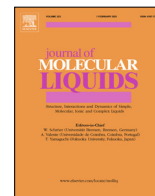




Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Translational and reorientational dynamics of ionic liquid-based fluorine-free lithium-ion battery electrolytes

Oleg I. Gnezdilov^a, Andrei Filippov^{b,c,*}, Inayat Ali Khan^c, Faiz Ullah Shah^{c,*}

^a Institute of Physics, Kazan Federal University, 420008 Kazan, Russia

^b Medical and Biological Physics, Kazan Medical University, 420012, Kazan, Russia

^c Chemistry of Interfaces, Luleå University of Technology, SE-97187 Luleå, Sweden

ARTICLE INFO

Article history:

Received 4 March 2021

Revised 20 June 2021

Accepted 12 July 2021

Available online xxx

Keywords:

Diffusion

Ionic liquid electrolytes

Lithium salt doping effect

Reorientational dynamics

ABSTRACT

The translational as well as reorientational mobilities of fluorine-free electrolytes prepared by mixing lithium furan-2-carboxylate Li(FuA) salt with tetra(*n*-butyl)phosphonium furan-2-carboxylate (P₄₄₄₄) (FuA) ionic liquid are thoroughly investigated. The diffusivity of ions and T_1 relaxation of protons belonging to various chemical groups of (P₄₄₄₄)⁺ and (FuA)⁻ ions and the Li⁺ ion present in these electrolytes are measured as a function of lithium salt concentration and temperature. The temperature dependence of correlation time for reorientational mobility of various chemical groups of (P₄₄₄₄)⁺ and (FuA)⁻ ions and the Li⁺ ion are estimated and used in calculations temperature dependence of the corresponding reorientational rates. It is shown that an increase in the concentration of lithium salt leads to a decrease in both the diffusion coefficients and the reorientation rates for all the chemical groups in concerted way. Activation energy of the reorientational rates for different chemical groups of the organic ions and the Li⁺ are discussed in details.

© 2021 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Ionic liquid-based electrolytes are emerging as promising electrolytes for lithium-ion batteries due to their unique properties such as negligible volatility, non-flammability, high thermal and electrochemical stability, high ionic conductivity, low melting point, and structural designability [1–7]. The structural designability of ionic liquids (ILs) is facilitating their tunability for various electrochemical applications. In the context of electrolytes, the addition of Li-salts to ILs is changing their physicochemical properties by the interactions between Li⁺ ions and the anions of ILs and thus effecting their overall performance as electrolytes in batteries. Therefore, a thorough understanding of the Li⁺ ion interactions with the anions of ILs is of utmost importance before their application in batteries.

Understanding the molecular basis of ionic conductivity of ionic liquid – lithium salt solutions have attracted extensive attentions during the last two decades due their increasing electrochemical energy storage applications [4–17]. Microstructures [18,19], ionic mobility [4–12] and cation–anion interactions in ionic liquids-

based lithium-ion battery electrolytes with fluorinated anions have been extensively studied. However, fluorinated anions have high risk of decomposition and formation of hydrofluoric acid and thus adversely affect the environment, service life and overall performance of a battery [20,21].

The translational dynamics of individual ions in the microscopic scale lengths is studied by using pulsed-field gradient spin-echo (PGSE) ¹H and ⁷Li NMR [5–10,17,22,23], while re-orientational correlation times in the molecular level scale are obtained from temperature dependences of longitudinal NMR relaxation times of corresponding “magnetic” nuclei [8,24,25]. These studies have proposed the plausible mechanisms of ionic mobility and Li⁺ ion transference behaviour within the conventional ionic liquid-based electrolytes. Bearing in mind the significance of electrochemical energy storage devices, the development of new ionic liquid-based electrolytes that are fluorine-free and potentially safe are urgently required to improve both the performance and service life of next-generation batteries.

This study is focused on the investigation of translational and reorientational dynamics of novel ionic liquid-based electrolytes comprising fluorine-free anion, furan-2-carboxylate, that is derived from lignocellulosic biomass. The 2-furoate anion is produced from furfural, a product of the dehydration of sugars present in various agricultural byproducts [26,27]. The aromatic furan-2-carboxylate anion in combination with a phosphonium cation offers high ther-

* Corresponding authors at: Chemistry of Interfaces, Luleå University of Technology, SE-97187 Luleå, Sweden (A. Filippov, F. U. Shah).

E-mail addresses: andrei.filippov@ltu.se (A. Filippov), faiz.ullah@ltu.se (F. Ullah Shah).

<https://doi.org/10.1016/j.molliq.2021.117001>

0167-7322/© 2021 The Author(s). Published by Elsevier B.V.

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

mal stability, acceptable ionic conductivity, and wide electrochemical stability window, which are the desirable features of electrolytes for Li-ion batteries [28]. A simple, economical, and environmentally benign synthetic procedure using water as a solvent can prepare this IL. The electrochemical properties of the mixtures of lithium furan-2-carboxylate Li(FuA) salt with tetra(*n*-butyl)phosphonium furan-2-carboxylate (P₄₄₄₄)(FuA) in different molar ratios are recently reported [23]. In this study, the influence of Li(FuA) salt concentration in (P₄₄₄₄)(FuA) IL on the reorientational and translational ionic mobilities is studied by ¹H and ⁷Li PGSE-NMR to understand the underlying mechanisms of interactions between different ionic species in the electrolyte.

2. Materials and methods

2.1. Sample preparation

Chemical syntheses of tetra(*n*-butyl)phosphonium furoate (P₄₄₄₄)(FuA) IL and lithium furoate salt Li(FuA) are described earlier [23,28,29]. The purity and successful synthesis of both the Li-salt and the IL are confirmed by NMR. The structures and abbreviations of the ionic components of these electrolytes are shown in Fig. 1. The electrolytes are prepared by mixing 2.5 to 10 mol% of Li(FuA) with (P₄₄₄₄)(FuA) IL. All the samples were kept in a vacuum oven at 60 °C for 5 days until the water content was less than 280 ppm as determined by Karl Fischer titration (using Metrohm 917 Coulometer).

