ELSEVIER

Thermochimica Acta 357–358 (2000) 97–102

thermochimica
acta

www.elsevier.com/locate/tca

Thermal properties of imidazolium ionic liquids

Helen L. Ngo, Karen LeCompte, Liesl Hargens, Alan B. McEwen*

Covalent Associates, Inc, 10 State St., Woburn, MA 01801, USA

Abstract

We investigated the thermal properties of several imidazolium salts using DSC and TGA/SDTA data. Many of these salts are liquids at sub-ambient temperatures. These ionic liquids form glasses at low temperatures and have minimal vapor pressure up to their thermal decomposition temperature (>400°C). Thermal decomposition is endothermic with the inorganic anions and exothermic with the organic anions investigated. Halide anions drastically reduce the thermal stability of these salts (<300°C). We have observed that aluminium catalyzes the decomposition of the salts containing the inorganic fluoride anions. The imidazolium cations are thermally more stable than the tetraalkyl ammonium cations. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: TGA/SDTA; Ionic liquids; Thermal properties

1. Introduction

Salts based on the imidazolium cation have low melting points, with many being liquids at room temperature. The solvating properties of these ionic liquids, their high conductivity (ca. 10 mS/cm), and their wide window of electrochemical stability (ca. 4 V) make these materials excellent candidates for a range of applications, including catalysis, supercapacitors, and photovoltaics [1–10].

The dependence of the thermal properties on imidazolium and anion structure was investigated. The chemical abbreviations and structures of the investigated salts are detailed in Scheme 1. We also compare the imidazolium salts to tetraethyl ammonium (TEA) and tetrabutyl ammonium (TBA) salts. Previous work has looked at the pyrolysis of 1,3-dialkyl-imidazolium halides at 220–260°C [11]. Chan et al. found the dealkylation of imidazole quaternary salts consistent with a S_N2 mechanism, where the halide attacked the primary alkyl groups preferential to secondary positions. We have determined that the imidazolium salts have lower melting points and are thermally more stable than the lithium ion analogs [12]. We were interested in comparing the thermal properties of the salts containing the conjugate base of the superacids bis(trifluoromethylsulfonyl)imide (Im), bis(perfluoroethylsulfonyl)imide (Beti), and tris(trifluoromethylsulfonyl)methide (Me) [13].

2. Experimental

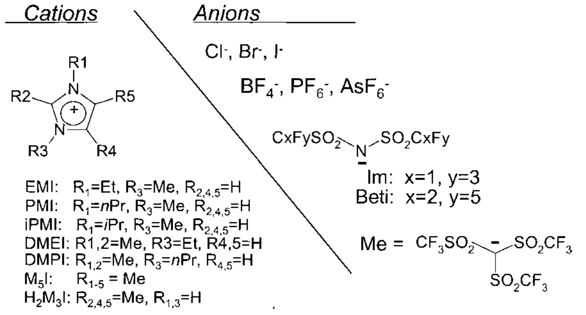
The imidazolium salts were synthesized according to standard procedures and dried before use [1–10,12]. For example, EMIBeti was synthesized from the reaction of EMICl with LiBeti in acetonitrile and used after drying at 100°C under vacuum. A Mettler DL18 Karl Fischer titrator was used to determine water content of the samples (typically <20 ppm).

Thermal analysis was performed on a Mettler DSC821^e and TGA850 using the STAR analysis software. Differential scanning calorimetry (DSC) data

---

* Corresponding author. Tel.: +1-781-938-1140.
E-mail address: mcewen@covalent.tiac.net (A.B. McEwen)

0040-6031/00/$ – see front matter
PII: S0040-6031(00)00373-7



Scheme 1. Structure of imidazolium salts investigated and chemical abbreviations.

were obtained in sealed aluminium pans, closed in a dry box (Vacuum Atmospheres dry box under an Ar atmosphere with <10 ppm H_2O), with a cooling and heating rate of 10°C/min. Thermogravimetric analysis (TGA) data were obtained either in an alumina (Al_2O_3) pan or in an aluminium (Al) pan sealed in a dry box. Using the Mettler Stinger technology the sample was pierced while being inserted into the instrument's dry N_2 atmosphere. The TGA data were collected at 20°C/min under N_2. The scanning differential thermal analysis (SDTA) data were obtained simultaneously with the TGA data. Temperatures reported from DSC data are curve peaks, freezing points being exothermic upon cooling and melting points being endothermic upon heating. Temperatures reported from TGA data are the onset, as determined from the step tangent. The decomposition was determined to be endothermic if the SDTA sample temperature decreased with the weight loss.

3. Results and discussion

We first describe our investigation of the phase transition dependence (DSC data) on salt structure followed by a discussion of thermal stability (TGA/SDTA data).

