Physicochemical study of diethylmethylammonium methanesulfonate under anhydrous conditions

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ABSTRACT

The protic ionic liquid diethylmethylammonium methanesulfonate ([DEMA][OMs]) was analyzed in depth by differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy,

Raman spectroscopy and broadband dielectric spectroscopy (BDS) under anhydrous conditions. Karl Fischer titration, NMR and FT-IR spectra confirmed the high purity of [DEMA][OMs]. The melting point (37.7 °C) and the freezing point (14.0 °C) obtained by DSC agree well with the values determined by BDS (40.0 °C and 14.0 °C). The dc conductivity (σ_{dc}) above the melting/freezing point obeys Vogel-Fulcher-Tammann (VFT) equation well and thus the proton conduction in [DEMA][OMs] is assumed to be dominated by the vehicle mechanism. In contrast, the σ_{dc} below the melting/freezing point can be fitted by the Arrhenius equation separately and therefore the proton conduction is most likely governed by the proton-hopping mechanism. The non-negligible influence of previously reported low water contents on the physicochemical properties of [DEMA][OMs] is found, indicating the importance of reducing water content as much as possible for the study of “intrinsic” properties of protic ionic liquids.

I. INTRODUCTION

Recently, protic ionic liquids (PILs), which are prepared by proton transfer from a Brønsted acid to a Brønsted base, have attracted research attention because of their excellent physicochemical properties which can include relatively low volatility, high thermal stability and high conductivity.¹⁻⁵ For these reasons PILs are widely used in fuel cells, sensors and supercapacitors, as well as in other electrochemical devices.⁶⁻¹⁰ PILs have proton-donor and proton-acceptor sites, which form a hydrogen-bonded network.^{2,11} Therefore, comprehensive studies of typical PILs will offer more knowledge about them.

The PIL [DEMA][OMs] has a σ_{dc} of $2.22 \times 10^{-2} \text{ S cm}^{-1}$ at 120 °C and was first reported by Nakamoto and Watanabe in 2007.¹² This compound has been investigated

as electrolytes or green solvents.^{12–21} Overall, the related studies can be divided into three groups. (1) The effect of the water content on the fundamental physical and chemical properties.^{13–16} For example, Schubert *et al.* studied the influence of water on the thermodynamic properties (*e.g.* vapor pressures, heat capacities, densities, and viscosities) of the binary mixtures of water and [DEMA][OMs].¹³ Martinelli *et al.* reported that the added water increased the self-diffusion of cations and anions and interacted primarily with the anion and slightly affected the ionicity of [DEMA][OMs].¹⁶ (2) The applications of [DEMA][OMs].^{17–19} For instance, Atilhan *et al.* showed that [DEMA][OMs] is suitable for pressure driven CO₂ capture processes that might lead to reduction in solvent regeneration cost.¹⁷ In addition, [DEMA][OMs] was employed to fill nano-pores of silica to enhance the ionic mobility.¹⁹ (3) Studies of the σ_{dc} and proton conduction mechanisms.^{19–21} Martinelli *et al.* found that the σ_{dc} of bulk [DEMA][OMs] obeys a VFT dependence, and that the charge transport mechanism is strongly associated with the vehicle mechanism.¹⁹ Yarger *et al.* measured the ionicity and transport properties of a series of diethylmethylaniline based PILs by nuclear magnetic resonance (NMR) spectroscopy, and concluded that the gas phase proton affinity is a better predictor of ionicity than the commonly used aqueous ΔpK_a .²⁰ Additionally, Krishnan *et al.* reported the proton transport mechanism (vehicle mechanism) of [DEMA][OMs] above the melting point.²¹

However, to the best of our knowledge, there have been no reports on the dielectric properties of [DEMA][OMs] and its proton conduction mechanisms below the melting/freezing point, restricting further understanding and applications of this PIL and its analogues. On other hand, the majority of previous reports^{13–19} used commercial [DEMA][OMs] (water content: around 7000 ppm¹⁸) as received without

further purification while other reports also indicated significant water content (*e.g.* about 2000 ppm²¹). Nevertheless, the influence of even lower water content on the physicochemical properties of [DEMA][OMs] has so far been **neglected**.

