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Observation of Highly Decoupled Conductivity in Protic Ionic Conductors

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Ionic liquids (ILs) are key materials for the development of a wide range of emerging technologies. Protic ionic liquids, an important class of ILs, have long been envisioned as promising anhydrous electrolytes for fuel cells. It is well known that in comparison to all other cations, proton exhibits abnormally high conductivity in water. Such superprotonic dynamics was expected in protic ionic conductors as well. However, many years of extensive studies led to the disappointing conclusion that this is not the case and most protic ionic liquids display subionic behavior. Therefore, the relatively low conductivity seems to be the main obstacle for the application of protic ionic liquids in fuel cells. Using dielectric spectroscopy, herein we report the observation of highly decoupled conductivity in newly synthesized protic ionic conductor. We show that its proton transport is strongly decoupled from the structural relaxation, in terms of both temperature dependence and characteristic rates. This finding offers a fresh look on the charge transport mechanism in PILs and also provides new ideas for design of anhydrous materials with exceptionally high proton conductivity.

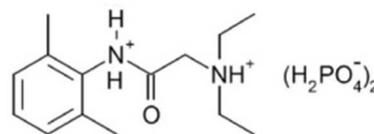
Introduction

Ionic liquids have been the focus of intensive scientific investigations for many years, due to their promising applications in batteries, supercapacitors, biology, and pharmacology among others.^{1,2,3,4} Ionic liquids can be classified as protic, aprotic, and zwitterionic, based on their chemical composition. Protic ionic liquids (PILs) are typically formed by proton transfer from Brønsted acids to Brønsted bases. Because of their low vapor pressure, high thermal stability, high open circuit voltage and efficiency at low current density, protic ionic liquids have been widely viewed as promising anhydrous electrolytes in fuel cells.^{5,6,7,8,9,10} However, the relatively low proton conductivity of PILs still remains the bottleneck for their application.

From a fundamental point of view, two types of charge transport mechanisms, vehicle and Grotthuss mechanism,^{11,12} have been recognized for proton conductors. In the vehicle mechanism, the proton migration is achieved through the translational diffusion of charged large molecular units (vehicles) which carry the protons. In the Grotthuss mechanism, protons hop within the hydrogen bonding network connecting one molecule (vehicle) to another. It is generally accepted that the Grotthuss mechanism is responsible for the abnormally high proton mobility in water as well as phosphoric acid.¹³ It is also speculated that the presence of Grotthuss-type mechanism might decouple proton transport from the motion of bulkier carrier molecules and give rise to superprotonic behavior.

Thus, it is expected that by choosing the right chemical structure for Brønsted acid-base pair, one can create a hydrogen bonding network for fast proton transport in anhydrous environment. Therefore, the possibility of synthesizing superprotonic ionic liquids remains an open question.

Herein we report the discovery of highly decoupled conductivity in newly synthesized protic ionic conductor lidocaine di-(dihydrogen phosphate) (Scheme 1).



Scheme 1. Chemical structure of lidocaine di-(dihydrogen phosphate).

Our results demonstrate that the ionic diffusion in this material has significantly weaker temperature dependence than its structural relaxation and is unusually high in the vicinity of the glass transition. This behaviour is in sharp contrast to aprotic ionic liquids and the earlier studied PILs with phosphate anion like e.g. carvedilol dihydrogen phosphate.^{14,15} Our Walden plot analysis reveals that this PIL should be classified as superprotonic conductor. Surprisingly, the observed degree of decoupling in the examined material and the

conductivity level around the glass transition are even stronger than that in phosphoric acid, which is believed to have a highly efficient Grotthuss mechanism.¹⁶ That is why in this paper the ionic transport properties of phosphoric acid (H_3PO_4 , 85%) and carvedilol dihydrogen phosphate are also reported as a reference.

Experimental

Sample characterization.

The investigated material lidocaine di-(dihydrogen phosphate) was obtained by modified reaction crystallization method reported by Koehler and Hefferen.¹⁷ The lidocaine base was dissolved in room temperature in anhydrous diethyl ether. White crystalline powder of lidocaine di- (dihydrogen phosphate) was precipitated by adding excess of H_3PO_4 (85%). The obtained powder was washed with diethyl ether and dried under dry nitrogen flow at room temperature to constant mass. Stoichiometry of the salt was confirmed using HPLC. Amorphous anhydrous form of examined samples was obtained by quench cooling of the melt. The values of T_m and T_g for studied material, determined by means of DSC technique, are equal to: $454 \pm 1\text{K}$ and $305 \pm 1\text{K}$, respectively.

Dielectric measurements.

