Journal of Non-Crystalline Solids 541 (2020) 120133

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Charge transport and glassy dynamics in a room temperature ionic liquid-[BMPyr][TFSI]

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ARTICLE INFO

Keywords:
Charge transport
Glassy dynamics
Broadband dielectric spectroscopy
Differential scanning calorimetry
Ionic liquids

ABSTRACT

In this paper, thermal and spectroscopic investigations on a room temperature ionic liquid, 1-Butyl-1-methyl pyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMP*yr*][TFSI]) were carried out using differential scanning calorimetry and broadband dielectric spectroscopy over wide temperature to study the molecular mobility, charge transport properties, and conductivity relaxation. The quantum mechanical calculations were used to study its polar nature. The isochronal cooling and heating were measured to get an estimation of the glass transition temperature. The study revealed that [BMPyr][TFSI] is an intermediate fragile system with a fragility index of 96.3 and T_g around 182 K. A strong translational–rotation coupling of the [BMPyr][TFSI] molecules were observed in the glassy state due to intermolecular Johari Goldstein relaxation. It showed an excellent agreement with the coupling model predictions. The conductivity behavior of [BMPyr][TFSI] follows Johncher's power law, and its temperature dependence well fits with the Arrhenius equation having an activation energy of 686.3 kJ/mol. The glass transition temperature obtained from DSC, isochronal cooling data and heating data were in good agreement.

1. Introduction

Room temperature ionic liquids (RTILs) have attained a growing interest among the physical chemistry and chemical physics research communities as well as to the industry [1]. RTILs are defined as molten salts composed of organic cations and inorganic anions with unique properties such as chemical and thermal stability, nonvolatility, the colossal range of fluidity, fast iono-mobility, high conductivity, and wide electrochemical window, all of which mark them as a promising candidate in electrochemical applications [2,3]. The diverse availability of anions and cations offers a wealth of materials with diverse structural formations and interactions. Such complex ion pair formations and its diverse dynamics influence the effectively available ion concentration, its transport characteristics and the conductivity beyond its simple viscosity dependence. Thus, the fundamental perspective of RTILs is very much essential to elucidate information regarding its diverse morphology, dynamics and transport properties in the glassy and supercooled liquid state. Thus a growing number of researchers and engineers have been focusing on different applications of RTILs due to their unique properties.

Apart from this point of view, this study can be useful to investigate the glassy dynamics and ionic conductivity of RTILs, since the chemical composition of RTILs plays a vital role in deciding its physiochemical properties. Some studies in this direction have been reported for the estimation of complex dielectric functions in ionic liquids (ILs) using quasielastic neutron scattering [4], mechanical relaxation [5], dielectric relaxation [6–11], light scattering [12], adiabatic calorimetry [12], and quasielastic Raman scattering [13–15], etc. Among them, broadband dielectric spectroscopy (BDS) can be considered as a versatile tool to measure the dielectric function and to expound information associated with it. BDS successfully probes the charge transport mechanism in the ILs with its ability to probe molecular fluctuations and ionic hopping in the broad frequency range from 10^{-2} to 10^{7} Hz over a wide temperature range.

This work intends to report the charge transport mechanism and glassy dynamics of a highly conductive RTIL, 1-Butyl-1-methyl pyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMP*yr*][TFSI]), and to elucidate the strong connection between conductivity relaxation (corresponding to the structural α- relaxations in nonionic glass formers) and secondary β-relaxations. In this perspective, one can assume that the pyrrolidinium cation $[Pyr]^+$ will be a better option since it acts as a source of secondary dynamics due to its non aromatic structure. Typically, ILs with aromatic cations like imidazolium fail to resolve the secondary β- relaxation in the glassy state due to delocalization of charge. Among all the possible derivatives of pyrrolidinium cation, BMPyr-cation can be considered as a stable one due to the presence of

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https://doi.org/10.1016/j.jnoncrysol.2020.120133
Received 24 January 2020; Received in revised form 11 April 2020; Accepted 21 April 2020
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equation. It is found that the dielectric data during heating from the deep glassy state could excellently be explained in modulus formalism for ionic conducting glass formers and could be well fitted with the Havriliak Nigami equation. Its temperature-dependent behavior strictly follows a non-Arrhenius VFT behavior in supercooled liquid and Arrhenius behavior in the glassy state. The study revealed that [BMPyr][TFSI] is a fragile intermediate system with fragility index 96.3 and T_g around 182 K. A strong translational–rotation coupling of the [BMPyr][TFSI] molecules were observed in the glassy state and which is considered as the precursor of structural α relaxation. It showed an excellent agreement of the JG and CM, $\tau_\beta(T)$ relaxation times emphasizing that the observed secondary relaxation is universal JG relaxation due to intermolecular interaction in the glassy state and excluded the possibilities for intramolecular rotation well evidently by Musiał et al. The conductivity behavior of [BMPyr][TFSI] follows Johncher's power law, and its temperature dependence well fits with the Arrhenius equation with an activation energy of 686.3 kJ/mol. The glass transition temperature obtained from DSC, isochronal cooling data and heating data were in good agreement admitting a slight discrepancy of 1–2 K.