BDS can probe the electrical properties, (dielectric) relaxation phenomena and thermal phase transitions in a very wide range of temperatures and frequencies.²²⁻²⁴ Dielectric spectra can be represented in different ways, such as the (complex) permittivity, electrical conductivity spectra and the electric modulus, of which the electrical conductivity has the advantage of revealing the proton conduction mechanisms.²²⁻²⁴

In this paper, the thermal, spectroscopic and dielectric properties as well as the proton conduction mechanism of pure [DEMA][OMs] with an extremely low water content (98 ppm) was investigated in depth using DSC, NMR, FT-IR, Raman spectroscopy, and BDS (over a broad range of temperatures and frequencies). It is found that even a very low water content reported in the literature can still have non-negligible influence on the physicochemical properties of protic ionic liquids, indicating the importance of reducing water content as much as possible for the study of “intrinsic” properties of protic ionic liquids. The dielectric properties of [DEMA][OMs] and the proton conduction mechanisms below the melting/freezing point (in the solid state) are also investigated, which is a complement to previous studies.

II. EXPERIMENTAL DETAILS

A. Materials

[DEMA][OMs] ($[(\text{C}_2\text{H}_5)_2\text{CH}_3\text{NH}]^+[\text{CH}_3\text{SO}_3]^-$) was purchased from Iolitec Ionic Liquids Technologies GmbH (Heilbronn, Germany). [DEMA][OMs] was dried on a

Schlenk line *in vacuo* at 150 °C for 24 h to remove water and other volatile components. The purified samples were stored in a dry nitrogen environment prior to further characterizations.

B. Water content determination

The water content of dried [DEMA][OMs] was detected to be 98 ppm using a Mettler-Toledo C30S coulometric Karl Fischer titrator.

C. Differential scanning calorimetry (DSC)

DSC measurements were performed on a Mettler-Toledo DSC1 Star using hermetically sealed aluminum sample cups. DSC traces were obtained by performing heating and cooling cycles between $-70\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$ at a scanning rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Three consecutive heating/cooling cycles were measured for each test. The first two heating/cooling scans were performed to eliminate the thermal history. The melting point (T_m) and the freezing point (T_f) were assigned as the peak temperatures of the corresponding endothermic and exothermic peaks, respectively.

D. Fourier Transform Infrared (FT-IR) and Raman analysis

The FT-IR spectrum of [DEMA][OMs] at room temperature was measured between 3500 and 250 cm^{-1} with a resolution of 2 cm^{-1} using a Bruker VERTEX 70 FT-IR spectrometer equipped with a Platinum ATR accessory by accumulating 64 scans. Raman spectra between 3500 and 250 cm^{-1} were collected on the same FT-IR spectrometer Bruker Vertex 70 with a Raman module Bruker RAM II using a 250 mW laser source ($\lambda = 1064\text{ nm}$) at a resolution of 2 cm^{-1} with 64 scans.

E. Nuclear magnetic resonance (NMR) measurement

NMR spectra were measured on a Bruker AvanceTM III 400 MHz spectrometer at

ambient temperature. CDCl_3 was used as the solvent. ^1H -NMR (400 MHz, CDCl_3)/ppm: 10.30 (s, 1H); 7.30 (s, CDCl_3 solvent residual signal); 3.29–3.07 (m, 4H); 2.9–2.76 (m, 6H); 1.41 (t, $J = 7.28$ Hz, 6H), 0.00 (s, TMS reference). ^{13}C NMR (100.61 MHz, CDCl_3)/ppm: 77.20 (solvent residual signal); 50.32 (s); 39.35 (s); 38.88 (s); 9.13 (s); 0.00 (TMS reference).

F. Broadband dielectric spectroscopy (BDS)

The temperature and the frequency dependence of the complex conductivity of [DEMA][OMs] were studied by means of a Novocontrol BDS spectrometer with an active sample cell based on a high resolution impedance analyzer at frequencies between 421 mHz and 2.5 MHz. [DEMA][OMs] was placed in a stainless steel liquid cell and then heated from ambient temperature to 100 °C to ensure complete filling of the cell. The system was then cooled down to –100 °C. Afterwards, the sample was heated up again to 100 °C, and once again cooled down to –100 °C. In particular, the first two heating/cooling scans were performed to eliminate any thermal history effects. A Novocontrol Quatro Cryosystem was used to control the temperature by a dry nitrogen gas flow derived from liquid nitrogen. By correlating the amplitude and phase of the current passing through the dielectric sample capacitor with the applied AC voltage, the Alpha-Analyzer measured the complex impedance and capacity. Based on this data, the complex conductivity was calculated. The σ_{dc} was determined by a plateau in the conductivity vs. frequency plot in the usual way.^{23,24}