3.1. DSC

The calorimetric data were obtained by heating and cooling the sample. We typically observed substantial supercooling as the freezing points of the samples are significantly lower than the melting points (Fig. 1,

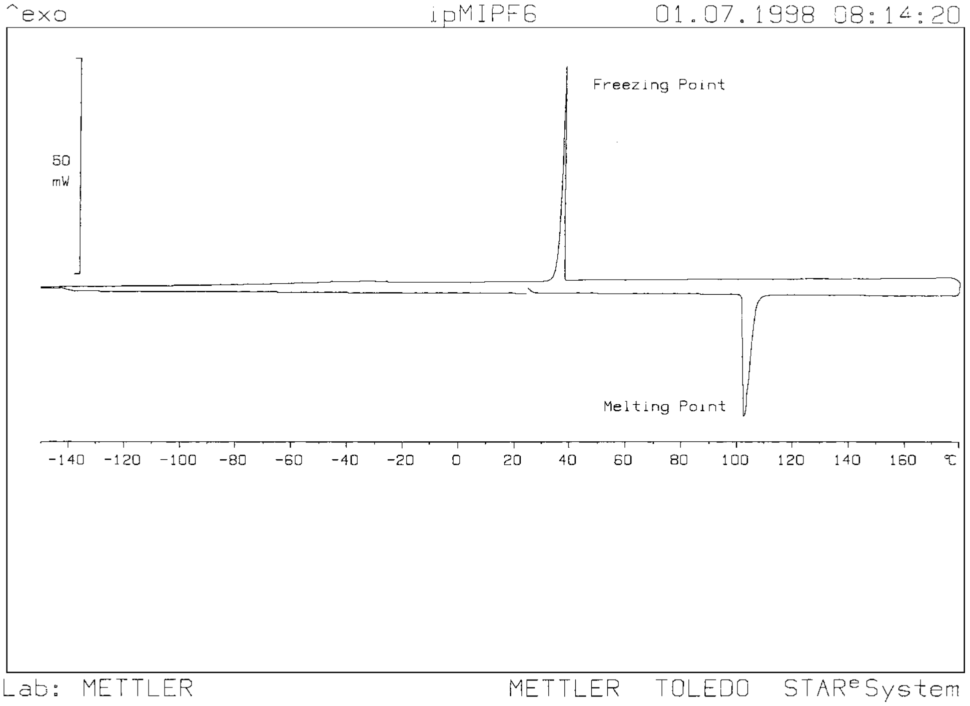


Fig. 1. Differential scanning calorimetry results for iPMIPF$_6$.

Table 1
Imidazolium and ammonium salt melting and freezing points as determined from DSC data

Salt	T_{mp}(°C)[a]	T_{fp}(°C)[a]	Observed supercooling (ΔT)
EMICl	89	33	56
EMIBr	79	30	49
EMII	79	39	40
PMICl	60	−140	200
iPMII	114	44	70
DMEICl	188	103	85
DMEIBr	141	92	49
DMPICl	138	43	95
H_2M_3Icl	194	168	26
M_5II	213	123	90
$TEABF_4$	72	45	27
$EMIBF_4$	11	−63	74
$TEAPF_6$	70	−58	128
$EMIPF_6$	62	5	57
$PMIPF_6$	40	−81	121
$iPMIPF_6$	102	35	67
$DMEIPF_6$	196	193	3
$DMPIPF_6$	78	18	60
M_5IPF_6	166	116	50
$EMIAsF_6$	53	−33	86
TEAIm	104	98	6
TBAIm	90	68	22
EMIIm	−15	−50	35
PMIIm	[b]	[b]	
iPMIIm	16	−29	45
DMEIIm	27	−18	45
DMPIIm	15[c]		
M_5IIm	118	108	10
TEABeti	83	75	8
EMIBeti	−1	−12	11
DMEIBeti	25	−25	50
DMPIBeti	34	−26	60
TEAMe	46	29	17
TBAMe	59	34	25
EMIMe	39	−34	73

[a] The temperature peak associated with a 1° phase transition observed upon cooling (T_{fp}, exotherm) and warming (T_{mp}, endotherm).

[b] Only a glass transition at −90°C was observed.

[c] Glass transition at −82°C.

Table 1). Many of these imidazolium ionic liquids have a glass transition around −80 to −100°C [12].

The salt melting points decrease with the larger more asymmetric imidazolium cations (e.g. EMI with C_s symmetry). The highest melting points are observed with the more symmetric (C_{2v}) M_5I cation. The lowest melting points are with the PMI cation, which has the longer propyl side chain. With the iso-propyl side chain (iPMI) the melting point increases to a value above that observed for EMI. The largest supercooling is observed with PMI, due to the larger alkyl side chain providing greater degrees of freedom and asymmetry. The salts containing the Im anion have lower melting points compared to the other anions investigated, while the halide salts display greater supercooling.

