# Protic Ionic Liquids Can Be Both Free Proton Conductors and Benign Superacids .

Younes Ansari*#, Kazuhide Ueno*$ and C. Austen Angell*

*Dept. of Chemistry and Biochemistry, Arizona State University,

# Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139 USA

$ Department of Chemistry and Biochemistry, Yokohama National University, Yokohama, Japan

**ABSTRACT**

**Superacids have been the source of much spectacular chemistry, but very little interesting physics despite the fact that the states of cations formed by transfer of the superacid proton to molecular bases, can approach that of the cations in free space. Indeed some of the very strongest acids, such as $HPF_6$ and $HAlCl_4$, have no independent existence due to lack of screening of the bare proton self-energy: their acidities can only be assessed by study of the conjugate bases. Here we show that, by allowing the protons of transient $HAlCl_4$ and $HAlBr_4$ to relocate on pentafluoropyridine, PFP - a very weak base that is stable to superacids - we can create glassforming protic ionic liquids (PILs) which are themselves superacids but, being free of superacid vapors, are of benign character. At $T_g$, conductivities exceed "good" ionic liquid values by 9 decades, so must be superprotonic. Anomalous Walden plots confirm superprotonicity.**

Systems in which the free motion of protons dominates the ionic conductivity, sometimes by many orders of magnitude, have been known for a long time but they are mostly low conductivity materials of little general interest[1]. Even the $CsHSO_4$-type anion rotator phase proton conductors only reach ~$10^{-2}$ $Scm^{-1}$ at 100ºC[2,3]. Amongst high conductivity materials rivaling aqueous solutions[4], ($10^{-1}$ $Scm^{-1}$ at 100ºC), the protic ionic liquids reported to date have all been vehicular conductors according to Walden plot assessments (in which equivalent conductivities are plotted against fluidities)[5,6]. The high conductivity systems ($\sigma > 10^{-1}$ S/cm at 100ºC) in which a significant free proton contribution has been identified, have nearly all involved water molecules in one way or another. The best known is concentrated (~4M) sulfuric acid, in which some 70% of the ionic current is carried by 'free' protons, and even the least hydrated case, phosphoric acid, widely studied for intermediate temperature fuel cells, usually needs 2 wt% water (10 mol%) to function effectively. In the present work, the total absence of water is guaranteed by the presence of a strongly hydrolyzing anion, $AlCl_4^-$.

In this contribution, we will describe how to decouple the protons from the possible vehicles by manipulating the properties of protic ionic liquids, PILs, to prepare superacidic and superionic versions, which might be expected to have their analogs in superprotonic solids. We have reported separately (seeTable1, Ref. k) how the superionic solid conductor $Li_3N$ can serve, at the opposite end of the proton activity spectrum, as a solid superbase and a progenitor of superbasic ionic liquids.

PILs, formed by transfer of protons from Brønsted acids to Brønsted bases, are a subclass of the burgeoning field of room temperature ionic liquids. The subclass has a chemistry that is dominated by the activity of the transferred proton. Although members of this subclass have been reported in the literature since 1876[7], it is only recently that there has been a concentrated attempt to characterize the state of the transferred proton and the driving force for its transfer. Without an adequate proton transfer driving energy (proton energy gap between acid and base components) highly ionic liquids cannot form.

In 2003, it was suggested[8] that, notwithstanding the anhydrous nature of the ionic liquids, the driving energy for proton transfer could be estimated approximately using the difference in $pK_a$ values borrowed from aqueous solution data tables. This has since been supported by a number of studies[9,10] though with some appropriate reservations[10]. Direct electrochemical interrogation of the ionic liquids[11], which may be supported by IR and NMR spectroscopic arguments [12,13], have shown that in many cases the energy levels are, almost quantitatively, those estimated from aqueous data (as indeed would be expected if the free energies of hydration of the cation and anion are about the same). This has permitted the construction of an energy level diagram for the anhydrous systems[14]. A new version of this diagram, updated from those in refs[15-17], is given in Table 1 below. Following Gurney[18], the relationships between different occupied/vacant (acid-base or donor/acceptor,) couples are given in energy units, eV, in addition to the $pK_a$ units common to aqueous acid chemistry.

Lacking any leveling solvent, the proton potential for any given acid-base couple is located midway between those of the parent acid and base levels in the proton energy level

