ISSN 1070-4272, Russian Journal of Applied Chemistry, 2011, Vol. 84, No. 7, pp. 1158–1164. © Pleiades Publishing, Ltd., 2011. Original Russian Text © O.E. Zhuravlev, N.V. Verolainen, L.I. Voronchikhina, 2011, published in Zhurnal Prikladnoi Khimii, 2011, Vol. 84, No. 7, pp. 1086–1092.

> PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

# Thermal Stability of 1,3-Disubstituted Imidazolium Tetrachloroferrates, Magnetic Ionic Liquids

O. E. Zhuravlev, N. V. Verolainen, and L. I. Voronchikhina

Tver State University, Tver, Russia

Received August 20, 2010

**Abstract**—Thermal stability of synthesized magnetic liquids, tetrachloroferrates of 1,3-disubstitued derivatives of imidazolium, was examined. An effect of the cation structure on thermal stability of ionic liquids was considered and a mechanism of thermal destruction was suggested.

**DOI:** 10.1134/S1070427211070068

In recent years a number of reviews, publications, and patents on various aspects of production and application of ionic liquids (IL) [1] grows. The ionic liquids are substances that are fluids at temperatures below 100°C and consist of bulk organic cations and various organic or inorganic anions. Ionic liquids are used as catalyst media and solvents.

An anion nature exerts a significant influence on IL properties: melting temperature, viscosity, density. If halides of transition metals (Fe, Co, Ni, Mn, etc.) are used in the ionic liquid as anion, then such ILs respond to magnetic field (they possess magnetic susceptibility). This new feature of IL [2] enabled isolation of similar compounds into group "magnetic ionic liquids" (MIL) and based on 1-butyl-3-methylimidazolium tetrachloroferrate their magnetic susceptibility was studied. Liquids under study are paramagnetic owing to the presence of stable tetrahedral anion  $FeCl_4^-$ .

Depending on the nature of the cation and anion ILs have different thermal stability. ILs can be decomposed under an action of other substances such as protic solvents, e.g., water which readily decomposes ionic liquids, and of high temperatures. In the latter case the decomposition temperature is determined by the nature of the organic cation. The alkylammonium salts are least stable and can be subjected to transalkylation and dealkylation by heating to 150°C, while imidazole and pyridine salts is much more stable.

Knowledge of the thermal stability of MILs enables determination of a temperature range, in which they can be used without any special precautions.

In the paper we examined the thermal stability of synthesized new magnetic ionic liquids: tetrachloroferrates, 1,3-disubstituted derivatives of imidazolium.

## EXPERIMENTAL

The spectra in the visible region were recorded on a spectrophotometer SF-56 in a solution of acetone, and IR spectra, on a Fourier spectrometer "Bruker" Equinox 55 between two plates. Data of a differential thermogravimetry was obtained on a device Q-1500 of MOM company (Hungary), the temperature range was 20–500°C, heating rate was 5°C min<sup>-1</sup>. Weight loss curves were recorded on an instrument "Perkin-Elmer" Pyris TGA, heating rate was 5 deg min<sup>-1</sup>, an air flow was 20 ml min<sup>-1</sup>.

Firstly based on the imidazole we synthesized  $1-(\beta$ -cyanoethyl) imidazole by a nucleophilic addition of acrylonitrile to the imidazole according to the scheme.

In a three-necked flask equipped with a stirrer, reflux condenser and dropping funnel 0.5 mol of imidazole dissolved in 50 ml of acetone were placed. Upon heating

Scheme of the synthesis of imidazole and magnetic ionic liquids



 $R = CH_2 = CH_2 - CN, CH_3; R' = C_4H_9, CH_2C_6H_5, CH_2CH_2CH_2CN, CH_2CH = CH_2, CH_2COOC_2H_5.$ 

and stirring 0.5 mole of acrylonitrile dissolved in 50 ml of acetone were added. The synthesis was carried out for 7 hours Acetone was distilled off. The resulting yellowish liquid was purified by distillation (bp =  $180^{\circ}$ C). The compound was characterized according to IR spectroscopy and elemental analysis.

Based on 1-(β-cyanoethyl)imidazole and 1-methyl-

imidazole (commercial product) quaternary salts of imidazolium were obtained by quaternization reaction with various agents (Table 1).

