ionic liquids. The solubility of ionic liquids in several organic solvents was determined.

Key words: room temperature molten salts, ionic liquids, IR spectra, UV–VIS spectra, thermogravimetry, solubility of ionic liquids.

INTRODUCTION

The continuing search for new materials is constantly revealing new substances with both useful and environmentally benign properties. Molten organic salts, such as the quaternary ammonium and imidazolium salts, are among the few classes exhibiting room temperature liquid-like behaviour and interesting solvent properties for both chemical reactions and extraction. Room temperature molten salt systems were reported first by Hurley & Wier [1] in 1951. In their work, fused mixtures of ethylpyridinium bromide and metallic chlorides were studied. Low temperature molten organic salts are viscous liquids that are composed entirely of ions and are liquid-like over a wide range of temperature (melting points are typically in the range from –40 to 70°C, in some cases as low as –90°C). In this sense, they resemble the ionic melts that may be produced by heating ordinary metallic salts such as NaCl to high temperatures. Liquids that are comprised entirely of ions could be called ionic liquids, and in this sense they are anhydrous aprotic solvents.

Ionic liquids have good electrochemical properties, for example, high conductivity and a wide electrochemical window (the range between the anodic

and cathodic decomposition potential limits of the solvent). In particular, this wide electrochemical window promises the potential use of these ionic liquids as unique solvents for electrochemical investigation. A great deal of work conducted with these liquids has involved electrochemical investigations and most notably for a variety of transition metal complexes. These complexes, which are unstable in other media, may be studied in ambient temperature melts [2]. Such liquids have been studied as new electrolytes for electrochemical cells and materials for solar panels.

The ionic liquids used have no measurable vapour pressure, are non-explosive and not oxidizing. It is reported that such ionic liquids are able to solvate a wide range of species including organic, inorganic, and organometallic compounds. It was the discovery of 1-ethyl-3-methylimidazolium [EMIm] based chloroaluminate ionic liquids [3] in 1982 that gave an impetus for a dramatic increase in activity in the area of ambient temperature ionic liquids. This is one of the most widely studied room temperature melt systems and is liquid at room temperature for compositions between 33 and 67 mole% $AlCl_3$.

A considerable limitation of aluminium-based ionic liquids arises from the fact that these ionic liquids are moisture sensitive and need to be protected scrupulously from the moisture and other oxide impurities; moreover, most transition metal complexes and organic substrates are not inert to the chloroaluminate compounds. These melts react with water in a highly exothermic manner with the evolution of hydrogen chloride and the formation of a white precipitate. This precipitate re-dissolves on stirring. It is suggested that, upon reaction with water, different aluminium hydroxy and chloroaluminoxy species may be formed [4]. This must be taken into account in precise studies, as water is an unavoidable impurity.

Air- and water-stable molten salts have been recently obtained using the weakly complexing anion in the imidazolium compound [5]. Unlike $[AlCl_4]^-$ anion, $[CF_3SO_3]^-$, $[BF_4]^-$, and $[PF_6]^-$ anions do not combine with their corresponding Lewis acids and therefore do not form polynuclear anions. Hence these salts are neutral stoichiometric compounds without the potential for acidity. Compounds are immiscible with water and can be purified by washing with water. Inertness and the more facile handling capability of such ionic liquids should greatly enhance the possibilities for their applications.

DIALKYLIMIDAZOLIUM MELTS

1,3-Dialkylimidazolium salts $[RR'Im]^+X^-$ appear to be so far the most stable and conductive ionic liquids. The R group of the cation is variable and may be used to fine-tune the properties of the ionic liquid, the R'group is mainly methyl group.

