

Maximum Electrical Conductivity of Associated Lithium Salts in Solvents for Lithium–Air Batteries

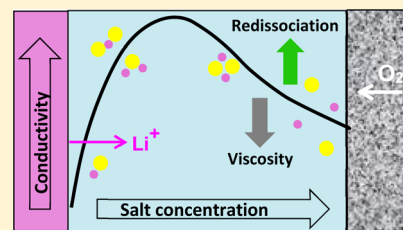
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Supporting Information

ABSTRACT: The choice of optimal electrolytes is crucial for improving the electrochemical performance of a lithium air battery because it determines the morphology of the discharge products in the cathode and the conductivity of the electrolyte. We have critically analyzed an important aspect related to the behavior of highly associated electrolytes, as those used in lithium–air batteries: the prediction of the concentration of maximum conductivity. Lithium triflate and lithium bis(trifluoromethyl sulfonyl)imide in glymes of low dielectric constant (1,2-di-methoxy-ethane and bis(2-methoxy-ethyl)ether) were used as a model of electrolytes exhibiting strong ionic clustering. The viscosity and lithium transference number of all the electrolytes were measured, and it was found that the correlation between the concentration of maximum conductivity and coefficient that describes the high-order dependence of the electrolyte viscosity with the concentration is no longer valid in these electrolytes because of the failure of Walden's rule, although a qualitative correlation with the salts' association constant was observed.



1. INTRODUCTION

Although Li–air batteries (LABs) are appealing energy storage and conversion devices because of a much larger theoretical energy density, as compared to Li-ion batteries (LIBs), their real performance is far from reaching the expected results in terms of the capacity and cyclability required for application in electric vehicles.^{1,2} Recent reviews on the status of LABs described the behavior of electrochemical and kinetic overpotentials.^{1,3} Surprisingly, the charge transport limitations during battery charge are much less severe than during discharge, mainly due to the oxygen reduction reaction (ORR) taking place at the cathode, where solid lithium peroxide (Li_2O_2) is deposited inside the pores of the carbon cathode. The morphology and thickness of these deposits partially determine the high overpotential and low capability of the LAB because of the limited electrical conductivity of Li_2O_2 .⁴

There have been several attempts to describe how the maximum of the specific conductivity of lithium electrolytes depends on the type of salt and solvent because, from the practical point of view, the maximum conductivity and lithium transference number would lead to the desirable minimum Ohmic overpotential during the operation of lithium batteries. Therefore, a choice of the best electrolyte (salt/glyme couple) could be based on maximizing the lithium ionic conductivity. Moreover, for the same lithium ionic conductivity, one would prefer the salt/glyme combination that requires a lower salt concentration and the solvent that satisfies other conditions,

such as low viscosity, low volatility, chemical stability, and so forth.⁵

The system lithium trifluoromethanesulfonate (LiTf) in bis(2-methoxy-ethyl)ether (diglyme) is the most studied of those analyzed in this work, and its ionic speciation has been previously reported by resorting to different approaches,^{6–8} which are described in detail in Section S1 of the [Supporting Information](#). It follows from that analysis that ion pairs are the dominant species all over the concentration range, although its contribution tends to decrease at high concentration because of the increasing contribution of triple ions. However, this speciation behavior could not account for the reduction of molar conductivity observed in the high concentration region^{6,8} neither can the speciation scheme neglecting triple ions but including LiTf dimers, as proposed by Petrowsky et al.,⁶ leading to an unexpected increase of the ionic conductivities with increasing salt concentration (see the [Supporting Information](#)).

In fact, more sophisticated models of ion clustering^{9–11} lead to the conclusion that in very low dielectric constant solvents (such as glymes), an electrolyte can redissociate at high concentrations, leading to the formation of essentially free ions, as it was observed experimentally.^{12,13} By considering that this redissociation phenomenon would increase the molar con-

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ductivity at high salt concentration, we conclude that the decreasing molar conductivity of strongly associated electrolytes in the high concentration regime is determined by the increase of the system viscosity, which is not well modeled by the electrical conductivity models. Thus, another aim of this work is to establish the relationship between the conductivity and viscosity of the salt/glyme systems as a function of the salt concentration, which would allow estimating the concentration of maximum specific conductivity.

