Molecular Origin of Enhanced Proton Conductivity in Anhydrous Ionic Systems

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S *Supporting Information*

ABSTRACT: Ionic systems with enhanced proton conductivity are widely viewed as promising electrolytes in fuel cells and batteries. Nevertheless, a major challenge toward their commercial applications is determination of the factors controlling the fast proton hopping in anhydrous conditions. To address this issue, we have studied novel proton-conducting materials formed via a chemical reaction of lidocaine base with a series of acids characterized by a various number of proton-active sites. From ambient and high pressure experimental data, we have found that there are fundamental differences in the conducting properties of the examined salts. On the other hand, DFT calculations revealed that the internal proton hopping within the cation structure strongly affects the pathways of mobility of the charge carrier. These findings offer a fresh look on the Grotthuss-type mechanism in protic ionic glasses as well as provide new ideas for the design of anhydrous materials with exceptionally high proton conductivity.
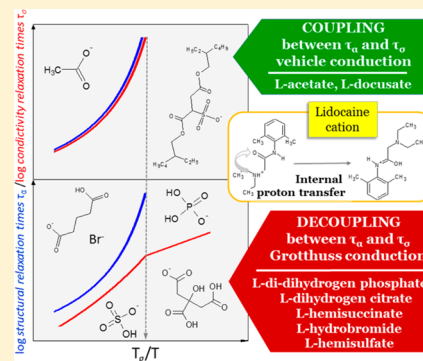
INTRODUCTION

Over the past decades, the understanding of proton transfer phenomenon at the molecular level has become a fundamental problem in many areas of science, from biological systems[1,2] to electrochemical devices.[3,4] Although a large portion of activities in the fields of molecular biology and pharmacology was dedicated to recognizing the biological consequences of intramolecular protonic charge diffusion in drugs and nucleic acids,[5−7] the effect of intermolecular proton transport on the physicochemical properties of ion-containing systems has attracted enormous attention of chemists and material scientists.[8,9] Following the latter research strategy, it has been demonstrated that proton conductors are promising electrolytes in fuel cells and batteries.[10] Unfortunately, most of these systems are water-saturated materials characterized by relatively poor proton conductivity in anhydrous conditions that limits their commercial application. To date, there are only few examples of dry superprotonic glasses and polymers.[11−14]

Therefore, one of the key challenges in advancing the electrochemical technology lies in new protic ionic liquids and solids characterized by long-term thermal stability and high electric conductivity at low relative humidity. To address these issues, there is a need to understand the molecular mechanism of enhanced proton transport in anhydrous ionic systems.

From a fundamental point of view, two types of charge transport mechanisms have been recognized for proton conductors. In the case of so-called vehicular mechanism, the charge transfer is associated with the motions of entire ions. A key feature of the other, frequently referred to as the Grotthuss-type, is the local proton hopping through the H-bond network.[15] As our knowledge has advanced, it has been found that the Grotthuss picture, originally proposed to explain the enhanced proton conductivity in water,[16] might decouple

Table 1. Characteristics of Protic Ionic Conductors Used in This Study

protic ionic salts used	T_g [K]	ΔC_P [J g/K]	T_m [K]	ΔH_m [J/g]	T_c [K]	ΔH_c [J/g]	ΔpK_a	$\sigma_{dc}(T_g)$ [S/cm]
L-HCl	307	0.41	343				13.96	5.02×10^{-14}
L-HBr	309	0.40	343	110.12			16.96	6.18×10^{-14}
L-hemisulfate	305	0.37	491	103.85	376	82.65	16.96	9.88×10^{-14}
L-di(dihydrogen phosphate)	308	0.43	454	96.80			5.99	6.68×10^{-10}
L-acetate	229	0.68	320	115.55			3.17	1×10^{-15}
L-dihydrogen citrate	298	0.56					5.03	1.63×10^{-13}
L-docusate	252	0.35					7.88	1×10^{-15}
L-hemisuccinate	274	0.75	390	123.71			3.72	3.57×10^{-14}

ΔC_P, jump in the heat capacity at T_g determined from TMDSC; T_g, glass transition temperature (from standard DSC, heating rate 10K/min); T_m, melting temperature; ΔH_m, enthalpy of fusion; T_c, temperature of crystallization onset; ΔH_c, enthalpy of crystallization process. All these parameters were determined by means of DSC technique while $\sigma_{dc}(T_g)$ values were measured by means of dielectric spectroscopy. ΔpK_a, defined as pK_a (base) − pK_a(acid), was calculated using ACD/ChemSketch version 12.0. The dielectric and calorimetric data for lidocaine HCl were taken from ref 33.

proton transport from the mass diffusion. It means that the conducting units (protons) become more mobile than the species controlling the structural relaxation. This is in contrast with the vehicle mechanism in which all species move at a similar rate.