The starting materials for the cationic part of ionic liquids are 1,3-dialkylimidazolium halides, mostly chlorides:

$$\left[\begin{array}{c} R \\ N \\ \oplus \end{array} N \right] \quad Cl^-$$
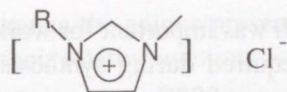
R = Methyl   MMIm Cl $C_5H_9N_2Cl$ m.p.124.5–128 °C
Ethyl   EMIm Cl $C_6H_{11}N_2Cl$ m.p. 87 °C
Propyl   PMIm Cl $C_7H_{13}N_2Cl$ m.p. 58–66 °C
Butyl   BMIm Cl $C_8H_{15}N_2Cl$ m.p. 65–69 °C

The anionic part of an ionic liquid can be based on different anions such as:
Aluminium halide – $[Al X_4]^-$ (X = Cl, Br, I)
Hexafluorophosphate – $[PF_6]^-$
Tetrafluoroborate – $[BF_4]^-$
Trifluoroacetate – $[CF_3COO]^-$
Trifluoromethanesulphonate – $[CF_3SO_3]^-$

Very often just mixing of imidazolium halide and the acid or salt containing related anion forms the ionic liquid:

$$\left[\begin{array}{c} R \\ N \\ \oplus \end{array} N \right] \quad X^-$$
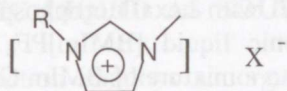
The resulting ionic liquids show very different properties:
[BMImCl]–AlCl₃   – hygroscopic;
[BMIm]–PF_6^- – hydrophobic;
[BMIm]–CH_3COO^- – water-soluble.

In our study the density and viscosity of hexafluorophosphate ionic liquid were measured: at 20 °C the density was 1.396 g/cm³ and the viscosity was 3.94 Pois. From the literature [6] data on chloroaluminate ionic liquid (neutral) are known: density 1.23 g/cm³ and viscosity 0.23 Pois at 30 °C. These measurements at different compositions show that chloroaluminate ionic liquids should not be considered as statistical aggregates of anions and cations, but preferentially as three-dimensional networks of anions and cations with certain structure. Hydrogen bonding between anion and imidazolium ring protons could influence the ion packing, and by this viscosity and melting points. The presence of a long alkyl chain at the N(1) of the imidazolium cation inhibits the crystallization of these liquids.

PREPARATION OF DIALKYLIMIDAZOLIUM MELTS

Two different types of ionic liquids based on the same 1-butyl-3-methyl-imidazolium cation, but using different anions – hexafluorophosphate and aluminium chloride – were made for this study. It was possible to prepare melts and load reaction vessels in an N_2-filled glove box maintained at less than 10 ppm

combined O_2 and H_2O, which was important for working with aluminium chloride. No other precautions are required during synthesis as these salts may be dried conveniently in a vacuum oven at 80 °C.

Starting materials were from Aldrich (Sigma-Aldrich Chemie GmbH, Germany) as provided: 1-methylimidazole, redistilled, 99+%; 1-chlorobutane, 99.5+%, HPLC grade; hexafluorophosphoric acid, 60 wt% solution in water; aluminium chloride, 99%. The ionic liquids were prepared following the procedures described in the literature [3]. Refluxing of equal molar amounts of 1-methylimidazole and 1-chlorobutane in a flask when heating and stirring at 70 °C for 48 h was the procedure used to prepare 1-butyl-3-methylimidazolium chloride (BMIm Cl). The resulting viscous liquid was allowed to cool to room temperature and then it was washed several times with small portions of ethyl acetate. After the washing, the remaining ethyl acetate was removed by heating at 70 °C under vacuum.

The starting material for the cationic part of the ionic liquid was 1-butyl-3-methylimidazolium chloride ($C_8H_{15}N_2Cl$), with a melting point at 65–69 °C. The anionic part was formed from hexafluorophosphate acid (HPF_6) or from $AlCl_3$.

The reaction of BMIm Cl with hexafluorophosphate acid affords the molten salt [7]. To prepare the ionic liquid [BMIm]PF_6^- hexafluorophosphoric acid (1.3 mol) was added slowly to a mixture of BMIm Cl (1 mol) in water. The upper acidic aqueous layer was decanted after stirring 12 h, and the lower ionic liquid portion was washed with water until the washings were no longer acidic. The ionic liquid was then heated under vacuum at 70 °C to remove any excess of water. The result was viscous liquid of a light golden colour.

The chloroaluminate ionic liquids were prepared by mixing aluminium chloride with the organic chloride. The amount of materials mixed depended on the mole ratio of the desired final product. To prepare the neutral ionic liquid [BMIm]$AlCl_4^-$, an equal molar amount of $AlCl_3$ was added to BMIm Cl. After mixing the two solids the liquid was obtained. Care must be exercised in mixing the organic chloride and the aluminium chloride since the reaction is highly exothermic.