For this purpose, it is convenient to analyze the dependence of the specific conductivity with the electrolyte molar concentration, usually described by the empirical equation proposed by Casteel and Amis¹⁴

$$\frac{\kappa}{\kappa_m} = \left(\frac{c}{c_m}\right)^a \exp\left[b(c - c_m)^2 - \frac{a}{c_m}(c - c_m)\right] \quad (1)$$

where κ_m represents the maximum specific conductivity and c_m represents the concentration at which it occurs. Two additional adjustable parameters, a and b , are needed to reproduce the experimental data over the entire concentration range. In spite of the fact that some attempts have been made to correlate the empirical parameters of the Casteel–Amis equation with properties of the solvent and the electrolyte,¹⁵ it is clear that eq 1 is just an empirical equation, without prediction power. Even more, the parameters obtained from the specific conductivity fit do not allow the prediction of the corresponding extremes observed in the molar conductivity at concentrations below c_m (see the Supporting Information).

There have been other attempts to describe how the maximum in the specific conductivity of lithium electrolytes depends on the system viscosity. Thus, Kondo et al.¹⁶ have proposed the following general equation for the specific conductivity, κ

$$\kappa(c) = \left(\frac{\eta_0}{\eta(c)}\right) \Lambda^0 \alpha c Q(\alpha c) \quad (2)$$

where $\eta_0/\eta(c)$ is the ratio of solvent to solution dynamic viscosity, Λ^0 is the infinite dilution molar conductivity, c is the salt molar concentration, α is the degree of dissociation, and $Q(c)$ gives the concentration dependence of the molar conductivity ($\Lambda = \kappa/c$), given, for instance, by the Fuoss–Hsia–Fernández Prini equation.¹⁷ The dependence of the viscosity with the salt concentration is expressed by the Jones–Dole equation

$$\eta(c)/\eta_0 = 1 + Ac^{1/2} + Bc + Dc^2 \quad (3)$$

where A is the Debye–Hückel term, while B and D are empirical parameters. For $c > 0.05$ mol dm⁻³, the term $Ac^{1/2}$, calculated from the properties of the salt and solvent, made a negligible contribution as compared to the higher orders terms.

According to eq 2, $Q(\alpha c) = (\Lambda\eta)/(\Lambda^0\eta_0)$ and, if the Walden product, $\Lambda\eta$, is almost constant all over the concentration range for the studied system, the maximum condition $dk/dc = 0$ leads to the simple expression¹⁶

$$c_{\max} = D^{-1/2} \quad (4)$$

The same equation was obtained by Chagnes et al.¹⁸ using the quasilattice theory, with $\Lambda = \Lambda^0 - Sc^{1/3}$. Thus, for systems where the Walden rule holds, the maximum of conductivity depends on the D coefficient of the Jones–Dole equation, which is related to the viscosity enhancement at high salt

concentration. The faster the viscosity increases with salt concentration, the lower the concentration at which the maximum conductivity is attained.

In this work, we will analyze the conductivity, lithium transference number, and viscosity behavior of two lithium salts, lithium trifluoromethanesulfonate (LiTf), and lithium bis(trifluoromethane sulfonyl)imide (LiTFSI), dissolved in 1,2-dimethoxyethane (DME) and diglyme, whose specific conductivities have been reported over a wide range of concentrations.^{6,8,19} These solvents were chosen because they exhibit good stability toward ORR intermediates, such as the superoxide anion radicals, produced upon discharge at the cathode of a LAB. For instance, Luntz and McCloskey¹ concluded that the system LiTFSI/DME is one of the more stable electrolytes, whereas Li et al.²⁰ indicated that LABs using DME as the solvent exhibit the highest yield of Li₂O₂ during discharge.

Li⁺ transference numbers measurements in these electrolytes are scarce. The diffusion coefficients of the Li⁺ and TFSI⁻ have been determined in DME, diglyme, triglyme, and tetraglyme by Watanabe and co-workers²¹ using PGSE NMR, in the concentration range 0.5–3.5 M at 303 K, while Lawson and co-workers²² determined the diffusion coefficients of Li⁺ and TFSI⁻ in DME between 0.5 and 2.0 M at 298 K employing diffusion-ordered spectroscopy (DOSY) NMR. From the measured diffusion coefficients, they estimated the Li⁺ ion transference number.

