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Physical Properties of Pyridinium Fluorohydrogenate, $[\text{pyridine} \cdot H^+][H_2F_3]^-$

Ryan Hulse · Rajiv Singh

Abstract Ionic liquids (ILs), also referred to as molten salts, have found application as electrolytes for batteries and super-capacitors, in electroplating baths, as designer solvents, and as reaction media. A few of the desired properties of a super-capacitor electrolyte are nonflammability, thermal stability, and electrochemical stability. ILs containing aromatic cations have been shown to have low viscosity which results in a high electrochemical conductivity. There is a delicate balance between increasing the thermal stability, or decreasing the melting point, and increasing the electrochemical conductivity of the IL. This study focuses on pyridinium fluorohydrogenate, $[\text{pyridine} \cdot H^+][H_2F_3]^-$. Pyridinium fluorohydrogenate has been synthesized by the reaction of pyridine and anhydrous hydrofluoric acid. This IL has a relatively high electrical conductivity ($\sim$98 $\text{mS} \cdot \text{cm}^{-1}$ at 23 °C), a wide electrochemical window, and a boiling point of 186 °C. A stable gel can also be formed by combining $[\text{pyridine} \cdot H^+][H_2F_3]^-$ and a super absorbent polymer such as polyacrylic acid. The gel adds mechanical stability to the matrix while not greatly affecting the conductivity of the IL.

Keywords Ionic liquids · Super-capacitor · Vapor pressure

1 Introduction

Room-temperature ionic liquids (RTILs) have found use as electrolytes for batteries, super-capacitors, and electroplating baths as well as designer solvents for organic reactions. An electrolyte for a super-capacitor should be low cost while also achieving the other desired characteristics of nonflammability, low volatility, and high chemical and thermal stability. One of the current electrolytes being used is 1.0 M

R. Hulse (✉) · R. Singh
Buffalo Research Laboratory, Honeywell International, Buffalo, NY 14210, USA
e-mail: ryan.hulse@honeywell.com

tetraethylammonium tetrafluoroborate in propylene carbonate which has an electrical conductivity of $\sim 12\,\mathrm{mS \cdot cm^{-1}}$ at room temperature.

2 Experimental

Pyridine (Aldrich, 99.5 % pure) and anhydrous HF (99 % pure) were used. A 120 ml polyethylene bomb was used as the reaction vessel. The inlet to the bomb was a dip leg fitted with a Teflon sparger that was positioned below the liquid level. The outlet from the bomb was passed through a series of two polyethylene Erlenmeyer flasks. The first flask was empty, and the second was filled with a 10 % KOH caustic solution. The exit of the second flask was vented inside a fume hood. Initially, the reaction bomb was filled with up to 30 ml of pyridine and placed in an ice bath. While the pyridine was cooling, the nitrogen was passed through the inlet of the bomb to ensure an inert dry atmosphere. After the pyridine had cooled to 0 °C, the nitrogen purge was shut off and anhydrous HF was introduced through the sparger into the liquid pyridine. Sufficient HF was allowed to flow into the reaction vessel to ensure 3 mol of HF per mol of pyridine was present in the reactor. The unreacted HF was scrubbed out of the exit gas in the caustic solution. After the HF had passed through the reaction vessel, the $[\mathrm{pyridine} \cdot \mathrm{H^+}][\mathrm{H_2F_3}]^-$ complex was purged with dry nitrogen for 12 h to ensure that all the excess HF was removed.

3 Analysis

The structure of the $[\mathrm{pyridine} \cdot \mathrm{H^+}][\mathrm{H_2F_3}]^-$ was confirmed by proton and fluorine NMR. The proton and fluorine NMR spectra are shown in Figs. 1 and 2, respectively. The proton NMR shows the expected pyridine triplet and a single peak that corresponds to the proton that is contained in the $[\mathrm{H_2F_3}]^-$ anion. The fluorine NMR indicates that there is only a single type of fluorine atom which is in agreement with the formation of $[\mathrm{pyridine} \cdot \mathrm{H^+}][\mathrm{H_2F_3}]^-$. These results are consistent with other researchers [1]. Carre [2] has shown the increase in density as HF is added to pyridine. The density reaches a maximum at ∼1 mol pyridine + 3 mol HF. The density at this point is $1.24\,\mathrm{g \cdot cm^{-3}}$ while the densities of pure HF and pure pyridine at 25 °C are $0.94\,\mathrm{g \cdot cm^{-3}}$ and $0.98\,\mathrm{g \cdot cm^{-3}}$, respectively. This significant increase in density indicates the formation of a new compound. This conclusion is reaffirmed when Carre plots the excess volume of the mixture of pyridine and HF (Fig. 3). The plot of the excess volume has a minimum at ∼ 1 mol pyridine + 3 mol HF with nearly ideal mixing between the minimum and each of the pure components. The large change in the excess volume can be explained by the formation of $[\mathrm{pyridine} \cdot \mathrm{H^+}][\mathrm{H_2F_3}]^-$. When excess-volume data are plotted assuming the density of $[\mathrm{pyridine} \cdot \mathrm{H^+}][\mathrm{H_2F_3}]^-$ to be $1.25\,\mathrm{g \cdot cm^{-3}}$, it shows ideal mixing occurs between pyridine and $[\mathrm{pyridine} \cdot \mathrm{H^+}][\mathrm{H_2F_3}]^-$ and a positive excess volume between $[\mathrm{pyridine} \cdot \mathrm{H^+}][\mathrm{H_2F_3}]^-$ and HF.