# Table 1. Proton free energy level diagram (Gurney inspired)

| Superacidic Electrolytes and very weak conjugate bases | Occupied proton level | Vacant proton level | pKa (H0) ref. $H_3O^+/H_2O$ | ε/eV vs $H_3O^+/H_2O$ | Refs |
|---|---|---|---|---|---|
| tetrachloroaluminic acid *(UnSt) | $(HAlCl_4)$ | $AlCl_4^-$ | -24.5 (NMR), -25 | 1.5 | a, b |
| hexafluoroantimonic | $HSbF_6$ | $SbF_6^-$ | -21.6 (H0), -23.6 NMR | 1.3, 1.4 | c,a |
| bis-Ntriflic acid, HTFSI/NTf2- | $(CF_3SO_3)_2NH$ | $(CF_3SO_3)_2N$ | -18 (H0), -19 NMR | | d,a |
| perchloric acid/perchlorate | $HClO_4$ | $ClO_4^-$ | -16 (H0), -16.1(NMR) | | e,c,a |
| triflic acid, HOTf/triflate | $CF_3SO_3H$ | $CF_3SO_3^-$ | -14.6 (H0), 14.6 (NMR)- | 0.86 | c, a, f |
| **Acid electrolytes** | **and** | **Weak bases** | | | |
| protonated hexabromobenzene | $HC_6Br_6^+$ | $C_6Br_6$ | ? | | g |
| pentafluoropyridinium/PFP-ine | $C_5F_5NH^+$ | $C_5F_5N$ | -13 | 0.77 | h |
| protonated triphenyl phosphate | $TPPOH^+$ | $TPPO$ | ? | | i |
| **Sulfuric acid** | **$H_2SO_4$** | **$HSO_4^-$** | **-10, -12, 11-14** | 0.59, **.71**, .8 | j, c, k |
| hydrogen chloride/chloride | $HCl$ | $Cl^-$ | -7 | 0.41 | f |
| tricyanomethane | $HC(CN)_3$ | $C(CN)_3^-$ | -5.1(est.) | 0.3 | l |
| methanesulfonic acid/mesylate | $CH_3SO_3H$ | $CH_3SO_3^-$ | -2, -2.6, -1.3 | 0.12, .15 | j,f,l |
| nitric acid/nitrate | $HNO_3$ | $NO_3^-$ | -0.43 | 0.025 | f |
| 2-fluoropyridinium/2-FPy-ine | $C_5H_4FNH^+$ | $C_5H_4FN$ | -0.25 | 0.015 | a |
| trifluoroacetic acid/acetate | $CF_3COOH$ | $CF_3COO^-$ | -0.25 | 0.015 | f |
| **Neutral Electrolytes:** | (change of sign at | reference level | $H_3O^+/H_2O$) | | |
| **Hydronium/Water** | **$H_3O^+$** | **$H_2O$** | **0** | **0** | |
| diphenylammonium/ine | $Ph_2NH_2^+$ | $Ph_2NH$ | 0.79 | -0.047 | |
| phosphoric acid/diHphosphate | $H_3PO_4$ | $H_2PO_4^-$ | 2.12 | -0.13 | m(Gurney) |
| hydrogen sulfate/sulfate | $HSO_4^-$ | $SO_4^{2-}$ | 1.92 | -0.11 | " |
| hydrofluoric acid/fluoride | $HF$ | $F^-$ | 3.2 | -0.19 | " |
| formic acid/format | $HCOOH$ | $HCOO^-$ | 3.75 | -0.22 | " |
| phenylamine (as base) | $C_6H_5NH_3^+$ | $C_6H_5NH_2$ | 4.6 | -0.27 | |
| acetic acid | $CH_3COOH$ | $CH_3COO^-$ | 4.75 | -0.28 | " |
| imidazolium/imidazole | $C_3N_2H_5^+$ | $C_3N_2H_4$ | 6.3,6.9 | -0.37 | |
| **hydrogen sulfide** | **$H_2S$** | **$HS^-$** | **7** | **-0.41** | |
| Bis- (trimethylsilyl)-ammonium | $((CH_3)_3Si)_2NH_2^+$ | $((CH_3)_3Si)_2NH$ | 7.5 | -0.44 | " |
| hydrazinium/hydrazine | $N_2H_5^+$ | $N_2H_4$ | 7.96 | -0.47 | |
| ammonium/ammonia | $NH_4^+$ | $NH_3$ | 9.23 | -0.55 | |
| ethylammonium/ethylamine | $C_2H_5NH_3^+$ | $C_2H_5NH_2$ | 10.63 | -0.63 | " |
| triethylamine, TEA | $(CH_3CH_2)_3NH^+$ | $(CH_3CH_2)_3N$ | 10.65 | -0.63 | |
| dicyanomethane (as acid) | $H_2C(CN)_2$ | $HC(CN)_2^-$ | 11.0 | -0.65 | |
| methylpyrrolidinium/ine | $(CH_2)_4CH_3NH_2^+$ | $(CH_2)_4CH_3NH$ | 11.7 | -0.65 | |
| **bisulfide/sulfide** | **$HS^-$** | **$S^{2-}$** | **12.4** | -0.69 | |
| guanidinium/guanidine | $(NH_2)_3C^+$ | $(NH_2)_2C=NH$ | 13.6 | -0.61 | |
| water/hydroxide | $H_2O$ | $OH-$ | 14 | -0.83 | |

In the Occupied/Vacant columns: $\Delta pK_a = 12$ (upper box), $\Delta pK_a = 11.1$ (lower box).

**References:**  a) see Hasani et al. refs. 28,29 (b) see ref. 35 (c) see Olah G. et al. ref. 25  (d) Thomazeau et al. J. Am. Chem. Soc 2003, 125, 5264 (e) Hammett and Deyrup, J. Amer. Chem. Soc., 54, 2721 (1932) (f) Ripin and Evans (Harvard 206) (g) D.K. Angell unpublished work (h) calculated using Advanced Chemical Software V. 11, 021944 (2011) ACDL Labs (i) M.R. Angell (unpublished work) (j) https://owl.oit.umass.edu/departments/OrganicChemistry/app... (k) C. A. Angell, (thermo. calcs. see *preprint arXiv:2001.01151*  (l) cyanoform: Wikipedia (m) Gurney, R.W. see ref. (18)

**Table 1.** Proton free energy level diagram for acids and their conjugate bases, referenced to the $H_3O^+/H_2O$ couple, and based on data measured or calculated for proton transfers in aqua. The difference between these values and those expected in the anhydrous PIL formed by transfer between pure acid and pure base, is discussed elsewhere[14,15], and is not expected, or often found[11,19], to be large.

========================================================================

diagram, as directly demonstrated by Kanzaki and co-workers[19,20] and confirmed in ref. [11]. The long arrow in Table 1 represents the proton transfer involved in forming the classic PIL ethylammonium nitrate EAN, which will accordingly have the intermediate proton potential 0.30 eV (pK$_a$ value 5.1).

The proton of any given proton transfer salt will relocate onto any stronger base that is introduced into the system. In this respect, protic ionic liquids have acidities akin to those of aqueous systems, although they do not contain any hydronium ions in terms of which the pH acidity is conventionally defined. A similar situation holds for solutions of acids in non-aqueous solutions such as those in the weak base DMSO discussed by many authors[21,22]. The present cases are distinguished by the absence of any solvent at all within which to establish a solution standard state.

In the present study we have sought conditions in which the above proton potential is raised into the superacid range *while maintaining high ionic liquid conductivity*. The latter requires that the energy gap across which the proton falls in forming the ionic liquid be at least 0.7 eV[8,14]. Having experienced the stability of the resonance-stabilized pyridine ring as a Bronsted base[23] we turned attention to the weak base limit of such systems represented by the pentafluoropyridine (PFP) molecule.