2.2. NMR diffusion and relaxation measurements

Pulsed gradient spin echo-nuclear magnetic resonance (PGSE-NMR) measurements were executed on a Bruker Avance III (Bruker BioSpin AG) NMR spectrometer. The working frequencies were 400.21 MHz for ¹H and 155.53 MHz for ⁷Li. The ⁷Li NMR spectra were indirectly referenced to 1.0 M LiCl(aq). NMR self-diffusion measurements were performed on ¹H and on ⁷Li with a PGSE-NMR probe Diff50 (Bruker).

The sample was placed in a standard 5 mm glass sample tube and closed with a plastic stopper to avoid direct contact with air. Prior to each measurement, the sample was equilibrated at a specific temperature for 30 min. The diffusional decays (DDs) were recorded using the stimulated echo (StE) pulse train. For single-component diffusion, the form of the DD can be described as [30]:

$$A(\tau, \tau_1, g, \delta) \propto \exp\left(-\frac{2\tau}{T_2} - \frac{\tau_1}{T_1}\right) \exp(-\gamma^2 \delta^2 g^2 D t_d) \quad (1)$$

Here, A is the integral intensity of the NMR signal, τ is the time interval between first and second radiofrequency pulses, τ_1 is the time interval between second and third radiofrequency pulses, T_1 and T_2 are longitudinal and transverse NMR relaxation times, respectively. γ is the gyromagnetic ratio for the magnetic nuclei (¹H and ⁷Li); g and δ are the amplitude and the duration of the gradient pulse; $t_d = (\Delta - \delta / 3)$ is the diffusion time; Δ is the time interval between two identical gradient pulses. D is the diffusion

coefficient. In the measurements, the duration of the 90° pulse was 7 μs, δ was in the range of (0.5 ÷ 2) ms, τ was in the range of (3 ÷ 5) ms, and g was varied from 0.06 up to the maximum of the gradient amplitude, 29.73 T m⁻¹. Diffusion time t_d was varied from 4 to 100 ms for the ¹H diffusion and in the range 200–700 ms for ⁷Li diffusion. The repetition time during accumulation of signal transients was 3.5 s.

¹H and ⁷Li T_1 NMR relaxation time measurements were performed with inversion-recovery (180°-τ-90°-Acq.) pulse sequence. Measurements were performed in the range of temperatures 293–363 K. Data was processed using Bruker Topspin 3.1 software.

3. Results and discussion

3.1. Ion diffusion

The ¹H NMR spectrum of the [Li(FuA)]_{0.025}[(P₄₄₄₄)(FuA)]_{0.975} electrolyte is shown in Fig. 2. The spectrum has ¹H resonance lines corresponding to the protons of methylene and methyl groups of the (P₄₄₄₄)⁺ cation: P-CH₂- (2.42 ppm), -CH₂-CH₂- (1.49 ppm) and -CH₃ (0.93 ppm), and the protons of (FuA)⁻ anion: 1 (7.34 ppm), 2 (6.89 ppm) and 3 (6.33 ppm). The lithium NMR spectrum of Li(FuA) has one resonance line at ~0.28 ppm (Fig. S3 in the ESI). Upon addition of Li(FuA) salt to the (P₄₄₄₄)(FuA) IL, two prominent changes are observed such as resonance line down-field shift and peak broadening suggesting that the local environment of Li⁺ ion changes [23].

The diffusional decays (DDs) for the electrolytes with all Li(FuA) concentrations and temperatures demonstrated single-exponential form, (Eq.(1)). A number of measurements are performed in the diffusion time range 4–100 ms and showed no time dependence of the form and slope of the DDs. Diffusion coefficients are obtained from DDs by fitting with Eq.(1). The variation of diffusion coefficients as a function of temperature is shown in Fig. 3.

The diffusion coefficients of ions in these electrolytes decrease in the order (FuA)⁻ > (P₄₄₄₄)⁺ > Li⁺ (Fig. 3). There is a quantitative correlation between ion diffusivity and size of the ions in these electrolytes: the bulkier (P₄₄₄₄)⁺ cation diffuses slower than (FuA)⁻ anion, which is in accordance with the previous study [23]. The diffusion coefficient of Li⁺ is less than both the organic ions, despite the fact that its size is almost a decimal order smaller than the organic ions. The dynamics of individual ions can be explained by the fast exchange of bound (in (P₄₄₄₄)(FuA) or the associates)

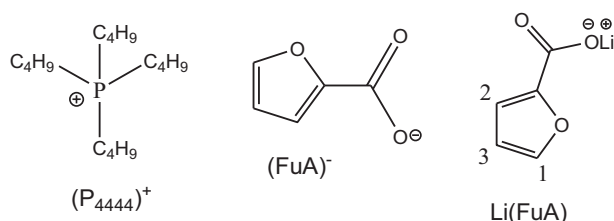


Fig. 1. Chemical structures of IL ions and Li-salt used in this study.

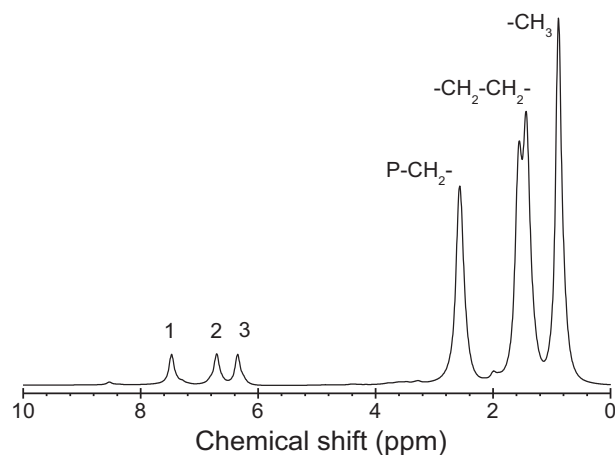


Fig. 2. ¹H NMR spectrum of [Li(FuA)]_{0.025}[(P₄₄₄₄)(FuA)]_{0.975} electrolyte with assignment of signals from protons of different chemical groups from (P₄₄₄₄)⁺ cation and (FuA)⁻ anion.

