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Revealing Fast Proton Transport in Condensed Matter by Means of Density Scaling Concept

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ABSTRACT: Herein, we investigate the charge transport and structural dynamics in the supercooled and glassy state of protic ionic material with an efficient interionic Grotthuss mechanism. We found that superprotonic properties of studied acebutolol hydrochloride (ACB-HCl) depend on thermodynamic conditions with the most favorable regions being close to the glass-transition temperature (T_g) and glass-transition pressure (P_g). To quantify the contribution of fast proton hopping to overall charge transport over a broad T–P space, we employed the density scaling concept, one of the most important experimental findings in the field of condensed matter physics. We found that isothermal and isobaric dc-conductivity (σ_0) and dynamic light scattering (τ_c) data of ACB-HCl plotted as a function of (TV)^[−1] satisfy the thermodynamic scaling criterion with the ratio η/η_c appearing as a new measure of fast charge transport in protic ionic glass-formers in the T–P plane. Such a universal factor becomes an alternative to the well-known Walden rule being limited to ambient pressure conditions.

INTRODUCTION

Charge transport through intermolecular proton hopping is considered essential for many chemical processes. In particular, it has been identified as the main mechanism underlying various biological functions and properties of such basic substances like proteins and water. Proton transport in condensed matter is, in turn, a fundamental phenomenon across a wide range of technologies and applications. For example, solid-state electrolytes with effective proton conductivity in anhydrous conditions have become a promising alternative for water-saturated fuel cell membranes that are useless above 100 °C.

Continuing the latest strategy, considerable attention of the scientific community has been focused on protic ionic (PI) glass-formers. A vital feature of these materials is their hassle-free transformation to the disordered glassy state by isobaric cooling or isothermal compression. Chemically, they are ion-containing liquids or solids obtained in proton transfer reaction from Bronsted acid (HA) to Bronsted base (B) and characterized by a substantial contribution of H-bonding to intermolecular interactions. Depending on the donor–acceptor capabilities of the parent compounds participating in this process, the neutralization reaction is more or less efficient resulting in fully or partially ionized products. The protic ionic systems composed solely of ions are characterized by charge transport of “vehicle” features, i.e., involving proton migration only via translational diffusion of cations (BH^+). On the other hand, in partially ionized protic glass-formers H^+ motions are additionally accessible through the Grotthuss pathways, i.e., local H^+ migration from one molecule to another by using “highways” made of hydrogen bonds. The latter mechanism, which gives a substantial contribution to charge transport, is found to be responsible for superionic properties of various PI glass-formers including phosphoric acid, which is considered to be the best proton conductor. Since fast intermolecular H^+ hopping along the Grotthuss paths is independent of ion diffusion, the basic physical quantities describing the PI system, i.e., molar conductivity (Λ_mol) and viscosity (η), become decoupled from each other.

Generally, two methods are providing a quantitative measure of decoupling phenomenon, and thereby proton transport efficiency. The first one is based on the Walden plot: log_{10} Λ_mol vs. log_{10}η^[−1]. If the experimental data are located in the superionic region of the Walden graph (i.e., above the ideal line determined for diluted KCl), then the lower exponent k indicates the greater decoupling. Note that k < 1. In an alternative approach, the decoupling index describing the time

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scale separation between structural reorientation \( (\tau_s = \eta/G^\infty) \) and electrical relaxation \( (\tau_e = \eta\gamma\rho/NaPhi/\rhoNaMu) \) at the temperature of liquid–glass transition, \( R(T_e) = \log_10\tau_e(T_e) - \log_10\tau_e(T_0) \), is employed.\(^{14,15}\) Importantly, the former method quantifies the proton transport over a broad \( T-P \) range while the latter one is limited to a single point, the \( T_e \) temperature, i.e., the region where \( \text{H}^+ \) hopping is the most efficient. Nevertheless, neither of these two procedures can be employed to provide a unified description of proton transport at various temperature and pressure conditions by using a single variable. This is because \( \text{H}^+ \) transfer becomes faster at elevated pressure, breaking the Walden rule and raising the decoupling index at the glass-transition pressure \( R(P_\text{g}) \) in comparison to \( R(T_\text{g}) \).\(^{14,15}\) Additionally, there is no correlation between the degree of decoupling at ambient conditions and its pressure dependence.\(^{16}\) In this context, the following question arises: How can we quantify the effectiveness of proton transport over a broad \( T-P \) thermodynamic space?