In a three-necked flask equipped with a stirrer, reflux condenser and dropping funnel 0.2 mole of 1-substituted imidazole dissolved in 50 ml, and 0.2 mole of a quaternizing agent were placed. Depending on the

Table	1.	Yield	and	physico	chemical	constants	of 1,3	3-disu	ubstituted	imidas	solium	chloride	2S
-------	----	-------	-----	---------	----------	-----------	--------	--------	------------	--------	--------	----------	----

			-	_				
Compd. no.	R	R'	M, g mol <sup>-1</sup>	Yield, %	mp, °C	Found, % Calculated, %		
						С	Н	
1	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	174.5	85	66–68	54.9 55.0	8.6 8.7	
2	CH <sub>3</sub>	$CH_2C_6H_5$	208.7	91	-23	63.1 63.3	6.2 6.3	
3	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CN	185.7	78	50-52	51.6 51.8	6.4 6.5	
4	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	158.6	82	Liquid	52.8 53.0	7.1 7.0	
5	CH <sub>2</sub> CH <sub>2</sub> CN	$C_4H_9$	213.7	55	"	56.3 56.2	7.7 7.6	
6	CH <sub>2</sub> CH <sub>2</sub> CN	CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	243.7	88	40-42	49.4 49.3	5.9 5.8	

 $\left[ R - N \stackrel{+}{\longrightarrow} N - R' \right] Cl^{-}$ 

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 84 No. 7 2011

structure of the quaternizing agent a synthesis time was ranged from 0.5 to 10 h. The yielded white crystalline substances were filtered, washed with dry cold ether and recrystallized from an acetone–ethyl acetate mixture of 1 : 2 ratio, dried under a vacuum for 1 day. All salts synthesized were crystalline substances of white or cream color.

Magnetic ionic liquids were prepared by mixing hot ethanolic solutions of ferric chloride(III) and imidazolium chlorides. The mixture was heated with constant stirring for 10–15 minutes. Ethanol was evaporated under a vacuum. Obtained MILs were washed with cold dry ether and dried under a vacuum over  $P_2O_5$  for a day. The composition and structure of MILs were confirmed by elemental analysis, IR spectroscopy and spectroscopy in the visible region (Fig. 1).

Synthesized magnetic ionic liquids were represented a painted liquid of green or brown colors. They were hydrophilic, soluble in water (they are highly hydrolyzed since anion  $\text{FeCl}_4^-$  is unstable in aqueous solution) and other polar solvents (dichloromethane, acetone,



**Fig. 1.** Absorption spectra in the visible region of HFeCl<sub>4</sub>·2H<sub>2</sub>O (7) and of several ionic liquids. (*D*) Absorption (rel. units), ( $\lambda$ ) wavelength (nm). (*1*–3) Compounds numbers in Table 2.



**Fig. 2.** Action of a constant magnet on the ionic liquid. (a) Bottom layer is an ionic liquid, upper layer is oil; (b) under the action of the constant magnet on system (a).

acetonitrile, ethanol). Physicochemical constants tetrachloroferrates of 1,3-disubstituted imidazolium are given in Table. 2.

Hydrated tetrachloroferric acid HFeCl<sub>4</sub>·2H<sub>2</sub>O. FeCl<sub>3</sub>·6H<sub>2</sub>O (1 mole) was dissolved in 30 ml of 36% HCl and extracted by ether in the form HFeCl<sub>4</sub>·2H<sub>2</sub>O. Ether was evaporated under a vacuum. The product was an amber-yellow crystals (mp = 46°C).

The spectra in the visible region indicate the presence in the composition of MIL of particle  $[FeCl_4^-]$  in the form of the anion. Spectra of MIL in the visible spectrum are comparable with HFeCl<sub>4</sub>·2H<sub>2</sub>O (Fig. 1) and have three characteristic bands of the ion  $[FeCl_4^-]$  at 534, 619, 688 nm, that agrees with published data for  $[FeCl_4^-]$ [3]. Similar spectra for MIL based on derivatives of imidazolium and FeCl<sub>3</sub> are presented in [4].

In the IR spectra of all examined compounds there exist absorption bands of imidazole ring ( $v_{C=C \text{ ring}} = v_{C-H_{arom}} = 3100-3150$ ;  $v_{as \text{ ring}} = 1460$ , 1165;  $v_{amide \text{ III}} = 625 \text{ cm}^{-1}$ ). Moreover, in the spectra of the derivatives there are absorption bands of functional groups (Table 3).