If we choose, as weak base to be protonated, the pentafluoropyridine molecule, pK$_a$ = -13 (by theoretical calculation[24]), as our base, then Table 1 shows that there are few choices available for the acid. To obtain an energy gap large enough to guarantee high ionicity, the acid must have strength comparable to, and preferably higher than, that of HSbF$_6$ (pK$_a \approx$ -21.6[25]).

Remembering the manner in which Brown and Pearsall[26] created, in 1951, a "brilliant green" protic ionic liquid at -80ºC, by using a transient HAlCl$_4$ [27] to protonate toluene, we adopted transient HAlCl$_4$ as the protonating agent - see the short red arrow in Table 1. Following Brown and Pearsall, dry HCl was bubbled through a stirred suspension of anhydrous AlCl$_3$ in PFP. Because our base, while very weak, is stronger than toluene we are able to carry out the protonation at ambient temperature, (after an initial heating to 50ºC to initiate the stirring action).

Bubbling HCl for 3 hours at ambient temperature dissolves all the AlCl$_3$, producing a mobile light brown ionic liquid that is found, by weight change measurement, to be only 90% AlCl$_4^-$, a result entirely consistent with the findings of Brown and Pearsall[26] in terms of increasing HCl pressure as the initially formed Al$_2$Cl$_7^-$ is converted to AlCl$_4^-$. Lowering the temperature of hydrochlorination to 0ºC by use of an ice bath, results in an increased HCl absorption to reach 94.9% AlCl$_4$-, but the stoichiometric absorption is only obtained when the system is changed to one in which the PFP is protonated by the stronger acid combination of HBr bubbling through a PFP +AlBr$_3$ suspension. This constitutes a confirmation of the often-controversial attribution of exceptional Lewis acidity for the aluminum halides and for AlBr$_3$ in particular. Indeed, a recent set of electronic structure calculations showed how the O-H$^+$ distance in a protonated basicity test molecule, 1,3-dimethyl-2-imidazolidinone (DMI), cation *in free*

*space* was only 0.035Å shorter than in the minimum energy structure when the cation was charge-compensated by the $AlBr_4^-$ anion[28].

All of these liquids are stable against crystallization at standard cooling rates, and exhibit glass transitions in the range -60 to -66°C, as shown in Figure 1. The $T_g$s are all higher than the typical $T_g$ values for proton transfer salts, cf. the classic case of ethylammonium nitrate, $T_g$ = -91.5°C [14]. The difference is consistent with the surprisingly high viscosity for the new salts which we characterize below.
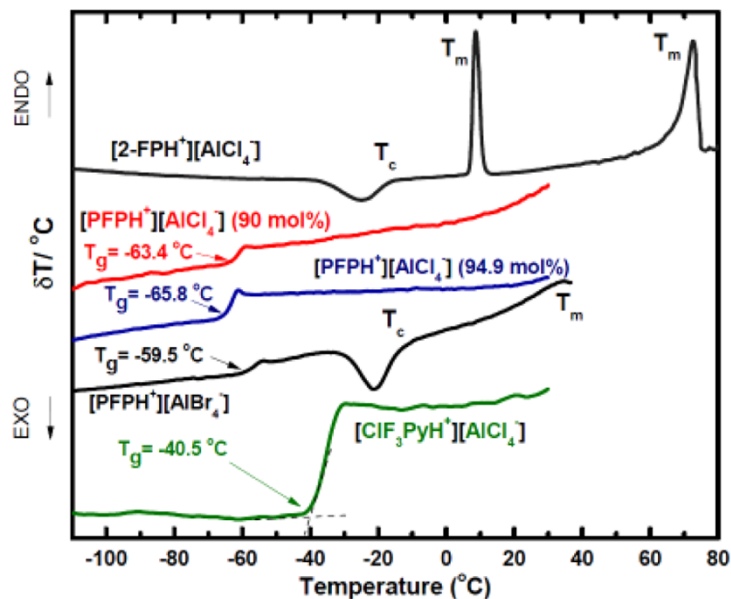


**Figure 1.** DSC upscans at $10Ks^{-1}$ for different proton transfer salts obtained by protonation of different weak bases by reaction with $HCl/AlCl_3$ and $HBr/AlBr_3$ at ambient pressure. PFP is pentafluoropyridine which is only completely protonated at ambient temperature by $HBr/AlBr_3$. The mixed anion cases, $AlCl_4^- + Al_2Cl_7^-$, are strong glassformers and show no crystallization during heating runs. They are further characterized below.

The Figure 1 endotherms for the stoichiometric $[PFPH^+][AlBr_4^-]$ case, and the more easily protonated, hence stoichiometric, case of the less-fluorinated pyridine base, $[2\text{-}FPy^+][AlCl_4^-]$, both reveal crystallization during reheating. Because of concern for the DSC instrument, no attempt was made to find the melting point of the former. The latter shows a strong solid-solid transition near 0°C presumably due to anion rotation, and a melting endotherm at around 70°C.

$[2\text{-}FPy^+][AlCl_4^-]$ was recently characterized as part of both $^1$H-N [28] and $^{15}$N NMR [29] spectroscopy studies of the protonating power of different Brønsted acids, and it was found that $AlCl_4^-$ is indeed a weaker base than $SbF_6^-$ (and $AsF_6^-$) as recognized in Table 1 above. According to Table 1, the midpoint $pK_a$ for the proton transfer salt $[PFPH^+][AlCl_4^-]$ should be -18.75, about the same as $HNTf_2$, so this protic ionic liquid should be a superacid. However, in contrast to $HNTf_2$ and other molecular superacids, it should *not* have a highly corrosive vapor. There are two separate reasons for this. Firstly, proton transfer ionic liquids of highly ionic character are like aprotic ionic liquids in having low vapor pressures[8]. Secondly, because $HAlCl_4$ is unstable[27], any acid vapors over $[PFPH^+][AlCl_4^-]$ superacid should consist only of HCl with a $pK_a$ of -7, and

in the case of the brominated analog, even the HBr pressure should be low. Therefore, to the extent that it remains liquid at ambient temperature, $[PFPH^+][AlCl_4^-]$, and especially its brominated analog, should serve as benign liquid superacids, e.g. they would not fume on exposure to the atmosphere, and would not threaten the internal surfaces of dry-boxes, and instruments therein, as observed with poorly stoppered triflic acid bottles, for instance.

