

Electrochemical properties of gel copolymer- electrolyte based on Phosphonium ionic liquid

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Abstract : Noble Poly (lithium 2-acrylamido-2-methyl propane sulfonate) and its copolymer with N-vinyl formamide based on trihexyl (tetradecyl) phosphonium acetate $[(C_6H_{13})_3P(C_{14}H_{29})CH_3COO]$; $P_{66614}CH_3COO$ and trihexyl (tetradecyl)phosphonium bis(trifluoromethane sulfonyl) amide $[(C_6H_{13})_3P(C_{14}H_{29})][TFSA]$; $P_{66614}TFSA$ were prepared and analyzed to determine their characteristics and properties. The ionic conductivity of a copolymer based $P_{66614}TFSA$ ionic liquid system exhibits a higher conductivity ($8.9 \times 10^{-5} Scm^{-1}$) than that of a copolymer based $P_{66614}CH_3COO$ system ($1.57 \times 10^{-5} Scm^{-1}$). The charge on the TFSA anion is spread very diffusely through the S-N-S core and particularly in the trifluoromethane groups, and this diffusion results in a decreased interaction between the cation and the anion. The viscosity of $P_{66614}TFSA$ (39 cP at 343 K) and $P_{66614}CH_3COO$ (124 cP at 343 K), which is very hydrophobic, was fairly high. High viscosity leads to a slow rate of diffusion of redox species. The ionic conductivity of copolymer of a phosphonium ionic liquid system also exhibits higher conductivity than that of a homopolymer system. Phosphonium ionic liquids were thermally stable at temperatures up to 400°C.

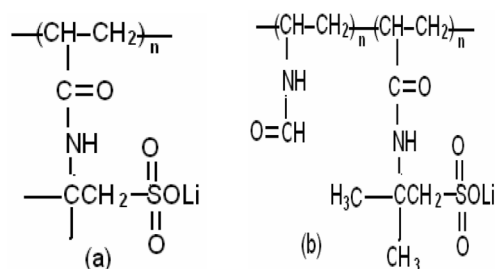
Keywords : phosphonium bis sulfonyl) amide, Trihexyl (tetradecyl) phosphonium acetate, Ionic conductivity, Viscosity, Thermally stable.

1. Introduction

Ionic liquids are electrochemically and thermally very stable, non volatile, non- flammable, they have a large stable liquid range, high conductivity, and have a superior solvating effect.¹⁻³⁾ In general ionic liquids have been used in polymer electrolyte samples as a charge carrier and a nonvolatile plasticizer. In particular, alkyl imidazolium based ionic liquids are capable of dissolving even molar concentrations of lithium salt and can function as electrolytic material in a lithium battery.^{4,5)} Whereas much attention has been paid to imidazolium ionic liquids recently, there has been very little research into

phosphonium ionic liquids. Imidazolium cation seems electrochemically unstable in a lithium battery system, however phosphonium ionic liquids are known to offer good chemical and thermal stability for various applications,⁶⁻⁸⁾ such as supercapacitor, dye-sensitized solar cells^{9,10)} and fuel cells, anodic polymerization of pyrrole, voltammetric measurements for various redox couples and photochemistry. Phosphonium ionic liquid cations have a higher stability and are less expensive than imidazolium ionic liquids. They have also not been researched into that much compared to imidazolium and pyridinium. The alkyl group (R_n) which is a very effective cation of tetraalkyl phosphonium, $[R_1R_2R_3R_4P]^+$ is a large and diverse group. Generally the large phosphonium cation can combine with relatively large anions to make viscous and

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Scheme1. (a) PAMPSLi (b)PAMPSLi/PVF