All synthesized tetrachloroferrates of substituted imidazolium give a response to the magnetic field. Visual observations of the system oil–MIL confirm that use of a small permanent magnet (with magnetic field 0.2 T) is sufficient to observe the magnetic attraction of the ionic liquid in the cell (l = 1 cm). Figure 2 shows snapshots visualizing the response of the synthesized 3-benzyl-1-methylimidazole tetrachloroferrate to the magnetic field. Oil was added to the system for better visibility.



**Fig. 3.** TG curves of 1,3-disubstituted imidasolium chlorides. ( $\Delta m$ ) the weight loss, %; (*T*) temperature, °C; the same for Figs. 4, 5. (*1*–3) Compounds numbers in Table 1.

Compd.	R	R'	$M$ , g mol $^{-1}$	Appearance	Density $\rho$ ,	Found, % Calculated, %			
110.					g cm <sup>3</sup>	Ν	Fe		
1	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	336.7	Greenish liquid	1.40	8.2 8.3	16.4 16.6		
2	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	370.8	Greenish-brown liquid	1.39	7.5 7.6	14.8 15.0		
3	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CN	347.7	The same	1.45	12.2 12.1	16.0 16.1		
4	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	321.0	Brownish liquid	1.46	8.8 8.7	17.3 17.4		
5	CH <sub>2</sub> CH <sub>2</sub> CN	C <sub>4</sub> H <sub>9</sub>	375.9	Brown liquid	1.45	11.3 11.2	14.8 14.9		
6	CH <sub>2</sub> CH <sub>2</sub> CN	CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	405.9	The same	1.58	10.5 10.4	13.5 13.7		

 Table 2. Yield and physicochemical constants of 1,3-disubstituted imidasolium chlorides

For comparison we have investigated the thermal stability of the original chlorides of 1,3-disubstituted imidazolium (Fig. 3). It is evident that the nature of the processes occurring during heating is similar: to 150–170°C practically all the salts are stable, then rapid weight loss occurs in one stage at a constant speed and at a temperature of 250–270°C the 100% weight loss occurs.

**Table 3.** Characteristics of vibration spectra of the synthesized magnetic ionic liquids

Compd. no. (Table 2)	Characteristic absorption bands, cm <sup>-1</sup>
1	$v_{-(CH_2)_3-CH_3} = 2960, 2880$
2	$v_{C-C_{arom}} = 1650, 1580, 1400;$ $v_{C-C_{arom}} = 3030, 3010$
3	$v_{-CH_{2}-} = 2958, 2877;$ $v_{CN} = 2256$
4	$v_{C=C} = 1647;$ $v_{=C-H} = 3093$
5	$v_{-(CH_2)_3-CH_3} = 2955, 2889;$ $v_{CN} = 2262$
6	$v_{-CH_2-} = 2958, 2877;$ $v_{-CH_2-COOH} = 1747$

In contrast to the original quaternary imidazolium salts their tetrachloroferrates are characterized by much greater heat stability and thermal decomposition process is a multi-stage (Fig. 4). All investigated tetrachloroferrates of substituted imidazolium are stable up to 400°C and gradually decompose in a range of 440–500°C. In all cases formation of undecomposed residue was found which was not identified.

Accounting for that all examined compounds in a salt structure have the same anion [FeCl<sub>4</sub>-], differences found



**Fig. 4.** TG curves of 1,3-disubstituted imidasolium tetrachloroferrates. (*1*–6) Compounds numbers in Table 2.

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 84 No. 7 2011

in the thermal stability can be caused by differences in the cation structure, namely, in the structure of a radical in position 3 of imidazole ring. The thermal stability of the hydtated tetrachloroferric acid was studied as reference in examination of an effect of the cation structure on the thermal stability of the synthesized ionic liquids (Fig. 5).

It is seen that this compound is stable at 80°C, then in a range of 80–200°C ( $T_{\text{max}} = 165$ °C) there is a rapid weight loss (50%) in one stage accompanied by an endothermic effect; in a range of 280–400°C, the small weight loss (6%); unburned residue (47%) remains after 500°C.

When replacing a hydrogen atom in the organic cation  $HFeCl_4$  by an organic cation the thermal stability of salts significantly increased, practically all the compounds are stable up to 400°C and lose 50% of the weight at 440–480°C. In all cases, the undecomposed residue is found at temperatures above 500°C.

