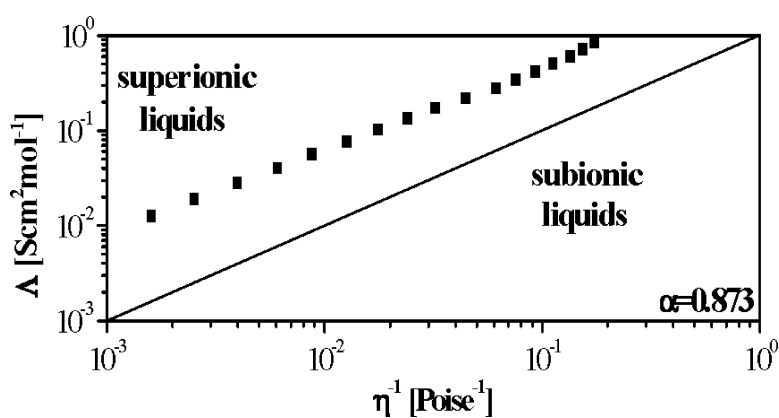


A Liquid Derivative of 12-Tungstophosphoric Acid with Unusually High Conductivity

Athanasios B. Bourlinos, Kannan Raman, Rafael Herrera,
 Qiang Zhang, Lynden A. Archer, and Emmanuel P. Giannelis

J. Am. Chem. Soc., **2004**, 126 (47), 15358-15359 • DOI: 10.1021/ja046821b • Publication Date (Web): 09 November 2004

Downloaded from <http://pubs.acs.org> on April 5, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

A Liquid Derivative of 12-Tungstophosphoric Acid with Unusually High Conductivity

Athanasios B. Bourlinos,[†] Kannan Raman,[†] Rafael Herrera,[†] Qiang Zhang,[‡] Lynden A. Archer,[‡] and Emmanuel P. Giannelis^{*†}

Department of Materials Science and Engineering and School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853

Received May 28, 2004; E-mail: epg2@cornell.edu

Thermally stable anhydrous proton conductors have recently attracted intense interest as electrolytes for high-temperature fuel cell applications.^{1–7} Among the gallery of protonic solid conductors, polyoxometalates (POMs) have been considered as possible electrolyte candidates in fuel cells. POMs consist of highly stable nanometer-size clusters generally containing early transition-metal ions octahedrally coordinated to oxygen.⁸ However, their protonic conductivity is highly sensitive to humidity and temperature,^{3,4} which limits their fuel cell application. Currently, efforts in using polyoxometalates have relied on POMs dispersed in a polymer matrix to form polymer nanocomposite membranes.^{1,3}

The present communication describes an alternative for attaining anhydrous proton conductors based on neat POMs. In particular, it describes a new family of POM-based liquid salts. The liquid POM derivatives are obtained by partial exchange of the surface protons of the POM core cluster by a bulky PEG-containing quaternary ammonium cation. The POM proton form can undergo partial proton exchange with monovalent ions leading to species with the general formula $H_{3-x}M_xPOM$ (M: monovalent cation, x : degree of proton substitution). Due to the remaining protons, the partially exchanged POMs are well-known for their acidic properties.⁹ Liquid POM salts offer several advantages: (i) they are solvent-free and zero vapor pressure liquids, (ii) they possess residual acidity and good thermal stability, and (iii) they exhibit much higher ionic conductivity than the corresponding anhydrous solid analogues.

The liquid salt was prepared by treating 10 g of the solid heteropolyacid $H_3PW_{12}O_{40}$ (Fisher Scientific) with 7 g of $(CH_3)(C_{18}H_{37})N^+[(CH_2CH_2O)_nH][[(CH_2CH_2O)_mH]Cl^-$ (Ethoquad 18/25, Akzo Nobel, $m + n = 15$) (POM/surfactant molar ratio $\sim 1:2$) at 75 °C for 4 h. The solid acid was gradually dissolved by simultaneous evolution of gas according to the reaction: $H_3POM + xS^+Cl^- \rightarrow H_{3-x}S_xPOM + xHCl$, where S^+ stands for the PEG containing ammonium cation. The resulting material was extracted, thoroughly washed with water and toluene, and dried at 75 °C. The final product is a viscous, optically transparent liquid (yield 40%). An aqueous solution of the liquid POM salt has a pH ~ 2 , suggesting the presence of residual protons after exchange.

The XRD patterns of the parent heteropolyacid and liquid derivative salt shown in Figure 1, top, reveal their crystalline and amorphous state, respectively. The latter is consistent with the liquid-state nature of the sample. The exchange reaction is confirmed by the presence of the characteristic cation absorption bands due to CH_3 , CH_2 , and $C-O$ vibrations. The neat heteropolyacid shows two absorption bands at 980 and 900 cm^{-1} corresponding to terminal $W=O$ and bridging $W-O-W$ groups, respectively.³ The same bands are also observed in the liquid derivative, confirming the presence of the core clusters in the liquid (Figure 1, bottom).