The electrical conductivity was measured with a Mettler Toledo InLab 730 conductivity meter fitted with an InLab730 electrode. The electrode is constructed of epoxy/graphite to ensure corrosion resistance in the case of any residual HF in the fluid. The conductivity range of the electrode is 0 mS to 1000 mS. The probe was

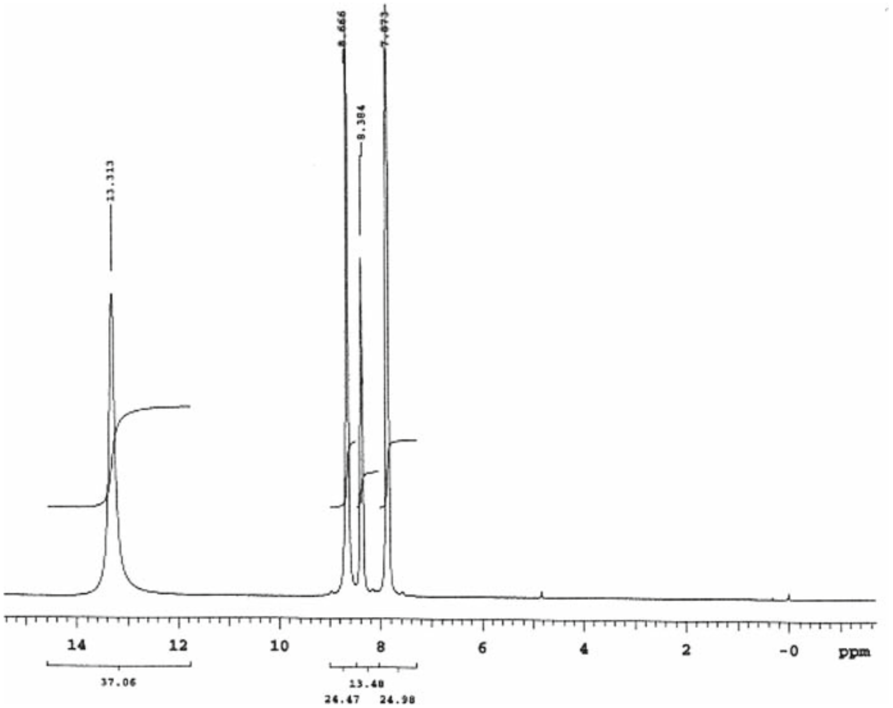

Fig. 1 Proton NMR of [pyridine $\cdot$ H^+][H_2F_3]$^-$

initially calibrated using 9.92 mS $\cdot$ cm^{-1} and 104.9 mS $\cdot$ cm^{-1} traceable conductivity calibration standards.

The electrochemical window was measured by a Princeton Applied Research PARSTAT 2273 poteniostat. The working, counter, and reference electrodes were constructed of glassy carbon, platinum foil, and silver wire, respectively. The scan rate was set at 50 mV $\cdot$ s^{-1}, and a 5.0 Hz filter was applied. The ionic liquid (IL) was continually blanketed under dry nitrogen to avoid any water impurities.

The vapor pressure was measured using a comparative ebulliometer. The setup and operation of the comparative ebulliometer is similar to that used by other researchers [3]. The ebulliometer was constructed of stainless steel and fitted with a sapphire window. A schematic of the comparative ebulliometer is shown in Fig. 4. The temperatures of the cells were measured by a Pt resistance temperature detector (RTD) which has a temperature range of −200 °C to 750 °C. The tip of the RTD was placed directly behind the sapphire window so that the condensate could be seen dripping off of the RTD. To ensure that there was no cross contamination between the reference and sample cells, a series of acetone/dry ice traps were installed in series between the cells. The cells were heated using electrical heating mantels. The condensers were cooled by using ethylene glycol that was maintained at 0 °C to ensure complete condensation. The reference fluid used in the ebulliometer was toluene. The vapor–pressure correlation for toluene was taken from the DIPPR database.