III. RESULTS AND DISCUSSION

A. Thermal analysis

The [DEMA][OMs] phase transitions are revealed by DSC measurements (Fig. 1). The melting point is 37.7 °C and the freezing point is 14.0 °C (both are peak

temperatures). The obtained melting and freezing points are in agreement with the values reported by other researchers. The melting point is significantly higher than the early reported value (10.6 °C),¹² which should be due to the high purity of [DEMA][OMs] we used. The entropy change, the enthalpy change and the melting or freezing point are correlated by Eq. (1):

$$\Delta S = \Delta H/T \quad (1)$$

where ΔS is the entropy change, ΔH the enthalpy change and T the melting or freezing temperature in Kelvin (K). The entropy changes at the melting and freezing points are calculated to be 18.2 J K⁻¹ mol⁻¹ and -37.8 J K⁻¹ mol⁻¹, respectively.

Figure 1. DSC thermograms of [DEMA][OMs] measured at 10 °C min⁻¹ for both the heating and cooling scans. The melting point is 37.7 °C and the freezing point is 14.0 °C (peak temperatures).

B. Structural analysis

Fig. 2 displays ¹H NMR spectrum of [DEMA][OMs] at ambient temperature. The resonance peaks a, b, c, d and e are associated with the diethylmethylammonium

cation, while peak f is related to the methanesulfonate anion. More specifically, peak a indicates the resonance associated with the exchangeable proton (N–H); it is the origin of conductive protons, which has a chemical shift of 10.3 ppm (s, 1H). Similarly, the chemical shifts of hydrogen atoms b, c, d, e and f are determined to be 3.24 ppm (m, 2H), 3.10 ppm (m, 2H), 2.83 ppm (s, 3H), 1.41 ppm (t, 6H) and 2.82 ppm (d, 3H), respectively. These results are in line with those reported by Martinelli *et al.* and Yarger *et al.*.^{19,20} It is noteworthy that the N–H proton is coupled with its neighboring methyl and methylene protons due to the multiplet peaks. The methylene protons may be unisochronous because they have different chemical shifts of 3.24 ppm (m, 2H) and 3.10 ppm (m, 2H), respectively. This phenomenon can be explained by the reason that the motion of alkyl side chains of the diethylmethylammonium cation is hindered by ionic interactions between the cations and the anions at ambient temperature due to the rotational barrier around the N–C bond.²⁵ The ratio of the integrated areas of peaks a, b, c, d, e and f are 1.01 : 2.00 : 2.05 : 2.99 : 6.00 : 3.01, which agree very well with the hydrogen atomic ratio of [DEMA][OMs]. The small additional peak at around 7.30 ppm is attributed to the residual signal of the solvent CDCl₃. No other peaks were detected, implying the absence of detectable impurities.

Figure 2. ^1H NMR spectrum of [DEMA][OMs] at ambient temperature. Insets: the chemical structure of [DEMA][OMs] and partial enlargement of the spectrum. The symbols a, b, c, d, e and f correspond to protons in different chemical environments. The small peak at around 7.30 ppm is ascribed to the residual signal of the solvent (CDCl_3).

For the ^{13}C NMR spectrum of [DEMA][OMs] (see Fig. S1, Electronic Supplementary Information), the resonance peaks labeled with “a”, “b” and “d” are associated with the cation, while the resonance peak marked with “c” is related to the methanesulfonate anion. The chemical shifts of carbon atoms a, b, c and d are confirmed to be 50.32 ppm (s), 39.35 ppm (s), 38.88 ppm (s), and 9.13 ppm (s), respectively. The ratio of the peak intensity matches the ratio of the number of carbon atoms for [DEMA][OMs]. The peak at around 77.20 ppm is due to the residual signal of the CDCl_3 solvent. These results confirm the purity of [DEMA][OMs].