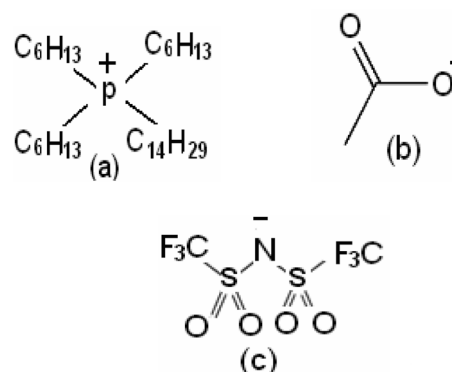
they exhibit different properties. Phosphonium ionic liquids seem to be good alternatives to other ionic liquids in many cases and need to be further researched. This basic data seems essential both for further research and to find practical uses and applications. In this work, new lithium polyelectrolyte-based on trihexyl (tetradecyl) phosphonium acetate ($P_{66614}CH_3COO$) and trihexyl (tetradecyl) phosphonium bis (trifluoromethane sulfonyl) amide ($P_{66614}TFSA$) were prepared and measured for conductivity, viscosity, thermal properties and stability.

2. Experimental

The monomer, lithium 2 acrylamide-2-methyl propanesulfonate (AMPSLi), was prepared by the reaction of 2 acrylamide-2-methyl propanesulfonic acid (Aldrich) with lithium carbonate (Aldrich) in a water solution placed in an ice bath; this monomer was polymerized at room temperature as the water was removed from the monomer aqueous solution by the water pump. The copolymer PAMPSLi/PVF was synthesized by polymerization of N-vinyl formamide (VF, Aldrich) with AMPSLi at $\sim 80^\circ\text{C}$ in the presence of a little $K_2S_2O_8$, initiator.⁹⁾ The polymer products, PAMPSLi and PAMPSLi/PVF [Scheme1], were dried under vacuum (~ 80 torr) at 65°C for at least 48 h. These alkylphosphonium ionic liquids ($[(C_6H_{13})_3P(C_{14}H_{29})]^+$, $TFSA^-$ and CH_3COO^-) were purchased from Cytec Industries and clean up as with $[(C_6H_{13})_3P(C_{14}H_{29})]Cl$. The water content of the samples was determined by Karl Fischer titration.¹¹⁾

trihexyl(tetradecyl) phosphonium bis(trifluoromethane sulfonyl) amide ($[(C_6H_{13})_3P(C_{14}H_{29})][TFSA]; P_{66614}TFSA$)

1H NMR δ_H (300 MHz; $CDCl_3$) 2.0~2.3(8 H, m, CH_2), 1.4~1.5(16 H, m, CH_2), 1.2~1.3 (32 H, m,

Scheme2. (a) P_{66614}^+ (b) CH_3COO^- (c) $TFSA^-$

CH_2), 0.79~0.85(12 H, m, CH_3)ppm. ES-MS: m/z 483 $[P_{66614}]^+$ ES- m/z 279 $[TFSA]^-$ Water content (Karl-Fisher): 141 ppm, Cl content :< 100 ppm

(tetradecyl) phosphonium acetate ($(C_6H_{13})_3P(C_{14}H_{29})CH_3COO$; $P_{66614}CH_3COO$;

1H NMR δ_H (300 MHz; $CDCl_3$) 2.0~2.3(8 H, m, CH_2), 1.4~1.5(16 H, m, CH_2), 1.2~1.3 (32 H, m, CH_2), 0.79~0.85(12 H, m, CH_3)ppm. ES-MS: m/z 483 $[P_{66614}]^+$ ES- m/z 59 $[CH_3COO]^-$

Water content(Karl-Fisher): 141 ppm, Cl content :< 100 ppm

The ionic liquid was dried and degassed before use. Trihexyl (tetradecyl) phosphonium acetate ($P_{66614}CH_3COO$) and trihexyl(tetradecyl) phosphonium bis (trifluoromethane sulfonyl) amide ($P_{66614}TFSA$) were mixed with 10 wt% polyelectrolyte and 90 wt% ionic liquid with ethanol and stirred over night. [Scheme2] The final products were dried under vacuum (~ 80 torr) at 65°C for at least 72 h.

Thermal analysis of samples was performed using a TA instruments differential scanning calorimeter (DSC Q100) at a scanning rate of 10°Cmin^{-1} over a temperature range of -150 to 150°C . Glass transition (T_g) and melting points (T_m) were determined as a function of composition

Impedance measurements were carried out in a small conductance cell from 25 to 65°C using the Eurotherm 2240E. Perkin Elmer thermogravimetric analyzer was used to test thermal stability of the ionic liquids and the scan rate was 10.0°C.min from room temperature to 800°C under a nitrogen atmosphere.