A well-established concept describing the dynamics of ion-containing systems (others as well) at various \( T-P \) conditions is based on the density scaling rule. According to this idea, dc-conductivity \( (\sigma_{dc} = \rhoNaMu\rho/\muNaWi) \), viscosity \( (\eta) \), structural relaxation time \( (\tau_s) \), diffusion \( (D) \), or any other dynamic quantity recorded over a broad \( T-P \) range can be expressed as a universal curve if plotted against \( TV^\gamma \), where \( T \) and \( V \) denote temperature and specific volume, respectively, and \( \gamma \) is the scaling exponent.\(^{17}\) The magnitude of parameter \( \gamma \) is related to the repulsive part of the effective short-range intermolecular potential,\(^{18}\) and thereby, it is usually associated with the structure of a given material. It is also directly connected to the thermodynamically defined Grüneisen constant \( (\gamma_G) \) and, thus, provides a bridge between the dynamics and thermodynamics.\(^{19}\)

It has been confirmed multiple times in the literature that the density scaling concept is satisfied for ionic systems regardless of the huge structural diversity of these materials and various types of intermolecular interactions existing between ions (electrostatics, van der Waals, \( \pi \)-stacking of the cation, and H-bonding).\(^{20-22}\) Importantly, the \( TV^\gamma \) scaling was found to be valid perfectly even when ion dynamics over a wide range of temperature, pressure, and density \( (\rho \text{ changes up to } 20\%) \)\(^{25}\) is considered. Additionally, for aprotic ionic systems, covering the supercooled liquid regime as well as the glassy state. Isobaric measurements at ambient pressure were carried out using a ALPHA High Grade Dielectric Analyzer (Novocntrol Technologies GmbH). For the isobaric measurements, the sample was placed between two stainless steel electrodes of the capacitor with a gap of 0.1 mm. The dielectric spectra of ACB-HCl were collected over a wide temperature range from 355 to 173 K. The temperature was controlled by the Novocntrol Quattro system, with the use of a nitrogen gas cryostat. The temperature stability of the system was better than 0.1 K. For the pressure-dependent dielectric measurements, we used a capacitor, filled with the ACB-HCl sample, which was next placed in the high-pressure chamber and compressed using silicone oil. Note that during the measurement the sample was in contact with stainless steel and Teflon. The pressure was controlled with an accuracy of 0.1 MPa. The temperature was controlled within 0.1 K employing a liquid flow provided by a Weiss fridge. The measurements were performed in the following pressure ranges: 20–160 MPa at 323 K; 20–290 MPa at 333 K; 0.1–425 MPa at 343 K; 20–500 MPa at 353 K.

Dynamic Light Scattering (DLS). For details of DLS measurements of ACB-HCl, see ref 26.

**PVT.** The PVT measurements were performed using a high-pressure dilatometer (a fully automated GNMIX).\(^{27}\) The details can be found in refs 28 and 29. PVT data in the pressure range up to 200 MPa, and from room temperature up to 433 K, were collected in the isobaric standard mode. The values for 0.1 MPa were obtained by extrapolation of the data measured in the range 40–200 MPa in steps of 40 MPa according to the Tait equation. In the studied range, the accuracy limit for the absolute values of the specific volume is within 0.002 cm\(^3\) g\(^{-1}\). Because PVT devices measure only the changes in the specific volume, it is necessary to correct the measured values by adding the specific volume under known, typically ambient conditions, which is 0.845 cm\(^3\) g\(^{-1}\) (determined by means of helium pycnometer at 0.1 MPa and 293.15 K).

**RESULTS AND DISCUSSION.** The conducting properties of ACB-HCl in the supercooled and glassy states were evaluated using ambient and high-pressure dielectric measurements. The representative electric conductivity spectra measured during isobaric cooling and