No information is available on the transference number of Li⁺ in LiTf/DME and LiTf/diglyme solutions. For this reason, we have measured the diffusion coefficients of the Li⁺ ion and the corresponding anions (Tf⁻ and TFSI⁻) in both solvents, using diffusion-ordered (DOSY) RMN spectroscopy, to determine the contribution of the lithium ion to the electrolyte conductivity.

Our aim is not to test these electrolytes under battery conditions, but use them as model systems to discuss why the assessment of the maximum specific conductivity based on eq 4 is not valid for low dielectric constant solvents, where strong ionic association leads to the breakdown of the Walden rule.

2. EXPERIMENTAL SECTION

2.1. Materials. Anhydrous bis(2-methoxy-ethyl)ether (Diglyme, DG, Sigma-Aldrich, 99.5% pure) and 1,2-dimethoxyethane (DME, Sigma-Aldrich, 99.5% pure) were used as received. Lithium trifluoromethanesulfonate (Li triflate, Sigma-Aldrich, 99.99%) and lithium bis(trifluoromethane sulfonyl)imide (LiTFSI, Sigma-Aldrich, 99.95%) were dried by heating at 140 °C under vacuum for more than 12 h. All chemicals were stored in an argon-filled MBRAUN glovebox with the oxygen content lower than 0.1 ppm, and the water content below 2 ppm. The water content of all of the solutions studied in this work content, measured using a Karl Fisher coulometer titrator (831 KFCoulometer, Metrohm), was less than 50 ppm.

2.2. Viscosity of LiTf and LiTFSI in DME and Dyglyme. The kinematic viscosity (ν) of the systems LiTf/DME, LiTf/DG, LiTFSI/DME, and LiTFSI/DG at different salt concentrations was measured with Cannon–Fenske (Ostwald modification) viscometers having constants 0.00266, 0.00632, and 0.0275 cSt s⁻¹, calibrated with water, to optimize accuracy over the entire range of measurement. The viscometer was filled inside the glovebox with the solution with a given salt concentration; its noncapillary arm was sealed with a septum,

taken out of the glovebox, and thermostated in a water bath at $(25 \pm 0.1)^\circ\text{C}$. Once the thermal equilibrium was achieved, the septum was removed, and measurements (by triplicate) were performed immediately to avoid solvent hydration.

To obtain the dynamic viscosity ($\eta = \nu/\rho$) of the solutions, it is necessary to know their densities, ρ , as a function of the salt concentration. For the systems LiTFSI/DG and LiTFSI/DME, this property is reported in the literature,¹⁹ while for the systems LiTf/DG and LiTf/DME, it was measured using a 10 cm³ picnometer. The picnometer was filled inside the glovebox, sealed with a septum, and thermostated at $(25 \pm 0.1)^\circ\text{C}$ in the same water bath as the viscometers. The dependence of the solution density with salt concentration was described with a second-order polynomial (eq S14), and the fitting parameters are summarized in Table S2 (the Supporting Information).

2.3. Diffusion Coefficients of Li⁺, Tf⁻, and TFSI⁻ Ions in DME and Diglyme. Diffusion-ordered (DOSY) NMR spectroscopy have been used for determining the diffusion coefficients of the solvent (glyme), Li⁺ cation, and X⁻ anion (X⁻ = Tf⁻ or TFSI⁻). Each electrolyte or pure solvent was placed into a 3 mm (o.d.) NMR tube up to a height of 5 cm. The length of the sample was intentionally made short so that it lay within the region of the constant magnetic field gradient and to minimize thermal convection.

The NMR measurements were performed on a Bruker AVANCE Neo 500 NMR spectrometer (¹H at 500.13 MHz, ¹⁹F at 470.59 MHz, ⁷Li at 194.37 MHz) equipped with a z-gradient amplifier and broadband observe probe (Bruker BBFO plus-AZ Smart Probe) with z-axis gradient coil having a maximum gradient strength of 55 G cm⁻¹. The 90° pulse lengths were 12.0 (¹H), 13.5 (⁷Li), and 15.0 (¹⁹F) μs . The self-diffusion coefficients were obtained at 25 °C, and the gradient strength was calibrated using the known self-diffusion coefficient of the “doped water” standard sample from Bruker ($1.91 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 298 K).