C. Vibrational analysis

Fig. 3 shows FT-IR spectrum of [DEMA][OMs] at ambient temperature in the region between 250 and 3500 cm^{-1} . At high wavenumbers, there are weak bands due to the low absorptivity of C–H and N–H groups. On the contrary, some sharp and strong peaks are found at low wavenumbers, which are mainly caused by the vibrations of the [OMs] anion, especially for the C–H and S–O stretching modes. The absence of O–H stretching bands between 3400 and 3500 cm^{-1} demonstrates the extremely low water content.^{26,27} In addition, the broadening of the bands in the region of 2200 – 3200 cm^{-1} indicates a strong hydrogen-bonded network in

[DEMA][OMs].^{28,29} In the case of ammonium-based PILs, this region is also a characteristic of ammonium structures and is associated with N–H stretching.^{25,28,30}

Figure 3. FT-IR spectrum of [DEMA][OMs] at ambient temperature.

The Raman spectrum of [DEMA][OMs] is recorded at ambient temperature between 250 and 3500 cm^{-1} (see Fig. S2, Electronic Supplementary Information). Most of Raman peaks have their equivalents in the FT-IR spectrum. For peaks at 2709, 2504 and 2360 cm^{-1} in FT-IR spectrum, it is difficult to find the corresponding peaks in the Raman spectrum, indicating that some infrared active vibrational modes are not Raman active. The observed FT-IR and Raman peaks and tentative vibrational assignments of [DEMA][OMs] are shown in Table I.^{25,28,30–37}

Table I. Observed FT-IR and Raman peaks and tentative vibrational assignments of [DEMA][OMs]. The peak positions are given in cm^{-1} (as = antisymmetric; s = symmetric; str = stretching; bend = bending; def = deformation; wag = wagging; roc = rocking; twi = twist).

Infrared bands and their assignments			Raman bands and their assignments		
Wavenumber/ cm^{-1}	Assignments	References	Raman shifts/ cm^{-1}	Assignments	References

3010	as N-H str	25,30	3010	as N-H str	32
2989	as CH ₃ str	31,32	2985	as CH ₃ str	32
2938	as CH ₂ str	31,32	2937	as CH ₂ str	32
2890	s CH ₃ str	31,32	2894	s CH ₃ str	32
2841	s CH ₂ str	31,32	2836	s CH ₂ str	32
2709	s N-H str	25,30			
2504	N-H str	28			
2360	N-H str	28			
1481	CH ₂ def	32	1455	CH ₂ def	32
1420	as CH ₃ def	33	1427	as CH ₃ def	33
1224	as SO ₃ str	32	1233	as SO ₃ str	33
1151	C-N str	32	1168	C-N str	32
1031	s SO ₃ str	33	1038	s SO ₃ str	33
978	CH ₃ roc	33	978	CH ₃ roc	33
885	C-N str	32	886	C-N str	32
835	CH ₂ roc	32	837	CH ₂ roc	32
767	C-S str	34	774	C-S str	33
550	SO ₃ bend	35	553	SO ₃ bend	37
523	as SO ₃ def	35	525	as SO ₃ def	35
458	SO ₂ rock	36	461	SO ₂ rock	37
344	CH ₃ wag	33	339	CH ₃ wag	33

D. Conductivity analysis

Fig. 4 shows 3D graphs of the real part of complex conductivity (σ'), the in-phase component of conductivity, as a function of frequency and temperature. Two jumps of σ' can be found at higher frequencies as the temperature increases to 40 °C (Fig. 4a) or decreases to 14 °C (Fig. 4b), respectively. The freezing point has a hysteresis of

26 °C compared with the melting point. Clearly, the conductivity jumps at phase transitions of melting or solidification. These two temperatures represent the melting and freezing points of [DEMA][OMs] and agree well with the DSC results.

Figure 4. Three-dimensional (3D) graphs of the real part of complex conductivity (σ') as a function of frequency (from 0.421 Hz to 2.5 MHz) and temperature (between -90 °C and 100 °C) for the heating scan (a) and the cooling scan (b).

In addition, taking the melting point or the freezing point as the demarcation, these curves can be divided into two parts. In the vicinity of the region below the melting point or the freezing point, the frequency-dependent conductivity curves show a plateau over a broad range of frequencies. At further lower temperatures, a plateau can be observed at higher **frequencies**. By contrast, in the region above the melting point or the freezing point, the frequency-dependent conductivity curves first exhibit a lower plateau at lower frequencies, which is due to the electrode polarization that results from interfacial effects.²²⁻²⁴ Then they gradually climb to a higher and flat plateau at higher frequencies. The boundary between these two plateaus shifts to higher frequencies as the temperature increases.