CRediT authorship contribution statement

K.P. Safna Hussan: Conceptualization, Formal analysis, Investigation, Writing - original draft. **Mohamed Shahin Thayyil:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Authors thankfully acknowledge UGC-MANF for fellowship with sanction number MANF2017-18-KER-78598. The authors also acknowledge the Central Sophisticated Instrumentation Facility (CSIF) of University of Calicut for the software support.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jnoncrysol.2020.120133.

Reference

[1] G. Jarosz, M. Mierzwa, J. Zio, M. Paluch, Glass transition dynamics of room-temperature ionic liquid 1-methyl-3-trimethylsilylmethylimidazolium tetrafluoroborate, J. Phys. Chem. B 115 (2011) 12709–12716.

[2] S. Hensel-bielowka, Z. Wojnarowska, M. Dzida, E. Zor, M. Geppert-rybczyn, T. Peppel, K. Grzybowska, Y. Wang, A.P. Sokolov, M. Paluch, Heterogeneous nature of relaxation dynamics of room- temperature ionic liquids (EMIm) 2 [Co(NCS) 4] and (BMIm) 2 [Co(NCS) 4], J. Phys. Chem. C 119 (2015) 20363–20368, https://doi.org/10.1021/acs.jpcc.5b07123.

[3] S.A. Katsyuba, T.P. Griaznova, A. Vidis, P.J. Dyson, Structural studies of the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate in dichloromethane using a combined DFT-NMR spectroscopic approach, J. Phys. Chem. B 113 (2009) 5046–5051, https://doi.org/10.1021/jp8083327.

[4] K.L. Ngai, M. Shahin Thayyil, L.M. Wang, Quasielastic neutron scattering evidence of coupling of caged molecule dynamics to JG β-relaxation, J. Mol. Liq. 247 (2017) 300–303, https://doi.org/10.1016/j.molliq.2017.10.011.

[5] B. Jakobsen, K. Niss, N.B. Olsen, Dielectric and shear mechanical alpha and beta relaxations in seven glass-forming liquids, J. Chem. Phys. 123 (2005) 1–9.

[6] K.P. Safna Hussan, T. Mohamed Shahin, K.R. Vijisha, A. Anu, The interplay between charge transport and CO_2 capturing mechanism in [EMIM][SCN] ionic liquid - A broadband dielectric study, J. Phys. Chem. B 123 (2019) 6618–6626, https://doi.org/10.1021/acs.jpcb.9b03929.

[7] Z. Wojnarowska, K. Kolodziejczyk, K.J. Paluch, L. Tajber, K. Grzybowska, K.L. Ngai, M. Paluch, Decoupling of conductivity relaxation from structural relaxation in protic ionic liquids and general properties, Phys. Chem. Chem. Phys. 15 (2013) 9205–9211, https://doi.org/10.1039/C3CP50627D.

[8] C. Gainaru, E.W. Stacy, V. Bocharova, M. Gobet, A.P. Holt, T. Saito, S. Greenbaum, A.P. Sokolov, Mechanism of conductivity relaxation in liquid and polymeric electrolytes: direct link between conductivity and diffusivity, J. Phys. Chem. B 120 (2016) 11074–11083, https://doi.org/10.1021/acs.jpcb.6b08567.

[9] Z. Wojnarowska, K. Grzybowska, L. Hawelek, A. Swiety-Pospiech, E. Masiewicz, M. Paluch, W. Sawicki, A. Chmielewska, P. Bujak, J. Markowski, Molecular dynamics studies on the water mixtures of pharmaceutically important ionic liquid lidocaine HCl, Mol. Pharm. 9 (2012) 1250–1261, https://doi.org/10.1021/mp2005609.

[10] J. Sangoro, C. Iacob, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa, A. Stoppa, J. Hunger, R. Buchner, F. Kremer, Electrical conductivity and translational diffusion in the 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid, J. Chem. Phys. 128 (2008) 14–19, https://doi.org/10.1063/1.2921796.

[11] K. Adrjanowicz, K. Kaminski, P. Wlodarczyk, K. Grzybowska, M. Tarnacka, D. Zakowiecki, G. Garbacz, M. Paluch, S. Jurga, Molecular dynamics of the supercooled pharmaceutical agent posaconazole studied via differential scanning calorimetry and dielectric and mechanical spectroscopies, Mol. Pharm. 10 (2013) 3934–3945.

[12] F. Pabst, J. Gabriel, P. Weigl, T. Blochowicz, Molecular dynamics of supercooled ionic liquids studied by light scattering and dielectric spectroscopy, Chem. Phys. 494 (2017) 103–110, https://doi.org/10.1016/j.chemphys.2017.08.004.