HCl is characterized by efficient interionic proton transport supported by intramolecular \( \text{H}^+ \) hopping. Herein, we investigate the isothermal and isobaric dc-conductivity and structural relaxation behavior of ACB-HCl in terms of the density scaling concept. We found that \( \tau_e(T, P) \) and \( \sigma_{dc}(T, P) \) dependences, determined from dynamic light scattering–phonon correlation spectroscopy (DLS) experiments and broadband dielectric spectroscopy (BDS) measurements, respectively, recalculated to \( TV^\gamma \) representation, both satisfy the scaling law, however with different \( \gamma \) coefficients. Additionally, a further decrease of \( \gamma_e \) is observed when the liquid–glass transition is passed through. On the other hand, the thermodynamic quantities seem not to be sensitive to fast proton hopping.
K). From Figure 2a, it is also obvious that the value of log10 \( \sigma \) is equal to 103 s). As is clearly visible, the contribution of dc-conductivity to the \( \sigma' \) spectra significantly decreases with cooling and squeezing which is due to a dramatic decrease of ion mobility in the vicinity of the liquid-glass transition. The values of \( \sigma_{dc}(T, P) \) determined directly from the plateau on \( \sigma' \) spectra are presented in Figure 2a. When an isobaric dependence of dc-conductivity is considered, a clear crossover from the super-Arrhenius (Vogel–Fulcher–Tamman-like)\(^{31-33} \) to Arrhenius-type behavior is visible at a certain temperature (\( T^{\text{vft}} = 314 \) K). Note that \( T^{\text{vft}} \) perfectly matches with the calorimetric \( T_g \) of ACB-HCl (\( T_g^{\text{MDSC}} = 315 \) K). From Figure 2a, it is also obvious that the value of log10 \( \sigma_{dc}(T_g) \) is equal to \( -12 \) which corresponds to the time scale of charge transport of 0.17 s. This is about three decades above the values characterizing ion transport in classical aprotic ionic liquids (AILs) \( \left( \sigma_{dc}(T_g) = 10^{-15} \text{ S/cm} \right) \).\(^{34} \) At the same time, \( \langle \tau_{\text{kww}} \rangle(T_g) \), determined from the DLS experiment, being an equivalent of structural relaxation time \( \tau_{\text{rr}} \) reaches \( 10^8 \) s at \( T_g \) (see Figure 2b). This confirms that the charge transport of ACB-HCl is significantly faster than structural reorientation in the vicinity of the liquid–glass transition (\( R_m(T_g) = 3 \)). Specifically, the charge diffusion is continued when the rotational motions of the ACB molecules are already frozen. Importantly, a similar picture appears at high-pressure conditions. Namely, each isotherm reveals a change from one Arrhenius-like behavior to another. The crossover point always occurs at an isochronal structural relaxation time (data not shown). Nevertheless, \( \sigma_{dc} \) determined at the liquid–glass transition continuously increases with pressure (see inset to Figure 2a), thereby indicating a higher contribution of Grothuss-type conduction to the charge transport in densified ACB-HCl. However, in comparison to other protic ionic glassformers, the decoupling degree in the studied hydrochloride salt does not change much at elevated pressure, which suggests rather insignificant fluctuations of the H-bonded network in densified material. The physical parameter quantifying this effect is the dlog10\( R_m/dP \) coefficient defined as the derivative of log10\( R_m(P) \)/\( P \) dependence. For ACB-HCl, it is equal to 1.27 GPa\(^{-1} \) and indicates that a pressure of 1.27 GPa\(^{-1} \) causes an increase of dc-conductivity by one decade. It is much lower than dlog10\( R_m/dP \) reported for low-molecular PI glassformers;\(^{35} \) however, at the same time, it is comparable to a pressure coefficient of \( R_m \) found for protic polymerized ionic liquids.\(^{36} \) In the context of a different efficiency of H\(^+ \) hopping in ACB-HCl at ambient and elevated pressures, searching for a new parameter quantifying proton transport over the entire \( T-P \) space is fully justified. To verify the suitability of exponent \( \gamma \) for this purpose, we examine the density scaling concept for supercooled and glassy ACB-HCl.
To test the scaling behavior of dynamic data of ACB-HCl, the $\sigma_{0k}$ and $(A_{KWW})$ measured at various $T$–$P$ conditions need to be expressed as a function of volume. For this purpose, the pressure–volume–temperature ($PVT$) relation for ACB-HCl was additionally determined. The obtained set of $V(T, P)$ data is displayed in the 3D plot in Figure 3. A standard picture presenting a decrease of $V$ with cooling and squeezing is observed. Additionally, each collected $V(T, P)$ curve shows crossover behavior, similar to that previously recorded for $\sigma_{0k}(T, P)$ data and denoting a transition from a supercooled to a glassy state. It is noteworthy that the $T_r(P_r)$ behavior taken directly from the crossover of isobaric $V(T)$ data is in good agreement with the $T_r(P_r)$ line constructed from crossover points of $\sigma_{0k}(T, P)$ dependences as well as $T_r(P_r)$ determined from $(A_{KWW})$ data by using the isochronal definition of $T_r = T(\log_{10}(T_{KWW}) = 3)$ (see inset to Figure 3). This result strongly confirms that the data obtained in three different experiments are consistent with each other.