Figure 5. σ_{dc} of [DEMA][OMs] as a function of the reciprocal temperature recorded during heating and cooling scans. The reported conductivities of [DEMA][OMs] from Ref. 19 and 21 are also shown.^{19,21} Water contents: 98 ppm (this work); ~7000 ppm (ref. 19); ~2000 ppm (ref. 21).

σ_{dc} can be obtained by fitting the plateau of conductivity curves. Fig. 5 plots σ_{dc} as a function of the reciprocal temperature. Overall, the values of σ_{dc} during the

heating and cooling processes overlap with each other except near the phase transition temperatures, and all curves are **nonlinear**. The σ_{dc} values of [DEMA][OMs] in the molten state are obviously lower than previously reported values because ionic conductivities are sensitive to water content (this work: 98 ppm; ref. 19: around 7000 ppm; ref. 21: around 2000 ppm),^{19,21} further confirming the high purity of the sample in this work. It has been shown that **the** water content (e.g. >7000 ppm)⁴ has significant influence on the physicochemical properties of [DEMA]-based PILs.^{4,16} However, the impact of even far lower water contents on [DEMA][OMs] have so far been neglected. From the dielectric perspective, this reveals that even a seemingly negligible water content reported in the literature (e.g. about 7000 ppm or 2000 ppm)^{19,21} can still have non-negligible influence on the physicochemical properties (e.g. the σ_{dc}) of protic ionic liquids, indicating the importance of reducing water content as much as possible for studying “intrinsic” properties of protic ionic liquids. In another way, [DEMA][OMs] with actually non-negligible water content (e.g. 2000 ppm) is in essence a “water-in-PIL” or “water-in-salt” system rather than a pure PIL.

Using extrapolation of the conductivity of [DEMA][OMs] as a function of added water at 25 °C, Martinelli *et al.*¹⁶ estimated the σ_{dc} of the anhydrous [DEMA][OMs] at 25 °C to be 3–4 mS cm⁻¹. It is shown here that during the cooling process in the supercooled liquid state (Fig. 5) the σ_{dc} of pure [DEMA][OMs] is 2.98 mS cm⁻¹ and 2.72 mS cm⁻¹ at 26 °C and 24 °C, respectively. Thus the ionic conductivity at 25 °C is determined to be 2.85 mS cm⁻¹ using interpolation method, which is in line with the extrapolated value, indicating again the high purity of our sample.

Figure 6. (a) VFT fit curves and (b) the activation energies (E_a) for the ionic conduction process in [DEMA][OMs] at temperatures above the melting/freezing point during the heating/cooling scan.

In order to further study the ionic conduction behavior, typical equations such as the Arrhenius equation and VFT law are used to fit the temperature dependence of the σ_{dc} . For the data above the melting/freezing point, the VFT equation³⁸⁻⁴⁰ shown in Eq. (2) is used to describe the ionic conduction behavior, as the temperature dependence of σ_{dc} shows a significant deviation from Arrhenius behavior:

$$\sigma_{dc}(T) = \frac{A}{\sqrt{T}} \exp\left(\frac{-B}{T-T_0}\right) \quad (2)$$

where A is proportional to the concentration of carrier ions, B the pseudo activation energy for ion conduction, and T_0 the ideal glass transition temperature or the Vogel temperature, at which free volume or configurational entropy becomes zero and ionic conduction is completely frozen.^{41,42} A , B and T_0 are all adjustable parameters. The VFT fit curves are shown in Fig. 6a with the corresponding parameters listed in Table II. The σ_{dc} as a function of the reciprocal temperature obeys the VFT equation very well with excellent correlation coefficients (R^2) (Table II). The fit value of T_0 is about 220 K for both processes. Because σ_{dc} follows the VFT equation and the ionic liquid is in the liquid state, the proton conduction is mainly governed by the vehicle mechanism.⁴³⁻⁴⁵ Interestingly, in the three cases of low water content (this work: 98 ppm; ref. 19: around 7000 ppm; ref. 21: around 2000 ppm), the ionic conduction in [DEMA][OMs] in the molten state all follows the vehicle mechanism,^{19,21} implying that the water content does not alter the proton conduction mechanism in the low water content region for [DEMA][OMs] in the molten state.

