High Pressure as a Key Factor to Identify the Conductivity Mechanism in Protic Ionic Liquids

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In this Letter we report the relation between ionic conductivity and structural relaxation in supercooled protic ionic liquids (PILs) under high pressure. The results of high-pressure dielectric and volumetric measurements, combined with rheological and temperature-modulated differential scanning calorimetry experiments, have revealed a fundamental difference between the conducting properties under isothermal and isobaric conditions for three PILs with different charge transport mechanisms (Grotthuss vs vehicle). Our findings indicate a breakdown of the fractional Stokes-Einstein relation and Walden rule when the ionic transport is controlled by fast proton hopping. Consequently, we demonstrate that the studied PILs exhibit significantly higher conductivity than one would expect taking into account that they are in fact a mixture of ionic and neutral species. Thus, the examined herein samples represent a new class of "superionic" materials desired for many advanced applications.

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Ionic liquids (ILs), composed solely of ions, are molten salts that can be found in the liquid state at a wide temperature range including room temperature conditions [1,2]. Their unique physical and chemical properties, such as high thermal and electrochemical stability, high ionic conductivity, and very low vapor pressure, make them attractive candidates for a wide variety of applications in modern technologies. The progress in most of these areas requires a fundamental understanding of the charge transport mechanism in ILs.

Ionic liquids are classified into two categories: aprotic and protic ionic liquids (PILs). PILs are formed by proton transfer reactions between Brönsted acids (HA) and bases (B) [3,4] according to the following equation, $HA + B \Leftrightarrow A^- + BH^+$. Ideally, this reaction results in individual cations and anions in PILs. However, the proton transfer may be less than complete in reality, and the obtained liquid is consequently a mixture of ionic and neutral species. In this context it should be noted that the degree of proton transfer from acid to base strongly affects the properties of PILs. Thus, the question of "how ionic is PIL" becomes of general significance. One way for assessing the ionicity of PILs is to construct the Walden plot that relates the ionic mobility, represented by molar conductivity Λ_{mol}, to the viscosity of the medium η [5]. According to the Walden rule the molar conductivity is controlled by fluidity $1/\eta$, and $\Lambda_{\text{mol}} \cdot \eta \approx$ const. The Walden plot presents the $\log \Lambda_{\text{mol}}$ vs $\log (1/\eta)$ and has an "ideal line" with the slope 1, typically calibrated using the dilute KCl solution [6,7]. The ideal line corresponds to the case where all ions are dissociated and their diffusion is coupled to the viscosity of the liquid. Most of PILs fall well below this calibration line, because incomplete ionization in these systems results in lower free ion concentration and, consequently, lower conductivity than what would be expected on the basis of the Walden rule. For this reason PILs are frequently regarded as "poor" ionic liquids.

Earliest studies have shown that in general one can distinguish two types of charge transport mechanisms in protic ionic conductors: vehicle and Grotthuss-type. In the vehicle mechanism the charge transfer is connected with the molecular diffusion, while in the Grotthuss-type mechanism it is realized through the proton migration in the hydrogen-bonded network [8]. The second mechanism is usually considered as the source of abnormally high proton mobility in water and phosphoric acid [9]. However, there is still no evidence that the Grotthuss mechanism exists in protic ILs. High pressure measurements (up to now almost completely unexplored approach in PILs studies) might provide new insights into this issue. Compression of a liquid not only reduces interatomic distances but also changes intermolecular interactions [10], affecting liquid fluidity and ion transport. From this point of view it is of general significance to examine the Walden criterion of PILs under high pressure conditions. Despite their promise for unraveling the details of the proton conductivity mechanism, which are not accessible in the usual temperature dependent studies, systematic high pressure measurements have not been carried out for PILs.

In this Letter, we examine the charge transport mechanism of two protic ionic liquids containing the same organic cation, carvedilol, and two different anions, chloride and dihydrogen phosphate. Neat carvedilol base is also examined as a reference. High pressure conductivity measurements, combined with rheology, allow us to test the fractional Stokes-Einstein relation and Walden rule at elevated pressure for the studied protic ionic conductors.

