Journal of Molecular Liquids 152 (2010) 9–13

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Effects of cation and anion on physical properties of room-temperature ionic liquids

Shiro Seki [a,*], Takeshi Kobayashi [a], Yo Kobayashi [a], Katsuhito Takei [a], Hajime Miyashiro [a], Kikuko Hayamizu [b], Seiji Tsuzuki [b], Takushi Mitsugi [c], Yasuhiro Umebayashi [c]

[a] Materials Science Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), 2-11-1, Iwado-kita, Komae, Tokyo 201-8511, Japan
[b] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Center 5, Tsukuba, Ibaraki 305-8565, Japan
[c] Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan

ARTICLE INFO

Available online 20 October 2009

Keywords:
Room-temperature ionic liquid
Viscosity
Density
Temperature dependence
Molecular design

ABSTRACT

To investigate the effects of the cation and anion on the physical properties of room-temperature ionic liquids, the temperature dependences of the viscosity and density of 12 (7 cationic, 6 anionic) room-temperature ionic liquids were measured and analyzed. The effects of the cation were investigated using chainlike and cyclic (aromatic and non-aromatic) nitrogen-based room-temperature ionic liquids, and amide-type ($N(SO_2C_xF_{2x+1})_2$, $x=0, 1, 2$) anions and anions of various shapes were used to investigate the effects of the anion.

1. Introduction

Room-temperature ionic liquids are liquid (molten) salts that exist–for certain salts–in a liquid state at and above room-temperature because of the particular kinds of interactions between certain cations and anions. In recent years, the research and development of room-temperature ionic liquids (RTILs) to achieve the functions of low-flammability, low-volatility, low-viscosity, and high electrochemical stability have been actively promoted. These functions depend on the molecular formulas of their cations and anions. Against such a background, applications such as various electrochemical devices (lithium secondary batteries [1–3], fuel cells [4,5], electric double-layer capacitors [6], dye-sensitized solar cells [7], field-effect transistors [8,9] etc.), tribology solvents [10], synthetic solvents [11], and biomass solvents [12] as functional uses of RTILs have been developed. In the case of the above-mentioned applications, the relatively high viscosity of RTILs is a serious problem. Therefore, if the relationships between the viscosity and the molecular structure of RTILs are quantitatively clarified, it will be possible to design low-viscosity RTILs. To clarify the molecular origin of the macroscopic physical properties of RTILs, spectroscopic and theoretical investigations on the RTILs in terms of physical properties including the bulk ones have been widely carried out in many fields. However, reports on the detailed analysis of the density of RTILs and its temperature dependence (expansion degree) are very few [13,14]. It is well known that dynamic properties (for example, diffusion, fluxion and viscosity) of liquids are strongly correlated with molar volume of liquids (solutions, RTILs) as a thermodynamic quantity [15–17]. However, the molar volume should be intrinsically static thermodynamic quantities [18,19], thus, more experimental and theoretical efforts should be needed to confirm the quantitatively strict correlation with dynamic physical properties at the molecular level. To this purpose, it is indispensable to obtain experimental molar volume (density) and viscosity for a wide range of RTIL samples in a wider temperature region. In this study, we performed precise density and viscosity measurements of 12 RTILs with seven different cations and six different anions, and the correlation between the arrangement of the structure and the physical properties was examined.

2. Experimental

2.1. Samples

To investigate the cationic species of RTILs, six different bis (trifluoromethanesulfonyl)-amide-anion-based RTILs were used. The cation species were 1-ethyl-3-methylimidazolium (EMIm, M_w(cation): 111.17), 1-ethyl-2,3-dimethylimidazolium (EDMIm, M_w(cation): 125.20), *N*-methyl-*N*-propylpyrrolidinium (P_{13}, M_w(cation): 128.24), *N*-methyl-*N*-propylpiperidinium (PP_{13}, M_w(cation): 142.26), 1-ethyl-2,3,5-trimethylpyrazolium (ETMP, M_w(cation): 139.22), and trimethyl propylammonium (TMPA, M_w(cation): 102.20) (Fig. 1).

On the other hand, to investigate the anionic species of RTILs, seven different EMIm-cation-based RTILs were used. The anion species were bis (pentafluoroethanesufonyl) amide ($N(SO_2C_2F_5)_2$, M_w(anion): 380.16), bis(trifluoromethanesulfonyl) amide ($N(SO_2CF_3)_2$, M_w(anion): 280.15), bis(fluorosulfonyl) amide ($N(SO_2F)_2$, M_w(anion): 180.13), trifluoromethanesulfonate (SO_3CF_3, M_w(anion): 149.07), tetrafluoroborate (BF_4, M_w(anion): 86.80), thiocyanate (SCN, M_w(anion): 58.08), and dicyanamide ($N(CN)_2$, M_w(anion): 66.04). Measurement matrix for cations and anions of RTILs used in this study was shown in Table 1. All samples were dried in a vacuum chamber at 323 K for more than 48 h and stored in a dry

* Corresponding author. Tel.: +81 3 3480 2111; fax: +81 3 3480 3401.
E-mail address: s-seki@criepi.denken.or.jp (S. Seki).