3.2. TGA and SDTA

Thermal decomposition is strongly dependent on the salt structure. With certain ions it is also dependent

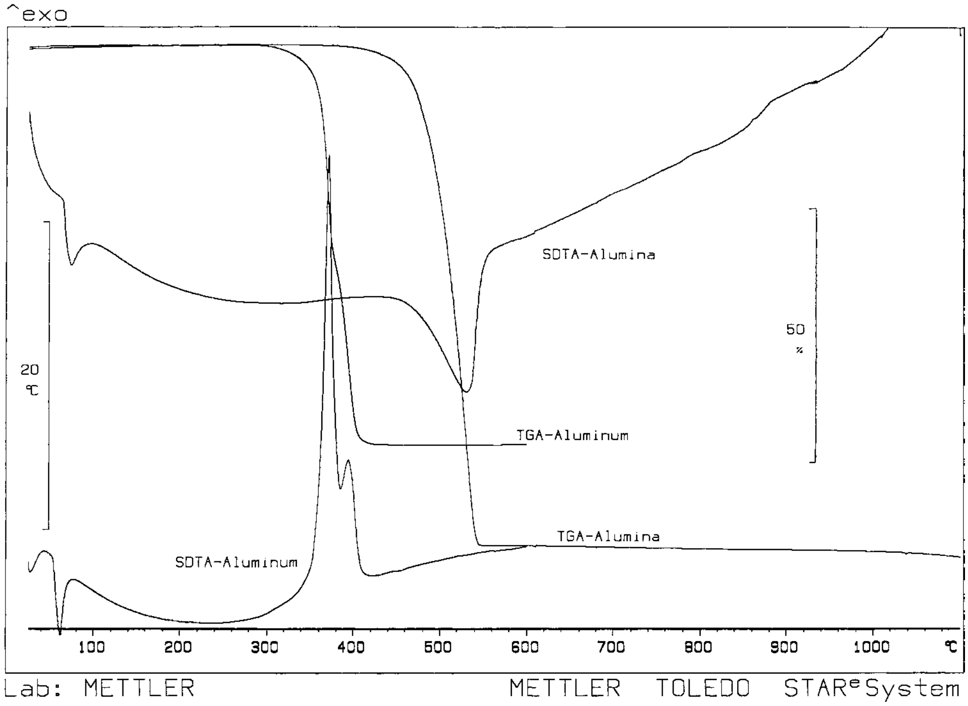


Fig. 2. TGA and SDTA results for $EMIPF_6$, comparing aluminium (Al) and alumina (Al_2O_3) pans.

on the sample pan composition. As exemplified by $EMIPF_6$ (Fig. 2), the thermal decomposition is catalyzed at a lower temperature by aluminium and the decomposition becomes exothermic. The imidazolium PF_6 salts are strongly affected by pan composition (Table 2), displaying 100°C lower thermal stability in the presence of aluminium compared to alumina. Therefore, our discussion will focus on the data obtained from alumina pans.

Increasing the substitution of the imidazolium ions (i.e. EMI to DMPI to M_5I) increases the thermal stability due to the removal of the ring hydrogens. The removal of the C(2) hydrogen (e.g. DMPI salts) has the largest effect due to the acidity of this proton. With an iso-propyl group at nitrogen (e.g. iPMI) the thermal stability decreases, likely due to the facile elimination of the stabilized secondary cation. This elimination is endothermic with iPMIIm, compared to the higher temperature exothermic decomposition normally observed with the Im containing salts.

Several general observations can be summarized. The imidazolium cations tend to be thermally more stable than the tetraalkyl animonium cations. The relative anion stabilities observed are: PF_6>Beti >Im≈BF_4>Me≈AsF_6≫I, Br, Cl. Salts composed of the organic anions, Im, Beti and Me, undergo exothermic decomposition in contrast to the inorganic anion salts. This exothermicity is likely due to the sulfonyl groups present. The lower temperature endothermic decomposition of the tetraalkyl ammonium salts (compared to the imidazolium salts) with these organic anions indicates a different lower temperature mechanism (e.g. alkyl group elimination) for the thermal decomposition of ammonium salts.

The decomposition temperature for these imidazolium salts is not sensitive to the presence of oxygen, as similar thermal decomposition behavior is observed in both O_2 and N_2 analysis environments. For example, with $EMIPF_6$ similar onset temperature is observed in both O_2 and N_2 atmospheres; however, in the presence of oxygen the decomposition becomes exothermic midway through the observed weight loss.

