

Influence of Aromatic and Unsaturated Substituents on Physical and Electrochemical Properties of Phosphonium Ionic Liquids

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Room-temperature ionic liquids (RTILs) have been regarded as potential electrolytes for various electrochemical systems due to the fact that RTILs have unique physicochemical properties such as no measurable vapor pressure, high thermal stability and low flammability, etc. Another advantage of RTILs is a designability of the chemical structures. Although many kinds of RTILs have been already investigated, interests in phosphonium RTILs have been increasing for their considerable advantages such as chemical and thermal stabilities. Recently, we have designed and proposed several RTILs based on quaternary phosphonium cations containing unsaturated carbon-carbon bonds in combination with a conventional anion, bis(trifluoromethylsulfonyl)amide ($N(\text{SO}_2\text{CF}_3)_2^-$, TFSA) anion.^{1,2} In this work, we report and summarize the findings of recent extensive researches on the RTILs based on quaternary phosphonium cations containing aromatic and unsaturated substituents (Figure 1) together with bis(fluorosulfonyl)-amide ($N(\text{SO}_2\text{F})_2^-$, FSA) anion.

The preparation and purification of phosphonium RTILs were carried out according to the procedures described in our previously published papers.^{1,2} The phosphonium RTILs were prepared by aqueous ion exchange reactions of the precursor phosphonium chlorides or bromides with lithium TFSA or potassium FSA. The resulting crude RTILs was extracted by dichloromethane, and then purified by washing with pure water several times until no residual bromide anion was detected with the use of AgNO_3 . The RTILs was dried under high vacuum for at least 8 h at 100 °C prior to use. The physicochemical and electrochemical properties such as conductivity (ac impedance method), viscosity (cone-plate type viscometer), density, melting point (DSC), thermal decomposition temperature (TGA) and electrochemical window (linear sweep voltammetry) were measured under argon atmosphere.

All the phosphonium RTILs prepared in this work were hydrophobic because of the hydrophobicity of TFSA and FSA anions. Table 1 lists the physicochemical properties of the FSA-based phosphonium RTILs. When a carbon-carbon double bond was introduced into an alkyl chain of the phosphonium cation, such phosphonium RTILs exhibited lower viscosity and higher conductivity than the corresponding unsubstituted phosphonium RTILs. Similar results were obtained in the case of TFSA-based phosphonium RTILs.² In this series of RTILs, $\text{P}_{222(\text{Al})}$ -FSA showed the lowest viscosity and highest conductivity because of its small cation size. On the other hand, the benzylphosphonium-based RTIL ($\text{P}_{222(\text{Bz})}$ -FSA) showed relatively high viscosity and low conductivity when

compared to the corresponding unsubstituted RTILs, which might be due to the positive charge enhanced by an electron-withdrawing effect of the phenyl group. Similar tendency was observed in the phenylphosphonium-based RTILs ($\text{P}_{11\text{P}(101)}$ -FSA and $\text{P}_{1\text{PP}(101)}$ -FSA); however, $\text{P}_{11\text{P}(101)}$ -FSA exhibited the lowest viscosity and highest conductivity in such phosphonium RTILs. The influence of the carbon-carbon double bond and the phenyl group on electrochemical and thermal stabilities of the phosphonium RTILs will be also reported and discussed.

References

1. K. Tsunashima, E. Niwa, S. Kodama, M. Sugiyama and Y. Ono, *J. Phys. Chem. B*, **113**, 15870 (2009).
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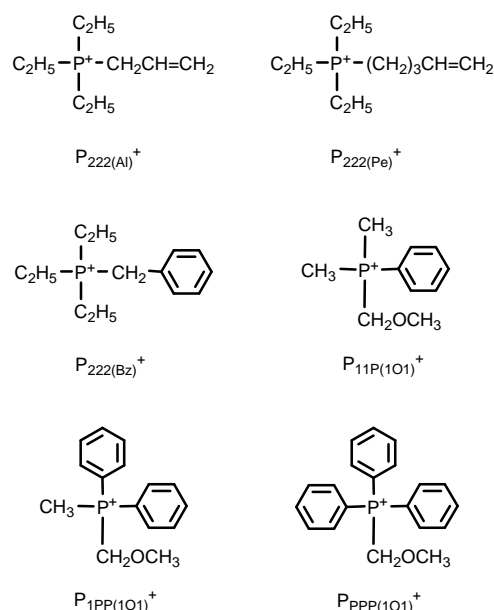


Figure 1 Structures of phosphonium cations investigated in this work.

Table 1 Physicochemical properties of ionic liquids based on phosphonium cations containing aromatic and unsaturated substituents.

Ionic liquid	$T_m / ^\circ\text{C}$	$d / \text{g cm}^{-3}$ at 25°C	$\eta / \text{mPa s}$ at 25°C	$\sigma / \text{mS cm}^{-1}$ at 25°C
$\text{P}_{222(\text{Al})}$ -FSA	6	1.28	44	5.4
$\text{P}_{222(\text{Ph})}$ -FSA	-36	1.24	64	3.8
$\text{P}_{222(\text{Bz})}$ -FSA	-34	1.30	191	1.3
$\text{P}_{11\text{P}(101)}$ -FSA	21	1.38	60	3.0
$\text{P}_{1\text{PP}(101)}$ -FSA	< -50	1.37	252	0.66
$\text{P}_{\text{PPP}(101)}$ -FSA	115	-----	-----	-----