Since the examined carvedilol salts exhibit higher conductivity than expected by the Walden plot analysis they can be classified as new examples of superionic conductors in which σ is controlled by fast proton hopping. Additionally, our analysis demonstrates that at ambient and elevated pressures one of the examined PILs exhibits anomalously large decoupling of conductivity from structural relaxation—it is even stronger than that in phosphoric acid [11], which is believed to have a highly efficient Grotthuss mechanism.

To examine the proton conductivity we chose two salts of carvedilol (chemical structures are presented in the Supplemental Material [12]): carvedilol-hydrochloride (C-HCl) and carvedilol-dihydrogen phosphate (C phosphate). The dielectric data of C phosphate at ambient pressure were taken from Ref. [13] while the relaxation spectra of the other two compounds were measured by a Novocontrol Alpha analyzer in broad frequency and temperature ranges. 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. [14]. Following the standard practice [15–18], we have chosen the electrical modulus $M^*(f)$ and conductivity $\sigma^*(f)$ representations to describe the ion dynamics of carvedilol salts, and the permittivity representation $\varepsilon^*(f)$ to investigate the structural relaxation of the carvedilol base (C base). These three complex quantities are related to each other by the following equation [15]:

$$M^*(f) = \frac{1}{\varepsilon^*(f)} = \frac{i2\pi f \varepsilon_0}{\sigma^*(f)}. \tag{1}$$

Similarly to other ionic liquids, the conductivity relaxation peak of C salts [i.e., the maximum in $M''(f)$], originating from the ionic motion, moves toward lower frequencies with cooling [Fig. 1(a)]. However, the temperature dependence is markedly reduced below certain temperature. The temperature dependence of dc conductivity relaxation times, $\tau_\sigma = 1/2\pi f_{\max}$ ($f_{\max}$ is the frequency of the M'' maximum), suddenly changes from Vogel-Fulcher-Tammann -like to Arrhenius behavior [Figs. 1(b) and 1(c)]. This is a manifestation of the liquid-glass transition of examined ionic glass formers. It is interesting that the kink of the $\tau_\sigma(T)$ curve for C phosphate occurs at a much shorter conductivity relaxation time ($\tau_\sigma \sim 0.01$ s) than in the case of C-HCl ($\tau_\sigma \sim 10$ s). In this context, it should be stressed that the T_g temperature is usually defined as the temperature at which the structural relaxation time τ_α is equal to 1000 s [15] and viscosity is on the order of 10^{12} Pa $\cdot$ s. This suggests that in the case of examined ionic liquids there is a significant separation between the time scale of conductivity and structural relaxation in the vicinity of the glass transition. Surprisingly, in the case of the sample with dihydrogen phosphate anion, this separation is even greater than that found in H_3PO_4 [11].