By performing partial differentiation of Eq. (2) in its logarithmic form with respect to T and noting Eq. (3), temperature-dependent activation energies (E_a) for the transport process of ionic conduction can be obtained, yielding Eq. (4).^{46,47}

$$E_a = RT^2(\partial \ln \sigma / \partial T) \quad (3)$$

$$E_a = RBT^2/(T-T_0)^2 - RT/2 \quad (4)$$

Clearly, E_a is a function of T because R , B and T_0 are constants in Eq. (4). Fig. 6b shows the temperature dependence of E_a of ionic conduction of [DEMA][OMs]. The E_a , which fall in the range between 10–50 kJ mol⁻¹, increase rapidly with decreasing

temperatures, which can be interpreted as due to the probability of ionic movement going to zero at T_0 rather than at 0 K according to the VFT equation (Eq. (2)).⁴² It is observed that E_a during the cooling scan are slightly higher than those during the heating scan.

Figure 7. Arrhenius curve-fitting of the σ_{dc} of [DEMA][OMs] in the low temperature range between -90 °C and 14 °C. The temperature range from 14 °C to 40 °C during the heating scan is **not** taken for fitting as it is near the melting transition, showing a deviation from Arrhenius behavior which is also observed in some other protic organic salts.^{2,7}

E_a in the solid (frozen) state is calculated using the Arrhenius equation (Eq. (5)):

$$\sigma_{dc}(T) = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where σ_0 is the pre-exponential factor in $S\ cm^{-1}$, E_a the activation energy in $kJ\ mol^{-1}$, and R the universal gas constant.² Both the heating and cooling curves can be divided into two parts: from -90 °C to -50 °C and then from -50 °C to 14 °C (heating scan); from 14 °C to -50 °C and subsequently from -50 °C to -90 °C (cooling scan). These

four parts are fitted separately.

Table II. Fit results of [DEMA][OMs] for both the heating and cooling processes.

Processes	$T/^{\circ}\text{C}$	$A/(\text{S K}^{1/2} \text{ cm}^{-1})$	B/K	T_0/K	$\sigma_0/(\text{S cm}^{-1})$	$E_a/(\text{kJ mol}^{-1})$	R^2 ^a
Heating	[+40,+100]	2.03	286	221	—	—	0.9999
	[−50,+14]	—	—	—	2.18×10^8	70.5	0.9991
	[−90,−50]	—	—	—	7.09×10^{14}	98.7	0.9993
Cooling	[+100,+14]	2.38	301	220	—	—	0.9999
	[+14,−50]	—	—	—	1.96×10^9	75.0	0.9999
	[−50,−90]	—	—	—	1.55×10^{15}	100	0.9991

^a R^2 : correlation coefficient for VFT or Arrhenius fit results.

The Arrhenius fit results are shown in Table II and Fig. 7. The excellent correlation coefficients indicate the curves obey the Arrhenius equation well. Interestingly, the temperatures of the crossover points that divide the respective heating or cooling scan into two parts are both -50°C , which agrees well with the calculated T_0 (about -53°C) obtained from the VFT curve-fitting (Table II). In fact, at the temperature of calculated T_0 , σ_{dc} is around $2.5 \times 10^{-9} \text{ S cm}^{-1}$. To some degree, it confirms that at T_0 the ionic conduction is frozen due to theoretically zero free volume.^{41,42} The Grothuss (proton hopping mechanism) and the vehicle mechanisms have been proposed to explain the proton conduction in solid compounds.^{48,49} Below the melting point and freezing point it is difficult to move freely for charge carriers. Additionally, the curves follow the Arrhenius equation well. Therefore, it could be inferred that the proton hopping mechanism is the underlying main proton conduction mechanism in the solid (frozen) state (e.g. from -90°C to 14°C).