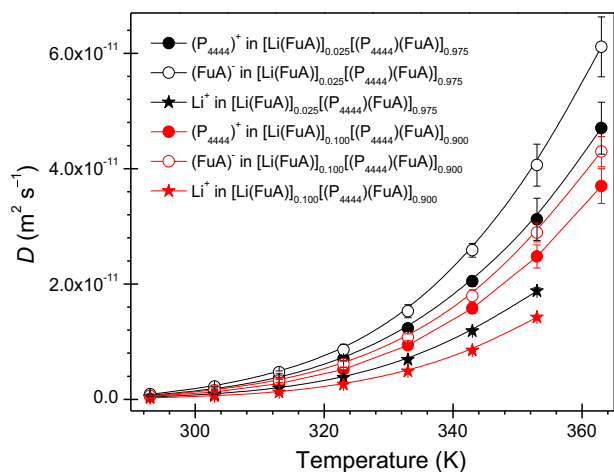


Fig. 3. Diffusion coefficients D of ions in 2.5 mol% Li-salt and 10 mol% Li-salt electrolytes.

and free states of the $(P_{4444})^+$ cation and $(FuA)^-$ anion. However, the lifetime of ions in these electrolytes is less than the minimal diffusion time of the experiment (4 ms) and the ionic diffusivity is provided by fast mobility of the free ions $(P_{4444})^+$ and $(FuA)^-$ [23]. An increase in Li(FuA) salt concentration leads to a monotonous decrease in the diffusion coefficients of $(P_{4444})^+$, $(FuA)^-$ and Li^+ over the whole studied range of Li salt concentrations. The same effect has been observed earlier for different ionic liquids-based electrolytes [6–8,17,24,31]. The $(P_{4444})^+$ and $(FuA)^-$ ions present in the associates are in the conditions of fast-exchange with the surrounding ions, while the Li^+ ions are found to be in slow-exchange with the surrounding ions and remain mainly in the associates [23].

3.2. T_1 NMR relaxation

Longitudinal (spin–lattice) NMR relaxation (T_1) of magnetic nuclei is conditioned by the reorientational mobilities of corresponding chemical groups [32]. Thus, T_1 relaxation reveals changes in a chemical group reorientation rates occurring with variation of the chemical composition and temperature. Hayamazu *et al.* have reported on the translational (self-diffusion) and local (reorientational correlation times of ions, τ_c , obtained from spin-lattice NMR relaxation, T_1) molecular motions of cations and anions in two selected ILs based on $(BF_4)^-$ anion and either $(EMIm)^+$ or $(BMIm)^+$ cations [25]. They have demonstrated that translational diffusion of cations is related to the molecular librational motion, while self-diffusion of $(BF_4)^-$ is predominantly coupled with the reorientational motion. A similar set of NMR techniques has been used to study both the rotational and the translational motions of methylimidazolium cations combined with bis(trifluoromethanesulfonyl)amide and bis(fluorosulfonyl)amide anions and their corresponding binary mixtures with lithium salts [33].

Temperature dependences of the longitudinal NMR relaxation time T_1 for protons of different chemical groups within $(P_{4444})^+$ cation, $(FuA)^-$ anion and also that of Li^+ ion are presented in Figs. 4–6. Minima on T_1 for protons of chemical groups of ions are inside or just near the range of the experimental temperatures (Figs. 4–6). The values and the corresponding temperatures for minima of T_1 of protons of different chemical groups of ions are shown in Table 1.

Here minima for anions are located at temperatures $1000/T \sim 3.4$ ($T \sim 272$ K) and T_1 at minimum is ~ 700 ms. An increase in temperature in the range from 293 K to 363 K has a stronger

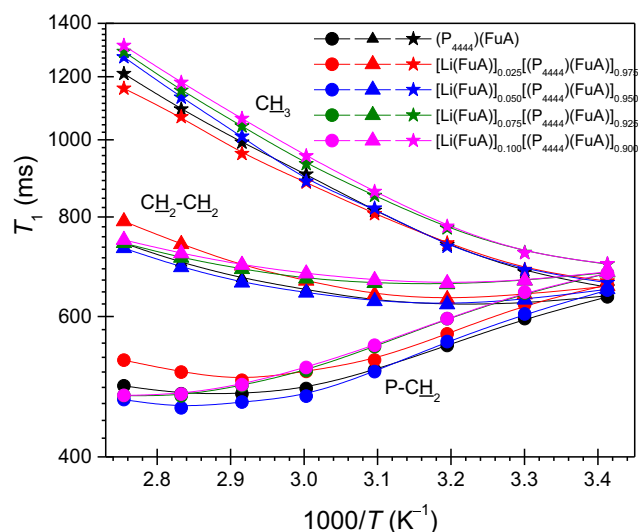


Fig. 4. T_1 for protons of the $(P_{4444})^+$ cation in the neat IL and in the electrolytes.

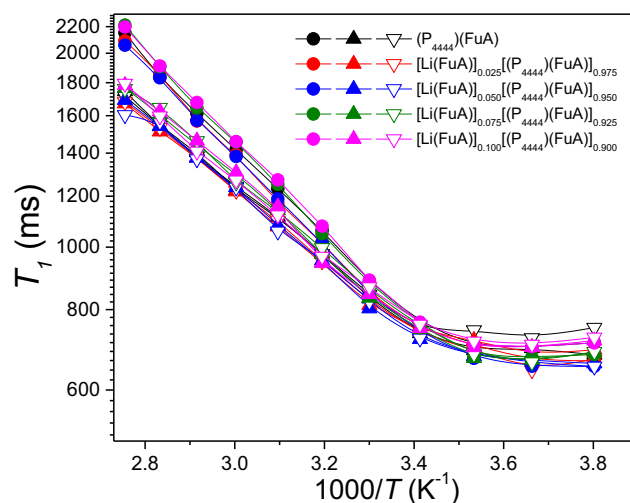


Fig. 5. T_1 for protons of the aromatic $(FuA)^-$ anion in the neat IL and in the electrolytes. Symbols correspond to proton of groups 1 (circles), 2 (up triangles) and 3 (down triangles).

effect on the T_1 of proton at position 1 than that of positions 2 and 3. This is related to the higher activation energy for local motion of the proton at position 1. There is a clear trend of increasing T_1 with an increase in Li(FuA) salt concentration and the effect is more prominent in the higher temperatures. The variation of T_1 with Li(FuA) salt concentration at lower temperatures is $\sim 4.1\%$ of its mean value, while at higher temperatures the variation of T_1 is $\sim 28\%$ of the mean value. Fig. 6 represents a temperature dependence for T_1 of Li^+ ion. Here, the minima for Li^+ ion are at temperatures 373 K and T_1 at minimum is ~ 40 ms. In the low-temperature range, T_1 increases with the concentration of Li(FuA) salt by $\sim 18\%$. In the electrolyte system composed of cross-linked poly(ethylene oxide-propylene oxide) random copolymer and glymes doped with $LiN(SO_2CF_3)_2$ salt, the T_1 of Li^+ ion at minimum (~ 323 K) is ~ 0.15 s [24]. Another study revealed that the minimum of T_1 is reached at 293–323 K with the T_1 values of 0.2–0.5 s for three quaternary ammonium ILs doped with Li salt [8].