[EMIm]Cl-$AlCl_3$ and other halogenoaluminate ionic liquids exhibit Lewis acid–base chemistry, which can be controlled by varying the molar ratio of the two components. This makes the ionic liquid interesting as a non-aqueous reaction medium [8].

The Lewis acidity of these melts is determined by chloride activity. The melt equilibrium in the room temperature chloroaluminate liquid can be described by two equilibria:

$$AlCl_3 + Cl^- \leftrightharpoons AlCl_4^-$$

$$AlCl_3 + AlCl_4^- \leftrightharpoons Al_2Cl_7^-$$
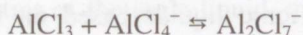
The former is dominant in basic melts, where the $AlCl_3/ImCl$ mole ratio is less than 1, and the latter in acidic melts, where the ratio is greater than 1. This means

that over much of the liquid range the anions present in significant quantities are Cl^-, $AlCl_4^-$, and $Al_2Cl_7^-$, and their relative amounts are controlled by the reaction:

$$2AlCl_4^- \leftrightharpoons Al_2Cl_7^- + Cl^-$$

The heptachloroaluminate ion is a strong Lewis acid, while chloride ion is the conjugate Lewis base. Neutral melt is one where the mole ratio is exactly 1 and only $AlCl_4^-$ ion is present. It has been found possible to buffer acidic melts to neutrality with solid alkali metal chlorides [9]. We prepared one basic ionic liquid (molar ratio $AlCl_3$/[BMIm]Cl was 0.7) and one acidic ionic liquid (molar ratio $AlCl_3$/[BMIm]Cl was 1.3). They had different colour: the basic was light green, the acidic was darker and brownish, and they also had different viscosity with the acidic being less viscous. The actual molar ratio for the basic ionic liquid used is also the limit of the single phase for room temperature (20°C). At lower molar ratios of $AlCl_3$/[BMIm]Cl a white solid residue can be seen which disappears at heating.

IONIC LIQUID AS SOLVENT

Traditional solvent extraction employs an organic solvent and an aqueous solution as the two immiscible phases. Ionic liquids represent a novel class of non-aqueous solvents and may now also be considered as a novel medium for liquid–liquid extraction, and used for the design of novel liquid–liquid extraction systems [7].

We decided to test the miscibility of ionic liquids with different organic solvents (Table 1). Equal volumes of an ionic liquid and the solvent were mixed in a test tube and the existence of separate layers was estimated.

Table 1. Ionic liquid solubility in other liquids

No.	Solvent	ε	[BMIm]PF$_6^-$	[BMImCl]–AlCl$_3$ Basic	[BMImCl]–AlCl$_3$ Acid
1	Water	80.1	Immiscible	Reacting	Reacting
2	Propylene carbonate	64.4	Miscible	Miscible	Miscible
3	Methanol	33.0	Miscible	Reacting	Reacting
4	Acetonitrile	26.6	Miscible	Miscible	Miscible
5	Acetone	20.7	Miscible	Miscible	Reacting
6	Methylene chloride	8.93	Miscible	Miscible	Miscible
7	Tetrahydrofuran	7.58	Miscible	Miscible	Reacting
8	Trichloroethylene	3.39	Immiscible	Immiscible	Immiscible
9	Carbon disulphide	2.64	Immiscible	Immiscible	Immiscible
10	Toluene	2.38	Immiscible	Miscible	Reacting
11	Hexane	1.90	Immiscible	Immiscible	Immiscible

{[BMIm]$^+$PF$_6^-$} is stable and shows solubility in organic solvents whose dielectric constant is higher than 7 except water. {[BMIm]Cl · AlCl$_3$} is different

because of its reactivity, which depends also on the ratio of imidazolium chloride and $AlCl_3$ used to make the ionic liquid. $AlCl_3$ rich ionic liquid (acidic) is more reactive and there are only a few solvents that do not react with this kind of ionic liquid. For acetone, toluene, and tetrahydrofuran some kind of solvatation takes place, but this is characteristic of only the acidic ionic liquid. This shows that solvents with possible donor or acceptor properties added to the ionic liquid may act differently in acidic and basic liquids. It has been recognized that there are specific ion–ion interactions, which are particularly important in the basic melt. The indications of such interactions were found as surprisingly large increases in viscosity when the system became basic. This suggests the onset of some kind of structure/order in the melt, resulting in an increase in viscosity.