0167-7322/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molliq.2009.10.008

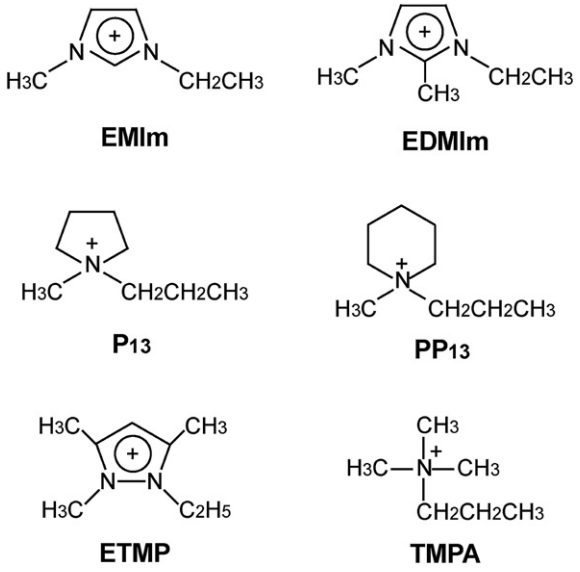

Fig. 1. Chemical structures of cation species of room-temperature ionic liquids used in this study.

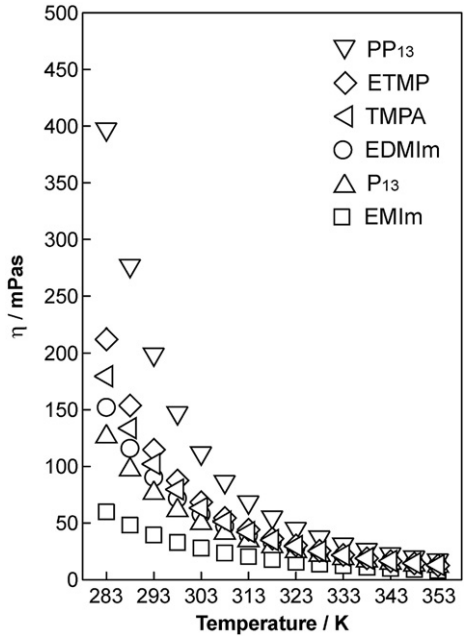

Fig. 2. Temperature dependence of viscosity (η) for $N(SO_2CF_3)_2$-anion-based room-temperature ionic liquids upon cooling (80 °C–10 °C).

argon-filled glove box ($[O_2]<0.4$ ppm, $[H_2O]<0.1$ ppm, Miwa Mfg. Co., Ltd.) before measurements.

2.2. Measurements

The viscosity (η/mPas) and density (ρ/g cm^{-3}) measurements were carried out using a thermo-regulated SVM3000G2 Stabinger-type viscosity and density/specific gravity meter (Anton Paar). The measurements were performed during cooling from 80 °C to 10 °C at 5 °C intervals with stopper to avoid any moisture and air contaminations.

2.3. Calculations of molecular frame volume of RTILs

Molar volume of RTILs $V_{measure}$/cm^3 mol^{-1} (at 30 °C), based on the measured density ρ/g cm^{-3} and molecular weight M_w/g mol^{-1} ($V_{measure}=M_w/\rho$), can be divided into two terms, i.e., $V_{measure}=V_{intra}+V_{inter}$. V_{intra} and V_{inter} represent volume for the molecular frame and that governed by inter-molecular interaction, respectively (Table 2). In other words, V_{intra} and V_{inter} are the excluded and the free (void) volumes of the given liquid. In addition, V_{intra} can be evaluated by using adequate van der Waals radii for the composing atoms and molecular geometries yielded by quantum mechanical calculations [20]. In this work, we adapted van der Waals radii proposed by Bondi [21], and molecular geometries optimized at MP2/6-311G** level of theory. All of geometry optimizations were carried out for the isolated ions in gas phase. If some conformers should be considered, we adapted sole the global minimum one. Ab initio calculations were performed by using *Gaussian*03 suites.

Table 1
Measurement matrix for cations and anions of room-temperature ionic liquids used in this study.

Cation/Anion	$N(SO_2C_2F_5)_2$	$N(SO_2CF_3)_2$	$N(SO_2F)_2$	SO_3CF_3	BF_4	SCN	$N(CN)_2$
EMIm	A	B	C	D	E	F	G
EDMIm		H					
P_{13}		I					
PP_{13}		J					
ETMP		K					
TMPA		L					

3. Results and discussion

3.1. Effects of cations of RTILs

Fig. 2 shows the temperature dependence of viscosity (η) for the six $N(SO_2CF_3)_2$-anion-based RTILs. The obtained viscosities increased in the order EMIm < P_{13} < EDMIm < TMPA < ETMP < PP_{13} at all measured temperatures. The values of η at 30 °C ($\eta_{30\,°C}$) were 28 (EMIm), 50 (P_{13}), 58 (EDMIm), 63 (TMPA), 68 (ETMP), and 112 mPas (PP_{13}). Also, a linear relationship with temperature was obtained for all samples. The obtained viscosities did not depend on M_w(cation) but depended on the cationic structure. In general, the increase in η was associated with a structural change from a five-membered ring to a six-membered ring and an increase in the size of substitutional groups on the cation ring. Viscosity is thought to be determined by the inter-molecular frictional force in the RTIL, in particular, it is affected by the molecular shape. For example, a significant decrease in viscosity was reported upon introducing a flexible ether oxygen on the alkyl chain in quaternary-ammonium-cation-based RTILs [22,23]. Furthermore, although the atomic weight of phosphorus is larger than that of nitrogen, a decrease in viscosity has been achieved by the substitution of phosphorus for nitrogen as the center atom species in quaternary-

Table 2
Calculated molecular frame volume (v_{frame}, unit per molecule) of six cations and seven anions at the MP2/6-311G** level.

Cation	EMIm	EDMIm	P_{13}	PP_{13}	ETMP	TMPA
Volume/Å^3	117.56	134.041	150.252	165.861	150.386	127.059
Anion	$N(SO_2C_2F_5)_2$	$N(SO_2CF_3)_2$	$N(SO_2F)_2$	SO_3CF_3	BF_4	SCN	$N(CN)_2$
Volume/Å^3	202.072	149.503	96.231	81.447	49.368	44.545	55.607