The predominant T_1 relaxation mechanism is assumed to be the spin-rotation. Since H has a spin $I = 1/2$, the dipolar-dipolar relaxation mechanism determines the T_1 of protons. The classical

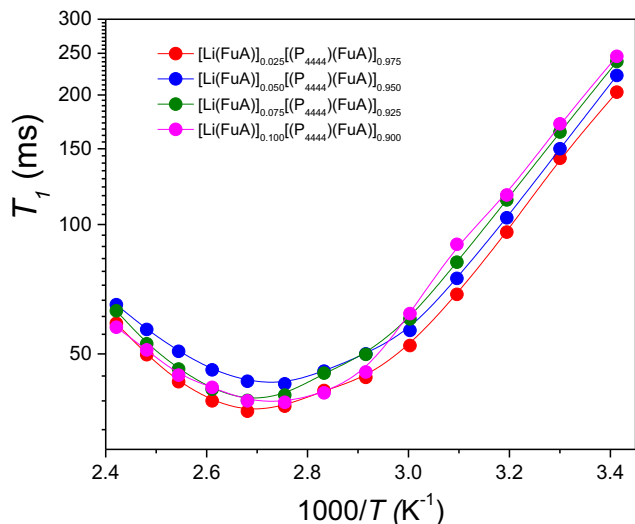


Fig. 6. T_1 for Li^+ in the electrolytes with different concentrations of $\text{Li}(\text{FuA})$.

Bloembergen, Purcell and Pound equation [34] can be used to estimate the correlation time τ_c for the motion of dipoles:

$$\frac{1}{T_1} = C \left(\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{4\omega_0^2 \tau_c^2} \right) \quad (2)$$

where ω_0 is the observed frequency and τ_c is the correlation time of the dipolar interaction. C is:

$$C = \frac{3}{10} \gamma^4 \hbar^2 \sum_j \frac{1}{r_j^6} \quad (3)$$

where r is the atomic distance between protons. The term $\omega_0 \tau_{c0} = 0.616$ at minimum of T_1 . Therefore, correlation times at minima for the protons of the organic ions and lithium are $\tau_{c0}(\text{H}) \sim 2.45 \cdot 10^{-10}$ s and $\tau_{c0}(\text{Li}) \sim 6.31 \cdot 10^{-10}$ s, respectively. Minima for $(\text{P}_{4444})^+$ cation are: CH_3 ($1000/T \sim 3.45$, $T \sim 290$ K) with the relaxation times T_1 at the minimum in the range 650–700 ms; $\text{CH}_2\text{-CH}_2$ ($1000/T \sim 3.3$; $T \sim 303$ K) and shifted to ($1000/T \sim 3.15$, $T \sim 318$ K) with a trend to increase T_1 from 630 to 670 ms as the concentration of $\text{Li}(\text{FuA})$ increases to 7.5 and 10 mol%; and P-CH_2 ($1000/T \sim 2.85$, $T \sim 351$ K) T_1 at minimum is near 480 ms. Values of correlation times of chemical groups of $(\text{P}_{4444})^+$ calculated using Eq.(2) are presented in Fig. S4 of the ESI. The constant C in Eq.(2) is calculated from the minima of T_1 (Fig. 4,5) and it is in the range from $2.71 \cdot 10^9$ to $3.7 \cdot 10^9$ Hz for the protons of $(\text{P}_{4444})^+$ cation and $\sim 2.5 \cdot 10^9$ Hz for the protons $(\text{FuA})^-$ anion. These values are matching well to the values of for Li doped electrolytes reported earlier [8,24,25]. The calculated values of correlation times are presented in Fig. S4 of the ESI.

The contribution of quadrupolar interactions in the spin–lattice relaxation is the strongest one for viscous liquids [35]. The change in Li^+ ($I = 3/2$) T_1 with correlation time closely follow [36]:

$$\frac{1}{T_1} = \frac{\omega_Q^2}{50} \left(\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right) \quad (4)$$

where $\omega_Q = 2\pi\nu_Q$ is the hyperfine quadrupolar coupling constant. It is assumed based on the Li^+ ion cubic symmetry that the T_1 relaxation is related also with the translation diffusion of this ion: one-flip time of the translational displacement [8]. It is not straight forward to calculate ω_Q , which is very important in calculating the correlation time from the model described by the Eq. (4). To do this, we used several approaches as described here in details. The first approach is based on the measurement of outer sidebands of ^7Li solid-state state MAS NMR spectrum [35]. Because the studied system is liquid, we measured ^7Li MAS NMR spectrum of the solid $\text{Li}(\text{FuA})$ in the temperature range from 283 to 323 K. The two representative ^7Li MAS NMR spectra of the $\text{Li}(\text{FuA})$ salt are shown in Fig. S5 of the ESI. The value of the most outset sideband does not depend on temperature and gives $\nu_Q \sim 130$ kHz. In another approach, the factor before brackets in Eq.(4) is directly estimated from the temperature and the value of minimum T_1 in Fig. 6 and Table 1. In this case, $(\omega_Q)^2/50$ is $1.71 \cdot 10^{10}$ Hz^2 that corresponds to $\nu_Q = 147$ kHz. The minimum of T_1 is reached at 373 K and the values of correlation times are in the range from $1.4 \cdot 10^{-9}$ to $1.5 \cdot 10^{-8}$ s. This is a range of typical correlation times of Li^+ in various electrolytes [8,24]. For example, the correlation times for Li^+ are in the range from $5 \cdot 10^{-10}$ to $8 \cdot 10^{-9}$ s [24] and in the range from $2 \cdot 10^{-10}$ to $3 \cdot 10^{-9}$ s [8] in previously studied electrolytes. The temperature dependences of correlation times in Arrhenius coordinates for all the ions in the electrolytes with the minimum (2.5 mol%) and maximum (10 mol%) concentrations of Li salt are shown in Fig. 7.