It has been demonstrated that the most efficient experimental method to examine the degree of coupling and decoupling of different molecular motions and consequently to identify the conductivity mechanism in ionic and nonionic systems is dielectric spectroscopy.[17−19] In this type of measurements, the specific separation between the time scale of charge and mass diffusion is manifested by a well-defined break of the temperature dependence of dc conductivity (σ_{dc}) or conductivity relaxation times (τ_σ), from the Vogel−Fulcher−Tammann-like ($T > T_g$) to Arrhenius behavior ($T < T_g$), observed at τ_σ much shorter than 10^2 s. Nevertheless, the greatest advantage of this method is an unusual opportunity to investigate the σ_{dc} and τ_σ behavior at elevated pressure, both at isobaric and isothermal conditions. Interestingly, it has been demonstrated that compression markedly enhances the decoupling of charge transfer from the structural relaxation when conductivity of ionic system is governed by fast proton hopping in accordance with the Grotthuss-mechanism.[17,20,21] This finding indicates that, in contrast to ambient conditions, at elevated pressure when the H-bonded network is strongly reinforced the proton transport is much more efficient.

The dielectric experiments performed so far clearly indicate that the Grotthuss-type transport, reflected in the anomalous electrical conductivity behavior $\sigma_{dc}(T,P)$, gives rise to super-protonic properties of phosphoric acid,[22] hydrated acidic polymers,[23] and nonionic azole membranes[24] as well as some anhydrous organic protic salt systems formed via neutralization of a Brønsted acid with a corresponding base.[13,25,26] Surprisingly, in the case of conventional imidazolium-based protic ionic liquids (ILs) the charge transfer is mostly coupled to structural relaxation.[14,27] The reason lies in the complete ionization of these systems combined with a low value of self-dissociation coefficient of the cation with both nitrogen atoms protonated. Therefore, there is a growing interest to design new anhydrous salts with a chemical structure providing exceptionally high proton conductivity.

In this study, we examine the proton transfer mechanism in seven newly synthesized protic ionic salts based on the same cation, lidocaine, and various organic and inorganic anions containing different number of proton-active sites and characterized by different proton donor/acceptor capability. The systems of interest, having various ionization degrees,

enable us to provide a resolution to the long-standing question of factors controlling the enhanced proton conductivity in anhydrous ionic materials. To address this issue, we investigate the interplay between the charge transport and structural dynamics by means of isothermal and isobaric dielectric measurements as well as various calorimetric methods. Additionally, to describe the possible pathways of mobility of the charge carrier the experimental data were accompanied by DFT calculations.

■ MATERIALS AND METHODS

Examined Ionic Conductors. In this paper, we have examined the proton transfer ability of seven newly synthesized lidocaine based systems. A detailed synthesis protocol is described in Supporting Information. Among the studied systems lidocaine docusate and lidocaine hydrogen citrate are liquid at room condition while the other salts take the form of white, crystalline powders with the melting points summarized in Table 1. To investigate the ions transport properties of lidocaine salts the crystalline samples were converted to the amorphous form by means of simple vitrification technique. The water content of the examined ILs was determined by Karl Fischer titration and it was lower than 60 ppm, that is, 0.006 wt %.

Dielectric Measurements. The dielectric spectra of examined samples were measured using a Novocontrol Alpha Analyzer Concept 80. The measurements were conducted in a stainless steel electrodes (diameter = 20 mm) capacitor with a gap of 0.1 mm. The high-pressure experiments were performed in a Unipress system with a custom flat parallel capacitor. A detailed description of the high-pressure equipment can be found in ref.[28].

Calorimetric Measurements. The frequency dependency of the calorimetric glass transition temperature was measured by temperature modulated differential scanning calorimetry (TMDSC) employing a PerkinElmer Pyris Diamond DSC (1.6 × 10^{-3} Hz < f < 0.1 Hz) and a Mettler Toledo Flash DSC 1 (0.3 Hz < f < 50 Hz). A step response multi frequency data analysis was applied.[29] For the highest frequencies (40 Hz < f < 13 kHz) a chip based AC calorimeter was used.[30] All measurements were performed in a dry nitrogen atmosphere and the samples were dried in the instruments prior to the measurements.