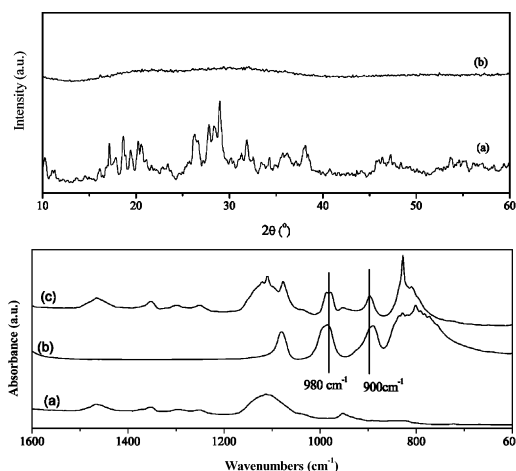


Figure 1. Top: XRD patterns of the parent heteropolyacid (a) and liquid derivative (b). Bottom: FTIR spectra of S^+Cl^- (a), neat heteropolyacid (b), and liquid salt (c).

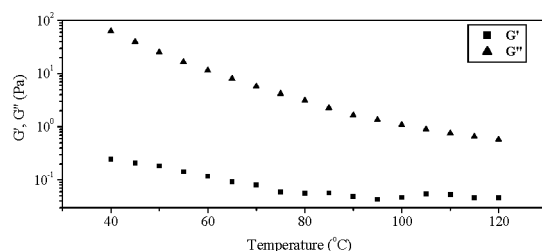


Figure 2. Temperature dependence of G' and G'' of the liquid POM salt.

The TGA trace of the POM liquid salt shows weight losses above 160 and 300 °C, which are attributed to the gradual decomposition of the organic cation (total 39% w/w) (see Supporting Information). The liquid POM contains less than 1 wt % H_2O . The parent solid heteropolyacid shows a loss of ~ 10 wt % at 120 °C, corresponding to the loss of water with no other decomposition up to 500 °C. Assuming a general formula $H_{3-x}S_xPW_{12}O_{40}$ for the liquid derivative, we conclude that $x \approx 2.0$ (i.e., the average number of surfactant cations per cluster is two). Anal. calcd. for $H_1S_2PW_{12}O_{40}$: C, 24.8; H, 4.3. Found: C, 26.8; H, 4.2; Cl, 0.02.

DSC analysis shows a second-order transition at -35 °C (see Supporting Information), most likely corresponding to the glass transition (T_g) and thus explaining its liquid state appearance. The S^+Cl^- surfactant used to modify the parent POM clusters exhibits a second-order transition at -61 °C, followed by a first-order transition at -7 °C. We thus conclude that the transition observed is unique to the POM liquid derivative and not just the surfactant.

The corresponding rheological behavior is shown in Figure 2. A viscous-like, fluid behavior is seen through the measured

[†] Department of Materials Science and Engineering.

[‡] School of Chemical and Biomolecular Engineering.

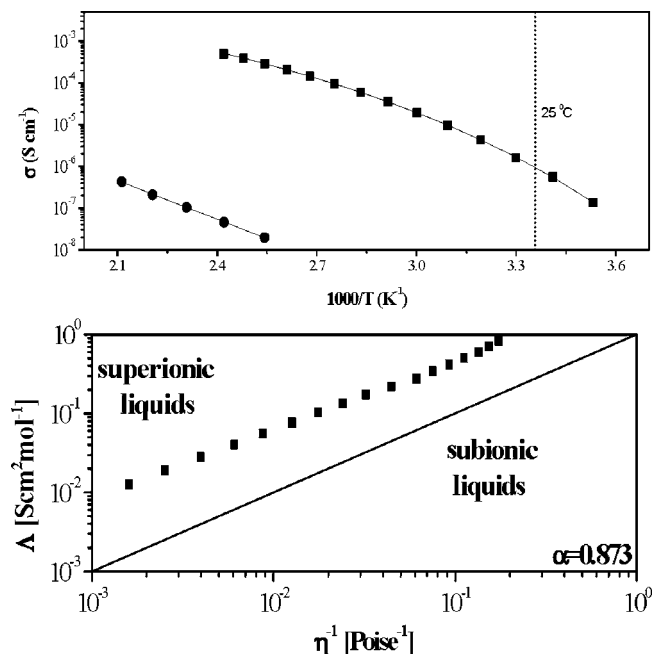


Figure 3. Top: conductivity of the POM liquid salt (■, VTF type) and of a potassium-exchanged POM solid (●, Arrhenius type) as a function of temperature. Bottom: Walden plot of POM liquid salt.

temperature range, suggested by the higher shear-loss modulus G'' compared to the storage modulus G' .¹⁰ Additionally, the fluidity (reciprocal viscosity) dependence on temperature follows a Vogel–Tamman–Fulcher (VTF) behavior. The viscosity at room temperature is 75 Pa s and it drops to 0.5 Pa s at 120 °C (see Supporting Information).