We now turn to the original motivation for this work, namely, the search for free proton mobility. The new ionic liquids are indeed highly conductive and have some unusual conductivity characteristics that we will describe below: they imply highly decoupled proton motion.

In Figure 2, we present the specific conductivities, determined using a cell with variable cell constants (0.587, 0.906 and 1.690). We compare the data with those of the classical PIL, ethylammonium nitrate, EAN, and also a related ionic liquid of the stronger base, 2-fluoropyridinium tetrachloroaluminate, $[2\text{-}FPH^+][AlCl_4^-]$ that we have prepared in the same way as $[PFPH^+][AlCl_4^-]$. In this second case, the proton energy level for the couple $[2\text{-}FPH^+]/2\text{-}$ FP is much lower onTable 1 - only 0.1 eV above the $[H_3O^+]/[H_2O]$ reference level. We find that, in the initial stage of the synthesis, in which anhydrous $AlCl_3$ is mixed with the 2-FP, a liquid adduct is formed exothermically, so that the subsequently bubbled HCl is reacting with a liquid rather than with a solid as in the previous case. During the HCl bubbling, the reaction mixture adds a mass that corresponds quantitatively (within 1 %) with the formation of the $AlCl_4^-$ anion. This PIL is a solid at 25°C, with melting point near 55°C, as indicated in Fig. 2.
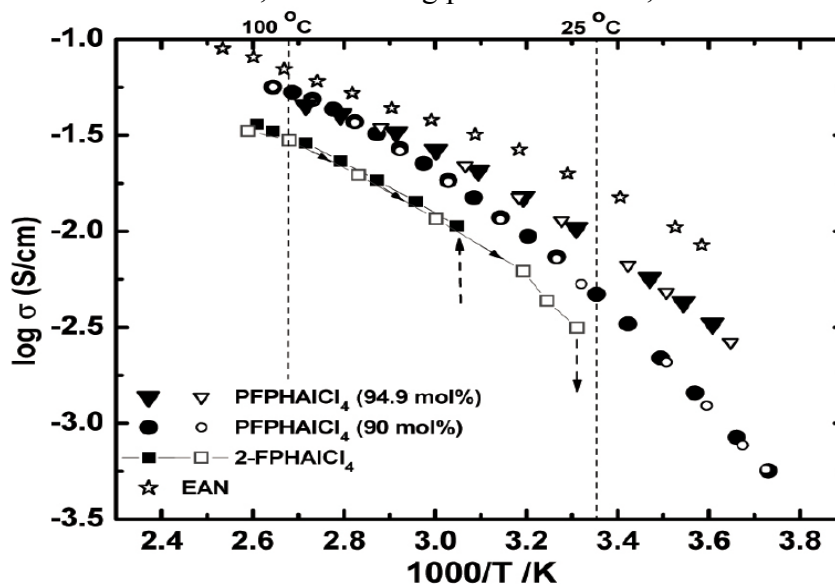


**Figure 2.** Ionic conductivity of the PILS of this work (*solid symbols for measurements made during slow heating and open symbols of same shape for measurements made during slow cooling*). Comparison is made with the much-studied case of the classical protic IL ethylammonium nitrate, EAN, which has a notably smaller temperature dependence of conductivity, doubtless a reflection of its lower $T_g$. The data for the superacidic PILs are clearly non-Arrhenius and a natural extrapolation to lower temperatures indicates a value of ~$10^{-6}$ Scm$^{-1}$ at the $T_g$ of -65.8°C for the 94.9 % $AlCl_4^-$ case. This implies a ~9 orders of magnitude decoupling of conductivity from viscosity relaxation times (see text and Eqs. (1-3)). The fully protonated 2-fluoropyridiniumAlCl$_4$ liquid has a higher melting point (up arrow) and a lower conductivity. Unlike the others, it also crystallizes before reaching ambient temperature (down arrow).

===================================================================

Figure 2 shows that the conductivity of the $[2\text{-FPH}^+][\text{AlCl}_4^-]$ liquid, which has a mean $pK_a$ value in the acidic but not superacidic domain, is also high at 100°C. However, it is not as high as those of the PFP-based liquids *despite the fact that the liquid viscosity is clearly lower at this temperature (see Figure 3)*. We will quantify this interesting difference below, after noting some special aspects of the superacidic liquid conductivities.

Firstly, the high conductivity confirms, via implied high ionicity, that the proton potential energy level of the donor (transient $\text{HAlCl}_4$) must lie at least 10 $pK_a$ units, or 0.59 eV, above that of the $pK_a = -13$ acceptor level of $[\text{PFPH}^+/\text{PFP}])$ (see Table 1), consistent with the $^1\text{H}$ and $^{15}\text{N}$ NMR assessments of refs[28][29] for $\text{HAlCl}_4$. This means the PIL produced by the proton transfer would have the mean potential $pK_a = -18$ or higher, thus confirming its superacidic character. Secondly, Figure 2 shows that the conductivities of the new $[\text{PFPH}^+][\text{AlCl}_4^-]$ PILs are lower than that of the familiar ethylammonium nitrate EAN, but also that their temperature dependences are higher. This itself could just reflect the difference in glass temperatures $T_g$ already noted in discussion of Figure 1. But it is the conductivity *relative to* the viscosity that is of greatest interest. This relation is most clearly expressed by comparing the ion conductive with the viscous (or structural) properties, directly in units of time. It is most simply done at $T_g$ where the structural relaxation time is known from many sources to be essentially the same as the enthalpy relaxation time, at the value 100s for DSC scan rates of 20Ks$^{-1}$ or 200s for scan rates of 10Ks$^{-1}$. Then the "decoupling ratio" [30] (or "decoupling index" [31]) at the glass transition temperature, which we designate $R^*_\tau$, is given by