Simulation Details. All calculations were performed using the ORCA 3.02 quantum chemistry package.[31] Most of the calculations were done applying density functional theory (DFT) with B3LYP hybrid functional and D3 dispersion
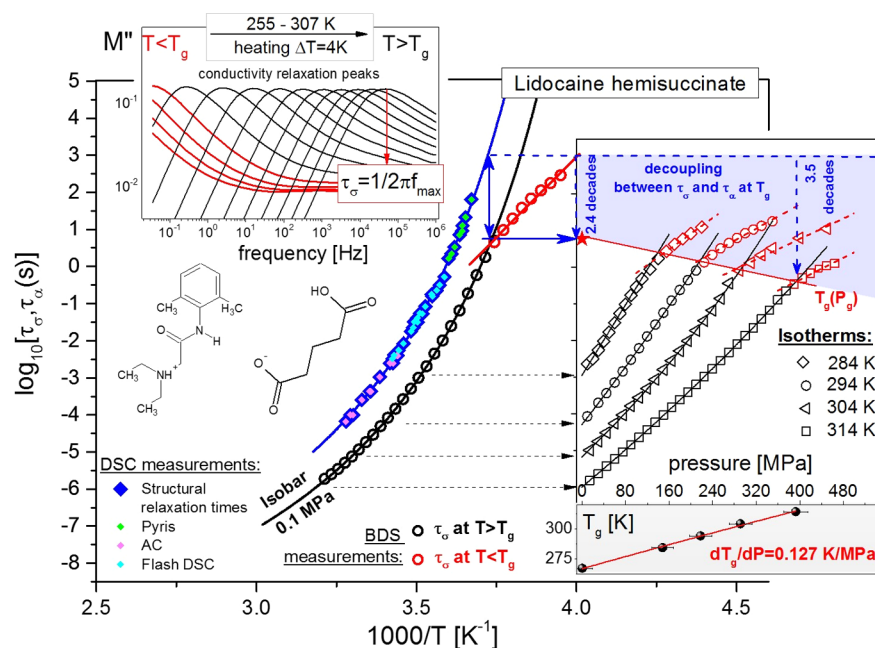
Figure 1. Main panel: the temperature dependence of conductivity relaxation time recorded by means of dielectric spectroscopy at ambient pressure both above (black circles) and below T_g (red circles); the structural relaxation times as a function of $1/T$ (blue diamonds) determined from the various calorimetric techniques. Inset panel (upper): dielectric loss modulus spectra due to conductivity relaxation at various temperatures in the liquid and glassy states for lidocaine hemisuccinate. Inset panel (lower): isothermal dielectric measurements of conductivity relaxation time of lidocaine hemisuccinate; the pressure dependence of T_g for this compound. The temperature dependence of τ_σ above T_g were parametrized by the VFT equation: $\tau_\sigma = \tau_{\sigma 0}\exp[B/(T - T_0)]$, whereas $\tau_\sigma(P)$ curves were described by the pressure counterpart of VFT law $\tau_\sigma = \tau_{\sigma 0}\exp[BP/(P - P_0)]$.[38]

corrections. Initial geometry scans were performed in 6-31G* basis set, whereas stationary point geometry optimizations were performed in 6-311G* basis set. In order to verify correctness of stationary states (minima and saddle point), vibrational analysis was performed. Moreover, to verify the DFT method, which sometimes enhances charge delocalization of the system, RI-MP2 method with the use of cc-pvdz basis set was employed.

RESULTS

General. The examined herein ionic compounds were designed as model systems to understand the molecular mechanism of charge transport in anhydrous protic conductors. As such, a lidocaine base (L), one of the most popular anesthetic agent, has been selected as the major component of the studied series. There are at least two fundamental reasons to justify this selection. Firstly, in X-ray investigations combined with the recent dielectric studies of lidocaine hydrochloride salt,[21] it was argued that lidocaine cations tend to link to each other forming strongly hydrogen bonded chains,[32] an excellent network for fast proton hopping. Secondly, we have found that under appropriate conditions the lidocaine molecule is able to undergo an intramolecular proton transfer reaction and consequently to exist as a mixture of two easily interconvertible constitutional isomers. Thus, one can expect that the unique chemical structure of lidocaine has a potential to favor the proton hopping in ionic systems. To shed more light on this, we have chosen seven different acids to create Brønsted pairs with lidocaine base. Some physicochemical properties of the newly synthesized salts are briefly listed in Table 1.

The initial thermal characterization of the studied systems has shown that these lidocaine salts are good glass formers, that is, they do not have a tendency to form an ordered structure from the amorphous state. The only exception is the

hemisulfate salt with a crystallization onset detected above 376 K. Nevertheless, this ionic conductor appears to be the most promising among the series of lidocaine salts produced. This is due to the sulfonate groups that are frequently regarded as a source of high proton conductivity of polymer electrolyte membranes.[34] Likewise, of a great importance is the dihydrogen phosphate salt due to the highly efficient Grotthuss mechanism confirmed in phosphoric acid.[22] On the other hand, the hemisuccinate, hydrogen citrate, and acetate salts were prepared to further advance our understanding of the relationships between the number of proton-active sites and ion transport properties of anhydrous protic conductors. This is in contrast with hydrobromide and docusate systems that are characterized by the smallest and the largest anion, respectively, among the produced salts.