[13] T. Yan, Y. Wang, C. Knox, On the dynamics of ionic liquids : comparisons between electronically polarizable and nonpolarizable models II, J. Phys. Chem. B 114 (2010) 6886–6904, https://doi.org/10.1021/jp9089112.

[14] G. Jarosz, M. Mierzwa, J. Zioło, M. Paluch, H. Shirota, K.L. Ngai, Glass transition dynamics of room-temperature ionic liquid 1-methyl-3-trimethylsilylmethylimidazolium tetrafluoroborate, J. Phys. Chem. B 115 (2011) 12709–12716, https://doi.org/10.1021/jp207291k.

[15] M.C.C. Ribeiro, Correlation between quasielastic raman scattering and configurational entropy in an ionic liquid, J. Phys. Chem. 111 (18) (2007) 5008–5015.

[16] M. Musia, Z. Wojnarowska, S. Cheng, K.L. Ngai, M. Paluch, Evidence of a fundamental mechanism governing conductivity relaxation in room-temperature ionic liquid, J. Phys. Chem. C 123 (2019) 22089–22094, https://doi.org/10.1021/acs.jpcc.9b07578.

[17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, C. J.R., G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, E.T. Vreven, J.A. Montgomery Jr, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, A. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, M.K. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, R.E.S.J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, K.M.O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. Ochterski, R.L. Martin, O.V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, D.F. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, GAUSSIAN 09 (Revision A.2) Gaussian, Inc., Wallingford, CT, D. J. Gaussian 09,. B.01, J (1998).

[18] K.P. Safna Hussan, T. Mohamed Shahin, S.K. Deshpande, Studies of ionogel structure and its electronic and optical characterization by ONIOM and other hybrid computational approaches, Mater. Today Proc. 5 (2018) 16272–16279, https://doi.org/10.1016/j.matpr.2018.05.119.

[19] K... Safna Hussan, M.S. Thayyil, V.K. Rajan, K. Muraleedharan, DFT studies on global parameters, antioxidant mechanism and molecular docking of amlodipine besylate, Comput. Biol. Chem. 80 (2019) 46–53, https://doi.org/10.1016/j.compbiolchem.2019.03.006.

[20] H. Ohno, K. Fujita, Electrochemical Aspects of Ionic Liquids, John Wiley & Sons, 2005, https://doi.org/10.1002/9781118003350.

[21] M. Shamsipur, A. Akbar, M. Beigi, M. Teymouri, Physical and electrochemical properties of ionic liquids 1-ethyl-3-methylimidazolium tetra fl uoroborate, 1-butyl-3-methylimidazolium tri fl uoromethanesulfonate and 1-butyl-1-methylpyrrolidinium bis (tri fl uoromethylsulfonyl) imide, J. Mol. Liq. 157 (2010) 43–50, https://doi.org/10.1016/j.molliq.2010.08.005.

[22] F. Trequattrini, A. Paolone, O. Palumbo, F.M. Vitucci, M.A. Navarra, S. Panero, Low frequency mechanical spectroscopy study of three pyrrollidinium based ionic liquids, Arch. Metall. Mater. 60 (2015) 385–390, https://doi.org/10.1515/amm-2015-0064.

[23] H. Tokuda, K. Hayamizu, K. Ishii, A. Bin, H. Susan, M. Watanabe, Physicochemical properties and structures of room temperature ionic liquids . 2 . variation of alkyl chain length in imidazolium cation, J. Phys. Chem. B 109 (2005) 6103–6110, https://doi.org/10.1021/jp044626d.

[24] J. Mijovic, B. Fitz, Dielectric Spectroscopy of Reactive Polymers, in: G. Schaumberg (Ed.), Applications of dielectric relaxation spectroscopy Novocontrol GmbH, 1998.

[25] A. Afzal, T. Mohamed Shahin, P.A. Sivaramakrishnan, M.K. Sulaiman, K.P. Safna Hussan, C.Y. Panicker, K.L. Ngai, Dielectric spectroscopic studies in supercooled liquid and glassy states of acemetacin, brucine and colchicine, J. Non Cryst. Solids 508 (2019) 33–45, https://doi.org/10.1016/j.jnoncrysol.2019.01.008.

[26] K.G. Sangeetha, K.K. Aravindakshan, K.P. Safna Hussan, Insight into the theoretical and experimental studies of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone N (4)-methyl- N (4)- phenylthiosemicarbazone - A potential NLO material, J. Mol. Struct. 1150 (2017) 135–145, https://doi.org/10.1016/j.molstruc.2017.08.078.

[27] K.P. Safna Hussan, M.S. Thayyil, S.K. Deshpande, T.V. Jinitha, Photoluminescent behavior of propylene carbonate and poly (methylmethacrylate) blend for transparent optoelectronic devices, AIP Conf. Proc. 1849 (2017), https://doi.org/10.1063/1.4984159.

[28] K.P. Safna Hussan, M.S. Thayyil, S.K. Deshpande, T.V. Jinitha, The entrapment of BaIb in PVP additives to form stable double active amorphous drug by hydrogen