Viscosity of the ionic liquids was measured with an AMVn Automated Microviscometer at 25°C , 70°C and the ionic liquids were sealed in the sample tube under a nitrogen atmosphere.

3. Results and Discussion

Ionic liquids were made from the trihexyl tetradecyl phosphonium cation, bis (trifluoromethane sulfonyl) amide anion, and acetate anion (Scheme2). These ionic liquids are very hydrophobic and highly viscous. Copolymer (PAMPSLi/PVF) were powder, but after they dissolved in the ionic liquids.

All Polyelectrolyte samples (10% polymer + 90% ionic liquid) were changed into gel-like samples. Fig.1 shows the thermal traces of (a) PAMPSLi/ P_{66614} CH₃COO (b) PAMPSLi/PVF/ P_{66614} CH₃COO (c) PAMPSLi/ P_{66614} TFSA (d) PAMPSLi/PVF/ P_{66614} TFSA. As you can see, the glass transition temperature of a PAMPSLi/PVF/ P_{66614} CH₃COO (-65.09°C) is higher than that of the PAMPSLi/PVF/ P_{66614} TFSA (-71.34°C) system. PAMPSLi/PVF/ P_{66614} TFSA (-71.34°C) and PAMPSLi/PVF/CH₃COO (-65.09°C) were also slightly lower than that of PAMPSLi/ P_{66614} TFSA (-70.97°C) and PAMPSLi/ P_{66614} CH₃COO (-64.12°C) respectively. That is, the glass transition temperature of a copolymer-type polyelectrolyte based phosphonium ionic liquid system is lower than that of a homopolymer system. These results anticipated that the ionic conductivity of copolymer system exhibits higher than that of a homopolymer system. But the difference in the glass transition temperatures was only slight. As you can see in Fig.1, all co-polymer based phosphonium ionic liquid systems did not exhibit a melting peak and between -150°C and 150°C except re-crystallization peak.¹²⁾ Comparing the T_g values of two copolymer systems, the conductivity of PAMPSLi/PVF/ P_{66614} TFSA system seems to be expected higher

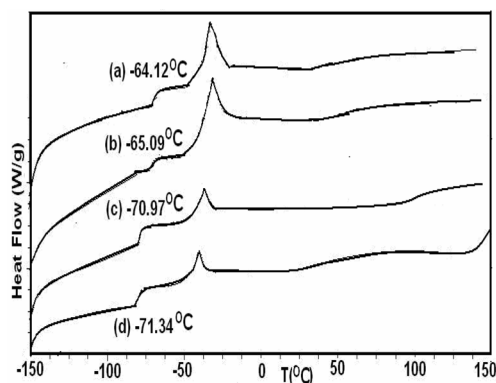


Fig. 1. DSC data of (a) PAMPSLi/ P_{66614} CH₃COO (b) PAMPSLi/PVF/ P_{66614} CH₃COO (c) PAMPSLi/ P_{66614} TFSA (d)PAMPSLi/PVF/ P_{66614} TFSA.

conductivity than that of PAMPSLi/PVF/CH₃COO

system. Fig.2 shows the conductivities of a copolymer based ionic liquid system and homopolymer system. At room temperature the ionic conductivity of copolymer systems [PAMPSLi/PVF/ P_{66614} TFSA ($8.9 \times 10^{-5} \text{Scm}^{-1}$) and PAMPSLi/PVF/CH₃COO ($1.57 \times 10^{-5} \text{Scm}^{-1}$) exhibit higher conductivity than those of homopolymer systems[PAMPSLi/ P_{66614} TFSA ($2.22 \times 10^{-5} \text{Scm}^{-1}$), PAMPSLi/ CH₃COO ($3.92 \times 10^{-6} \text{Scm}^{-1}$). The ionic conductivity of a copolymer system also exhibits nearly four times a higher conductivity than that of a homopolymer system. This behavior of higher conductivity of the copolymer sample can be explained by free lithium cations dissociated from the polymer backbone and reducing the repulsion of anions. Therefore these results support that the introduction of vinyl formamide into the copolymer type can increase the dissociation of lithium cations from the polymer backbone.¹³⁾ The ionic conductivity is increased as the temperature increasing. The ionic conductivities of these copolymer based phosphonium ionic liquids displayed a lower conductivity than that of copolymer based ionic liquid based imidazolium cation($5.4 \times 10^{-3} \text{Scm}^{-1}$).¹³⁾