$$R^*_\tau = \ <\tau_{\text{H})}>(T_g)/<\tau_\sigma>(T_g) \ = \ 2 \times 10^2/<\tau_\sigma>(T_g) \qquad (1)$$

and it is then just a matter of using equation (2) [30,31]

$$<\tau_\sigma> = e_0\varepsilon_\infty/\sigma_{dc} \qquad . \qquad\qquad\qquad (2)$$

to convert the measured conductivity to an average conductivity relaxation time. (Eq.(2) is the ionic conductivity analog of Maxwell's famous relation between high frequency shear modulus and viscosity, $\eta = G_\infty\tau$ [32].

Substitution in Eq.(2) of the value for $e_0$, the permittivity of free space (8.85 x 10$^{-14}$ Farad cm$^{-1}$) and a typical value of 10 ±5 for $\varepsilon_\infty$, then yields $<\tau_\sigma> \approx 9\pm5 \times 10^{-13}/ \sigma_{dc}$. So the decoupling index at $T_g$ is given by

$R^*_\tau = 2 \pm1 \times 10^{-14} \ \sigma_{dc(Tg)}$
or, in orders of magnitude,
$\log R^*_\tau = 14.3 + \log\sigma_{dc(Tg)}$ \qquad\qquad\qquad\qquad (3)

This relation tells us that when the conductivity is fully coupled to the structure ($R^*_\tau = 1$), the specific conductivity at $T_g$ should be 10$^{-14.3}$ Scm$^{-1}$, close to that reported for *a*protic ionic liquids (APLs), and very far below the 10$^{-6}$ Scm$^{-1}$ indicated by the data for our superacidic cases at their $T_g$, (see Figure 1) - as stated earlier. The conductivities of the superacidics of Figure 2 actually closely parallel those of the superionic $\text{LiAlCl}_4\text{-LiAlI}_4$ eutectic, which has a *measured* conductivity of 10$^{-5}$ Scm$^{-1}$ at its $T_g \approx -51°\text{C}^{33}$. Thus at $T_g$ the protons in our superacidic glass are, like the lithium ions in the above inorganic eutectic, decoupled from the viscosity by almost 9 orders of magnitude !.

Above $T_g$ the increasingly chaotic thermal motions in the expanding liquid structure cause the structural and conductivity times to rapidly approach one another, and the structural relaxation time becomes more difficult to determine because of the difficulty of measuring $G_\infty$ in the Maxwell relation[32], $\eta = G_\infty\tau$. Thus at higher temperatures it is more common and fruitful to compare the two properties using a Walden plot[34] in which the behavior is observed relative to that of an ideal coupled system (1M aqueous KCl). Except for aqueous strong acids and phosphoric acid, superionic (or superprotonic) behavior is rarely seen at high conductivities. Inorganic silver ion-containing liquid salts and, to a lesser extent, lithium ion conducting liquids[4] and some ionic liquids with protonated anions[35,36] may be exceptional (see Supporting Information, SI).

Viscosities were measured using a small volume Ubbelohde glass tube viscometer mounted in a rectangular aluminum temperature control (and temperature smoothing) block, with a viewing slit to observe when the flowing liquid meniscus passes the fiducial mark. Measurements with this device are less precise than those for conductivity, but are sufficient for our purpose. Data are shown in Figure 3. As expected from the differences in $T_g$, the viscosities of the new PILs are higher than those of the classical PIL, EAN, ($T_g = -91.5°C$ [14]. Also, the viscosity of the sample with the lower % conversion to $AlCl_4^-$, (i.e. that with the larger mole fraction of the larger $Al_2Cl_7^-$ anion), is the largest.
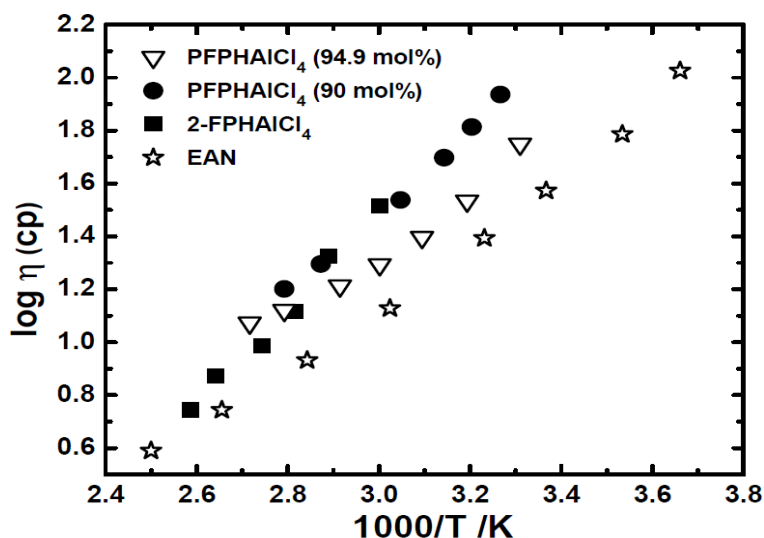


**Figure 3.** Arrhenius plots of viscosity data for two different levels of hydrochlorination of $AlCl_3$, (100% corresponding to complete conversion of $AlCl_3$ to $AlCl_4^-$.). Comparison is made with the 100% $[AlCl_4^-]$ salt of the stronger base $[2\text{-}FPH^+][AlCl_4^-]$, and with the classical PIL EAN (ethyl ammonium nitrate) from previous studies. Note the intermediate position of the PIL made from the intermediate base, monofluorinated pyridine, 2-FP.