Table 2
Thermogravimetric analysis results comparing ammonium and imidazolium salt decomposition dependence on pan material

Aluminium/stinger			Al_2O_3	
Salt	T_{onset} (°C)	SDTA	T_{onset} (°C)	SDTA
TEACl	–	–	264	endo
EMICl	285	endo	281	endo
EMIBr	–	–	311	endo
EMII	303	exo	310	endo
PMICl	282	endo	281	endo
iPMII	–	–	296	endo
DMEICl	287	endo	290	endo
DMEIBr	–	–	322	endo
DMPICl	286	endo	284	endo
H_2M_3ICl	–	–	253	endo
M_5II	303	exo	333	endo
$TEABF_4$	383	endo/exo	412	endo/exo
$EMIBF_4$	–	–	450	endo
$TEAPF_6$	–	–	388	endo
$EMIPF_6$	375	exo	481	endo
$PMIPF_6$	335	exo	440	endo
$iPMIPF_6$	332	exo	383	endo
$DMEIPF_6$	–	–	500	endo
$DMPIPF_6$	399	exo	–	–
M_5IPF_6	401	exo	487	endo
$EMIAsF_6$	416	exo	430	endo
TEAIm	439	endo	399	endo
TBAIm	403	endo	388	endo
EMIIm	455	exo	453	exo
PMIIm	452	exo	453	exo
iPMIIm	432	endo	409	endo
DMEIIm	–	–	456	exo
DMPIIm	462	exo	462	exo
M_5Iim	470	exo	466	exo
TEABeti	423	endo	397	endo
EMiBeti	423	exo	462	exo
DMEIBeti	–	–	420	exo
TEAMe	411	exo	397	endo
TBAMe	403	endo/exo	398	endo
EMIMe	450	exo	430	exo

4. Conclusions

Many of the imidazolium salts investigated are liquids at room temperature and below, displaying substantial supercooling characteristics. These ionic liquids have little vapor pressure up to their decomposition, providing a wide liquid range with no vapor pressure. The thermal stability of the imidazolium salts increases with increased alkyl substitution, as long as linear alkyl groups are used. The presence of nitrogen substituted secondary (and likely tertiary) alkyl groups decreases the thermal stability due to the facile elimination of the stabilized alkyl cations. With proper design, these ionic liquids offer unique solutions to a variety of technologies from catalysis and ‘solvent-free’ synthesis to electrochemical energy storage and optoelectronic devices.

Acknowledgements

We thank Richard Laura for his assistance. This work was financially supported by DOE contract DE F602-96ER82149 and NASA contract NAS3-98083.

References

[1] E.I. Cooper, J.M. O'Sullivan, in: R.J. Gale, G. Blomgren, H. Kojima (Eds.), Proceedings of the 8th International Symposium on Molten Salts, PV92-16, The Electrochemical Society Proceedings Series, Pennington, NJ 1992, p. 386.

[2] J.S. Wilkes, M.J. Zaworotko, J. Chem. Soc., Chem. Commun. (1992) 965.

[3] R.T. Carlin, H.C. De Long, J. Fuller, P.C. Trulove, J. Electrochem. Soc 141 (1994) L73.

[4] J. Fuller, R.T. Carlin, H.C. De Long, D. Haworth, J. Chem. Soc. Chem. Commun. (1994) 299.

[5] V.R. Koch, C. Nanjundiah, G.B. Appetecchi, B. Scrosati, J. Electrochem. Soc. 142 (1995) L116.

[6] V.R. Koch, L.A. Dominey, C. Nanjundiah, M.J. Ondrechen, J. Electrochem. Soc. 143 (1996) 788.

[7] P. Bonhôte, A.-P. Dias, M. Armond, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.

[8] N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhôte, H. Pettersson, A. Azam, M. Grätzel, J. Electrochem. Soc 143 (1996) 3099.

[9] A.B. McEwen, S.F. McDevitt, V.R. Koch, J. Electrochem. Soc. 144 (1997) L84.

[10] J. Fuller, R.T. Carlin, R.A. Osteryoung, J. Electrochem. Soc. 144 (1997) 3881.

[11] B.K.M. Chan, N.-H. Chang, M.R. Grimmett, Aust. J. Chem. 30 (1977) 2005.

[12] A.B. McEwen, H.L. Ngo, K. LeCompte, J.L. Goldman, J. Electrochemical Soc. 146 (5) (1999) 1687.

[13] I.A. Koppel, R.W. Taft, F. Anvia, S.-Z. Zhu, L.-Q. Hu, K.-S. Sung, D.D. DewMarteau, L.M. Yagupolskii, Y.L. Yagupolskii, N.V. Ignat'ev, N.V. Kondratenko, A.Y. Volkonskii, V.M. Vlasov, R. Notario, P.-C. Maria, J. Am. Chem. Soc. 116 (1994) 3047.