IV. CONCLUSIONS

Diethylmethylammonium methanesulfonate ([DEMA][OMs]), a typical protic ionic liquid, has been systematically studied for its thermal, structural, spectroscopic,

and ionic conduction properties under anhydrous conditions. The purity of [DEMA][OMs] is confirmed by NMR and FT-IR spectra as well as the σ_{dc} . The resonance peaks of ^1H -NMR and ^{13}C -NMR spectra are identified, and the vibrational bands of FT-IR and Raman spectra are tentatively assigned. In addition, the melting point and the freezing point obtained by DSC agree well with the values detected by BDS. Based on BDS analysis, the freezing point shows a hysteresis of 26 °C compared with the melting point. Furthermore, the ionic conduction above the melting/freezing point obey the VFT equation well and proton conduction is thus dominated by the vehicle mechanism. It is found that the water content does not change the proton conduction mechanism in the low water content region of [DEMA][OMs] in the molten state. However, the previously reported low water contents are found to have non-negligible influence on the physicochemical properties (*e.g.* the σ_{dc}) of [DEMA][OMs], implying the importance of reducing water content as much as possible for the study of “intrinsic” properties of protic ionic liquids. The ionic conduction below the melting/freezing point could be fitted by the Arrhenius equation and the proton conduction is presumed to follow the proton-hopping mechanism. The findings are expected to provide some insights for the development of fuel cell electrolytes based on protic ionic liquids.

SUPPLEMENTARY MATERIAL

See the supplementary material for ^{13}C NMR and Raman spectra of [DEMA][OMs] at ambient temperature.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

1. M. S. Miran, M. Hoque, T. Yasuda, S. Tsuzuki, K. Ueno, and M. Watanabe, *Phys. Chem. Chem. Phys.* **21**, 418 (2019).
2. J. Luo, A. H. Jensen, N. R. Brooks, J. Sniekers, M. Knipper, D. Aili, Q. Li, B. Vanroy, M. Wübbenhorst, F. Yan, L. Van Meervelt, Z. Shao, J. Fang, Z.-H. Luo, D. E. De Vos, K. Binnemans, and J. Fransaer, *Energy Environ. Sci* **8**, 1276 (2015).
3. D. E. Smith, and D. A. Walsh, *Adv. Energy Mater.* **9**, 1900744 (2019).
4. K. Wippermann, J. Giffin, S. Kuhri, W. Lehnert, and C. Korte, *Phys. Chem. Chem. Phys.* **19**, 24706 (2017).
5. P. Jannasch, J. Rehmen, D. Evans, and C. Karlsson, *J. Phys. Chem. C* **123**, 23427 (2019).
6. N. Yaghini, I. Abdurrokhman, M. Hasania, and A. Martinelli, *Phys. Chem. Chem.*

- Phys. **20**, 22980 (2018).
7. X. Chen, H. Tang, T. Putzeys, J. Sniekers, M. Wubbenhorst, K. Binnemans, J. Fransaer, D. E. De Vos, Q. Li, and J. Luo, J. Mater. Chem. A **4**, 12241 (2016).
 8. J. Luo, O. Conrad, and I. F. J. Vankelecom, J. Mater. Chem. A **1**, 2238 (2013).
 9. J. Luo, T. V. Tan, O. Conrad, and I. F. J. Vankelecom, Phys. Chem. Chem. Phys. **14**, 11441 (2012).
 10. Z. Zhu, X. Yan, H. Tang, H. Cai, M. Pan, H. Zhang, and J. Luo, J. Power Sources **351**, 138 (2017).
 11. W. Xu, and C. A. Angell, Science **302**, 422 (2003).
 12. H. Nakamoto, and M. Watanabe, Chem. Commun. 2539 (2007).
 13. C. Römich, N. C. Merkel, A. Valbonesi, K. Schaber, S. Sauer, and T. J. S. Schubert, J. Chem. Eng. Data **57**, 2258 (2012).
 14. N. C. Merkel, C. Römich, R. Bernewitz, H. Künemund, M. Gleiß, S. Sauer, T. J. S. Schubert, G. Guthausen, and K. Schaber, J. Chem. Eng. Data **59**, 560 (2014).
 15. N. Merkel, C. Weber, M. Faust, and K. Schaber, Fluid Phase Equilibr. **394**, 29 (2015).
 16. N. Yaghini, M. N. Garaga, and A. Martinelli, Fuel Cells **16**, 46 (2016).
 17. M. Atilhan, B. Anaya, R. Ullah, L. T. Costa, and S. Aparicio, J. Phys. Chem. C **120**, 17829 (2016).
 18. M. N. Garaga, M. Persson, N. Yaghinia, and A. Martinelli, Soft Matter **12**, 2583 (2016).
 19. M. N. Garaga, L. Aguilera, N. Yaghini, A. Matic, M. Perssonc and A. Martinelli,