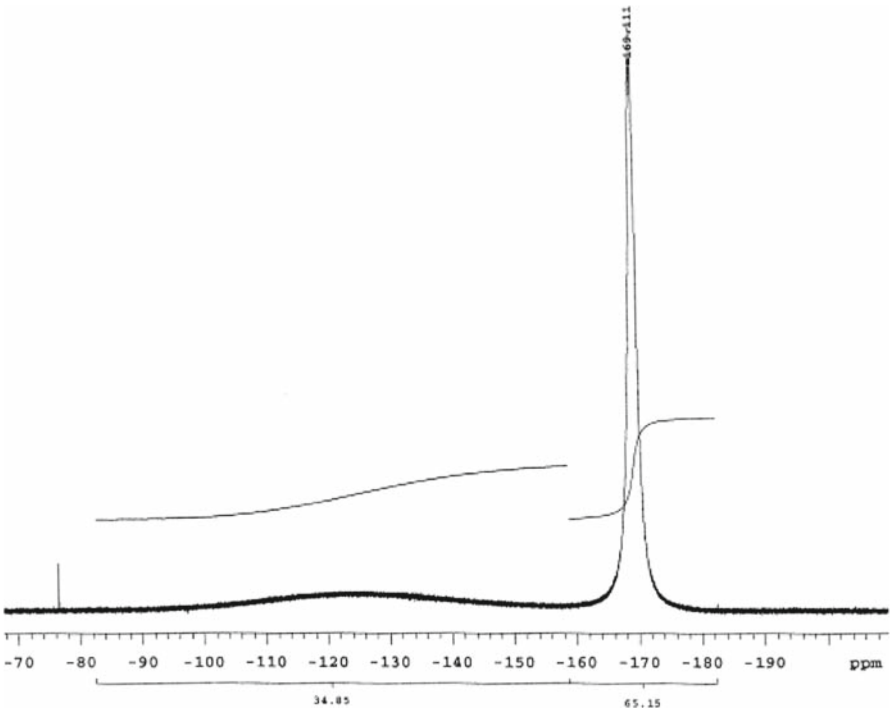

Fig. 2 Fluorine NMR of $[\text{pyridine}\cdot H^{+}][H_2F_3]^{-}$

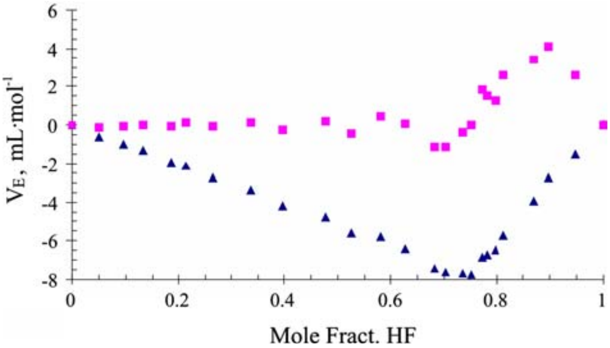

Fig. 3 Excess molar volume (V_E) of a pyridine and HF mixture, (▲) data reported by Carre [2], (■) assuming 1.25 g · ml^{-1} $[\text{pyridine}\cdot H^{+}][H_2F_3]^{-}$ density

4 Results

The electrical conductivity of $[\text{pyridine}\cdot H^{+}][H_2F_3]^{-}$ was measured to be 98 mS · cm^{-1} at 23 °C. This conductivity is nearly an order of magnitude higher than that of typical electrolytes. The $[\text{pyridine}\cdot H^{+}][H_2F_3]^{-}$ was thickened using 15 mass% sodium polyacrylic acid or 20 mass% potassium polyacrylic acid. Conductivities of 78 mS · cm^{-1}