3.3. Reorientational rates and diffusion

For comparison with another type of molecular motion, translational motion, the rates of reorientation ($1/\tau_c$) are more convenient than correlation times. Therefore, dependences obtained for correlation times are recalculated for those of rates of reorientation. The dependences of $1/\tau_c$ on the temperature are shown in Arrhenius coordinates in Fig. 8 (left ordinate) alongside with diffusion coefficients for comparison from Fig. 3 (right ordinate).

Fig. 8 represents the dependence of rates of reorientation of chemical groups in cation, anion and Li^+ on the temperature and concentration of $\text{Li}(\text{FuA})$ salt. Generally, the trend resembles to that of ionic diffusivity: $D_{(\text{FuA})^-} > D_{(\text{P}_{4444})^+} > D_{\text{Li}^+}$. Here, $1/\tau_{c(\text{FuA})^-} > 1/\tau_{c(\text{P}_{4444})^+} > 1/\tau_{c\text{Li}^+}$. However, within each ion there are also dependences of the reorientation rates on chemical group belonging to the ion. The rates of reorientations for the $(\text{P}_{4444})^+$ cation follow the order: $\tau_c^{-1}(\text{CH}_3^-) > \tau_c^{-1}(-\text{CH}_2\text{-CH}_2^-) > \tau_c^{-1}(\text{P-CH}_2^-)$, and for the $(\text{FuA})^-$ anion: $\tau_c^{-1}(1) > \tau_c^{-1}(2) \sim \tau_c^{-1}(3)$.

The addition of Li^+ ion decreases the rate of reorientation of all the chemical groups present in $(\text{P}_{4444})^+$ cation and $(\text{FuA})^-$ anion. It is highest for P-CH_2^- (by a factor of ~ 1.2), while for the other groups it is less (by a factor of ~ 1.05). Therefore, the effect of Li^+ addition to the electrolytes on the rate of reorientation is much less than that in the case of ion diffusivity. The addition of Li^+ ion also

Table 1

T_1 relaxation of chemical groups of ions in the $[\text{Li}(\text{FuA})]_x[(\text{P}_{4444})(\text{FuA})]_{1-x}$ electrolytes.

Ionic species	$(\text{P}_{4444})^+$			$(\text{FuA})^-$			Li^+
	CH_3^-	$-\text{CH}_2-\text{CH}_2^-$	P-CH_2^-	1	2	3	
Temperature at T_1 min, K	290	303–318	351	272	272	272	373
T_1 min (ms), for neat IL	650	630	480	700	697	705	
T_1 min (ms), for 2.5 mol% Li salt	664	630	480	666	693	644	36.8
T_1 min (ms), for 5.0 mol% Li salt	668	640	480	663	660	663	42.6
T_1 min (ms), for 7.5 mol% Li salt	698	650	477	675	668	663	39.0
T_1 min (ms), for 10 mol% Li salt	698	660	478	701	700	706	38.6

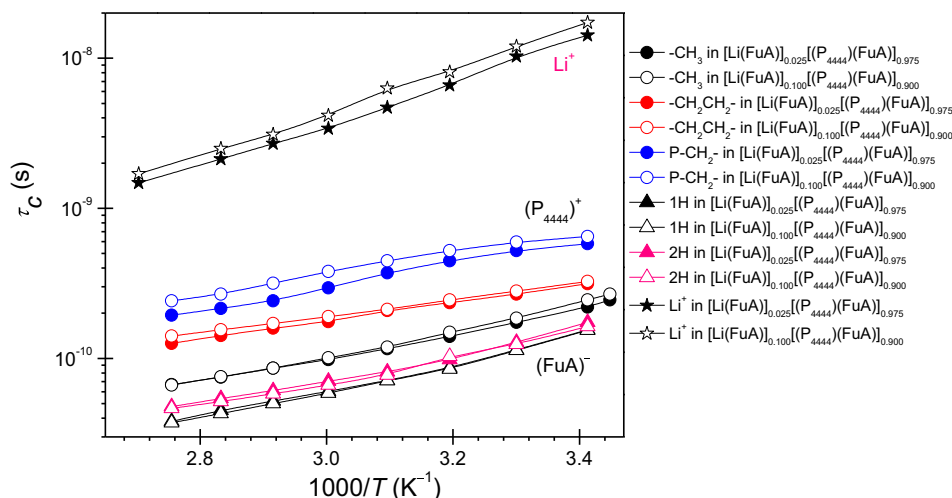


Fig. 7. Correlation times of local mobility as calculated for different chemical groups of the $(P_{4444})^+$ cation, $(FuA)^-$ anion and Li^+ ion in the electrolytes. The 1H and 2H are the furan ring protons from 1H NMR chemical shifts as shown in Figs. 1 and 2.

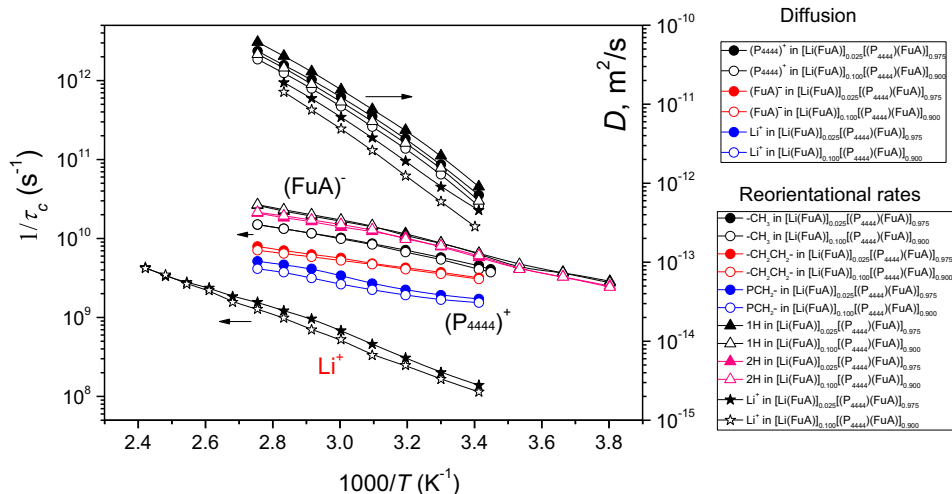


Fig. 8. Reorientation of chemical groups of $(P_{4444})^+$, $(FuA)^-$ and Li^+ (calculated from correlation times, Fig. 7) for chemical groups of different ions in the electrolytes (left ordinate). The temperature dependences of diffusion coefficients of the correspondent ions are shown for comparison (right ordinate). The 1H and 2H are the furan ring protons from 1H NMR chemical shifts as shown in Figs. 1 and 2.