To calculate the volume at each $T$–$P$ state point of ACB-HCl, $V(T, P)$ data were parametrized by the means of the equation of state (EOS)

\[
V = \frac{A_0 + A_1 \times (T - T_0) + A_2 \times (T - T_0)^2}{\{1 + \frac{T_{KWW}}{b_1} \times (P - P_0) \times \exp[b_2 \times (T - T_0)]\}^{1/\gamma_{KWW}}} \tag{1}
\]

where $A_0$, $A_1$, $A_2$, $T_{KWW}$, $b_1$, and $b_2$ are adjustable coefficients shown in Table 1 when $T_r = 300$ K and $P_r = 0.1$ MPa. Note that two sets of EOS parameters ($PVT$-1 and $PVT$-2) were used to describe $V(T, P)$ data in the supercooled and glassy states of ACB-HCl. Having this, it is now possible to plot the dc-conductivity data and structural relaxation times measured at various $T$ and $P$ as a function of volume. In Figure 4a, very peculiar behavior can be observed for isobaric $\sigma_{0k}(V)$ dependence; i.e., in contrast to $\sigma_{0k}(T)$ data, there is no crossover from the VFT to the Arrhenius behavior (see 2D projection). Thus, the liquid–glass transition of ACB-HCl becomes hidden when the changes of $\sigma_{0k}$ accompanying densification at $P = \text{const}$ are analyzed. This suggests temperature rather than free volume as a decisive factor in controlling the dynamics of the studied ACB-HCl. A similar result was obtained recently for other protic ionic glass-formers with efficient Grotthuss transports.\textsuperscript{38}

The next step toward verification of the scaling criterion in ACB-HCl is to determine the $\gamma$ exponent. According to the literature reports, there are several approaches to realize this goal. The simplest one is based on the analysis of volume dependences of isobaric and isothermal data ($\gamma_0$, $\gamma_1$, $\gamma_2$) along with the iso$\langle x \rangle$ lines ($x_i$, relaxation time, viscosity, conductivity) in terms of $\log_{10} T = f(\log_{10} V^{-1})$. Namely, $\gamma = d\log_{10} \tau_i / d\log_{10} (V^{-1})$. The exemplary horizontal surfaces intersecting the experimental curves at various iso$\langle x \rangle$ and iso$\langle y \rangle$ conditions for ACB-HCl are presented in Figure 4a, b, respectively. The insets, in turn, show double logarithmic plots of $T$ vs. $V^{-1}$ obtained along the chosen 2D planes. As presented, $\log_{10} T(\log_{10} V^{-1})$ dependences obtained using glassy ($G$) and supercooled (SL) EOS ($\sigma_{0k}(T, V)$ points as well as $(A_{KWW})(T, V)$ data are linear. Nevertheless, their slope, providing a direct estimate of the $\gamma$ parameter, is different in all these cases. Specifically, $\gamma_0(\text{SL}) = 1.86 \pm 0.03$, and $\gamma_0(\text{G}) = 1.81 \pm 0.03$, while $\gamma_0(\text{SL}) = 2.09 \pm 0.05$. Importantly, the same coefficients are obtained from an alternative method employing numerical fitting of BDS and DLS data with the use of the Avramov entropic model\textsuperscript{39} $A_{KWW}(G)$ or $	au_0(\gamma_0) = \sigma_{0k}(\gamma_0) \exp\left(\frac{A_{D}}{\gamma_0}\right)$ (see the lines in Figure 4 and Table 2 for fitting parameters: $\sigma_{0k}(\gamma_0)$, $\gamma_0$, $A_{D}$, and $D$).

Having the values of $\gamma$ already determined, one can verify the scaling concept for ACB-HCl. As presented in Figure 5, all isothermal and isobaric $(A_{KWW})$ dependencies illustrating the structural dynamics of supercooled ACB-HCl create a single curve when plotted as a function of scaling variable $T^{-1/\gamma+2}$.