The dielectric spectra of lidocaine di-(dihydrogen phosphate) were measured using a Novocontrol Alpha Analyzer. The measurement was conducted in stainless steel electrodes (diameter 20 mm) of the capacitor with a 0.1 mm Teflon spacer.

Rheological measurements.

Rheological measurements of lidocaine di-(dihydrogen phosphate) were carried out on an AR2000ex rheometer (TA Instruments). 20mm glass-covered parallel plates were used in order to avoid corrosion by the presence of high concentration of protons. The temperature was controlled using an environmental test chamber with nitrogen as the gas source.

Results and discussion

The dielectric relaxation spectra of lidocaine di-(dihydrogen phosphate), carvedilol dihydrogen phosphate and phosphoric acid (H_3PO_4 , 85%) are shown in Figure 1 using the electrical modulus representation traditional for ionic conductors. The prominent peak in the loss modulus (M'') is due to the conductivity relaxation of ions. Because of the high ion concentration, the primary structural relaxation within the lidocaine and carvedilol cations is completely masked by conductivity. Two important quantities can be determined from the M'' spectra: the dc conductivity (σ) can be calculated from M'' in the low-frequency region: $\sigma \approx 2\pi f \epsilon_0 / M''$; and the conductivity relaxation time can be estimated from the frequency corresponding to the M'' maximum: $\tau_\sigma = 1/(2\pi f_{\max})$.

The conductivity relaxation peak moves towards lower frequencies with the decrease of temperature (Figure 1). The curves measured below the glass transition temperature, T_g (determined by differential scanning calorimetry (DSC)), are shown in color. It can be seen that below T_g the shift of the conductivity peak with temperature is markedly reduced, i.e., the ionic transport becomes less sensitive to the change of temperature. The Arrhenius plot of temperature dependence of the conductivity relaxation time in each

sample has a clear kink at T_g (Figure 2). $\tau_\sigma(T)$ above T_g can be described by the Vogel-Fulcher-Tammann (VFT) equation, whereas the behavior below T_g is Arrhenius. Such a super-Arrhenius-to-Arrhenius transition of temperature dependence at T_g is commonly observed in ionic conductors.^{18,19}

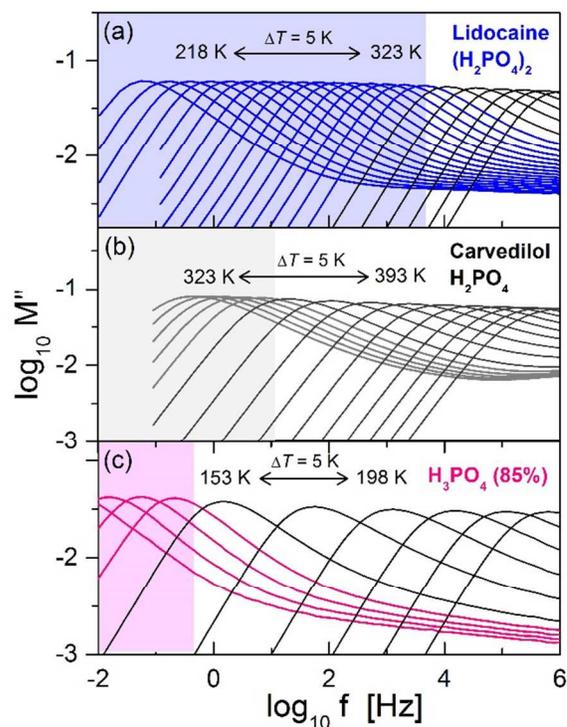


Figure 1. Electrical loss modulus M'' as a function of frequency for the three protic liquids: (a) H_3PO_4 , (b) carvedilol dihydrogen phosphate, and (c) lidocaine di-(dihydrogen phosphate). The spectra measured below T_g are presented in colour. The dielectric data for carvedilol dihydrogen phosphate and phosphoric acid were taken from ref [14] and [19], respectively.

To explore the relation of ionic transport to structural relaxation in lidocaine di-(dihydrogen phosphate), its structural relaxation times τ_α , determined from both rheology and temperature-modulated differential scanning calorimetry (TMDSC), are also shown in Figure 2. Here, the rheological τ_α is evaluated from the Maxwell relation $\tau_\alpha = \eta/G$, by using the measured viscosity and τ_α from TMDSC. The shear modulus G is used as a fit parameter to match the mechanical and calorimetric relaxation times. As can be easily seen, the structural relaxation time of lidocaine di-(dihydrogen phosphate) exhibits stronger temperature dependence than does the conductivity relaxation time. Most importantly, the conductivity relaxation of this system is orders of magnitude faster than its structural relaxation. At T_g , where $\tau_\alpha \sim 1000$ s, τ_σ is equal to $7.9 \cdot 10^{-5}$ s, and it is much shorter than that observed for both carvedilol dihydrogen phosphate ($2.4 \cdot 10^{-2}$ s), and H_3PO_4 (85%) ($3.3 \cdot 10^{-1}$ s). It means that the proton diffusion continues below T_g , but the cessation of rotational motion of the lidocaine molecule inhibits the migration, increasing τ_σ and reducing its sensitivity to T . Such decoupling of proton translation and host molecule reorientation has been reported before for procainamide hydrochloride, lidocaine HCl and lidocaine