An attempt was made to compare the chemistry in ionic liquids with that in a typical organic solvent [10]. From this point of view, toward solutes that are not very basic, a basic ionic liquid will behave like dimethylformamide. On the other hand, acidic ionic liquids are similar in acidity to trifluoroacetic acid.

Room temperature ionic liquids have been found to be excellent solvents, acting at the same time as catalysts for a number of reactions, such as the Friedel–Crafts reactions, Diels–Alder reactions, isomerizations, and hydrogenations. A good review and related references are given by Welton [11].

UV–VIS SPECTROSCOPY OF IONIC LIQUIDS

Good solvating properties together with large spectral transparency make ionic liquids suitable solvents for spectroscopic measurements especially in the ultraviolet–visible (UV–VIS) region. They can be used together with organic co-solvents that "solvate" the constituent ions of the ionic liquid, resulting in a decrease in the aggregation of these ions (lower viscosity and higher conductivity).

Figure 1 shows the UV–VIS spectra for BMIm Cl–$AlCl_3$ mixtures and $[BMIm]^+PF_6^-$ ionic liquid. An extremely weak band occurs at 360 nm. Additional

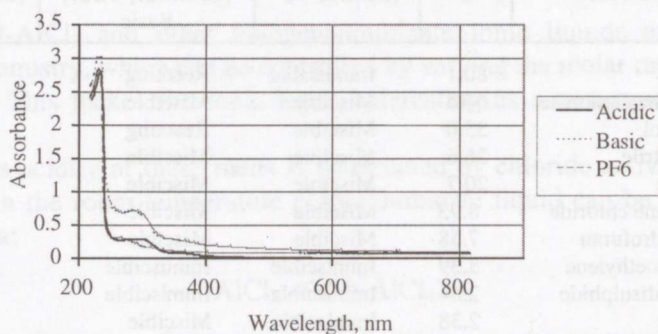Fig. 1. UV–VIS spectra of different ionic liquids: acidic and basic BMIm Cl–$AlCl_3$ mixture and $[BMIm]^+PF_6^-$. UV absorption spectra in the interval 200–800 nm were measured on HP8452A diode array spectrometer using 1 cm square silica cuvettes with tight closures. Samples of ionic liquids were 10 vol% of solutions in acetonitrile at 20 °C.

bands are observed at 300 nm for the acidic and at 290 nm for the basic liquid. In both cases the basic liquid has stronger bands. These bands may be due to protic impurities and they limit the useful spectral range of these ionic liquids. The rapidly rising UV cut-off reaches absorbance of unity at 250 nm for the basic and at 240 nm for the acidic and $[BMIm]^+PF_6^-$ ionic liquid. The shift in the UV cut-off to shorter wavelengths as the chloride concentration is increased is also regarded as an indication of specific cation–chloride anion interaction [12].

IR SPECTROSCOPY OF IONIC LIQUIDS

In the case of moisture stable ionic liquids IR spectroscopy helps to reveal impurities in the liquids. Figure 2d shows the spectrum of $[BMIm]^+PF_6^-$. The complete removal of water and the absence of other –OH species were confirmed by the lack of O–H stretching bands from 3400 to 3800 cm^{-1} in the infrared
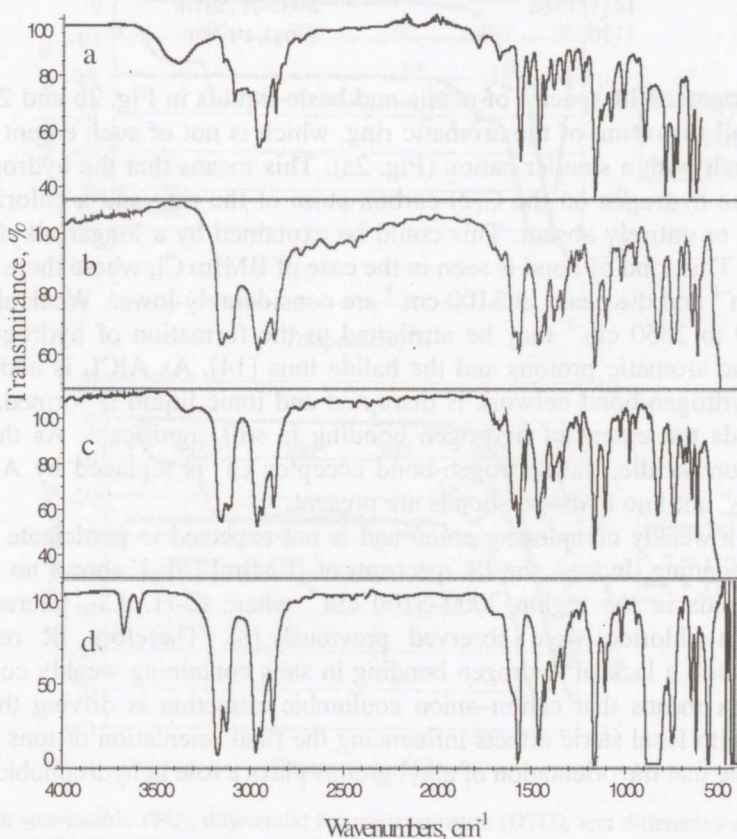