======================================================================

The Walden plot comparison is that of equivalent conductivity with inverse viscosity (i.e. fluidity) over a common range of temperatures. This is shown in Figure 4, where it is seen that each of the PFP-based samples lie *above* the ideal line - and well separated from the classic EAN case. Furthermore, the excess conductivity is *increasing* at higher temperature, rather than decreasing as in all the less acidic protic ionic liquid cases studied to date. The excess of conductivity, over that expected from viscosity in the classical EAN case at the same fluidity,

$10^{-1}$ poise, is almost half an order of magnitude, implying that well over half the current is carried by some non-vehicular mechanism. While this is far from the "proton sea" number one might have hoped to see from such a high proton activity ionic liquid, it is still a provocative number, and stands as an encouragement to seek other cases where the proton binding can be even weaker, or the temperature range can be extended further without loss of acid component.

The fact that the less-fluorinated but fully protonated case based on 2-fluoropyridine (2-FP) lies intermediate between the EAN and superacid cases in Figure 4 suggests that improvements might be possible. Full hydrochlorination may, however, not be desirable. Indeed $Al_2Cl_7^-$ is expected to be a weaker base than $AlCl_4^-$ just as $H_2S_2O_7$ is a stronger acid than $H_2SO_4$. Thus even weaker bases than PFP should be stably protonated at ambient temperature, as indicated in Table 1(see also SI).
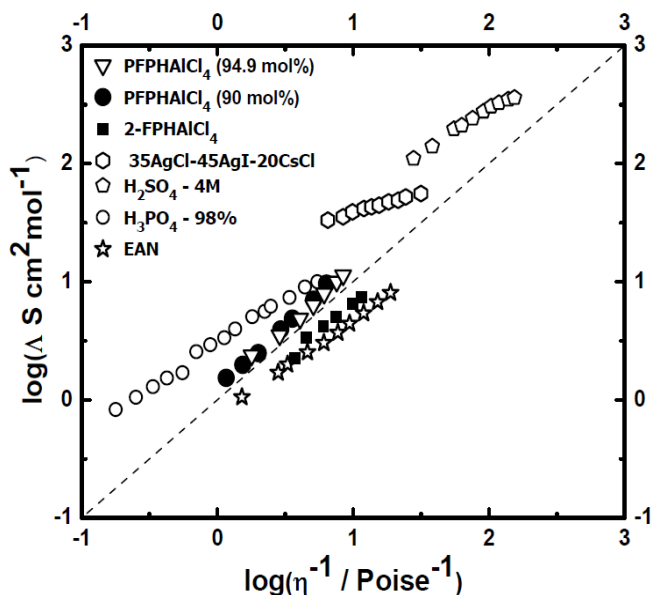


**Figure 4.** Walden plot for assessment of excess (superionic or super-protonic) contributions to the conductivity of ionic systems (calibrated by 1M KCl(aq) at 25°C) . Comparison of data for systems of the present study (filled symbols and empty triangles) is made with superprotonic systems 4M sulfuric and 98% phosphoric acids, a superionic silver halide-alkali halide glassformer, and with ethylammonium nitrate EAN. Note the intermediate position of the PIL made from the intermediate base monofluorinated pyridine.

================================================================

In this respect we await with interest, measurements of the ionic conductivity and conductivity/viscosity relations for the liquid of composition $[C(CH_3)_3^+]$ $[AlBr_4^-]$ reported recently by Krossing and coworkers[37], and its $Al_2Br_7^-$ relative. We note that neither $AlBr_4^-$ nor $Al_2Br_7^-$ nor their (slightly stronger base) chloride equivalents, are mentioned in earlier reviews of weakly coordinating anions[38,39] although popular but somewhat stronger bases such $PF_6^-$ and $SbF_6^-$, and even OTf$^-$, are recognized. Very large weakly coordinating anions described in the latter references resemble the 24 fluoride-containing anion of the salt $LiB[OC(CF_3)_2]_4$ (LiBPFPB

of ref.[40]), the molar volume of which is nearly 0.4 l !). This bis-pinacolatoborate salt is low melting (120ºC) but also of very low conductivity unless dissolved in low viscosity solvents like acetonitrile[40]. The 1M solution conductivities, though high, are not as high as for more moderate-sized anions like lithium bis-oxalatoborate (LiBOB). The properties of the monoprotic acid of the BPFPB anion are not known but the smaller acid  HBOB is not a very strong acid by the metric of $^1$H-N chemical shift[10] of the proton transfer ionic liquid diethylmethylammonium BOB.

There are some other relevant observations. Where Brown and Pearsall's toluenium pentachlorodialuminate decomposed by HCl loss at ambient temperature, toluenium pentabromodialuminate, has been obtained as a dark green ambient-temperature-stable liquid in our experiments[41] (See also SI). Since that time, bromoaluminate ionic liquid physical properties have been studied in detail by Hog et al. as aprotic ionic liquids with conventional cations like imidazolium, tetralkyl ammonium and phosphonium[42]. $C_6Br_6$ has been protonated by transient $HAlBr_4$ in our laboratory, but it crystallized before its conductivity could be measured (D. K. Angell unpublished work), and the very weakly basic oxygen of triphenyl phosphate has been protonated by both transient $HAl_2Cl_7$ and $HAl_2Br_7$ to give an ionic liquid of surprisingly high ionic conductivity considering the size of the cation (M. R. Angell (unpublished work). There are evidently many possibilities, including protonated fluoroethers, still to be explored. If nothing else, the $AlBr_4^-/Al_2Br_7^-$ ratio achieved during a HBr/AlBr$_3$ protonation at 1atm pressure of HBr, should provide, via the distinct $^{27}Al$ NMR resonances, a useful laboratory route to ordering and finally quantifying the basicities of very weak proton acceptors (like PFP and toluene) for general purposes.  It might be particularly useful for the creation of a library of benign superacidic PILs, of tunable low vapor pressures, for chemical synthesis applications.