Dielectric and Calorimetric Data. To examine the charge transport mechanism of lidocaine-based ionic conductors, dielectric measurements over a wide frequency, temperature and pressure range were performed. Following the standard practice, the complex electrical modulus representation $M^*(f) = M'(f) + iM''(f)$ has been adopted to analyze the experimental data.[35−37] Herein, it should be noted that physically the electric modulus corresponds to the relaxation of the electric field in the material when the electric displacement remains constant. Consequently, the M^* formalism represents the real dielectric relaxation process. This representation allows determination of two relevant quantities describing the ion dynamics in conducting materials, that is, the dc conductivity calculated from M'' in the low-frequency region, $\sigma_{dc} \approx 2\pi f \varepsilon_0/M''$, and the conductivity relaxation time estimated from the frequency corresponding to the M'' maximum, $\tau_\sigma = 1/2\pi f_{max}$. The representative modulus loss spectra $M''(f)$ of lidocaine hemisuccinate collected over a wide temperature range at
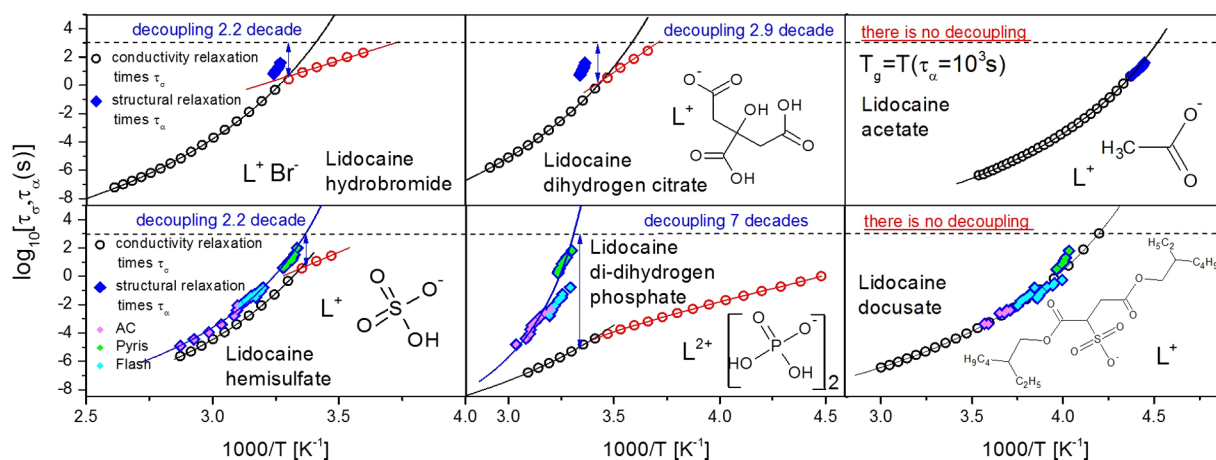
Figure 2. Temperature dependences of conductivity and structural relaxation times for six different lidocaine-based systems.
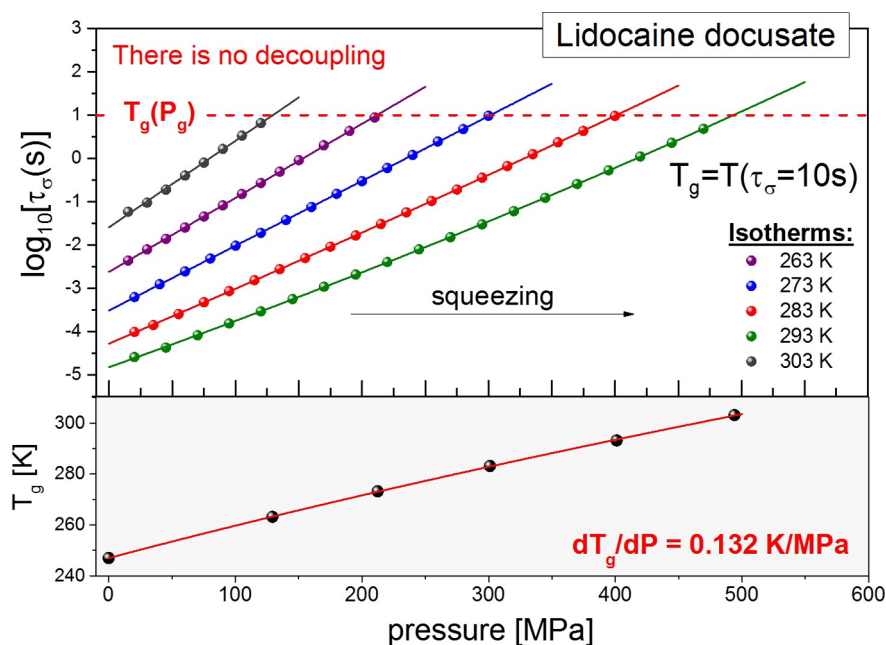

Figure 3. Isothermal dielectric measurements of conductivity relaxation time of lidocaine docusate. Solid lines denote fits of VFTp equation to the experimental data.

ambient pressure conditions are depicted in the upper inset of Figure 1.