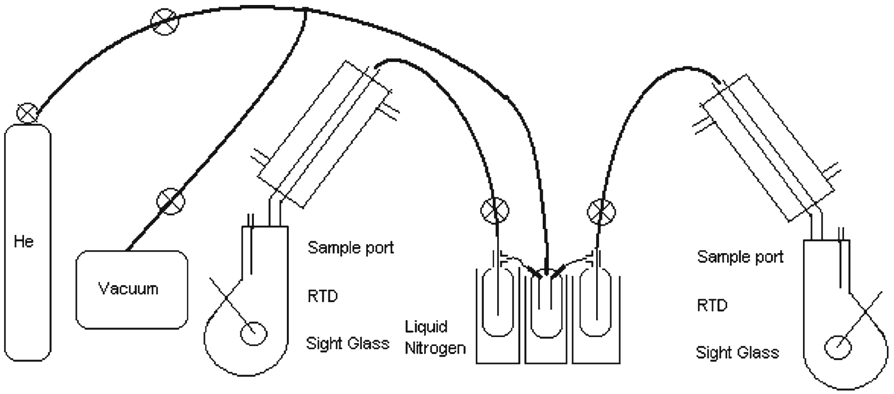

Fig. 4 Schematic of the comparative ebulliometer

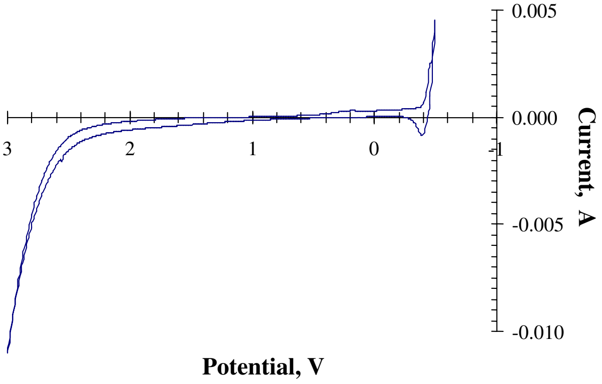

Fig. 5 Current/voltage curve of [pyridine · H^+][H_2F_3]$^-$

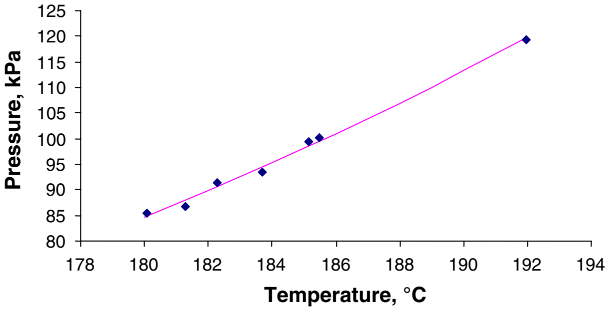

Fig. 6 Vapor pressure of [pyridine · H^+][H_2F_3]$^-$, (▲) experimental data and the line is the fit to the Antoine equations (Eq. 1)

and 74 mS · cm^{-1} were measured for the 15 mass% sodium polyacrylic acid and 20 mass% potassium polyacrylic acid, respectively. Gelling allows for a more mechanically stable electrolyte without significant loss in conductivity.

The cyclic voltammogram of [pyridine · H^+][H_2F_3]$^-$ is shown in Fig. 5. The anodic and cathodic limits are shown to be −2.01 and 0.24, respectively. There is a slight reduction peak centered at 0.42 V. This peak may be due to impurities in the sample.

The vapor-pressure data are shown in Fig. 6. The vapor-pressure data as fit by the Antoine equation can be expressed as follows:

$$\ln(P) = \frac{-6095.35}{T + 273.15} + 17.891 \tag{1}$$

where P is the vapor pressure in kPa and T is the temperature in °C. The normal boiling point of [pyridine · H^+][H_2F_3]$^-$ was determined to be 186 °C. The [pyridine · H^+][H_2F_3]$^-$ was continually blanketed with nitrogen to avoid corrosion of the stainless-steel vessel. There were no observed effects due to hysteresis. Initially as the [pyridine · H^+][H_2F_3]$^-$ began to boil, a white mist formed over the top of the liquid. As the fluid was continued to heat, the white mist dissipated and boiling and condensation could clearly be seen.

It is possible to separate a mixture of [pyridine · H^+][H_2F_3]$^-$ and water by simple distillation. Water is completely soluble in [pyridine · H^+][H_2F_3]$^-$, but due to the significant difference between the boiling point of water and [pyridine · H^+][H_2F_3]$^-$, they can be easily separated. Although the separation is possible, mixtures of [pyridine · H^+][H_2F_3]$^-$ and water are very acidic and highly corrosive.

5 Conclusions

A new IL has been identified that has the desired properties of a super-capacitor electrolyte. It is potentially low cost and nonflammable. The electrical conductivity was measured to be 98 mS · cm^{-1} at 23 °C. The boiling point is 186 °C, and the electrochemical window is 2.2 V indicating that it has both good thermal and electrical stability. This IL can also be gelled to increase the mechanical stability, and therefore, decrease the potential risk of spilling the IL out of the electrical device.

References

1. K. Matsumoto, R. Hagiwara, Y. Ito, Electrochem. Solid-State Lett. **7**, E41 (2004)
2. J. Carre, J. Fluorine Chem. **50**, 1 (1990)
3. L.A. Weber, A.M. Silva, Int. J. Thermophys. **17**, 873 (1996)