The measurements of the diffusion coefficients of the solvent, the anion, and the lithium ion were made by ¹H, ¹⁹F, and ⁷Li NMR, respectively. The stimulated-echo with bipolar gradients pulse sequence was used for the diffusion measurements. Diffusion coefficients, D , were obtained from the decay of the echo intensity I as a function of the gradient strength, g , to

$$I = I_0 e^{-D\gamma^2\delta^2g^2(\Delta - \frac{\delta}{3} - \frac{\tau}{2})} \quad (5)$$

where I is the spin-echo signal intensity, γ is the gyromagnetic ratio, δ is the gradient pulse length, and Δ is the gradient pulses spacing. The gradient strength was increased in 16 linear steps to a maximum value of 46 G cm⁻¹. Typical Δ values were 50–100, 240, and 100 ms for ¹H, ⁷Li, and ¹⁹F, respectively, while δ values were 1.7–2.6, 3.8–5, and 2.4–3.5 ms for ¹H, ⁷Li, and ¹⁹F, respectively. A recycle delay sufficient to allow for full relaxation (i.e., $>5T_1$) was used between each transient. All of the measured signal attenuations were well described by a straight line as expected for free diffusion. The diffusion coefficients and their errors were determined from the echo damping according to eq 5, using Dynamic Center software provide by Bruker.

3. RESULTS AND DISCUSSION

3.1. Viscosity and Ionic Clustering of LiTf and LiTFSI in Glymes: What Determines the Conductivity Max-

imum? The viscosities of the four systems studied in this work as a function of the salt concentration are shown in Figure 1.

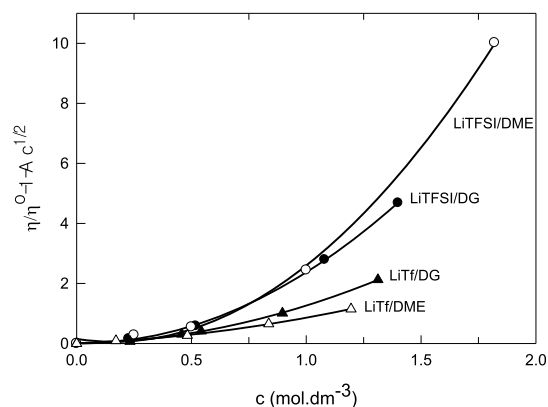


Figure 1. Jones–Dole plot for the viscosity at 25 °C: (Δ) LiTf/DME; (\blacktriangle) LiTf/DG; (\circ) LiTFSI/DME; (\bullet) LiTFSI/DG.

The results can be described with the Jones–Dole eq 3, and the adjustable parameters, along with the corresponding Debye–Hückel coefficient,²³ are summarized in Table 1. It is observed that the D coefficient for LiTFSI is much higher than that for LiTf in both glymes, as expected by the higher slope of the viscosity versus concentration curve for LiTFSI/DME and LiTFSI/diglyme in the concentrated region.

To test the validity of eq 4 to predict the concentration of maximum conductivity in these systems, we plotted in Figure 2a the specific conductivities at 25 °C for LiTFSI/DME,^{8,19} LiTFSI/DG,^{8,19} LiTf/DG,^{6,8} and LiTf/DME,⁸ over a wide range of concentrations. It should be noted that the data by Petrowsky et al.⁶ for LiTf/DG were measured at room temperature, without specifying the exact value of this parameter. The increasing order of c_m is LiTFSI/diglyme \approx LiTFSI/DME $<$ LiTf/diglyme $<$ LiTf/DME. The maximum conductivity of the LiTf/DME system has not been reached over the concentration range studied, but it is clear that it will lie above 1.4 mol dm⁻³.

As it can be observed in Figure 2b, the molar conductivity of these associated electrolytes exhibits a more complex behavior as a function of concentration, as compared to that of the specific conductivity. In the diluted region, Λ decreases with concentration because of the formation of neutral ion pairs, and goes through a minimum as the concentration approaches 0.01–0.02 mol dm⁻³ because above that concentration, the charged triplet ion population makes an important contribution to the charge transport. At higher concentrations, in the range 0.3–1.2 mol dm⁻³, a maximum in molar conductivity is observed for all of the systems owing to an increase of the neutral quadruplet ionic aggregates, and also because the increasing viscosity at high salt concentrations decreases the ionic mobilities.