As demonstrated, the maximum of the prominent M'' peak, related to the translational mobility of ions, moves toward lower frequencies with cooling. However, below a certain temperature this effect is markedly reduced. Concomitantly, at the same temperature where the spectra are getting closer the $\tau_\sigma(T)$ dependence reveals a well-defined break from the Vogel–Fulcher–Tammann–like to Arrhenius behavior (Figure 1). According to the latest reports on protic ionic conductors, the observed crossover is a manifestation of the liquid–glass transition of the ionic glass former.[13,17,20] In this context, it is crucial to note that the glass transition (T_g) is usually defined as the temperature at which the structural relaxation time (τ_α) reaches 1000 s.[36] However, for the hemisuccinate salt the conductivity relaxation time at the T_g point is even 100-fold faster than τ_α, $\tau_\sigma \sim 5$ s. This result suggests that in this case of the protic conductor there is a distinctive separation (decoupling) between the time-scale of ionic transport and

structural relaxation in the vicinity of the glass transition temperature, that is, the charge transfer is continued when the host dynamics became arrested. Nevertheless, to investigate this phenomenon in more detail it is necessary to obtain information on the temperature behavior of structural relaxation times of the studied ionic materials. Herein, the $\tau_\alpha(T)$ dependences were determined by means of various calorimetric techniques (details are presented in Supporting Information). As illustrated in Figure 1, from comparison of $\tau_\sigma(T)$ data of lidocaine hemisuccinate and its temperature dependence of τ_α determined over a six-decades range, it is obvious that the abrupt inflection of the conductivity relaxation curve occurs at $\log(\tau_\alpha/s) = 3$. As a consequence, the ions movement through the studied system is indeed decoupled from the structural dynamics. Furthermore, the application of pressure (P) as an external thermodynamic variable markedly enhances the decoupling between τ_σ and τ_α in the hemisuccinate salt, that is, the kink of the isothermal $\tau_\sigma(P)$ curve being a manifestation of glass transition pressure, P_g moves
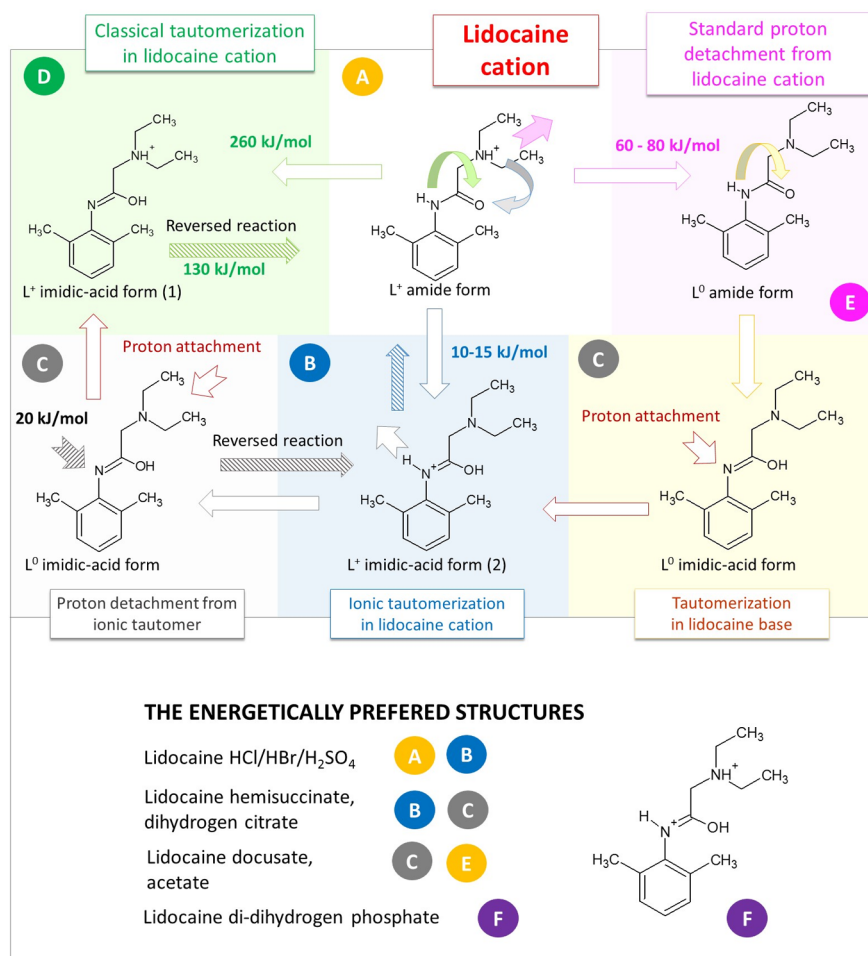
Figure 4. Possible pathways for proton transfer within the lidocaine structure.

toward shorter conductivity relaxation times as pressure increases. This is clearly visible in the lower inset panel of Figure 1. Because the crossover bending points on the $\tau_\sigma - P$ plot denote the $T_g(P_g)$ line, one can easily estimate the $dT_g/dP|_{P=0.1MPa}$ coefficient that reflects the pressure sensitivity of the glass transition temperature for the examined ionic conductor. Interestingly, the small value of $dT_g/dP = 0.127$ K/MPa for lidocaine hemisuccinate, much lower than those found for other protic ionic conductors,[17,39] reflects a weak compressibility of the sample probably caused by strongly hydrogen-bonded structure.