These results indicate that the organic cation in the ionic liquid composition participates in the formation of special crystal structure of IL. Depending on its nature the structure of a salt (domains, chains, lattices) may be different, as reflected, inter alia, on the thermal stability. Table 4 shows the thermal stability of the investigated magnetic ionic liquids. It should be noted that the investigated ionic liquids are characterized by multistage process of decomposition, with the exception of 1-methyl-3-butylimidazolium tetrachloroferrate (compound 1), which is characterized by a rapid decomposition in a single stage in a range of 400-500°C at a constant speed. The reason for increasing the thermal stability of these compounds should be considered as a result of strong Coulomb interactions between the cation and anion in comparison with an interaction of halide anions. It should also be noted that the ionic





liquids are a certain structure, not only ion pair, in which apart from the Coulomb interactions, the formation of hydrogen bonds is possible with protonated hydrogen atoms in position 2 of the imidazole ring that leads to a strengthening of the structure. Also the specific order of arrangement and alternation of cations and anions should be accounted for in the crystal lattice of the salt [5-7].

In the case of halides of 1,3-disubstituted imidazolium the process of salts decomposition starts at 150–170°C and is associated mainly with the decomposition of the cation. According to literature data [8–11] the initial stages of decomposition of the cation of the quaternary salts start with the rupture of alkyl-N<sup>+</sup>, and suggest two potentially possible reaction paths:  $\beta$ -elimination (E<sub>2</sub>) and nucleophilic substitution at the quaternary nitrogen (S<sub>N</sub>):

$$R^{4}N^{+}X^{-} - S_{N} + RX$$

In the case of halides of a substituted imidazolium we can assume that thermodestruction of the salts proceeds by a mechanism of intramolecular  $\beta$ -elimination with formation of a five center transition state [8]:



In this case, the anion Cl- acts as a nucleophile and simultaneously a heterolytic rupture of the C<sub>B</sub>-H and  $C_{\alpha}$ -N<sup>+</sup> occurs that takes place in the nucleophilic  $\beta$ -elimination. In the case of halide ions, the transition state is easily implemented, and, as a rule, chlorides (Cl-0.181 Å) are less thermally stable in an order Cl-, Br-, I<sup>-</sup>. When counterions are bulky, such as  $ClO_4$  (2.36 Å),  $NO_{\overline{3}}$  (2.53 Å), thermal stability of salts increases, due to the fact that they hardly take three-dimensional structure and impede the implementation of the transition state [12-14]. Similar results were obtained when studying the thermal stability of the quaternary ammonium tetrafluoroborate [15]. Slowing of the reaction of thermal decomposition of tetrafluoroborate is due to destabilization of the transition state due to steric repulsion of a more bulky anion. The presence in the

\_

Tal	ole	4.	T	hermal	stabilit	y of	tetrac	hloro	ferrates	of	su	bsti	tutec	l im	ic	laso	lium
-----	-----	----	---	--------	----------	------	--------	-------	----------	----	----	------	-------	------	----	------	------

	[FeCl <sub>4</sub> ]
--	----------------------

-

Comnd. no.				Wei	ght loss	, %, at <i>T</i>	C, °C	Residue	Residue after		
	R	R'	<i>T</i> <sub>50</sub> , °C	200	300	400	500		800°C	Fe <sub>calc</sub> , %	
				200	500	100	500	0			
1	CH <sub>3</sub>	$C_4H_9$	480	3	3	3	55	45	20	17	
2	CH <sub>3</sub>	$CH_2C_6H_5$	480	3	6	28	52	48	30	15	
3	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CN	500	0	0	24	50	50	16	18	
4	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	440	0	0	16	66	34	21	20	
5	CH <sub>2</sub> CH <sub>2</sub> CN	$C_4H_9$	400	2	20	50	72	28	16	14	
6	CH <sub>2</sub> CH <sub>2</sub> CN	CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	400	4	18	50	80	20	17	15	
7	HFe	200	50	50	53	53	47	28	24		

anion structure of the alkyl substituents leads primarily to the decomposition of the anion [16]. In all cases, the study of the thermal stability of 1,3-dialkylimidazolium alkylsulfates we observed a gradual weight loss (7– 16 wt%) in a range of 50–350°C, followed by a sharp loss of the weight at 350–400°C associated with decomposition of the cation of the ionic liquids.