To describe the conductivity (σ) of an electrolyte phase it is common to refer to the Nernst-Einstein equation.¹⁴⁾

The conductivity of polyelectrolyte is proportional to the concentration of charges in the material. It is clear that conductivity of ionic liquid is in proportion to the number of charge carriers. Therefore, disasso-

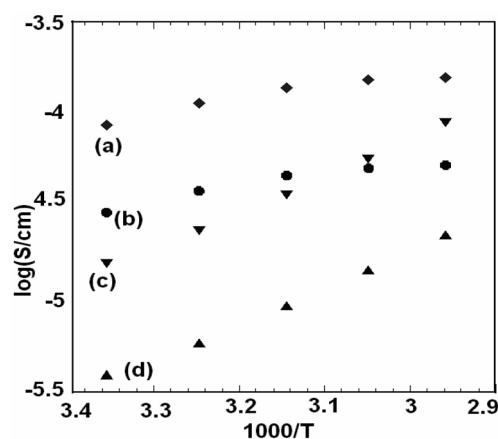


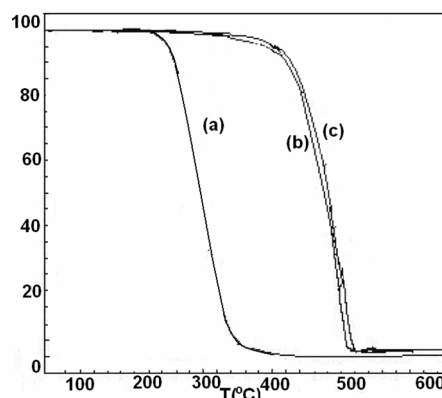
Fig. 2. Conductivity of (a) PAMPSLi/PVF/ P_{66614} TFSA (b) PAMPSLi/ P_{66614} TFSA (c) PAMPSLi/PVF/ P_{66614} CH₃COO (d) PAMPSLi/ P_{66614} CH₃COO.

ciation of an ionic liquid into cation and anions could be one of the most important factors in determining the conductivity of the liquid, as only the dissociated species are charge carriers in the systems. The relative basicity of anion seems to affect this dissociation process: the more basic the anion the more likely it is to exist in a paired and aggregated form. So it could be suggested that the higher conductivity of the PAMPSLi/PVF/P₆₆₆₁₄TFSA system compared to other phosphonium ionic liquid systems may be due to the weaker basicity of the dithiostructure. Furthermore, the charge on the TFSA anion is particularly diffused, spread through the S-N-S core and particularly through the trifluoromethane groups, and this diffusion results in a decreased interaction between the cation and the anion compared to other phosphonium ionic compounds with more localized anion charges.¹⁵⁾ It has become apparent that the bis(trifluoro methanesulfonyl)amide(TFSA) anion produces ionic liquids with substantially lower melting points and viscosity and higher fluidity than almost any other phosphonium anion. In particular, the organic salts of the TFSA anion are generally more hydrophobic and extremely stable, both thermally and electrochemically. P₆₆₆₁₄TFSA and P₆₆₆₁₄CH₃COO are quite viscous. This presumably reflects strong electrostatic interactions between ions. This high viscosity leads to a slow rate of diffusion of redox species. So it exhibits a slightly higher glass transition temperature than that of other ionic liquids. Furthermore, quaternary phosphonium cations that have a high molecular weight also contributed to an increased viscosity. Generally the viscosities of phosphonium ionic liquids are all greater than 200 cP at room temperature. P₆₆₆₁₄TFSA(298 K: 277 cP; 343 K: 39 cP) and P₆₆₆₁₄CH₃COO(298 K: 1380 cP, 343 K: 124 cP). These viscosity values are greater than other ionic liquids, presumably as a result of the larger size of the (C₆H₁₃)₃P (C₁₄H₂₉) cation. Viscosities vary with anions in the order TFSA⁻ < BF₄⁻ < Br⁻ < ~Cl⁻; That is, the large phosphonium cations can combine with relatively large anions to make less viscous. Table 1 was showed the viscosity of some phosphonium ionic liquid at 343 K. This data revealed that the viscosities increase with decreasing anion size.¹¹⁾ The ionic liquids with higher viscosities also exhibit lower conductivity. According to Eq. (1), conductivity of an ionic liquid is also proportional to the mobility of the charge carriers, on which the vis-