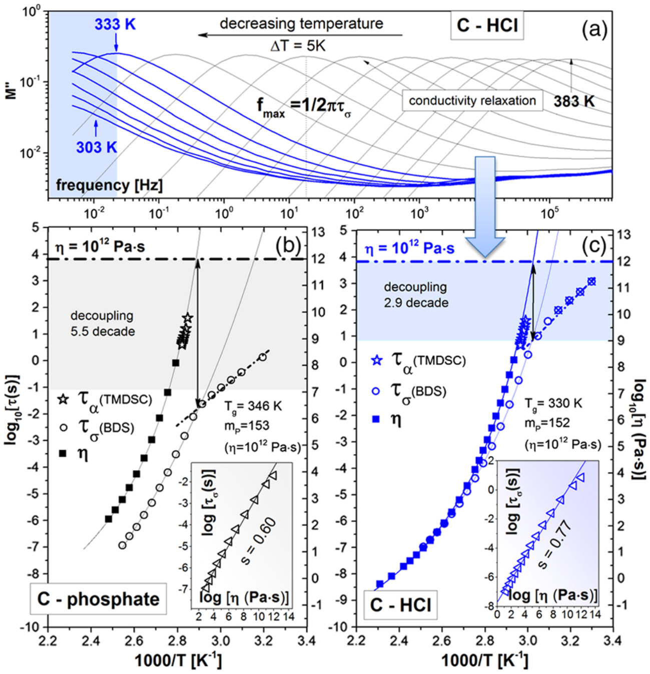

FIG. 1 (color online). (a) Dielectric loss modulus spectra due to conductivity relaxation at various temperatures in the liquid and glassy states for carvedilol HCl; (b) and (c) present the temperature dependence of viscosity, conductivity relaxation time, and structural dynamics of carvedilol salts. Open circles: conductivity relaxation time (τ_σ). Open stars: (τ_α) measured by TMDSC. Solid squares: viscosity (η). The solid lines are Vogel-Fulcher-Tammann fits to the experimental data. τ_σ shows weaker temperature dependence below T_g. Insets: relation of τ_σ to η. The τ_σ in the glassy states of C-HCl (crossed circles) were estimated by horizontal shift of the σ peak from the region above T_g to the temperatures below T_g.

To quantify the decoupling of ion diffusion from the structural relaxation, the temperature dependence of conductivity relaxation time are compared to that of $\tau_\alpha(T)$ and $\eta(T)$, determined by temperature-modulated differential scanning calorimetry (TMDSC) and rheology [Figs. 1(b) and 1(c)]. The TMDSC measurements were carried out by Mettler-Toledo DSC apparatus, and viscosity measurements were performed on an AR2000ex rheometer (TA Instruments) with 25 mm aluminum parallel plates. The calorimetric structural relaxation times $\tau_\alpha = 1/2\pi f$ were determined from the temperature dependences of the real part of the complex heat capacity $c'_p(T)$ obtained at different frequencies in the T_g region. The inflection of the $\tau_\sigma(T)$ curve in both cases occurs at $\eta = 10^{12}$ Pa $\cdot$ s, confirming its glass transition origin. The relationship between dc conductivity and structural relaxation for low-molecular-weight glass-forming liquids and polymers is usually discussed in terms of the phenomenological fractional Stokes-Einstein (fSE) relation [19], $\tau_\sigma \eta^s =$ const. In this case the double logarithmic plot of τ_σ vs η (the inset panels of Fig. 1) provides an estimate of the decoupling parameter s. It is equal to 0.60 and 0.77 for C phosphate and C-HCl, respectively. This decoupling behavior is in strong contrast to the neat C base where the slope s is close

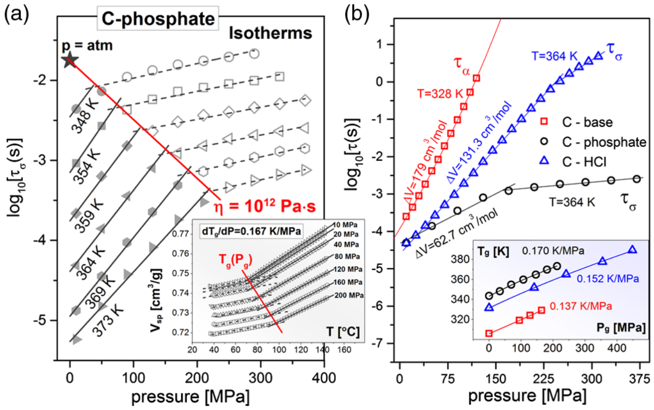

FIG. 2 (color online). (a) Isothermal dielectric measurements of conductivity relaxation time of carvedilol dihydrogen phosphate. The inset presents the temperature dependence of specific volume V_{sp} in the pressure range of 10–200 MPa for C phosphate. The data above T_g are fitted by the Tait equation [27,28] (solid lines). (b) Open circles and triangles denote isothermal dielectric measurements of the conductivity relaxation time of C phosphate and C-HCl, respectively. Open squares denote the pressure dependence of structural relaxation time of C base. The values of ΔV were calculated at $P = 0.1$ MPa for each isotherm. The inset presents the pressure dependence of the T_g temperature for C compounds. Solid lines are fits of the Andersson equation [29] to the experimental data. $T_g(P_g)$ values for C salts were taken from the isoviscosity line while the data for the C base was calculated as $P_g = P\ (\tau_\alpha = 1000\ \mathrm{s})$.