decreases the rate of reorientation of Li ions $\tau_c^{-1}(Li^+)$ by a factor ~ 1.26 .

However, an increase in temperature leads to a monotonous increase in the intensity of different types of motion (such as reorientational and ion diffusion) due to their thermal activation. Non-Arrhenius dependences are observed in $[Li(FuA)]_x[(P_{4444})(FuA)]_{1-x}$ electrolytes for diffusion coefficients that are typical for many ionic liquids [6–8,25,29,37,38]. The dependences have non-linear and convex form in the Arrhenius plot. This form, is supposedly, conditioned by the dynamic glass-transition temperature, $T_0 \gg 273$ K. Dynamic glass-transition temperatures obtained from NMR data are usually higher than that obtained from mechanical (viscosity) measurements. Glass transition temperature T_0 in a broad sense is the temperature below which certain type of motion is hindered or lacking due to a lowered thermal energy and the absence of needed free volumes for such type of motion. Therefore, T_0 may depend on the type of motion: for example, when the temperature is low enough, molecules may not diffuse, while reorientations of chemical groups might take place. If the temperature is decreased further, reorientation motion will also be stopped. Previously, the convex temperature dependence of diffusion coefficients for the

$[Li(FuA)]_x[(P_{4444})(FuA)]_{1-x}$ electrolytes (Fig. 8) is analyzed [23], and the T_0 and apparent activation energies for diffusion of ions are estimated using Vogel-Fulcher-Tammann (VFT) equation in the form for ion diffusivity [39]:

$$D = D_0 \exp\left(\frac{-E_D}{R(T - T_0)}\right) \quad (5)$$

where T_0 is an adjustable parameter and E_D is the apparent activation energy for diffusion, R is the gas constant. The values of T_0 and E_D obtained from data of Fig. 3 in such analysis are presented in the Table 2. As it is clear from Fig. 8, the dependence of reorientational rates τ_c^{-1} on temperature is also convex. Therefore, to describe these dependences we can, similar to the ion diffusion data, use a VFT type of equation for the reorientational rates:

$$\tau_c^{-1} = \tau_{c0}^{-1} \cdot \exp\left(\frac{-E_a^r}{R(T - T_0)}\right) \quad (6)$$

where $(\tau_{c0})^{-1}$ is an adjustable parameter, E_a^r is the apparent activation energy for reorientation of the chemical groups or the ion. The performed analyses demonstrated that the dynamic glass transition

Table 2

Apparent activation energy of ion diffusion for $(P_{4444})^+$, $(FuA)^-$ and Li^+ estimated by the VFT approach (Eq.(5)) and apparent energy of activation (kJ mol^{-1}) of reorientation rates of chemical groups of the neat $(P_{4444})(FuA)$ and the electrolytes obtained by VFT approach (Eq.(6)).

Chemical group	Reorientational rates of chemical groups		Ions	Diffusion of ions			
	E_a , kJ/mol	E_a , kJ/mol		Neat $(P_{4444})(FuA)$		10 mol% Li(FuA)	
	Neat $(P_{4444})(FuA)$	10 mol% Li(FuA)		T_0 , K	E_D , kJ/mol	T_0 , K	E_D , kJ/mol
CH_3 cation	3.3 ± 0.4	3.4 ± 0.4	$(P_{4444})^+$	172	11.6	175	11.2
CH_2-CH_3 cation	2.6 ± 0.4	2.2 ± 0.4					
P- CH_2 cation	3.1 ± 0.6	3.1 ± 0.6					
Anion group "1"	3.7 ± 0.6	3.6 ± 0.6	$(FuA)^-$	172	11.7	175	11.3
Anion group "2"	3.5 ± 0.6	3.4 ± 0.6					
Li^+	6.0 ± 0.6	5.9 ± 0.6	Li^+	172	11.6	175	11.7
	(2.5 mol% Li(FuA))			(2.5 mol% Li(FuA))	(2.5 mol% Li(FuA))		

temperatures for reorientation of chemical groups coincides with T_0 obtained from diffusion data of the corresponding ions. Particularly, for neat $(P_{4444})(FuA)$ IL T_0 is ~ 172 K, and for $[Li(FuA)]_{0.100}[(P_{4444})(FuA)]_{0.900}$ electrolyte T_0 is ~ 175 K. Therefore, both the reorientation and the ion diffusion are stopped almost at the same temperature in these electrolytes. The results of VFT analysis of the experimental data for τ_c^{-1} as shown in Fig. 8 are presented in Table 2 and in Table S1 of the ESI.

The activation energy of the reorientation are less by a factor of 2–3 than those of the ion diffusion. It is known that the reorientational mobility of ions and molecules is a prerequisite for translational mobility. The reorientational mobility characterizes the processes occurring on the molecules-size scale, while translational mobility obtained by PGSE NMR describes micrometer scale lengths. In this case, the displacement of ions are in the range from $6 \cdot 10^{-8}$ to $5 \cdot 10^{-6}$ m. An increase in the concentration of the Li-salt decreases the reorientational and diffusional mobilities in concerted way. The difference in activation energy as observed for reorientation of chemical groups and translational diffusion of ions shows that the translation motion is more energy consumptive, but the added salt does not have any significant influence on this aspect. The quality of the analysis of reorientational mobility as well as diffusion data may be further improved if both these types of experiments are performed in a broader temperature range, particularly at lower temperatures.