Fig. 2. Infrared spectra of different ionic liquids and 1-butyl-3-methylimidazolium chloride: a, BMIm Cl; b, basic BMIm Cl–AlCl$_3$; c, acidic BMIm Cl–AlCl$_3$; d, $[BMIm]^+PF_6^-$. IR transmission spectra in the interval 4000–500 cm^{-1} were measured on Nicolet Avatar 360 FT-IR spectrometer, using NaCl cell for liquids (film thickness 0.025 mm).

spectra of the final melts. Evidence for the presence of hydrogen bonding can be obtained from IR spectroscopy. The presence of a band in the region of 3050–3080 cm^{-1} is regarded as diagnostic of the presence of a strong, discrete C(2)...X-hydrogen bond [13].

In the region 4000–2000 cm^{-1} C–H stretching vibrations were observed. The peaks at >3100 cm^{-1} in the spectrum can be attributed to the ring C–H stretch, while those below 3000 cm^{-1} can be attributed to aliphatic stretches. Other bands are given in Table 2.

Table 2. Main IR bands (cm^{-1}) assigned according to [8]

Wavelength of the band, cm^{-1}	Vibration
3171, 3124	ν(C–H) aromatic, str
2966, 2939, 2878	ν(C–H) aliphatic, str
843	ν(PF)
1575, 1467	ν(ring), str sym
1431, 1386	MeC–H , asym
1170	(ring), str sym

Comparison of IR spectra of acidic and basic liquids in Fig. 2b and 2c reveals only a small distortion of the aromatic ring, which is not of such extent as in the case of a salt with a smaller cation (Fig. 2a). This means that the hydrogen bond between the hydrogen on the C(2) carbon atom of the ring and a chloride ion is very weak or entirely absent. This could be explained by a longer alkyl chain in the cation. This kind of bond is seen in the case of BMIm Cl, where there is a band at 3088 cm^{-1} and the peaks at 3100 cm^{-1} are considerably lower. Weak absorption from 2500 to 2850 cm^{-1} may be attributed to the formation of hydrogen bonds between the aromatic protons and the halide ions [14]. As AlCl$_3$ is added to the salt, the hydrogen-bond network is disrupted and ionic liquid is formed. In basic ionic liquids the extent of hydrogen bonding is still significant. As the liquids become more acidic, the hydrogen-bond acceptor Cl$^-$ is replaced by AlCl$_4^-$ and then Al$_2$Cl$_7^-$ until no hydrogen bonds are present.

PF$_6^-$ is a weakly complexing anion and is not expected to participate in strong hydrogen bonding. Indeed, the IR spectrum of [BMIm]$^+$[PF$_6$]$^-$ shows no hydrogen bonding bands in the region 3000–3100 cm^{-1} where C–H...Cl– interactions on imidazolium chloride were observed previously [8]. Therefore IR results are consistent with a lack of hydrogen bonding in salts containing weakly complexing anions. This means that cation–anion coulombic attraction is driving the overall structure, with local steric effects influencing the final orientation of ions [15]. It is also possible that the orientation of alkyl groups plays a role in hydrophobic effects.