The next step of our investigations was dedicated to dielectric and calorimetric studies of other lidocaine-based ionic compounds. From Figure 2, it becomes clear that the greatest separation between the time scale of conductivity and structural relaxation occurs near T_g of lidocaine di(dihydrogen phosphate). Surprisingly, in this system the charge diffusion is even faster than that found in the classical protonic conductor, H_3PO_4 acid.

Ranking the various lidocaine salts in terms of the decoupling force, the dihydrogen citrate salt takes the second place. On the other hand, a less pronounced difference between the ions translation and host molecule reorientation is observed for inorganic lidocaine salts, that is, hydrobromide and hemisulfate. These results stand in sharp contrast with the behavior of lidocaine acetate and docusate, where the ionic conductivity was found to be completely coupled to structural relaxation.

Interestingly, even compressing the sample up to 400 MPa was not able to separate τ_α and τ_σ (see Figure 3).

■ DISCUSSION

Internal Proton Transfer within the Lidocaine Cation. A varying degree of decoupling between charge diffusion and structural dynamics was observed when we applied the same experimental protocol to a series of protic compounds, based on one active pharmaceutical ingredient, lidocaine. It means that the chemical structure of the anion has a particularly strong influence on the charge transport properties of lidocaine salts. To provide the physical insight into this issue, theoretical calculation studies were performed. Because all the examined samples were formed by proton transfer reaction between Brønsted acids and bases, at the beginning, we considered the reversed reaction, that is, simple proton dissociation from the lidocaine cation (Figure 4, conversions A–E).

The energy needed for the standard proton detachment evaluated by DFT falls within the range of 60–80 kJ/mol. However, we have found that a much lower activation barrier is required for proton hopping from the nitrogen (R_3NH^+) to the oxygen atom of the carbonyl group ($R_2C=O$) (pathways A–B in Figure 4). Such an intramolecular proton migration implicates the rearrangement of chemical bonds in the lidocaine molecule, the charge displacement and finally the hydrogen dissociation from the R_2NH^+ group. This ionic tautomerization, markedly different than the classical amide-imidic acid

conversion (schemes A−B), requires only 10−15 kJ/mol and thus facilitates the charge diffusion through the system. However, only some of the examined anions appeared to work as efficient proton-relay molecules. Consequently, the fast proton conduction is a characteristic feature of some studied herein systems.

Proton Transfer Mechanism in Anhydrous Lidocaine Salts. We have found that among the chosen salts, the docusate structure sterically blocks the proton hopping, whereas the acetate anion readily accepts proton and acquires the form of energetically preferred neutral acetic acid. This is due to the poor donor capability of acetate anion as well as relatively low value of ΔpK_a for lidocaine acetate. As a consequence, at ambient and elevated pressure conditions the conductivity of these two ionic systems is governed by translational diffusion of large molecular species and therefore τ_α and τ_σ are fully coupled. Considerably different conductivity trace occurs in the case of hemisuccinate salt that is characterized by ΔpK_a similar to that established for L-acetate (see Table 1). The hydroxyl moieties actively involved in charge transfer combined with passable donor capability of anion and an extensive H-bonded network (see Figure S9 and Table S1 in Supporting Information) make the succinate structure an effective proton mediator. The representative proton migration pathway through the hemisuccinate ion, imposed by the external electric field, is visualized in Figure 5.
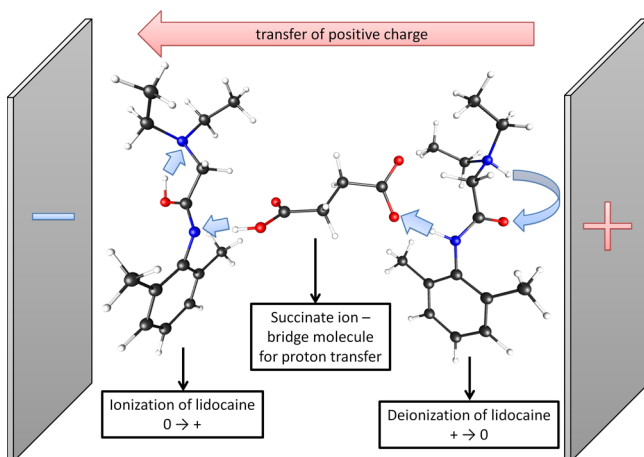

Figure 5. Representative proton migration pathway through the hemisuccinate anion imposed by the external electric field. The arrows on the right side of the figure indicate the internal proton transfer reaction within the lidocaine structure (A−B stage in Figure 4) and the proton detachment from R$_2$NH$^+$ group (B−C in Figure 4), respectively. On the other hand, the arrows on the left part of figure indicate the proton transfer between anion and L-molecule (C−B stage in Figure 4) and the proton hopping in lidocaine cation (B−A stage in Figure 4).