## Concluding remarks

Although Figure 4 shows what we had hoped to find - namely, that as the shielding of the proton by its environment becomes weaker, its mobility increasingly exceeds those of the entities to which it is normally bound - there are questions to resolve. In superionicity, (the behavior normally associated only with very small ions like Li$^+$ in solvent-free media, or small highly polarizable ions like Ag$^+$, e.g. the silver halide cesium halide melts[43] seen in  Figure 4), the decoupling is usually manifested by a Figure 4 slope much less than unity (fractional Walden rule). To a lesser extent, this is also true of the phosphoric and sulfuric acids (Figure 4) in which the excess conductivity is usually referred to as due to a Grotthus[44]) mobility mechanism.  By contrast, the decoupling in the present case seems to be *increasing* with increasing temperature, perhaps because the protons are becoming increasingly plasma-like at the higher temperatures. Unfortunately, higher temperature studies would require high pressure equipment to repress the loss of HCl or HBr, an effort that goes beyond the scope of this study. Such work, and more detailed studies at lower temperatures and in different systems, will be needed to clarify the various questions raised in the present study. Meanwhile, it is notable that, in a detailed study of phosphoric acid and its solutions in water over wide temperature ranges including T$_g$, the conductivity at T$_g$ only exceeded the ideal Walden rule value (Eq. (3) and following) by 4 orders of magnitude[45]. This is much less than the 9 orders or higher observed for the lithium and silver salt cases, and for the superacidic PILs of this study as discussed earlier. Finally, we note that although the logR*$_\tau$ value can reach values as high as 13 for exceptional cases of high T$_g$  glasses [31,46,] there has been no special mechanism assigned to the phenomenon beyond the "rattle and

drift" observed in computer simulation studies. If such $\log R^*_\tau$ values could be induced for our superacidic ionic liquids, we could have ambient temperature proton conductivities in the "weak metal" domain.

## References

(1)     Angell, C. A.; Bressel, R. D.; Gammel, P. M. Protonic semiconducting glasses from aqueous solutions. *J. Non-Cryst. Solids* **1972**, *7*, 295.

(2)     Haile, S. M.; Boysen, D. A.; Chisholm, C. R. I.; Merle, R. B. Solid acids as fuel cell electrolytes. *Nature*, *410*, 910.

(3)     Boysen, D. A.; Uda, T.; Chisholm, C. R. I.; Haile, S. M. High-performance solid acid fuel cells through humidity stabilization. *Science* **2003**, *303*, 68.

(4)     Xu, W.; Angell, Solvent-free electrolytes with aqueous solution - like conductivities. C. A. *Science* **2003**, *302*, 422.

(5)     MacFarlane, D. R.; Forsyth, M.; Izgorodina, E. I.; Abbott, A. P.; Fraser, K. *Phys.* On the concept of ionicity in ionic liquids.*Chem. Chem. Phys.* **2009**, *11*, 4962.

(6)     Angell, C. A.; W. Xu; Belieres, J.-P.; Yoshizawa, M. **2004,** *U.S. Patent 7,867,650, WO2004114445A1***.**

(7)     Ramsay, W. On picoline and its derivatives. *Phil. Mag.* **1876**, *2*, 269.

(8)     Yoshizawa, M.; Xu, W.; Angell, C. A. Ionic liquids by proton transfer: vapor pressure, conductivity, and the relevance of $\Delta pK_a$ from aqueous solutions. *J. Amer. Chem. Soc.* **2003**, *125*, 15411.

(9)     Miran, M. S.; Kinoshita, H.; Yasuda, T.; Susan, M. A. B.; Watanabe, M. Physicochemical properties determined by $\Delta pKa$ for protic ionic liquids based on an organic super-strong base with various Brønsted acids. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5178.

(10)     Davidowski, S. K.; Thompson, F.; Huang, W.; Amin, S. A.; Angell, C. A.; Yarger, J. L. NMR Characterization of ionicity and transport properties for a series of diethymethylamine based protic ionic liquids. *J. Phys. Chem B* **2016**, *120*, 4279.

(11)     Bautista-Martinez, J. A.; Tang, L.; Belieres, J.-P.; Angell, C. A.; Friesen, C. Hydrogen redox in protic ionic liquids and a direct measurement of proton thermodynamics. *J. Phys. Chem.* **2009**, *113*, 12586.

(12)     Stoyanov, E. S.; Kim, K.-C.; Reed, C. A. An NH Infrared vibration frequency scale for weakly basic anions. Implications for single-molecule acidity and superacidity.*J. Amer. Chem. Soc.* **2006**, *128*, 8500.

(13)     Belieres, J.-P.; Byrne, N.; Angell, Characterization of strong and super acids, using protic ionic liquids made with tertiary amine bases: The N-H chemical shift. C. A. *Abstracts of papers of the ACS (I&EC)* **2008**, *236* Meeting Abstract: 82.

(14)     Belieres, J.-P.; Angell, C. A. Protic ionic liquids: Preparation, characterization , and the proton transfer energy level diagram. *J. Phys. Chem.B* **2007**, *111*, 4926.

(15)     Angell, C. A.; Byrne, N.; Belieres, J.-P. Parallel developments in inorganic, aprotic, and protic ionic liquids: physical chemistry and applications. *Accounts of Chemical Research* **2007**, *40*, 1228.

(16)     Angell, C. A.; Xu, W.; Yoshizawa, M.; Belieres, J.-P.; Hayashi, A.; Lucas, P.; Videa, M.; Zhao, Z.-F.; Gervasio, D. Physical chemistry of ionic liquids, inorganic and organic, protic and aprotic. *Electrochemical aspects of ionic liquids, Ed. H. Ohno, Wiley Pub. Chapter 2,* **2011**.

(17)     Angell, C. A.; Ansari, Y.; Zhao, Z.-F. Ionic Liquids: Past, present and future. *Faraday Discussion* **2012**, *154*, 9.

(18)     Gurney, R. W. *Ionic Processes in Solution*; Dovers Publications: New York, **1962**.

(19)     Kanzaki, R.; Song, X.; Umebayashi, Y.; Ishiguro, S.-I. Thermodynamic study of the solvation states of acid and base in a protici onic liquid, ethylammonium nitrate, and its aqueous mixtures. *Chemistry Letters* **2010**, *39*, 578.