Table 1. Viscosity of some Phosphonium Ionic liquids at 343 K

Ionic liquid	Mw	Water content	Viscosity/cP
P ₆₆₆₁₄ TFSA	763	< 100 ppm	39
P ₆₆₆₁₄ BF ₄	570	0.7 wt%	*87
P ₆₆₆₁₄ Br	563	0.1 wt%	*116
P ₆₆₆₁₄ CH ₃ COO	542	< 100 ppm	124
P ₆₆₆₁₄ Cl	518.5	0.1 wt%	*133

*ref.[11];viscosity was measured at 343 K

**Fig. 3. Thermogravimetric traces for (a) emImTCM (b) P₆₆₆₁₄TFSA (c) P₆₆₆₁₄CH₃COO.**

cosity of the ionic liquid also depends.¹⁶⁾ The conductivity and viscosity for ionic liquids reveal the degree of association in the liquid. So the polyelectrolyte based on P₆₆₆₁₄TFSA displayed a higher conductivity than that of polyelectrolyte based P₆₆₆₁₄CH₃COO ionic liquid. Fig. 3 shows the thermogravimetric trace for P₆₆₆₁₄TFSA and P₆₆₆₁₄CH₃COO. A Perkin Elmer thermogravimetric analyzer was used to test the thermal stability of the ionic liquids and the scan rate was 10.0°C/min from room temperature to 700°C in a nitrogen atmosphere. It was found that two phosphonium ionic liquids were thermally stable up to over 400°C. Interestingly, two phosphonium ionic liquids also exhibited slower gravimetric decreases than those of the corresponding imidazolium ionic liquid. And a small amount of the residue tended to be left even after decomposition at high temperature.

4. Conclusion

The ionic conductivity of a copolymer polyelectrolyte based P₆₆₆₁₄TFSA ($8.9 \times 10^{-5} \text{ S cm}^{-1}$) exhibits higher

conductivity than that of a copolymer polyelectrolyte based on $P_{66614}CH_3COO$ system ($1.57 \times 10^{-5} S cm^{-1}$). The higher viscosity of $P_{66614}TFSA$ (298 K: 277 cP; 343 K: 39 cP) and $P_{66614}CH_3COO$ (298 K: 1380 cP, 343 K: 124 cP), which is very hydrophobic, leads to a decrease in conductivity. This is probably due to a less even charge distribution on the phosphonium cation leading to increased ionic interaction.¹⁷⁾ Phosphonium ionic liquids were thermally stable up to over 400°C. The advantages of a phosphonium system compared with other ionic liquid systems are density (higher viscosity) and lower cost; the disadvantage of a phosphonium system is its lower conductivity. It is believed that phosphonium-types are good alternatives to other ionic liquids and thus deserve further research.^{18,19)}