It can be easily seen that the examined anion, due to the dual proton active site, is able to act as a bridge between two neighboring lidocaine molecules: (i) the charged imidic-acid structure, being a consequence of internal tautomerization reaction and (ii) the neutral form existing in the system due to its incomplete ionization. These theoretical considerations were confirmed by experimental results, showing the decoupling between conductivity and structural relaxation times for lidocaine hemisuccinate in contrast to simple VFT behavior of $\tau_\sigma(T)$ reported in the case of acetate and docusate salts.

Additionally, the separation between the time scale of charge and mass diffusion in the succinate system becomes even greater under high pressure conditions. These findings indicate that compression not only reduces intermolecular distances but also markedly affects the H-bonded structure of compressed material and, thus, creates new pathways for fast proton hopping. In the light of these theoretical considerations supported by experimental data, one can state that at least two proton active moieties in the anion are required to enhance the Grotthuss conduction through the lidocaine systems. However, the more proton donors in chemical structure, the more efficient charge transfer is expected. Therefore, the dihydrogen citrate, dihydrogen phosphate, and hemisulfate anions are potentially better proton-relay molecules than the hemisuccinate form. However, as presented in Figure 2, the decoupling between the charge migration and structural relaxation at T_g is larger than that observed for hemisuccinate salt only in the case of dihydrogen citrate (3 decades) and phosphate (7 decades) systems. On the other hand, the time scale separation between τ_σ and τ_α is less pronounced in lidocaine hemisulfate. This apparently surprising result can be very easy explained if we take into account the ionization degree of this protic conductor. Namely, hemisulfate salts, just like L-hydrochloride and L-hydrobromide and in contrast to other examined herein lidocaine-based compounds, is composed solely of ions ($\Delta pK_a > 13$). However, according to the literature reports the ability of ionic system to fast proton conduction is strongly governed by nonconducting species that fulfill the role of extra H$^+$-donor/acceptor.[40,41] That is why in the sulfate salt (as well as in L-HBr) the Grotthuss mechanism is less effective than the charge diffusion in succinate system. As a consequence the decoupling index observed in L-sulfate is smaller than that calculated for L-hemisuccinate, despite the higher number of proton active sites in H$_2$SO$_4^-$ anion. Note that the proton transfer is still realized through the H-bonds connecting R$_2$N$^+$-H groups and acid sulfate anions, but importantly, there is no affinity of system to deionization.

Interestingly, the most efficient Grotthuss conduction among the systems studied herein is observed in the case of lidocaine di(dihydrogen phosphate). This is due to the doubly ionized lidocaine structure (form F in Figure 4) combined with the increased amount of anionic charge carriers that are characterized by a high proton donor/acceptor capability. Moreover, it should be stressed that the analysis of the L-di(dihydrogen phosphate) crystal structure has shown that this protic ionic compound is characterized by an extensive H-bonded network that is crucial in the Grotthuss-type transport mechanism (see Figure S10 and Table S1 in Supporting Information). Moreover, we have found that the amide group is assisted on both sides by two possibly partially deprotonated phosphate molecules. This arrangement may play an important role in a transfer of proton charge through delocalized covalent bonds of the amide moiety during the tautomerization process. Moreover, phosphate molecules on their own from a crown-like layered, self-assembled arrangement which looks like a promising route of proton transfer with possibly a lower activation energy due to already partial deprotonation and strong dislocation of protons (see Figure 6).