succinate^{20,21,22,23,24} but the degree of decoupling was much smaller in that cases.

The decoupling behavior is also reflected in the conductivity at T_g (Figure 3). According to the convention, the ionic conductivity in an “ideal” system (where ion diffusion is tightly coupled to structural relaxation) is $\sigma \sim 10^{-15}$ S/cm at T_g .²⁵ The conductivity of the three studied liquids at T_g is significantly higher than this value. In the case of lidocaine di-(dihydrogen phosphate), the difference is ~ 7 orders of magnitude. The decoupling phenomena in PILs stand in sharp contrast with the behavior of aprotic ionic liquids, where the ionic conductivity is found to be closely coupled to structural relaxation.^{26,27} Since the vehicular transport mechanism is available in both aprotic and protic ionic liquids, the strong decoupling behavior in PILs should come from Grotthuss-type mechanism, i.e. the proton hopping within the hydrogen-bonding network. To further demonstrate the existence of Grotthuss mechanism in PILs, we turn to the Walden plot analysis, which was employed in earlier studies of protic ionic liquids.^{28,29}

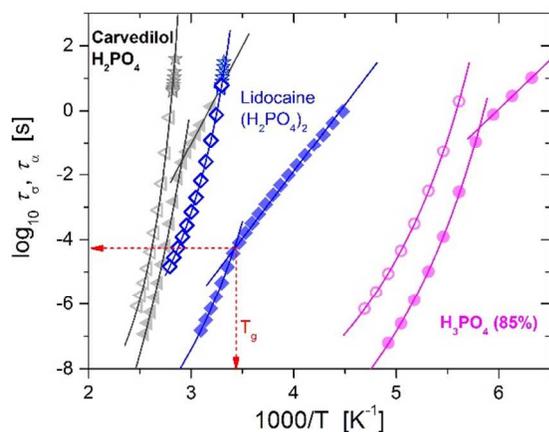


Figure 2 Temperature dependence of structural and conductivity relaxation times for the three protic ionic conductors. Filled symbols: conductivity relaxation time τ_σ from dielectric measurements. Stars: structural relaxation time τ_α from TMDSC measurements. Open symbols: structural relaxation time τ_α from viscosity measurements, calculated according to the Maxwell relation: $\tau_\alpha = \eta/G$. The moduli for carvedilol dihydrogen phosphate, lidocaine di-(dihydrogen phosphate), and H_3PO_4 (85%) are $2.0 \cdot 10^8$, $1.3 \cdot 10^7$, and $5.0 \cdot 10^7$ Pa (average of the other two PILs), respectively. The temperature dependence of conductivity above T_g can be well described by the VFT equation: $\sigma = \sigma_0 \exp[-B/(T-T_0)]$. The conductivity below T_g exhibits Arrhenius temperature, with activation energy of 58.0 ± 1.6 , 115 ± 3 , and 79.4 ± 0.9 kJ/mol for H_3PO_4 (85%), carvedilol dihydrogen phosphate, and lidocaine di-(dihydrogen phosphate), respectively.

This analysis was inspired by the classical Walden rule, which states that the molar conductivity (Λ) of an electrolyte is dictated by its macroscopic viscosity: $\Lambda\eta = \text{constant}$. In a Walden plot, the molar conductivity is presented as a function of fluidity ($1/\eta$) on a double-logarithmic scale (Figure 4). If the ionic transport is completely coupled to the structural relaxation, then the data would appear as a straight line with the slope of one. In order to classify ionic conductors, dilute KCl aqueous solution is typically chosen as a reference to present this ideal case. Because proton conductivity is the primary concern of this study, dilute HCl aqueous solution is

used as the reference. It should be noted that the HCl solution has much higher molar conductivity than KCl, due to the Grotthuss mechanism. Ionic conductors are classified as superionic (superprotic) if they stay above the ideal line. On the other hand, those below the ideal line are called subionic (subprotic) conductors.^{1,6,8}