(20)     Kanzaki; Uchida, K.; Hara, S.; Umebayashi, Y.; Ishiguro, S.; Nomura; S., Acid-Base property of ethylammonium nitrate ionic liquid directly obtained using ion-selective field effect transistor electrode. *Chem. Lett.* **2007**, *36*, 684.

(21)     Bordwell, F. G. Equilibrium acidities in dimethyl sulfoxide solution. *Accounts of Chemical Research* **1988**, *21*, 456

(22)     Whitesides, G. M.; Biebuyck, H. A.; Folkers, J. P.; Prime, K. L. Acid-base interaction in wetting. *J. Adhesion Sci. Technol.* **1991**, *5*, 57.

(23)     Shuppert, J. W.; Angell, C. A. *J. Phys. Chem.* Proton NMR studies of the Lewis acid-base reactions between pyridinium chlorides and the acids $ZnCl_2$ and $AlCl_3$.J. Phys. Chem. **1980**, *84*, 538.

(24)     ACDL-Labs *Advanced Chemical Software* **2011**, *11*, 021944.

(25)     Olah, G. A.; Prakash, G. K. S.; Molnar, A.; Somner, J. *Superacid Chemistry 2nd ed. Hoboken, NJ, Wiley and sons* **2009**.

(26)     Brown, H. C.; Pearsall, H. W. The action of the catalyst couple aluminum chloride-hydrogen chloride on toluene at low temperatures ; the nature of Friedel-Crafts complexes. *J. Amer. Chem. Soc.* **1952**, *74*, 191.

(27)     Brown, H. C.; Pearsall, H. W. The catalytic halides. I. A study of thecatalyst couple, aluminum chloride-hydrogen chloride, and the question of the existence of $HAlCl_4$. *J. Am. Chem. Soc.* **1951**, *73*, **5347**.

(28)     Hasani, M.; Yarger, J. L.; Angell, C. A. *Chem. Euro.  J* **2016**, *22*, 13312.

(29)     Hasani, M.; Amin, S. A.; Yarger, J. L.; Davidowski, S.; Angell, C. A. On the use of a protic ionic liquid with a novel cation to study anion basicity.  *J. Phys Chem B* **2019**, *123*, 1815.

(30)     Macedo, P. B.; Moynihan, C. T.; Bose R., The role of ionic diffusion in polarization in vitreous ionic conductors. *Phys. Chem. Glasses* **1972**, *13*, 171.

(31)     Angell, C. A. Mobile ions in amorphous solids. *Annu. Rev. Phys. Chem.* **1992**, *43*, 693.

(32)     Maxwell, J. C. On the dynamical theory of gases. *Phil. Trans. Roy. Soc. Lon.* **1867**, *157*, 49.

(33)     Angell, C. A.; Xu, W.; Yoshizawa, M.; Hayashi, A.; Belieres, J.-P.; Lucas, P.; Videa, M. *Chemistry of  Ionic Liquids, ed H. Ohno. Wiley Interscience, Chap. 2,* **2005**.

(34)     Xu, W.; Cooper, E. I.; Angell, C. A. Ionic liquids: ion mobilities, glass temperatures, and fragilities *J. Phys. Chem. B* **2003**, *107*, 6170.

(35)     Jankowski, P.; Matuszek, K.; Treskow, M.; Armand, M.; MacFarlane, D. R.; Johansson, P.  Anion amphiproticionic liquids as protic electrolyte matrices allowing sodium metal plating. *Chem. Commun.* **2020**, *55*, 12523.

(36)     Mizuno, F.; Belieres, J.-P.; Kuwata, N.; Pradel, A.; Ribes, M.; Angell, C. A. Highly decoupled ionic and protonic solid electrolyte systems in relation to other relaxing systems and their energy landscapes. *J. Non-Cryst. Solids* **2006**, *352*, 5147.

(37)     Scholz, F.; Himmel, D.; Scherer, H.; Krossing, I. Superacidity or not? Synthesis, characterisation, and acidity of the room temperature ionic liquid *Chem.  Eur.* **2013**, *19*, 109.

(38)     Strauss , S. H. *Chem. Revs.* The search for larger and more weakly coordinating anions. **1993**, *93*, 927.

(39)     Krossing, I.; Raabe, I. Noncoordinating anions - fact or fiction? A survey of likely candidates. *Angew. Chem. Int. Ed.* **2004**, *43*, 2066.

(40)     Xu, W.; Angell, C. A. A Fusible orthoborate lithium salt with high conductivity in solutions.  *Electrochem. and Solid State Letters* **2000**, *3*, 366.

(41)     Ansari, Y. Novel anhydrous superprotonic ionic liquids, and membranes for application in mid-temperature fuel cells. *Ph. D Thesis, Arizona State University, Chapter 6, p92* **2013**, 92.

(42)     Hog, M.; Schneider, M.; Krossing, I. Synthesis and characterization of bromoaluminate ionic liquids. *Chemistry -A European Journal* **2017**, *23*, 9821.

(43)     Liu, C.; Sundar, H. G. K.; Angell, C. A. Silver alkali halide glasses and a vitreous analog of the RbAg4I5 superionic conductor.  *Mat Res. Bull* **1985**, *20*, 525.

(44)     Grotthus, C., J. T. Sur la décomposition de l'eau et des corps qu'elle tient en dissolution à l'aide de l'électricité galvanique. *Ann. Chim.* **1806**, *58*, 54.

(45)     Wang, Y.; Lane, N. A.; Sun, C.-N.; Fan, F.; Zawodzinski, T. A.; Sokolov, A. P. Ionic conductivity and glass transition of phosphoric acids. *J. Phys. Chem. B* **2013**, *117*, 8003–8009

(46).   Angell, C. A.; Ngai K. L.; McKenna, G. B; McMillan, P. F.; Martin, S. W, Relaxation in glassforming liquids and amorphous solids. *J. Appl. Phys.* **88**, 3113 (2000).