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Synthesis of novel proton-conductive ionic liquids from 1-*H*- and 1-alkylimidazoles and hypophosphorous acid

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Abstract

Hitherto unknown 1-*H*- and 1-alkyl-3*H*-imidazolium hypophosphites have been synthesized from imidazole, 1-alkylimidazoles and hypophosphorous acid (50% aqueous solution) under mild conditions (room temperature, 30 min) in 90-95% yields. Their structure is proved by ^{1}H, ^{13}C, ^{31}P NMR and IR techniques and composition is confirmed by the data of elemental analysis. The synthesized 3*H*-imidazolium hypophosphites are viscous glycerol-like yellow liquids. They represent promising proton-conductive ionic liquids and can be employed to impart conductivity to the dielectric polymeric materials that is demonstrated on the example of industrial dielectric microporous track films from polyethylene terephthalate (PETF). The comparative analysis of IR spectra of the 3*H*-imidazolium hypophosphites, initial PETF film and PETF films impregnated by the synthesized ionic liquids shows that the latter are incorporated into the initial PETF film. The films, obtained by modification of PETF with imidazolium hypophosphites, possess high proton conductivity 1.92-$3.81 \cdot 10^{-4}$ $S \cdot cm^{-1}$ (according to the data of impedance spectroscopy) whereas the electric conductivity of the initial PETF film does not exceed 10^{-11}-10^{-12} $S \cdot cm^{-1}$. The temperature dependence of proton conductivity (σ) obtained for PETF film modified with 1-methyl-3*H*-imidazolium indicates that σ value increases in the range from $3.81 \cdot 10^{-4}$ to $1.53 \cdot 10^{-3}$ $S \cdot cm^{-1}$ at 303-363 K. Activation energy of the proton transfer process for this sample is 18.85 kJ/mol·K. Thus, application of novel proton-conductive ionic liquids for modification of industrial dielectric microporous PETF track film with through micropores (a model of proton-conductive membrane for the fuel elements) increases by 7 orders the electric conductivity of this film.

References

[1] R. Martinez-Palou. Microwave-assisted synthesis using ionic liquids. *Mol. Divers.* **2010**. Vol.14. No.1. P.3-25.

[2] L.-C. Chen, H.-M. Wang, R.-S. Hou, H.-T. Cheng. An Efficient Protocol for the Friedlander Quinoline Synthesis Using the Lewis Acidic Ionic Liquid Choline Chloride·$ZnCl_2$. *Heterocycles.* **2009**. Vol.78. No.2. P.487-493.

[3] W. Wu, G. Wu, M. Zhang. Highly selective synthesis of 2,6-Dimethylnaphthanlene by green catalysts – N-alkyl-pyridinium halides-aluminum chloride ionic liquids. *Applied Catalysis A: General.* **2007**. Vol.326. No.2. P.189-193.

[4] Y. Deng, F. Shi, J. Beng, K. Qiao. Ionic liquid as a green catalytic reaction medium for esterifications. *J. Mol. Cat. A: Chem.* **2001**. Vol.165. No.1-2. P.33-36.

[5] S. Sunitha, S. Kanjilal, P.S. Reddy, R.B.N. Prasad. Liquid-liquid biphasic synthesis of long chain wax esters using the Lewis acidic ionic liquid choline chloride·$ZnCl_2$. *Tetrahedron Lett.* **2007**. Vol.48. No.39. P.6962-6965.

[6] Y. Xin-hua, C. Min, D. Qi-xun, C. Xiao-nong. Friedel-Crafts acylation of anthracene with oxalyl chloride catalyzed by ionic liquid of [bmim]Cl/$AlCl_3$. *Chem. Eng. J.* **2009**. Vol.146. No.2. P.266-269.