to unity (see Supplemental Material [12]). Herein, the question arises: Why do the examined protic conductors have different degrees of decoupling? A possible explanation for various time scales of τ_σ and τ_α in tested materials involves the role of fast proton transport through the hydrogen-bonded network. Recently, it has been shown that the Grotthuss mechanism gives rise to the high conductivity in phosphoric acid [9]. Thus, one should expect that the excess conductivity of C phosphate is due to the proton hopping through its dense H-bonded network. This would explain the difference between C phosphate and C-HCl, where the H bonds are formed only by cations. Additionally, one should also expect that in the case of PILs with no H bonds, the Grotthuss mechanism does not take place and, consequently, ionic transport is coupled to structural relaxation through the vehicle mechanism.

If the above explanation is true, then it should be possible to control the decoupling phenomenon and consequently recognize the conduction mechanism (Grotthuss vs vehicle) in PILs by modification their hydrogen-bonded structure using high pressure techniques. The experiments performed previously for van der Waals liquids [20] and aprotic ionic conductors [21,22] have shown that their conductivity and structural relaxation times vary in a similar manner under pressure. On the other hand, the recent high pressure results for PILs did not reveal a universal behavior. For example, a slight increase in decoupling between τ_σ and τ_α with pressure was reported for the hydrochloride salts of procainamide [23] and lidocaine [24], while the decoupling is pressure independent in verapamil HCl [25]. To test the effect of pressure on the decoupling phenomenon in carvedilol salts, we have performed isothermal high-pressure dielectric measurements. As illustrated in Fig. 2(a), the kink of the τ_σ-P curve (a manifestation of T_g) in C phosphate moves toward shorter conductivity relaxation times with increasing pressure. This means that compression markedly enhances the decoupling of ionic conductivity from the structural relaxation in this compound. The crossover bending points on the τ_σ-P plot mark the isoviscosity line. These results provide estimation of the pressure dependence of T_g [inset in Fig. 2(b)] that is in good agreement with the value determined from pressure-volume-temperature (PVT) measurements [inset in Fig. 2(a)]. The same procedure has been employed for the analysis of C-HCl and C base as well. However, in the latter case the dielectric spectra were examined in the permittivity representation and T_g was defined as $T_g = T\ (\tau_\alpha = 1000\ \mathrm{s})$.

A very useful parameter to quantify the effect of P on the relaxation time in glass-forming liquids is the activation volume, defined as $\Delta V^{\#} = 2.303RT(d\log\tau/dP)_T$, where τ can be either structural (τ_α) or conductivity relaxation time (τ_σ). In the framework of the transition state theory, $\Delta V^{\#}$ is interpreted as the difference between the volumes occupied by the relaxing units in activated and ground (energy minimum) states. To calculate the activation volume of structural relaxation in studied samples at T_g and ambient pressure, we use the relationship between $\Delta V^{\#}_{\alpha}$, the steepness index m_P, and dT_g/dP coefficient: $\Delta V^{\#} = 2.303Rm_P dT_g/dP$ [10]. It appears that activation volume for structural relaxation at T_g is essentially the same in these materials: $\Delta V^{\#}_{\alpha} = 486\ \mathrm{cm}^3/\mathrm{mol}$ for C base and C phosphate, and 451 $\mathrm{cm}^3/\mathrm{mol}$ for C-HCl, slightly larger than the molar volume of carvedilol ($V_{\mathrm{mol}} = 313\ \mathrm{cm}^3/\mathrm{mol}$). In contrast to structural relaxation, the conductivity activation volume, $\Delta V^{\#}_{\sigma}$, determined at the same T-P conditions is considerably lower for chloride and dihydrogen phosphate salts: 225 and 85 $\mathrm{cm}^3/\mathrm{mol}$, respectively. Moreover, the conductivity activation volume of C phosphate is more than two times lower than that of C-HCl. These results indicate that the sensitivity of the α relaxation to pressure remains about the same for all the examined samples while the effect of pressure on the conductivity depends strongly on the system. Consequently, the size of the mobile units will have an influence on the value of $\Delta V^{\#}$—roughly speaking, the larger particle responsible for charge transfer the higher activation volume. This suggests that proton hopping through the hydrogen-bonded network contributes significantly to the charge transport in carvedilol phosphate. What is also interesting—the stronger is the temperature decoupling between η and σ, the weaker is the sensitivity of the conductivity to pressure. It turns out that this finding is valid not only in the case of carvedilol salts but also holds for another protic conductors [23–25].