To assess the validity of eq 4 for predicting the concentration of maximum specific conductivity for these systems, we compare in Table 2 the experimental values of c_m along with the values calculated using eq 4. Also included in this table is the experimental c_m measured by Barthel et al.²⁴ for the system LiBF₄/DME, which exhibits a strong ionic association, similar to the system LiTf/DME.

The concentration of maximum conductivity estimated through eq 4 is, in all cases, around 0.35–0.50 mol dm⁻³ lower than the experimental ones. This behavior differs from

Table 1. Parameters of the Jones–Dole Equation at 25 °C

system	A (dm ^{3/2} mol ^{-1/2}) ^a	B (dm ³ mol ⁻¹)	D (dm ⁶ mol ⁻²)	R ²
LiTf/DME	0.04135	0.333	0.526	0.9994
LiTf/DG	0.03824	0.137	1.093	0.9997
LiTFSI/DME	0.04522	-0.806	3.452	0.9970
LiTFSI/DG	0.04165	-0.0587	2.434	0.9998

^aCalculated using eq 6-9-4 from ref 23. The ionic conductivities in both glymes were taken from Table S1 in the Supporting Information. Viscosities at 25 °C are 0.423 mPa s for DME and 0.984 mPa s for diglyme, while the relative dielectric constants are 7.20 for DME and 7.36 for diglyme.⁸

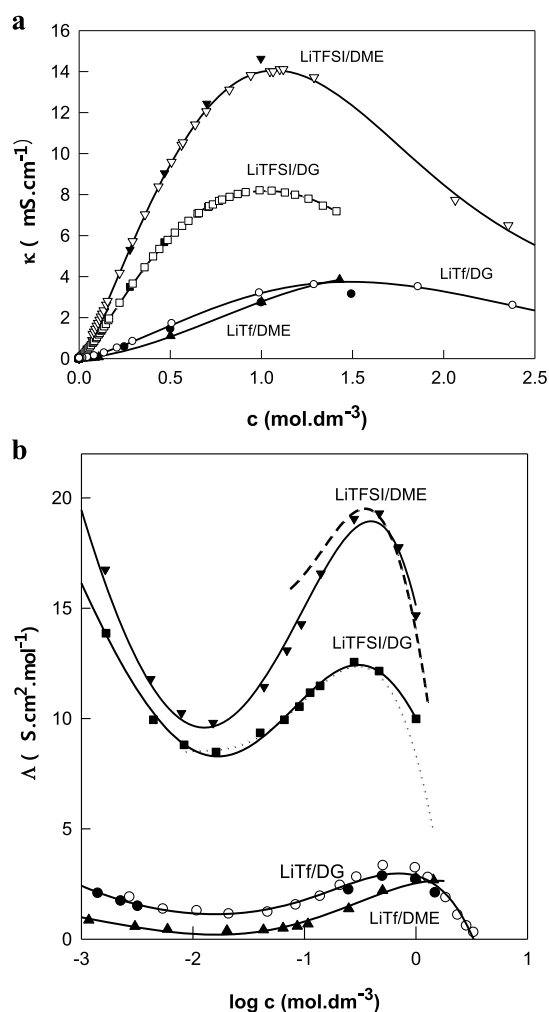


Figure 2. (a) Specific conductivity at 25 °C of: LiTf/DME (▼) Horwitz et al.,⁸ (▽) Brouillette et al.;¹⁹ LiTFSI/DG (■) Horwitz et al.,⁸ (□) Brouillette et al.;¹⁹ LiTf/DME (▲) Horwitz et al.;⁸ LiTf/DG (●) Horwitz et al.,⁸ (○) Petrowsky et al.⁶ (room temperature); (b) molar conductivity at 25 °C. Symbols as in (a), with (---) data by Brouillette et al.¹⁹ for LiTFSI/DME; (····) data by Brouillette et al.¹⁹ for LiTFSI/DG.

that found by Kondo et al.¹⁶ for the system LiPF₆/PC (propylene carbonate), where the experimental c_m is 0.79 mol dm⁻³, while the calculated with eq 4 is 0.78 mol dm⁻³. For several lithium salts (LiBF₄, LiPF₆, LiAsF₆, and LiTFSI) in γ -butyrolactone, it was found that the experimental c_m varies between 0.97 and 1.02 mol dm⁻³, in good agreement with the calculated c_m , ranging from 0.91 to 1.15 mol dm⁻³.¹⁸

The agreement between experimental and calculated c_m is not so close in the case of LiTf or LiTFSI in the glymes studied in this work, even when the order of c_m is predicted by eq 4, as observed in Table 2. A plausible explanation for that is the difference between the dielectric constant of DME (7.20) or diglyme (7.36), as compared with solvents with higher dielectric constant, such as propylene carbonate ($\epsilon = 64.4$) or γ -butyrolactone ($\epsilon = 41.7$). The Walden rule, that is the invariance of the product $\Lambda\eta$ with salt concentration, is approximately obeyed for the high-dielectric constant solvents, where the lithium salt is almost completely dissociated, leading to eq 4, as shown in the Introduction section.