The ionic conductivity measured by impedance spectroscopy¹¹ as a function of temperature is shown in Figure 3. The conductivity follows again VTF behavior throughout the temperature range with a conductivity of 6×10^{-4} S cm⁻¹ at 140 °C. We suspect that the main contribution to the conductivity is the smaller, more mobile protons, compared to the bulky POM clusters and quaternary ammonium counterions. In comparison, a partially exchanged POM solid (e.g., K⁺ derivative) with the same number of protons exhibits much lower conductivity under anhydrous conditions. The temperature dependence of the solid analogue is also Arrhenius-like rather than the VTF behavior observed for the liquid derivative.

One way of assessing the ionicity of ionic liquids is based on the classical Walden rule ($\Lambda\eta = \text{constant}$) that relates the ionic mobility, represented by the equivalent conductivity Λ to the fluidity $\phi = \eta^{-1}$.^{6,12} For ideal ionic solutions (i.e., fully dissociated ions of equal mobility), the ideal behavior lies on the diagonal of Figure 3, bottom. Behavior below the diagonal indicates that there is a high degree of correlation between cations and anions (e.g., ion-pairing) so that the conductivity is less than expected for certain fluidity. In contrast, behavior that lies above the diagonal is characterized as superionic and is associated with conduction mechanisms that are more efficient than the Walden mechanism.

Superionic slip of small ions in some melts and the Grothuss mechanism for certain protonic solutions are examples of such behavior. Recently Angell and co-workers have shown that these arguments can be extended to ionic liquids.^{6,12}

The behavior for the POM liquid derivative falls above the diagonal, suggesting that ion movement is characterized by a mechanism that is more efficient than the Walden ideal behavior.

While we are yet to identify the conduction mechanism, it is clear that the conductivity is higher than that expected from the corresponding fluidity. The slope on the conductivity vs fluidity plot is about 0.9, suggesting that the ion relaxation modes are highly coupled to the matrix modes.

Finally, while the connection between high conductivity and vapor pressure is not obvious, Angell and co-workers have suggested that both depend on the formation of an “ideal” quasi-lattice.¹² The more uncorrelated the motion of the cations and the anions, the higher the conductivity but also the larger the Madelung energy of the liquid and, hence, the larger the energy that is required to remove an ion pair into the vapor phase resulting into a lower vapor pressure. On the basis of Figure 3, bottom, we suggest that the POM liquid derivative exhibits a low vapor pressure, which is beneficial for high-temperature fuel cell and catalytic applications.

In summary, we are reporting a cluster-based ionic liquid by partially replacing the proton ions of a heteropolyacid with a PEG-containing quaternary ammonium cation. The liquid salt exhibits proton conductivity 4 orders of magnitude higher than that of its solid analogue and super-ionic behavior. The liquid-like character and proton transport properties under anhydrous conditions make this new class of materials possible candidates for fuel cell or catalytic applications.

Acknowledgment. We gratefully acknowledge the support by AFOSR and the Cornell Center for Materials Research (CCMR).

Supporting Information Available: Figures showing TGA trace of the liquid POM derivative, DSC traces of the liquid POM derivative and neat surfactant, and temperature dependence of viscosity. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Li, Q. F.; He, R. H.; Jensen, J. O.; Bjerrum, N. J. *Chem. Mater.* **2003**, *15*, 4896.
- (2) Haile, S. M.; Boysen, D. A.; Chisholm, C. R. I.; Merle, R. B. *Nature* **2001**, *410*, 910.
- (3) Kim, Y. S.; Wang, F.; Hickner, M.; Zawodzinski, T. A.; McGrath, J. E. *J. Membr. Sci.* **2003**, *212*, 263.
- (4) Nakamura, O.; Ogino, I.; Kodama, T. *Solid State Ionics* **1981**, *3–4*, 347.
- (5) Appleby, A. J. *J. Power Sources* **1994**, *49*, 15.
- (6) Xu, W.; Angell, C. A. *Science* **2003**, *302*, 422.
- (7) Susan, M. A. B. H.; Noda, A.; Mitsushima, S.; Watanabe, M. *Chem. Commun.* **2003**, 938.
- (8) Katsoulis, D. E. *Chem. Rev.* **1998**, *98*, 359.
- (9) Moser, W. R., Ed. *Advanced Catalysts and Nanostructured Materials: Modern Synthetic Methods*; Academic Press: San Diego, CA, 1996; p 592.
- (10) Zhang, Q.; Archer, L. A. *Langmuir* **2002**, *18*, 10435.
- (11) Macdonald, J. R., Ed. *Impedance Spectroscopy: Emphasizing Solid Materials and Systems*; Wiley: New York, 1987; p 346.
- (12) Xu, W.; Cooper, E. I.; Angell, C. A. *J. Phys. Chem. B* **2003**, *107*, 6170.

JA046821B