In the case of the investigated 1,3-disubstituted imidazolium tetrachloroferrates the presence in the structure of the bulky anion  $[FeCl_4^-]$  (3.7 Å) even in the larger extent complicates the implementation of the transition state that leads to a significant increase in the thermal stability compared to the initial halides. 1-Methyl-3-butylimidazolium tetrachloroferrate should be considered as the most thermally stable among the compounds (Table 4, compound 1), which up to 450°C is stable and decomposes in one step. Compounds 2-4 are stable up to 450°C, their decomposition occurs in two stages. It should be noted that for these compounds we observed decomposition also after 500°C, and the undecomposed residue after 800°C corresponds to the theoretically calculated content of the iron in the salt. Compounds 5, 6 in the series of investigated MILs are the least stable; replacement of methyl group in the structure of imidazole by  $\beta$ -cyanoethyl group leads to a decrease in the thermal stability, the decomposition of salt starts after 250°C, and the process is multi-stage and corresponds to the gradual destruction of the bonds  $C-N^+$ .

## CONCLUSIONS

(1) The ionic liquids were synthesized. They contained anion  $[FeCl_4^-]$  and various cations based on 1.3-disubstituted imidasolium.

(2) It was established that all studied magnetic ionic liquids were stable up to 380–400°C, in air the decomposition were carried out in several stages with formation of the undecomposed residue.

(3) We demonstrated that the cation nature is of a key factor in the thermal stability of the studied salts.

(4) It was established that the hydrated tetrachloroferric acid were thermally stable up to 80°C, at 200°C it lost 50% of weight, the decomposition proceeded in one stage. Replacement of hydrogen atom by an organic cation leads to a significant increase in the thermal stability of the compound.

#### ACKNOWLEDGMENTS

This work was supported by the Foundation for Assistance to Small Innovative Enterprises in Science and Technology, project no. 6972r/9585.

## REFERENCES

- Vygodskii, Ya.S., Lozinskaya, E.I., and Shaplov, A.S., *Ros. Khim. Zh.*, 2004, vol. 48, no. 6, pp. 40–50.
- 2. Hayashi, S. and Hamagushi, H., Chem. Lett., 2004,

vol. 33, pp. 1590–1593.

- 3. Friedman, H.L., J. Am. Chem. Soc., 1952, vol. 74, pp. 5–10.
- Hayashi, S., Saha, S., and Hamagushi, H., *IEEE Transactions on Magnetics*, 2006, vol. 42, no. 1, pp. 12–14.
- Rico, E.D., Sesto, T.M., and McClesky, *Chem. Commun.*, 2008, vol. 48, pp. 447–449.
- Yoshida, Y., Muroi, K., and Otsuka, A., *Inorg. Chem.*, 2004, vol. 43, pp. 1458–1462.
- 7. Holbrey, J.D., Reichert, W., and Rogers, R.D., *Dalton Trans.*, 2004, vol. 15, pp. 2267–2271.
- 8. Ingold, C.K., *Structure and Mechanism in Organic Chemistry*, Ithaca: Cornell Univ., 1969, 2nd ed.
- 9. Sykes, P., A Guidebook to Mechanism in Organic Chemistry, 2nd edn., London: Longmans, 1966.

- 10. Zhu, J., Morgan, A.B., Lamelas, F.J., and Wilkie, C.A., *Chem. Mater.*, 2001, vol. 13, pp. 3774–3780.
- 11. Becker, H., *Einfuhrung in die Elektronentheorie organischchemischer Reaktionen*, Berlin: Wissenschaften, 1974.
- Sokol'skaya, L.I., Semenov, V.A., Osipova, E.S., and Zhukova, N.G., *Zh. Prikl. Khim.*, 1987, vol. 60, no. 5, pp. 1127–1131.
- 13. Vasilenok, Yu.I., Zashchita polimerov ot staticheskogo elektrichestva (Protection of Polymers from Static Electricity), Leningrad: Khimiya, 1975.
- Bonhote, P. and Dias, A., *Inorg. Chem.*, 1996, vol. 35, pp. 1168–1178.
- 15. Ryzhkov, Yu.A. and Voronchikhina, L.I., *Zh. Prikl. Khim.*, 1994, vol. 67, no. 5, pp. 821–824.
- Holbrey, J. and Richrrd, W., *Green Chem.*, 2002, vol. 4, pp. 407–413.