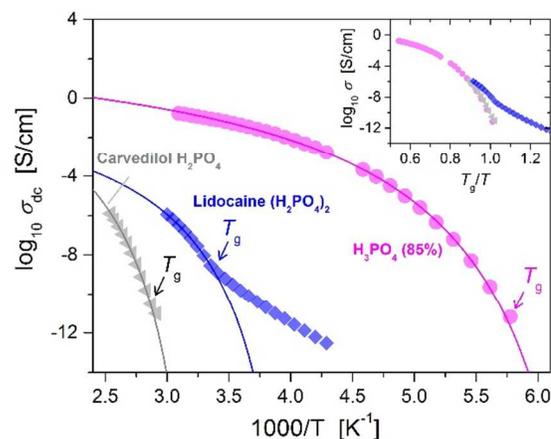


Figure 3 Temperature dependence of ionic conductivity. Solid lines: Fits of conductivity above T_g using the VFT equation $\sigma = \sigma_0 \exp[-B/(T-T_0)]$. Inset: T_g -scaled Arrhenius plot.

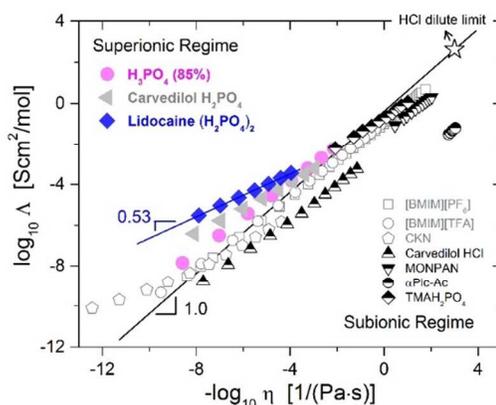


Figure 4 Relation of molar conductivity (Λ) to fluidity ($1/\eta$) for various ionic liquids and melts. [BMIM][PF₆] (1-butyl-3-methyl-imidazolium hexafluorophosphate) and [BMIM][TFA] (1-butyl-3-methyl-imidazolium trifluoroacetate) are aprotic ionic liquids. CKN stands for ionic melt $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$.³⁰ Carvedilol hydrochloride¹⁴, MONPAN (hydroxyethylammonium)³¹, α Pic-Ac (α -picolinium acetate)³² and TMAH₂PO₄ (trimethylammonium dihydrogen phosphate)³³ are protic ionic liquids. The open black star represents the dilute HCl aqueous solution at room temperature. The line with slope of 1.0 is the “ideal” Walden line that divides the plot into superionic (above) and subionic (below) regimes.

Earlier studies, mostly in the high temperature regime, classified PILs as subionic conductors, i.e., they fell below the ideal line.^{1,7,8} It was therefore concluded that the Grotthuss mechanism does not exist in PILs.¹ In contrast, carvedilol dihydrogen phosphate, lidocaine di-(dihydrogen phosphate), and H_3PO_4 (85%) appear in the superionic (superprotic) regime in the entire studied temperature range (Fig.4). The data can be described by a fractional Walden rule: $\Lambda\eta^f$

= constant, with $\alpha < 1$. The case of $\alpha = 1$ would correspond to the classical Walden rule, where ionic transport and structural relaxation are closely coupled. The slope α of carvedilol dihydrogen phosphate and lidocaine di-(dihydrogen phosphate) is 0.62 ± 0.01 and 0.53 ± 0.01 , respectively. This suggests that their ionic transport is strongly decoupled from structural relaxation. Fig.4 includes literature data for several aprotic and protic ionic liquids for a comparison. Aprotic ionic liquids typically exhibit only very weak decoupling between ionic conductivity and structural relaxation.^{26,27,34} Protic ionic liquids hydroxyethylammonium (MOPAN) and α -picolinium acetate (α Pic-Ac) are in the subionic regime.⁸ Similar to carvedilol dihydrogen phosphate and lidocaine di-(dihydrogen phosphate), trimethylammonium dihydrogen phosphate (TMAH_2PO_4)²⁵ also seems to exhibit superprotonic behavior and decoupling of conductivity from structural relaxation. It should be noted, however, that the reported conductivity in TMAH_2PO_4 displays unusual temperature dependence – its super-Arrhenius-to-Arrhenius transition occurs far above T_g . Such a behavior has never been observed in other ionic supercooled liquids. The validity of the TMAH_2PO_4 therefore requires further verification.