- Phys. Chem. Chem. Phys. **19**, 5727 (2017).
20. S. K. Davidowski, F. Thompson, W. Huang, M. Hasani, S. A. Amin, C. Austen Angell, and J. L. Yarger, J. Phys. Chem. B **120**, 4279 (2016).
21. J. L. Lebga Nebane, S. E. Rock, J. Franclemont, D. Roy, and S. Krishnan, Ind. Eng. Chem. Res. **51**, 14084 (2012).
22. F. Kremer, and A. Schonhals, Broadband Dielectric Spectroscopy, Springer, Berlin, (2003).
23. M. Wübbenhorst, and J. van Turnhout, J. Non-Cryst. Solids **305**, 40 (2002).
24. J. Leys, M. Wübbenhorst, C. Preethy Menon, R. Rajesh, J. Thoen, C. Glorieux, P. Nockemann, B. Thijs, K. Binnemans, and S. Longuemart, J. Chem. Phys. **128**, 064509 (2008).
25. M. Kazuki, H. Syu, Y. Tomoaki, and S. Kazuhisa, B. Chem. Soc. Jpn. **83**, 328 (2010).
26. J. Luo, O. Conrad, and I. F. J. Vankelecom, J. Mater. Chem. **22**, 20574 (2012).
27. J. P. Belieres, and C. A. Angell, J. Phys. Chem. B **111**, 4926 (2007).
28. J. Luo, J. Hu, W. Saak, R. Beckhaus, G. Wittstock, I. F. J. Vankelecom, C. Agert, and O. Conrad, J. Mater. Chem. **21**, 10426 (2011).
29. A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y. M. Tan, T. Welton, and J. A. Zora, J. Chem. Soc., **Dalton Trans.** 3467 (1995).
30. E. S. Stoyanov, K. C. Kim, and C. A. Reed, J. Am. Chem. Soc. **128**, 8500 (2006).
31. J. Pacansky, W. Koch, and M. D. Miller, J. Am. Chem. Soc. **113**, 317 (1991).
32. A. L. Verma, Spectrochim. Acta, **27**, 2433 (1971).

33. J. H. R. Clarke, and L. A. Woodward, *Trans. Faraday Soc.* **62**, 2226 (1966).
34. E. Davies, Y. Huang, J. B. Harper, J. M. Hook, D. S. Thomas, I. M. Burgar, and P. J. Lillford, *Int. J. Food Sci. Tech.* **45**, 2502 (2010).
35. D. H. Johnston and D. F. Shiver, *Inorg. Chem.* **32**, 1045 (1993).
36. S. P. Gejji, K. Hermansson, and J. Lindgren, *J. Phys. Chem.* **97**, 6986 (1993).
37. J. R. Durig, L. Zhou, T. Schwartz, and T. Gounev, *J. Raman Spectrosc.* **31**, 193 (2000).
38. H. Vogel, *Phys. Z.* **22**, 645 (1921).
39. G. S. Fulcher, *J. Am. Ceram. Soc.* **8**, 339 (1925).
40. G. Tammann, and W. Z. Hesse, *Z. Anorg. Allg. Chem.* **156**, 245 (1926).
41. S. Seki, M. A. B. H. Susan, T. Kaneko, H. Tokuda, A. Noda, and M. Watanabe, *J. Phys. Chem. B* **109**, 3886 (2005).
42. C. A. Angell, *J. Electrochem. Soc.* **112**, 1224 (1965).
43. A. Noda, M. A. B. H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu, and M. Watanabe, *J. Phys. Chem. B* **107**, 4024 (2003).
44. W. Münch, K. D. Kreuer, W. Silvestri, J. Maier, and G. Seifert, *Solid State Ionics* **145**, 437 (2001).
45. J. Lin, L. Wang, T. Zinkevich, S. Indris, Y. Suo, and C. Korte, *Phys. Chem. Chem. Phys.* **22**, 1145 (2020).
46. J. R. Sanders, E. H. Ward, and C. L. Hussey, *J. Electrochem. Soc.* **134**, 325 (1986).

47. K. Wippermann, J. Wackerl, W. Lehnert, B. Huber, and C. Korte, *J. Electrochem. Soc.* **163**, F25 (2016).
48. K. D. Kreuer, *Chem. Mater.* **8**, 610 (1996).
49. P. Colomban, *Proton Conductors: Solids, Membranes and Gels—Materials and Devices*, Cambridge University Press, Cambridge (1992).

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