In contrast, because of the strong association of the lithium salts in the low-permittivity glymes, the Walden rule does not hold, as can be seen in Figure 3. The Walden product, $\Lambda\eta$, is not constant as a function of concentration, but it goes through a minimum for all of the studied systems and, consequently, $Q(\alpha c) = (\Lambda\eta)/(\Lambda^0\eta_0) \neq 1$ in eq 2, and eq 4 is no longer valid. In fact, the Walden rule is not obeyed even in the diluted region ($c < 10^{-3}$ mol dm⁻³) because of the strong ion pairing occurring in these solvents. In summary, the application of eq 4 to lithium salts in low dielectric constant solvents for predicting maximum conductivity concentration is invalidated by the failure of those systems to obey the Walden rule. In spite of that, there is a qualitative correlation between c_m and $D^{-1/2}$ that would allow us to predict that the lithium salt/solvent system with the larger viscosity versus concentration slope in the high concentration region should exhibit the conductivity maximum at lower salt concentration.

3.2. Concentration of Maximum Conductivity and the Ionic Association. The values of the association constants, K_A and K_T , determined from the conductivity data⁸ using the Fuoss and Kraus procedure (eqs S6–S9) described in the Supporting Information are summarized in

Table 2. Experimental (c_m^{exp}) and Calculated (c_m^{cal}) Concentrations of Maximum Specific Conductivity and Association Constants of Lithium Salts in Glymes

system	c_m^{exp} (mol dm ⁻³)	c_m^{cal} (mol dm ⁻³)	K_A (dm ³ mol ⁻¹) ^a	K_T (dm ³ mol ⁻¹) ^a
LiTf/DME	>1.4	1.38	2.7×10^7	129
LiTf/DG	1.29	0.95	9×10^5	60
LiTFSI/DME	1.07	0.54	5×10^4	17
LiTFSI/DG	1.02	0.64	1.5×10^4	54
LiBF ₄ /DME ^b	2.1		2.3×10^7	31

^aValues of K_A and K_T obtained by fitting the molar conductivity of the dilute systems to the Fuoss–Kraus equation.⁸ ^bData from Barthel et al.²⁴

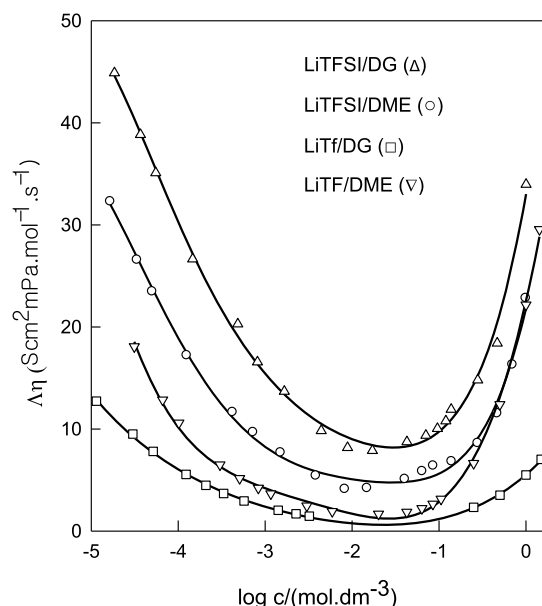


Figure 3. Walden plot at 25 °C of: LiTFSI/DG (Δ); LiTFSI/DME (\circ); LiTf/DG (\square); LiTf/DME (∇). The $\Delta\eta$ product for LiTf/DME was augmented for a factor 10 for a better comparison.

Table 2. It is observed that there is a good correlation between the strength of the ionic association and concentration of maximum conductivity: the systems which exhibit stronger ionic association, such as LiTf and LiBF₄ in DME, reach the maximum conductivity at higher concentration than those with weaker association, such as LiTFSI in DME or diglyme.