Now we return to the main topic of this Letter—the relation between ionic transport and structural relaxation in PILs under the condition of high compression, which will be discussed in terms of the fSE relation and Walden rule. To examine the pressure behavior of the exponent s^P in fSE rule for C salts the values of τ_σ and η measured at 1 atm and at P_g (the pressure at which glass transition occurs in the isothermal experiments) have been plotted in Figs. 3(a) and 3(b). As one can see the data obtained for isothermal and isobaric pathways do not superimpose onto each other, as opposed to the recent finding for aprotic ionic conductors [21]. Moreover, in both examined PIL samples the exponent s under isothermal conditions is significantly smaller than that estimated at ambient pressure. It is equal to 0.26 and 0.60 for C phosphate and C-HCl, respectively. Note that the dashed lines [Figs. 3(a) and 3(b)] linking the points from the isothermal measurements are only guide for the eyes, as the viscosity behavior of examined PILs as a function of pressure is not known. To resolve this issue, high pressure viscosity measurements should be performed. However, this kind of experiment is technically complicated, especially close to the liquid-glass transition region. To circumvent this difficulty we propose a new analytical method, which is based on the temperature-volume version of the Avramov entropic model [26] and the thermodynamic scaling concept, to determine the pressure dependence of viscosity using ambient pressure rheological data and PVT experiments. The detailed description of the applied procedure is explained in the Supplemental Material [12]. As shown in Fig. 3 the results of this procedure (solid lines) agree well with the experimentally determined points (open symbols) at T_g. These observations suggest that for PILs with Grotthuss-type conductivity the decoupling exponent s is generally pressure dependent, and the fractional Stokes-Einstein relation, strictly speaking, is not applicable. This raises the next question: *does the fSE relation also break down under high pressure for PILs with no Grotthuss conduction?* To put more light on this problem, we have performed a similar analysis for verapamil hydrochloride (VH)—a protic ionic liquid which does not create H bonds and where there is no kink in the $\tau_\sigma(P)$ curve even up to 400 MPa [25]. As presented in Fig. 3(c) isobaric and isothermal data for VH can be scaled onto a single line with the slope $s = 0.9$. This result strongly supports the idea that the fSE relation breaks down when the conductivity of PIL is controlled by the Grotthuss mechanism.

Since the ionic transport is usually analyzed in terms of molar conductivity, $\Lambda_{\mathrm{mol}} = \sigma/n$, where n is molar concentration of ions, in the next step of our studies we examine the physical properties of C salts in terms of the fractional Walden rule, $\Lambda_{\mathrm{mol}}\eta^k = \mathrm{const}$, with the exponent $k \leq 1$. Analysis of Λ_{mol} of C salts reveals that it is surprisingly similar for the two PILs in the supercooled liquid state (lower inset in Fig. 4), while their $\eta(T)$ are significantly different (upper inset in Fig. 4). On the other hand, below T_g the effect of temperature on Λ_{mol} is markedly reduced in both cases and, more importantly, the molar conductivity is significantly higher in C phosphate than in its hydrochloride analog (Fig. 4).