4. Conclusions

The diffusivity of ions and T_1 relaxation of protons in various chemical groups of $(P_{4444})^+$ and $(FuA)^-$ and the Li^+ ion in fluorine-free electrolytes comprising $Li(FuA)$ and $(P_{4444})(FuA)$ are performed as a function of lithium salt concentration and temperature. The temperature dependence of correlation times of reorientational mobility of various chemical groups of $(P_{4444})^+$ cation, $(FuA)^-$ anion and Li^+ ion are estimated and used to calculate corresponding reorientational rates at variable temperatures. It is demonstrated that an increase in the concentration of lithium salt leads to decrease in both the ion diffusion coefficients and the reorientation rates. The activation energy of reorientational rates of the organic ions and the Li^+ is significantly lower than that of the ion diffusion, and independent on the amount of added lithium salt. These new findings could be very useful for understanding the molecular basis of ionic conductivity of ionic liquid-based electrolytes.

CRedit authorship contribution statement

Oleg I. Gnezdilov: Methodology, Investigation, Software. **Andrei Filippov:** Methodology, Investigation, Writing – original draft, Writing - review & editing. **Inayat Ali Khan:** Data curation.

Faiz Ullah Shah: Conceptualization, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The Kempe Foundation in memory of J. C. and Seth M. Kempe is gratefully acknowledged for the financial support in the form of a stipend for IAK (grant number: SMK-1838). The financial support from the Swedish Research Council (project number: 2018-04133) is gratefully acknowledged for supporting this work. O.I. G. acknowledges the subsidy allocated to the Kazan Federal University for the state assignment in the sphere of scientific activities (project number: 0671-2020-0051).

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2021.117001>.

References

- [1] M. Watanabe, M.L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K. Dokko, Application of ionic liquids to energy storage and conversion materials and devices, *Chem. Rev.* 117 (2017) 7190–7239.
- [2] B. Scrosati, J. Garche, Lithium batteries: status, prospects and future, *J. Power Sources* 195 (2010) 2419–2430.
- [3] G.B. Appetecchi, M. Montanino, S. Passerini, Ionic Liquid-Based Electrolytes for High-Energy Lithium Batteries, in: Visser, A.E.; Bridges, N.J.; Rogers, R.D. (Eds.), *Ionic Liquids: Science and Applications*. ACS Symposium Series 1117, Oxford University Press, Inc., American Chemical Society, Washington, DC, USA, 2013, pp. 67–128.
- [4] T. Tamura, T. Hachida, K. Yoshida, N. Tachikawa, K. Dokko, M. Watanabe, New glyme-cyclic imide lithium salt complexes as thermally stable electrolytes for lithium batteries, *J. Power Sources* 195 (2010) 6095–6100.
- [5] B. Gélinas, M. Natali, T. Bibienne, Q.P. Li, M. Dollé, D. Rochefort, Electrochemical and transport properties of ions in mixtures of electroactive ionic liquid and propylene carbonate with a lithium salt for lithium-ion batteries, *J. Phys. Chem. C* 120 (2016) 5315–5325.
- [6] F.U. Shah, O.I. Gnezdilov, R. Gusain, A. Filippov, Transport and association of ions in lithium battery electrolytes based on glycol ether mixed with halogen-free orthoborate ionic liquid, *Sci. Rep.* 7 (2017) 16340.
- [7] F.U. Shah, O.I. Gnezdilov, A. Filippov, Ion dynamics in halogen-free phosphonium bis(salicylate)borate ionic liquid electrolytes for lithium-ion batteries, *Phys. Chem. Chem. Phys.* 19 (2017) 16721–16730.
- [8] K. Hayamizu, S. Tsuzuki, S. Seki, Transport and electrochemical properties of three quaternary ammonium ionic liquids and lithium salt doping effects studied by NMR spectroscopy, *Chem. Eng. Data* 59 (2014) 1944–1954.
- [9] T. Frömling, M. Kunze, M. Schönhoff, J. Sundermeyer, B. Roling, Enhanced lithium transference numbers in ionic liquid electrolytes, *J. Phys. Chem. B* 112 (2008) 12985–12990.