[7] E.J. Angueira, M.G. White. Surer acidic ionic liquids for arene carbonylation derived from dialkylimidazolium chlorides and MCL_3 (M = Al, Ga, or In). *J. Mol. Cat. A: Chem.* **2007**. Vol.277. No.1-2. P.164-170.
[8] J.T. Yoke, J.F. Weiss, G. Tollin. Reactions of triethylamine with copper(I) and copper(II) halides. *Inorganic Chem.* **1963**. Vol.2. No.6. P.1209-1216.
[9] Y. Chauvin, B. Gilbert, I. Guibard. Catalytic dimerization of alkenes by nickel complexes in organochloroaluminate molten salts. *Chem. Commun.* **1990**. Vol.23. P.1715-1716.
[10] T. Welton. Ionic liquids in catalysis. *Coord. Chem. Rev.* **2004**. Vol.248. No.21-24. P.2459-2477.
[11] X. Chen, Y. Peng. Chloroferrate(III) Ionic Liquid: Efficient and Recyclable Catalyst for Solvent-free Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones. *Catal. Lett.* **2007**. Vol.122. No.3-4. P.266-269.
[12] P. Hapiot, C. Lagrost. Electrochemical reactivity in room-temperature ionic liquids. *Chem. Rev*. **2008**. Vol.108. No.7. P.2238-2264.
[13] D. Wei, A. Ivaska. Applications of ionic liquids in electrochemical sensors. *Anal. Chim. Acta.* **2008**. Vol.607. No.2. P.126-135.
[14] S.Z.E. Abedin, M. Polleth, S.A. Meiss, J. Janek, F. Enders. Ionic liquids as green electrolytes for the electrodeposition of nanomaterials. *Green Chem.* **2007**. Vol.9. No.6. P.549-553.
[15] W.D. Qin, H.P. Wei, S.F.Y. Li. 1,3-Dialkylimidazolium-based room-temperature ionic liquids as background electrolyte and coating material in aqueous capillary electrophoresis. *J. Chromatogr. A*. **2003**. Vol.985. No.1-2. P.447-454.
[16] J.S. Wilkes, M.J. Zaworotko. Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. *Chem. Commun.* **1992**. Vol.13. P.965-967.
[17] N.V. Shvedene, D.V. Chernyshev, I.V. Plentev. Ionic liquids in electrochemical sensors. *Zh. Mend. Russ. Che. Soc.* **2008**. Vol.52. No.2. P.80-91. (russian)
[18] M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou. Ionische Flüssigkeiten für die Synthese funktioneller Nanopertikel und anderer anorganischer Nanostrukturen. *Angew. Chem.* **2004**. Vol.116. No.38. P.5096-5100.
[19] J. Dupont, J.D. Scholten. On the structural and surface properties of transition-metal nanoparticles in ionic liquids. *Chem. Soc. Rev*. **2010**. Vol.39. No.5. P.1780-1804.
[20] K.L. Luska, A. Moores. Ruthenium nanoparticle catalyst stabilized in phosphonium and imidazolium ionic liquids: dependence of catalyst stability and activity on the ionicity of the ionic liquid. *Green Chem*. **2012**. Vol.14. No.6. P.1736-1742.
[21] M. Freemantle. NATO workshop examines the industrial potential of green chemistry using room-temperature 'designer solvents. *Chem. Eng. News*. **2000**. Vol.78. No.20. P.37-50.
[22] M. Abe, Yu. Fukaya, H. Ohno. Extraction of polysaccharides from bran with phosphonate or phosphinate-derived ionic liquids under short mixing time and low temperature. *Green Chem.* **2010**. Vol.12. P.1274-1280.
[23] H.T. Vo, Yo.J. Kim, Eu.H. Jeon, C.S. Kim, Ho.S. Kim, H. Lee. Ionic-Liquid-Derived, Water-Soluble Ionic Cellulose. *Chem. Eur. J.* **2012**. Vol.18. P.9019.
[24] H.T. Vo, V.T. Widyaya, J.J., Kim S. Hoon, H. Lee. Hydrolysis of ionic cellulose to glucose. *Bioresource Technology*. **2014**. Vol.167. P.484-489.
[25] C. Chiappe, G.C. Demontis, V.Di Bussolo, M.J.R. Douton, F. Rossella, Ch.S. Pomelli, S. Sartinia, S. Caporali. From pollen grains to functionalized microcapsules:a facile chemical route using ionic liquids. *Green Chem.* **2017**. Vol.19. P.1028-1033.
[26] J.P. Maciejewski, H. Gao, J.M. Shreeve. Synthetic Methods for Preparing Ionic Liquids Containing Hypophosphite and Carbon-Extended Dicyanamide. *Anions Chem. Eur. J.* **2013**. Vol.19. P.2947-2950.
[27] M. Doyle, S. Choi, G. Proulx. High-temperature proton conducting membranes based on perfluorinated ionomer membrane-ionic liquid composites. *J. Electrochem Soc*. **2000**. Vol.147. P.34-37.
[28] M. Galiński, A. Lewandowski, I. Stępniak. Ionic liquids as electrolytes. *Electrochimica Acta.* **2006**. Vol.51. P.5567-5580.
[29] L.G. da Trindade, L. Zanchet, J.C. Padilha, F. Celso, S.D. Mikhailenko, M.R. Becker, M.O. de Souza, R.F. de Souza. Influence of ionic liquids on the properties of sulfonated polymer membranes. *Mat. Chem. Phys.* **2014**. Vol.148. P.648-654.
[30] C. Schmidt, T. Glück, G. Schmidt-Naake. Modification of Nafion Membranes by Impregnation with Ionic Liquids. *Chem. Eng. Technol*. **2008**. Vol.31. No.1. P.13-22.
[31] Encyclopedia of polymers. Ed. V.A. Kargin et al. Vol.3. *Moscow: Soviet Encyclopedia.* **1974**. P.941. (russian)
[32] R.R. Shagidullin, A.V. Chernova, V.S. Vinogradova, F.S. Mukhametov. Atlas of IR spectra of organophosphorus compounds. *Moscow: Nauka*. **1989**. P.336. (russian)