The classical Walden plot analysis (Fig. 4) demonstrates that at ambient pressure the C phosphate is clearly in the superionic regime, in contrast to the C-HCl that falls in the subionic regime, especially at high temperatures. Thus, for the same viscosity conditions the charge transport in C

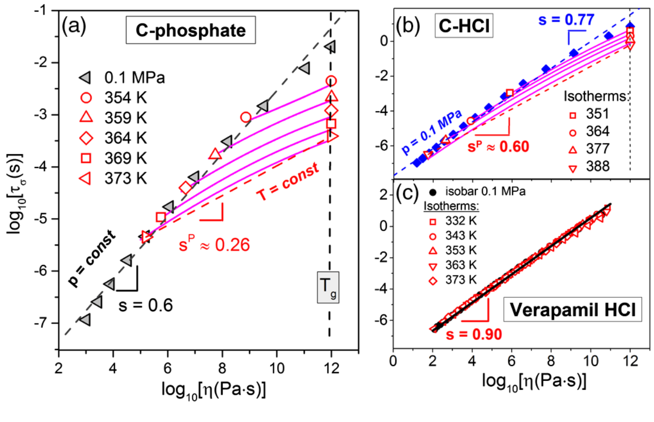

FIG. 3 (color online). Test of the fractional Debye-Stokes-Einstein relation (fDSE) at ambient and elevated pressures for carvedilol salts (with Grotthuss conducting mechanism) [panels (a) and (b)] and verapamil HCl (vehicle mechanism) [panel (c)]. Closed triangles, diamonds, and circles indicate the data collected at ambient pressure while open symbols are the data recorded under high pressure. Solid lines are determined using the pressure dependence of viscosity generated by the Avramov entropic model.

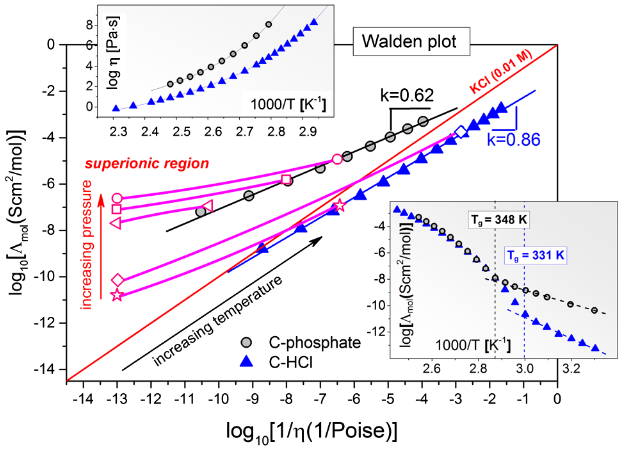

FIG. 4 (color online). Walden plot under high pressure conditions for C salts. Closed symbols: isobaric measurements. Open symbols: isothermal measurements. The ideal line is constructed from the data of KCl aqueous solution. The insets present the molar conductivity and viscosity as a function of $1/T$ for C phosphate (solid circles) and C-HCl (solid triangles), respectively.

phosphate is significantly faster than that in C-HCl. As discussed already, this is due to the proton hopping through the dense H-bond network created by carvedilol and dihydrogen phosphate ions. These data indicate that supercooled C phosphate can be classified as a new example of very desirable superionic conductors. Moreover, the high pressure studies reveal that compressing the PILs significantly improves their conduction properties at the same viscosity. Consequently, by squeezing the sample it is possible to transform poor ionic liquids into superionic liquids. The enhanced proton transport at the same viscosity or structural relaxation time should originate from the deformation of the hydrogen-bonded network under high pressure.

In summary, the examined carvedilol salts are new examples of PIL materials in which the ion transport can be strongly decoupled from structural relaxation. Their activation volumes of conductivity relaxation are considerably lower than the activation volume of structural relaxation, indicating an enhanced proton transport through the Grotthuss mechanism. The high pressure conductivity measurements combined with the $\eta(P)$ data, reveal that the fractional Walden rule and Stokes-Einstein relation are pressure dependent in PILs with the Grotthuss-type proton transport mechanism. In contrast, for verapamil HCl—a protic conductor in which decoupling of ionic transport from structural relaxation is pressure independent, the isobaric and isothermal data can superimpose onto each other. Additionally, the Walden plot analysis suggests that the examined carvedilol dihydrogen phosphate should be classified as a new example of superprotonic conductors, especially in the condition of high compression. This is because it exhibits high conductivity despite the fact that it contains ionic and neutral species.

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