- [10] V.L. Martins, N. Sanchez-Ramirez, M.C.C. Ribeiro, R.M. Torresi, Two phosphonium ionic liquids with high Li^+ transport number, *Phys. Chem. Chem. Phys.* 17 (2015) 23041–523051.
- [11] M. Brinkkötter, G.A. Giffin, A. Moretti, S. Jeong, S. Passerini, M. Schönhoff, Relevance of ion clusters for Li transport at elevated salt concentrations in $[\text{Pyr}_{1201}][\text{FTFSI}]$ ionic liquid-based electrolytes, *Chem. Commun.* 54 (2018) 4278–4281.
- [12] H. Yoon, G.H. Lane, Y. Shekibi, P.C. Howlett, M. Forsyth, A.S. Best, D.R. MacFarlane, Lithium electrochemistry and cycling behaviour of ionic liquids using cyano based anions, *Energy Environ. Sci.* 6 (2013) 979–986.
- [13] S. Seki, K. Takei, H. Miyashiro, M. Watanabe, Physicochemical and electrochemical properties of glyme- $\text{LiN}(\text{SO}_2\text{F})_2$ complex for safe lithium-ion secondary battery electrolyte, *J. Electrochem. Soc.* 158 (2011) A769–A774.
- [14] K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko, M. Watanabe, Correlation between battery performance and lithium ion diffusion in glyme–lithium bis(trifluoromethanesulfonyl)amide equimolar complexes, *J. Electrochem. Soc.* 159 (2012) A1005–A1012.
- [15] B. Dilasari, Y. Jung, G. Kim, K. Kwon, Effect of cation structure on electrochemical behavior of lithium in $[\text{NTF}_2]$ -based ionic liquids, *ACS Sustainable Chem. Eng.* 4 (2016) 491–496.
- [16] R. Wibowo, S.E.W. Jones, R.G. Compton, Investigating the electrode kinetics of the Li/Li^+ in a wide range of room temperature ionic liquids at 298 K, *J. Chem. Eng. Data* 55 (2010) 1374–1376.
- [17] M. Brinkkötter, A. Mariani, S. Jeong, S. Passerini, M. Schönhoff, Ionic liquids in Li salt electrolyte: Modifying the Li^+ transport mechanism by coordination to an asymmetric anion, *Adv. Energy Sustainability Res.* (2020) 2000078.
- [18] T. Mendez-Morales, J. Carrete, O. Cabeza, O. Russina, A. Triolo, L.J. Gallego, L.M. Varela, Solvation of lithium salts in protic ionic liquids: A molecular dynamics study, *J. Phys. Chem. B* 118 (2014) 761–770.
- [19] O. Russina, R. Caminita, T. Mendez-Morales, J. Carrete, O. Cabeza, L.J. Gallego, L. M. Varela, A. Triolo, How does lithium nitrate dissolve in a protic ionic liquid?, *J. Molec. Liq.* 205 (2015) 16–21.
- [20] Z. Lu, L. Yang, Y. Guo, Thermal behavior and decomposition kinetics of six electrolyte salts by thermal analysis, *J. Power Sources* 156 (2006) 555–559.
- [21] H. Yang, G.V. Zhuang, P.N. Ross Jr, Thermal stability of LiPF_6 salt and Li-ion battery electrolytes containing LiPF_6 , *J. Power Sources* 161 (2006) 573–579.
- [22] K. Yuan, H. Bian, Y. Shen, B. Jiang, J. Li, Y. Zhang, H. Chen, J. Zheng, Coordination number of Li^+ in nonaqueous electrolyte solutions determined by molecular rotational measurements, *J. Phys. Chem. B* 118 (2014) 3689–3695.
- [23] I.A. Khan, O.I. Gnezdilov, A. Filippov, F.U. Shah, Ion transport and electrochemical properties of fluorine-free lithium-ion battery electrolytes derived from biomass, *ACS Sustain. Chem. Eng.* 9 (2021) 7769–7780.
- [24] K. Hayamizu, Y. Aihara, W.S. Price, Correlating the NMR self-diffusion and relaxation measurements with ionic conductivity in polymer electrolytes composed of cross-linked poly(ethylene oxide-propylene oxide) doped with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, *J. Chem. Phys.* 113 (2000) 4785–4793.
- [25] K. Hayamizu, S. Tsuzuki, S. Seki, Y. Umebayashi, Multinuclear NMR studies on translational and rotational motion for two ionic liquids composed of BF_4^- anion, *J. Phys. Chem. B* 116 (2012) 11284–11291.
- [26] E. Taarning, I.S. Nielsen, K. Egeblad, R. Madsen, C.H. Christensen, Chemicals from renewables: Aerobic oxidation of furfuryl and hydroxymethylfurfural over gold catalysts, *ChemSusChem* 1 (2008) 75–78.
- [27] J.P. Lange, E. van der Heide, J. van Buijtenen, R. Price, Furfural – a promising platform for lignocellulosic biofuels, *ChemSusChem* 5 (2012) 150–166.
- [28] I.A. Khan, O.I. Gnezdilov, Y.-L. Wang, A. Filippov, F.U. Shah, The effect of aromaticity in anion on the cation-anion interactions and ionic mobility in fluorine-free ionic liquids, *J. Phys. Chem. B* 124 (2020) 11962–11973.
- [29] I.A. Khan, F.U. Shah, Fluorine-free ionic liquid-based electrolyte for supercapacitors operating at elevated temperatures, *ACS Sustainable Chem. Eng.* 8 (2020) 10212–10221.
- [30] J.E. Tanner, Use of the stimulated echo in NMR diffusion studies, *J. Chem. Phys.* 52 (1970) 2523–2526.
- [31] A. Filippov, O.I. Gnezdilov, N. Hjalmarsson, O.N. Antzutkin, S. Glavatskih, I. Furó, M.W. Rutland, Acceleration of diffusion in ethylammonium nitrate ionic liquid confined between parallel glass plates, *Phys. Chem. Chem. Phys.* 19 (2017) 25853–25858.
- [32] M. Levitt, Spin dynamics. Basics of nuclear magnetic resonance, second ed., Wiley & Sons, New York, 2008.
- [33] K. Hayamizu, S. Tsuzuki, S. Seki, Y. Umebayashi, Nuclear magnetic resonance studies on the rotational and translational motions of ionic liquids composed of 1-Ethyl-3-methylimidazolium cation and bis(trifluoromethanesulfonyl) amide and bis(fluorosulfonyl)amide anions and their binary systems including lithium salts, *J. Chem. Phys.* 135 (2011) 084505.
- [34] D.D. Traficante, Relaxation: An Introduction, in *Encyclopedia of Nuclear Magnetic Resonance*, Grant, M. D., Harris, R. K., Eds.; Wiley: New York, 1966, Vol. 6, p. 3988.
- [35] J. Skibsted, N.C. Nielsen, H. Bildsøe, H.J. Jakobsen, Satellite transition in MAS NMR spectra of quadrupolar nuclei, *J. Magn. Reson.* 95 (1991) 88–117.
- [36] L.G. Werbelow, Relaxation theory for quadrupolar nuclei, in *Encyclopedia of Nuclear Magnetic Resonance*, ed. Grant, D. M.; Harris, R. K. Willey, New York, 1996, pp. 4092–4101.
- [37] A. Noda, K. Hayamizu, M. Watanabe, Pulsed-gradient spin-echo ^1H and ^{19}F ionic diffusion coefficient, viscosity, and ionic conductivity of non-chloroaluminate room-temperature ionic liquids, *J. Phys. Chem. B* 105 (2001) 4603–4610.
- [38] H. Tokuda, K. Hayamizu, K. Ishii, A.B.H. Susan, M. Watanabe, Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation, *J. Phys. Chem. B* 109 (2005) 6103–6110.
- [39] (a) H. Vogel, Das Temperaturabhängigkeitsgesetz der Viskosität von Flüssigkeiten, *Physikalische Zeitschrift* 22 (1921) 645–646;
(b) G.S. Fulcher, Analysis of recent measurements of the viscosity of glasses, *J. Am. Ceram. Soc.* 8 (1923) 339–355;
(c) G. Tammann, W.Z. Hesse, The dependence of the viscosity on the temperature in supercooled liquids, *Anorg. Allg. Chem.* 156 (1926) 245–257.