On the other hand, the $T$–$P$ dc-conductivity data form two separate master curves for supercooled and glassy regimes, respectively. Thus, the density scaling concept is obeyed for ACB-HCl in each formalism; however, the value of exponent $\gamma$ is $T_{KWW}$-sensitive and depends on the physical variable being chosen to express the ion dynamics. When the structural relaxation is investigated, the scaling coefficient $\gamma_r$ of ACB-HCl is similar to the exponents characterizing aprotic ionic liquids (e.g., 1-octyl-3-methylimidazolium tetrafluoroborate [C\textsubscript{8}MIM][BF\textsubscript{4}], $\gamma_0 = 2.25$; 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C\textsubscript{6}MIM][NTf\textsubscript{2}], $\gamma_0 = 2.45$)\textsuperscript{16} and protic salts (verapamil HCl $\gamma_0 = 2.45$\textsuperscript{40}), all with “vehicle” transport being decisive. Thus, by exploring solely the diffusion of cations and anions (structural relaxation, viscosity) in terms of the scaling concept, it is not possible to identify the

| Table 1. Coefficients of the EOS Equation (eq 1) along with Standard Deviations |
|---------------------------------------------|-------------|-------------|-------------|-------------|
| $A_0/\text{cm}^3\text{g}^{-1}$ | $A_1/10^3/\text{cm}^3\text{g}^{-1} \text{K}^{-1}$ | $A_2/10^3/\text{cm}^3\text{g}^{-1} \text{K}^{-2}$ | $T_{KWW}$ | $b_1/\text{MPa}$ | $b_2/10^3/\text{K}^{-1}$ |
|---------------------------------------------|-------------|-------------|-------------|-------------|-------------|
| $PVT$-1\textsuperscript{4} | 0.8525 ± 0.0001 | 4.51 ± 0.02 | \(-2.39 ± 0.98\) | 11.3 ± 0.1 | 3084.2 ± 16.0 | 3.11 ± 0.04 |
| $PVT$-2\textsuperscript{6} | 0.8527 ± 0.0001 | 2.26 ± 0.12 | 72.8 ± 7.4 | 15.1 ± 0.8 | 3416 ± 34 | 2.76 ± 0.02 |

\textsuperscript{4}Supercooled liquid state.\textsuperscript{6}Glass.
charge carriers. Generally, this is the second time when the decrease of 13% is observed from ACB-HCl, the dihydrogen phosphate, a material with e40 a broad transport mechanism being decisive in a given system. On the other hand, the parameter describing the dc-conductivity behavior over a broad T–P space seems to be sensitive to the type of charge carriers taking part in the conduction process, namely, the larger the contribution of proton hopping to overall conductivity and decoupling even more pronounced than they are for ACB-HCl. In the context of the presented results, the ratio γα/γσ can be indeed treated as a new measure of the decoupling phenomenon and, thus, the efficiency of proton transport in supercooled ionic glass-formers over a broad T–P thermodynamic space. An important question arises immediately: Is the relation between scaling exponent and thermodynamic variables established in ref 41 for van der Waals liquids also valid in the case of PI glass-formers? Following this issue, we verify the formula that links the parameter γ with thermodynamic Grüneisen constant γG:

\[ γ = \frac{γ_{\text{EOS}}}{D} + γ_G \]  

As mentioned above, the γEOS is determined directly from PVT data and characterizes the repulsive part of the intermolecular potential. For ACB-HCl, it is equal to 11.3 in supercooled liquid state. On the other hand, parameter D is obtained from the fitting of the experimental T–V surface by means of the Avramov entropic model. Since we have collected two sets of dynamic data for ACB-HCl, describing the behavior of dc-conductivity and structural relaxation over a wide T–V space, we have two different γ coefficients and two different parameters D. Nevertheless, by using both these data sets, a nonphysical Grüneisen constant is obtained. This is because the ratio γEOS/D is larger than the scaling parameter γ (see Table 3). Interestingly, in the past, the validity of eq 2 was confirmed for several van der Waals liquids and aprotic ionic system 1-butyl-1-methylpyrrolidinium bis(oxalate)borate [C4MPYR][BOB] species.41 However, in all these cases the value of γ was around 4, i.e., 2 times higher than the coefficients determined for ACB-HCl. Importantly, the negative value of γG is obtained also for other protic ionic glass-formers, i.e., hydrochloride salts of lidocaine, carvedilol, as well as carvedilol H2PO4 (see Table 3 for γEOS, D, and γG). This indicates that eq 2 is broken for PI materials. In this context, it is interesting to calculate the real Grüneisen constant for protic conductors. For this purpose, we determine γG directly from the thermodynamic variables:

\[ γ_G = \frac{V α_T}{C_V \kappa_T} \]  

where V is a specific volume, αT the isobaric thermal expansion coefficient, and κT the isothermal compressibility. The C_V is the heat capacity at a constant volume that can be converted to the
Table 3. Dynamic and Thermodynamic Parameters of Selected Protic Ionic Glass-Formers

|                     | ACB-HCl |  carbediol HCl | carbediol HPO4 | lidocaine HCl |
|---------------------|---------|----------------|----------------|--------------|
| \( \gamma \)        | 1.8°    | 2.13°          | 1.12°          | 2.40°        |
| \( \gamma_{ex} \)   | 11.3    | 11.92          | 9.83           | 10.48        |
| \( D \)             | 4.57°   | 4.95°          | 4.95°          | 3.05°        |
| \( \gamma_{ex} / D \)| 5.37°   | 2.40°          | 1.98°          | 3.43°        |

- Determined from BDS data. *Determined from DLS data. *Estimated using group contribution method. *Taken from ref 48.

heat capacity at constant pressure \( C_p \) that, in turn, is easily available in DSC measurements: \( C_V = C_p - {\gamma \nu_a}^2/\kappa \). Since all the thermodynamic quantities defining \( \gamma \) depend on \( T - P \) conditions, the common practice is to define the Grüniesen constant at the liquid–glass transition of the given system. Having already determined all the quantities appearing in eq 3 (see Table 3), we calculated the value of the exponent \( \gamma_a(T_g) = 0.64 \) for ACB-HCl. Interestingly, the \( \gamma_a(T_g) \) value below unity is found also for other protic materials (see Table 3). On the other hand, the obtained values are around twice lower than \( \gamma_a(T_g) \) for classical aprotic ionic liquids 1.1 < \( \gamma_a(T_g) < 1.5 \) (e.g., 1-buty1-3-methylimidazolium bis-(pertrifluorosulfonyl)imide [C4MIM][BET]) = 1.3; [C4MPYR][BOB] = 1.5; 1-butyl-3-methylimidazolium bis-(trifluorosulfonyl)imide [C4MIM][NF2] = 1.32) and the van der Waals systems (e.g., BMPC = 2.26; OTP = 1.2). Such a low value of \( \gamma_a(T_g) \) found for ACB-HCl and other protic glass-formers is most likely due to their relatively high isobaric heat capacity since the other parameters (\( V_{ex}, \sigma_n, \) and \( \kappa \)) stay typical for AILs. Since the molar heat capacity generally increases linearly with the molar mass and molar volume of the IL, one can expect that the high \( C_p \) of protic materials studied herein is due to their heavy cations containing more bonds storing thermal energy and having more degrees of freedom than the classical cations of ILs, i.e., imidazolium or pyrrolidinium-based. The proton transport between cations and anions is of rather less importance.

### CONCLUSIONS

In this paper, we have investigated the molecular dynamics of the ACB-HCl protic ionic glass-former with efficient inter- and intramolecular proton transport. Due to the contribution of Grothuss conduction, the charge transport of ACB-HCl is markedly faster than the structural relaxation, especially in the vicinity of the liquid–glass transition and under high-pressure conditions. To quantify the effectiveness of \( H^+ \) hopping over a wide \( T - P \) range, we took advantage of the density scaling concept. We found that \( T W \) scaling is satisfied for ACB-HCl despite the significant contribution of H-bonding to intermolecular interactions. However, the exponent \( \gamma \) depends on the dynamic quantity under investigation. The \( \gamma_a \) (obtained from scaling of \( \sigma_n(T, P) \) data) in contrast to \( \gamma_a \) (from analysis of structural dynamics) is sensitive to the type of charge carrier participating in the conduction process; i.e., it decreases when the efficiency of \( H^+ \) hopping is higher, and generally it is \( \approx 2 \) times smaller than \( \gamma_a \) of AILs. Consequently, the ratio \( \gamma_a / \gamma_a \) can be considered as a new measure of decoupling between charge and mass transport in protic ionic systems, and thereby the contribution of the Grothuss mechanism to overall conductivity at various \( T - P \) state points. At the same time, the proton dynamics is not detectable by revising the thermodynamic quantities characterizing a given system. The Grüniesen constant \( \gamma_a \) of protic ionic glass-formers, although markedly lower than \( \gamma_a \) reported for AILs, reflects the complex structure of the cation rather than H-bonding interactions and H hopping.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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