THERMAL ANALYSIS OF IONIC LIQUIDS

One of the advantages of ionic liquids is their thermal robustness, resulting in a large thermal operating range, which, in turn, enables excellent kinetic control for reactions proceeding in these liquids.

Thermogravimetry and differential thermal analysis were performed for air-stable ionic liquid both in air and in nitrogen (Fig. 3). In the case of [BMIm]PF_6^- the wide range of thermal stability was confirmed. This ionic liquid starts to degrade at a temperature of 350°C and degradation proceeds very rapidly after 400°C. The picture is very similar in air and in nitrogen, which points to similar thermal degradation process in both atmospheres, and there is no oxidation in the case of heating in air.
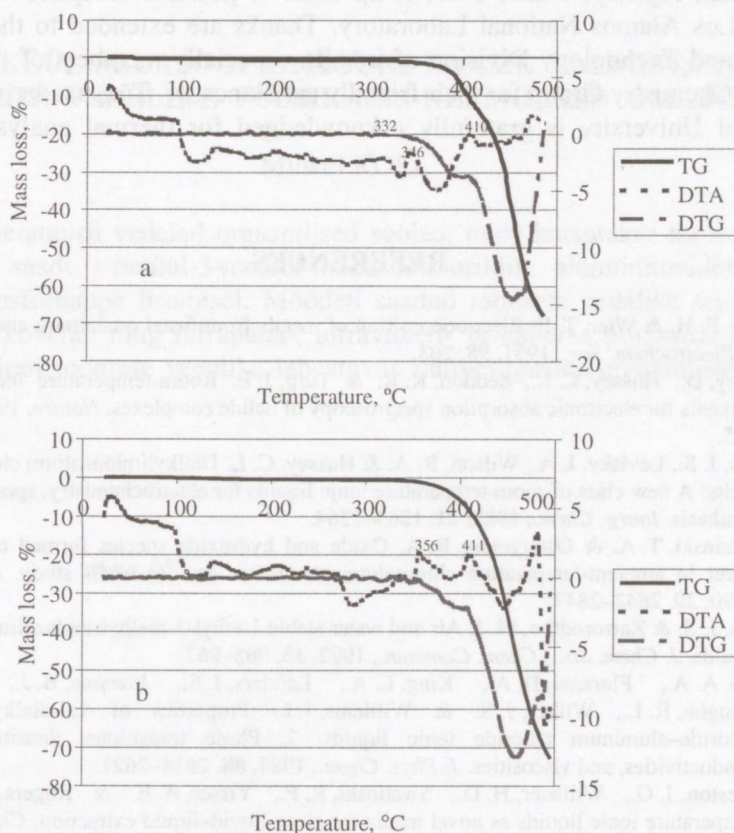

Fig. 3. Thermogravimetric (TG), differential thermogravimetric (DTG), and differential calorimetric (DTA) curves of [BMIm]$^+$$PF_6^-$ in air (a) and in nitrogen (b). Thermal analysis of ~200 mg of sample was performed on MOM TA analyser (Hungary). Program rate was 5°C/min and gas flow 25 l/h.

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CONCLUSIONS

Ionic liquids appear to be undemanding, convenient to use, and inexpensive to manufacture. They are good solvents for catalyst precursors and the possibility of using them in conjunction with Lewis acids makes them interesting industrial scale candidates as solvents for catalytic reactions. Advantage can be taken of the solubility of catalysts or reactants, and the insolubility of the reaction products of the catalytic reaction in these solvents.

ACKNOWLEDGEMENTS

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DIALKÜÜLIMIDASOOLKATIOONI BAASIL VALMISTATUD IOONSETE VEDELIKE FÜÜSIKALIS-KEEMILISED OMADUSED

Mihkel KOEL

Toatemperatuuril vedelad orgaanilised soolad, mida kutsutakse ka ioonseteks vedelikeks, saadi 1-butüül-3-metüül-imidasoolkloriidile alumiiniumkloriidi või heksaflorofosforhappe lisamisel. Mõõdeti saadud ioonsete vedelike termogravimeetrilised kõverad ning infrapuna-, ultraviolett- ja nähtava piirkonna spektrid. Samuti määrati ioonsete vedelike lahustuvus mitmesugustes orgaanilistes lahustites.