The prediction of c_m is important for choosing the best electrolyte for LABs because a lower c_m implies the use of lower amount of lithium salt. However, one should also aim to maximize the specific conductivity in order of decreasing the Ohmic overpotential. Thus, one is tempted to say that the maximum conductivity will be higher for the system with weaker ionic association. However, it is inferred from Figure 2 that the system LiTFSI/DME is the one exhibiting the best maximum conductivity for a LAB, even when it is most associated than the couple LiTFSI/diglyme. The reason for that behavior is that the ionic conductivities of the charged ions (Li^+ , X^- , Li_2X^+ , and LiX_2^-) are mainly determined by the viscosity of the media, and DME has almost half viscosity as compared to diglyme.

Combining both criteria, minimum amount of lithium salt and maximum conductivity, it is clear from Figure 2a that LiTFSI/DME is the best electrolyte of those studied in this work, including the LiBF₄/DME electrolyte reported by Barthel et al.,²⁴ whose maximum conductivity is half (7.2 mS cm⁻¹) of that found for LiTFSI/DME and would require more than double of salt concentration.

It could be argued that the relevant parameter for determining the best electrolyte is not the maximum salt conductivity, but the Li^+ ionic conductivity, λ_{Li^+} . Thus, the Li^+ transference number, t_{Li^+} , is required to assess $\lambda_{\text{Li}^+} = t_{\text{Li}^+} \kappa / c$. This parameter can be obtained from the ionic diffusion coefficients reported in Table 3, by resorting to the expression

$$t_{\text{Li}^+} = \frac{D_{\text{Li}}}{D_{\text{Li}} + D_{\text{X}}} \quad (6)$$

The last column in Table 3 summarizes the t_{Li^+} values for the four systems studied, which in all cases are close to 0.5, with

Table 3. Diffusion Coefficients of Li^+ (D_{Li}), Anion (D_{X}), and Solvent (D_{S}), and Transference Number of Li^+ Ion, in 1 M Solutions at 25 °C

system	($10^{10} D_{\text{Li}} \text{ m}^2 \text{ s}^{-1}$)	($10^{10} D_{\text{X}} \text{ m}^2 \text{ s}^{-1}$)	($10^{10} D_{\text{S}} \text{ m}^2 \text{ s}^{-1}$)	t_{Li^+}
LiTFSI/DG	1.83 ± 0.01	2.04 ± 0.02	3.69 ± 0.04	0.473 0.454 ^a
LiTFSI/DME	4.47 ± 0.02	4.36 ± 0.04	9.72 ± 0.11	0.506 0.502 ^a 0.47 ^b
LiTf/DG	2.15 ± 0.02	2.18 ± 0.02	4.98 ± 0.05	0.497
LiTf/DME	6.10 ± 0.04	6.30 ± 0.05	16.0 ± 0.2	0.492

^aData from ref 21 at 30 °C. ^bData from ref 22.

the LiTFSI/DME system exhibiting the larger Li^+ transference number. For the systems LiTFSI/DME and LiTFSI/DG, the agreement with previously published data^{21,22} is quite good. Therefore, it can be concluded that this electrolyte at concentration close to 1 M will have the highest Li^+ ionic conductivity.

The diffusion coefficient order is $D_{\text{solvent}} > D_{\text{X}^-} \approx D_{\text{Li}^+}$ for all of the electrolytes, as it has been observed for LiTFSI/DME between 0.5 and 2.0 M²² (averaged $t_{\text{Li}^+} = 0.48$). Other authors found that the diffusion order is $D_{\text{solvent}} > D_{\text{TFSI}^-} > D_{\text{Li}^+}$ in diglyme, triglyme, and tetraglyme at concentrations up to 2 M^{22,26,27} implying that $t_{\text{Li}^+} < 0.5$ in all of them, changing to $D_{\text{solvent}} > D_{\text{Li}^+} > D_{\text{TFSI}^-}$ at concentrations above 2 M. Thus, in the very concentrated regime ($c \approx 3$ M), t_{Li^+} can increase, reaching values close to 0.54, which are not high enough to compensate the decrease in the specific conductivity with increasing concentration in that region, as observed in Figure 2b.