Acknowledgements

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References

1. Wataru Ogihara, Satiko Washiro, Hiromitsu nakajima, and Hiroyuki Ohno, 'Effect of Cation Structure on the Electrochemical and Thermal Properties of ion Conductive Polymers Obtained From Polymerizable Ionic Liquids' *Electrochimica Acta* **51**, 2614 (2006).
2. Qing Dai, David B. Menzies, D. R. Macfarlane, Stuart R. Batten, Stewart Forsyth, Leone Spiccia, Yi-Bing Cheng, and Maria Forsyth, 'Dye Sensitized Nanocrystalline Solar Cells Incorporating Ethylmethylimidazolium-based Ionic Liquid Electrolytes' *C.R.Chimie* **9**, 617 (2006).
3. Hiroyuki Ohno, Masahiro Yoshizawa, and Wataru Ogihara, 'Development of New Class of Ion Conductive Polymers Based on Ionic Liquid' *Electrochimica Acta* **50**, 255 (2004).
4. Thomas E. Sutto, Hugh C. De long, and Paul C. Trulove 'Physical Properties of Substituted Imidazolium Based Ionic Liquids Gel Electrolyte' *Z.Naturforsch.* **57a**, 839 (2002).
5. R. T. Carlin, J. Fuller, W. K. Kuhn, M. J. Lysaght, and P. C. Trulove, 'Electrochemistry of Room-temperature Chloroaluminate Molten Salts at Graphitic and Nongraphitic Electrodes' *J. Appl. Electrochem.* **26**, 1147 (1996).
6. J. Sun, M. Forsyth, D. R. Macfarlane, 'Room- temperature Molten Salts Based on Quarternary Ammonium ion' *J. Phys. chem. b*, **102**, 8858 (1998).
7. D. R. Macfarlane, P. Meakin, J. Sun, N. Amini, and M. Forsyth, 'Ionic Liquids Based on Imidazolium, Ammonium and Pyrrolidinium Salts of the dicyanamide Anion' *Phys. chem. b*, **103**, 4164 (1999).
8. H. Matsumoto, H. Sakaebe, K. Tatsumi, and J. Power Sources, **146**, 45 (2005).
9. R. E. Ramirez and E. M. Sanchez, 'Molten Phosphonium Iodides as Electrolytes in Dye-sensitized Nanocrystalline Solar Cells' *Energy Mater. Sol. Cells*, **90**, 2384 (2006).
10. R. E. Ramirez, L. C. Torres Gonzalez, and E. M. Sanchez, 'Electrochemical Aspects of Asymmetric Phosphonium Ionic Liquids' *J. ElectroChem. Soc.*, **154**, B 229 (2007).
11. N. Ito, S. Arzhanysev, M. Heitz, and M. Maroncelli 'Solvation Dynamics and Rotation of Coumarin 153 in Alkylphosphonium Ionic Liquids' *J. Phys. Chem. B* **108**, 5771 (2004).
12. J. Sun, D. R. Macfarlane, and M. Forsyth, 'Lithium Polyelectrolyte-ionic Liquid Systems' *Solid state ionics* **147**, 333 (2002).
13. E. H. Cha, S. A. Lim, J. H. Park, D. W. Kim, and D. R. Macfarlane, 'Ionic Conductivity Studies of Gel Polyelectrolyte Based on Ionic Liquid' *J. Power Sources*, **178**, 779 (2008).
14. J. Sun, D. R. Macfarlane, and M. Forsyth, 'Lithium Polyelectrolyte-ionic Liquid Systems' *solid state Ionics* **147**, 333 (2002).
15. Jennifer M. Pringle, Jake Golding, Krisztian Baranyai, Craig M. Forsyth, Glen B. Deacon, Janet L. Scott, and Douglas R. Macfarlane 'The Effect of Anion Fluorination in Ionic Liquids-physical Properties of a Range of bis (methanesulfonyl) Amide Salts' *New Journal of Chemistry*, **127**, 1504 (2003).
16. R. Y. Bruce 'Organic Chemistry', *Prentice Hall*, 1995.
17. Katsuhiko Tsunashima, Masashi Suiya, 'Physical and Electrochemical Properties of Low-viscosity Phosphonium Ionic Liquids as Potential Electrolytes.' *Electrochemistry Communications* **9**, 233 (2007).
18. James Vauhan, Jack Tu, and David Dreisinger, 'Ionic Liquid Electro-Deposition of Reactive metals' *J. Minerals, Metals & Materials Society*.
19. C. Bradaric *et al.*, in *Ionic Liquids, as Green Solvents Progress and Prospects*, R. Rogers and K. Seddon, Editors, p.41 American Chemical Society (2003).