Conductivity Behavior of Examined Systems. Considering the molecular origin of enhanced proton conduction it is also necessary to explore the temperature dependence of electrical conductivity σ_{dc} for the studied herein ionic conductors. As summarized in Figure 7, the ionic conductivity
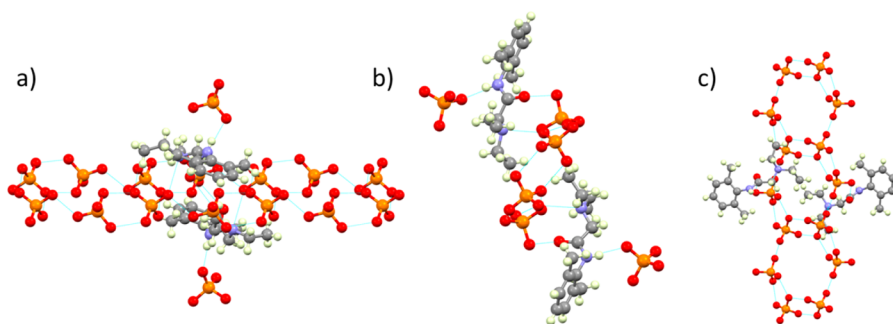
Figure 6. Crown cluster motifs of phosphate molecules along: (a) *a* axis, (b) *b* axis, and (c) *c* axis with exemplar amide "bridges" of lidocaine molecules. Some molecules of lidocaine were removed for clarity purposes.
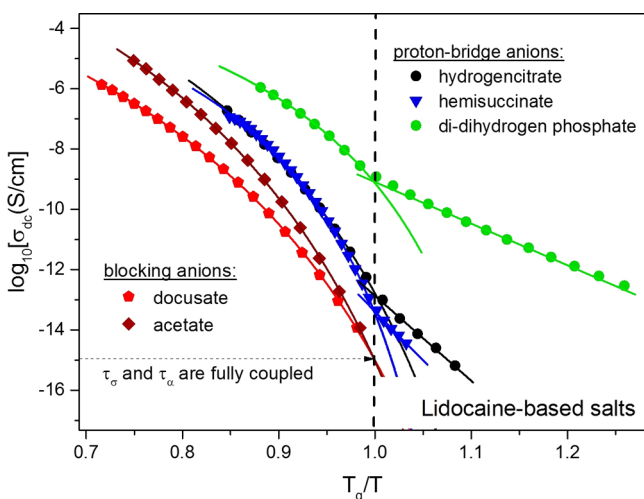

Figure 7. T_g-scaled Arrhenius plot for the conductivities of examined ionic glasses.

of docusate and acetate lidocaine salts is 10^{-15} S/cm at T_g, which is in a good agreement with the literature statements on the ideally coupled ionic glasses. However, with the increased number of proton active sites in the chemical structure of anion the $\sigma_{dc}(T_g)$ is also raised.

In the case of lidocaine di(dihydrogen phosphate), the difference is ~7 orders of magnitude. This indicates that the excess proton conductivity is revealed not only in the decoupling phenomenon but also gives a real contribution to the value of electrical conductivity of ionic systems. Furthermore, due to the Grotthuss-type mechanism, σ_{dc} of glasses being a mixture of ions and neutral species (like the hemisuccinate salt) is even higher than that found for completely ionized salts (e.g., lidocaine HBr; see the data in Table 1).

Taking these facts together one can state that the examined herein dihydrogen phosphate, dihydrogen citrate, and hemisuccinate lidocaine salts can be classified as new examples of anhydrous superprotonic conductors for potential fuel cell applications. However, as indicated by our experimental data the most promising is phosphate-based material. Interestingly, among the dry proton conductors identified so far, mostly phosphate salts can be found (e.g., carvedilol dihydrogen phosphate or trimethylammonium dihydrogen phosphate). Thus, when designing an anhydrous materials with exceptionally high proton conductivity, the phosphate anion is of particular interest. On the other hand, it is better to avoid: (i) a large anions that sterically blocks the proton transfer; (ii)

anions with only one proton active sites and poor proton donor/acceptor capability; (iii) sulfate groups that seems to be a source of high proton conductivity only in the case of polymer electrolyte membranes because the dc-conductivity of these systems is realized mainly by the vehicular mechanism.

■ SUMMARY

We conclude this article by highlighting the factors controlling the enhanced proton conductivity in anhydrous ionic materials. As demonstrated by theoretical and experimental data, systems characterized by an internal charge transfer reaction are potential proton conductors for various electrochemical applications. This is because the tautomerization process markedly reduces the energy required for fast proton hopping between the ions and neutral species. However, based on the dielectric studies of various lidocaine salts supported by DFT calculations we have shown that regarding the ability of given system to fast proton conduction the ionization degree should be also discussed. ΔpK_a value must be high enough to meet the criteria of ionic liquid; however, at the same time, it cannot be too exaggerated since a nonconductive species fulfill the role of efficient H^+-carriers. Considering the molecular origin of fast proton transport in ionic systems one should also take into account the characteristics of H-bond network in examined material, the number of active sites in the chemical structure of ions as well as their proton donor/acceptor capability. This is because all these factors together significantly facilitate the Grotthuss mechanism by creating a shortcut for charge transport and consequently cause a relatively large separation between the time scale of charge and mass diffusion that is observed experimentally as a characteristic crossover of $\tau_\sigma(T)$ dependence.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information file contains: synthesis of the examined ionic conductors, details of calorimetric experiments and characteristic of hydrogen bonds network in crystal structures of selected lidocaine salts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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