It is worth noting that the maximum conductivity is not the unique descriptor in the search for the best electrolyte for LABs. Recently, Aurbach and co-workers²⁵ observed that the degree of association of the lithium salt in the solvent is even more important than the donor number for determining the efficiency of the discharge reaction in the cathode. This is due to the fact that for highly associated salts (i.e., LiTf in DME) a “top-down” Li_2O_2 precipitation mechanism takes place, favored by the reduce affinity of the Li^+ ion toward the metastable superoxide anion, which can diffuse far away from the cathode surface before being associated with a Li^+ ion to form LiO_2 , which then disproportionates into Li_2O_2 . Through this mechanism, the Li_2O_2 growth can expand in all directions, forming large deposits and improving the cell capacity.

According to this hypothetical discharge mechanism, the system LiTf/DME would be the best choice as the electrolyte for a LAB,⁸ but it needs to be probed experimentally if the stronger association of the LiTf/DME couple leads to a better LAB performance than that of LiTFSI/DME, having higher conductivity and, consequently, lower Ohmic overpotential. Also the long term stability of both electrolytes should be determined under the operation conditions of a LAB. These aspects will be analyzed in a forthcoming work.

4. CONCLUSIONS

Electrolytes formed by LiTf and LiTFSI dissolved in low dielectric constant glymes, such as DME and diglyme, have been analyzed as models of strongly associated electrolytes for LABs.

For the four systems studied in this work, the electrical molar conductivities exhibit a complex dependence with salt concentration because of the presence of different ionic species that could contribute (free and triple ions) or not (ion pairs and quadruplets) to the conductivity. We suggest that the redissociation of lithium salts can occur in the high concentration regime, and the reduction of the molar conductivity of strongly associated electrolytes under that condition is mainly due to the increase of the system viscosity, which is not well modeled by the electrical conductivity models. For this reason, we focused on the relationship between the concentrations of maximum specific conductivity of these electrolytes with the coefficient D of the Jones–Dole equation describing the concentration dependence of the solution viscosity.

We conclude that, even when eq 4 fails in these types of electrolytes due to the fact that the Walden rule is not obeyed, a qualitative correlation between c_m and $D^{-1/2}$ is observed, predicting that the conductivity maximum will occur at lower salt concentration for that lithium salt/solvent system whose viscosity increases quicker with increasing salt concentration. It was also found that the lithium salt/solvent couple which exhibits weaker ionic association reaches the maximum conductivity at lower concentration, as is the case of LiTFSI as compared to LiTf in both solvents.

In the search for the best LAB electrolyte, one should prefer the system with a lower c_m , implying a lower amount of lithium salt, and that with a higher specific conductivity, to reduce the Ohmic overpotential of the battery. Comparing the systems studied in this work, LiTFSI/DME is that having the best maximum conductivity reached at a low salt concentration (1.07 mol dm^{-3}). This couple also exhibits the highest Li^+ ion transference number at that concentration ($t_{\text{Li}^+} \approx 0.51$), which assure the best Li^+ ionic conductivity among the studied electrolytes.

We observed that the couple LiTFSI/DME has almost double-specific conductivity than LiTFSI/diglyme around 1 mol dm^{-3} in spite of being more associated. The reason for that behavior is that the viscosity of DME is almost half of the viscosity of diglyme, with this parameter, instead of the speciation, being what determines the conductivity.

We have also considered the role of ionic association of the lithium salt in the solvent in relation to the mechanisms of the discharge reaction in the cathode. It has been proposed that highly associated salts (i.e. LiTf in DME) will promote a “top-down” Li_2O_2 precipitation mechanism, leading to larger deposits and, consequently, to higher LAB capacity. If that is the case, the couple LiTf/DME could be a better choice than the couple LiTFSI/DME, even when it exhibits a lower conductivity. Thus, this work prompts for further studies on both electrolytes to decide which one leads to a better LAB performance.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b00864.

Thermodynamics of ion aggregation in solvents of low dielectric constants, how the association constants can be obtained from electrical conductivity measurements, and speciation of lithium salts in glymes from conductivity and IR spectroscopy data; calculation of

the ionic conductivities of lithium salts at infinite dilution using the fractional Walden rule; density of lithium salts in the studied glymes; and calculation of the extremes of the molar conductivity of strongly associated electrolytes from the Casteel–Amis equation (PDF)

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Notes

The authors declare no competing financial interest.

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