It is widely believed that phosphoric acid has an “optimal” structure for proton transport.^{13,19} The frustrated hydrogen-bonding structure of phosphoric acid gives rise to a proton migration mechanism that is very close to the true Grotthuss mechanism.¹¹ As a result, the intrinsic conductivity of phosphoric acid is among the highest of all known substances. In addition, the proton transport in phosphoric acids decouples from the structural relaxation in the vicinity of glass transition.¹⁹ Surprisingly, the degree of decoupling in carvedilol dihydrogen phosphate and lidocaine di-(dihydrogen phosphate) is even higher than in H_3PO_4 (85%): they not only lie above H_3PO_4 (85%) on the Walden plot, showing superprotonic behavior, but also exhibit much smaller slope α . This strongly decoupled superprotonic behavior, combined with the high conductivity at T_g , clearly points to the existence of a highly efficient Grotthuss-type transport mechanism in these PILs. Here, it should be emphasized that while decoupled ionic conductivity has been reported for polymeric proton conductors (especially phosphoric acid based polymers),^{35,36} in the literature one can find only few reports on the Grotthuss-type mechanism in protic ionic liquids. The current study demonstrates that by choosing the right structure for the base, a high degree of decoupling between proton conductivity and structural relaxation can be achieved in protic ionic liquids. Recent studies suggested¹³ that high proton conductivity in phosphoric acid is caused by the frustration in hydrogen-bonding network. Following this suggestion we speculate that addition of carvedilol and lidocaine to phosphoric acid leads to even stronger frustration of the H-bonds and consequently to sharp rise in proton conductivity at the same structural relaxation time (Figure 4). In addition, the size of carvedilol and lidocaine is much larger than the

size of a proton. This asymmetry in the size of relaxing unit may also play an important role in decoupling.

Conclusions

In summary, in contrast to the general behavior of aprotic ionic liquids, strong decoupling of ionic transport from structural relaxation has been found in protic ionic conductors close to their liquid-glass transition. Proton transport progressively switches from the vehicle to hopping mechanism as the temperature is lowered towards T_g . The conductivity relaxation of lidocaine di-(dihydrogen phosphate) at T_g is orders of magnitude faster than its structural relaxation. Walden plot analysis suggests that they should be classified as superprotonic conductors. The observed highly decoupled ionic conductivity suggests that the Grotthuss conduction mechanism, originally proposed for water, also exists in anhydrous protic ionic liquids. While earlier investigations failed to identify such a mechanism, the present study provides the first crucial experimental evidence for the existence of Grotthuss mechanism in PILs. Although important details of the transport mechanism and the reason for unusually high proton conductivity in lidocaine di-(dihydrogen phosphate) remain to be explained, the discovered decoupled conductivity proves the feasibility of design of efficient anhydrous proton conductors for various electrochemical applications.

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Notes and references

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Observation of Highly Decoupled Conductivity in Protic Ionic Conductors

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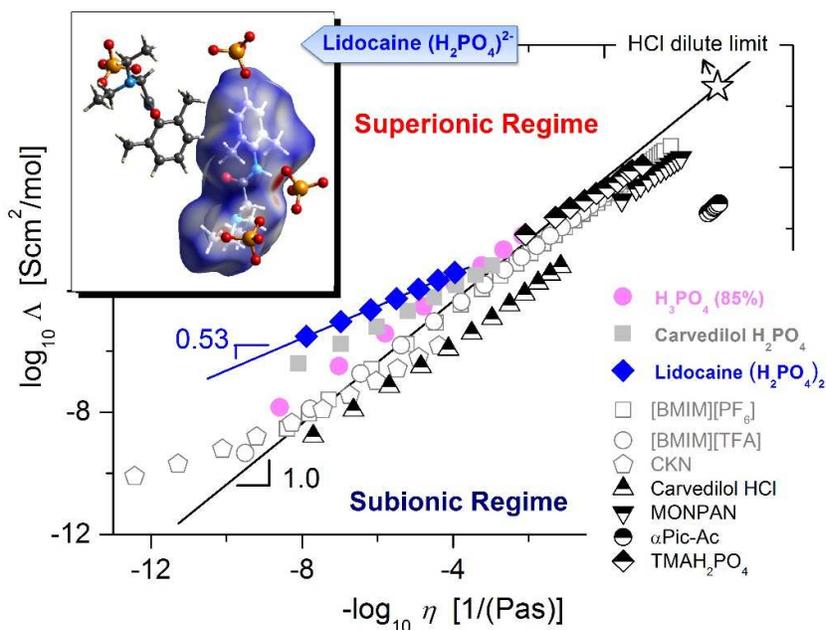
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Using dielectric spectroscopy, we report the observation of highly decoupled conductivity in newly synthesized protic ionic conductor lidocaine di-(dihydrogen phosphate).