



Change of Conductivity with Salt Content, Solvent Composition, and Temperature for Electrolytes of LiPF₆ in Ethylene Carbonate-Ethyl Methyl Carbonate

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We measured the electrolytic conductivities of the electrolytes of LiPF₆ in ethylene carbonate-ethyl methyl carbonate at different salt contents, solvent compositions, and temperatures in the ranges of their practical values. To these data, we fitted a fourth degree trivariate polynomial and obtained a close fit. We then plotted this function as surface and contour plots in the coordinates of salt content and solvent composition for a series of temperatures. These plots showed the change of conductivity with the simultaneous changes of salt content and solvent composition and the influence of temperature on this change, thus mapping the locations for the optimal combinations of salt content and solvent composition for maximum conductivity of the electrolytes at desired temperatures. Here we also discuss and interpret qualitatively the trends found in the change of conductivity with salt content, solvent composition, and temperature, based on the dependency on the same variables of these three factors: the number of dissociated ions in the electrolyte, the dielectric constant of the solvent, and the viscosity of the electrolyte.

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Electrolytic conductivity of an electrolyte in an electrochemical device, such as a battery, a capacitor, or a fuel cell, is an important property whose values greatly affect the performance of the device. As the ion-carrying medium between the electrodes, an electrolyte with a high conductivity enhances the current-carrying capability of the overall device by offering low resistance to the conduction of ion. This practical importance has prompted extensive studies on the conductivities of many nonaqueous electrolytes of lithium salts and their dependency on salt content, solvent composition, and temperature.¹⁻¹⁵ Studies of this nature, however, are mostly empirical, as values of concentration which are practical for real electrochemical devices are well beyond the limits within which theoretical models have met with success. Furthermore, these studies have mostly been restricted to those on change of conductivity with essentially a single variable; therefore, their utility in the optimization of an electrolyte when more than one variable can be simultaneously adjusted has been limited. There has been a case where conductivity of an electrolyte is plotted as a surface in the space of salt content and solvent composition, but the trends for the change of conductivity with these variables are difficult to observe because of the unwarranted irregularities in the surface of the function representing the conductivity.⁷

The purpose of this work is to measure and interpret the electrolytic conductivities of a particular electrolyte system, LiPF₆ in ethylene carbonate-ethyl methyl carbonate (EC-EMC), at different salt contents, solvent compositions, and temperatures in the ranges of their practical values, and to observe the trends in the change of conductivity with the simultaneous changes of salt content and solvent composition at different temperatures. These trends can be used to locate the optimal combinations of salt content and solvent composition for maximum conductivity at desired temperatures, and may also have a more general significance of providing guidance on how conductivities of other electrolyte systems with a similar constitution will change with the same variables.

The electrolytes we have chosen for this study, LiPF₆ in EC-EMC, exhibit wide electrochemical stability windows that enable them to withstand low reduction potentials at which lithium ions get reduced and high oxidation potentials at which some highly energetic oxides operate as cathodes. They also have moderately high

electrolytic conductivities and relatively wide liquid ranges. For these reasons, these electrolytes have been widely adopted in lithium battery research and development.^{7,16-19} In addition, these electrolytes often supercool to temperatures well below their liquidus temperatures under normal conditions, a favorable property for their low temperature use. The degree of this supercooling, however, is sensitive to and can be severely diminished by the presence of foreign materials, especially carbon particles.¹⁶ Furthermore, the solvent system of these electrolytes, EC-EMC, has been well studied for its liquid-solid phase equilibria,²⁰ its supercooling behavior,¹⁶ and its role in passivating and therefore protecting graphite.^{19,21}

On these electrolytes of LiPF₆ in EC-EMC, we measured the conductivities at different salt contents, solvent compositions, and temperatures in the ranges of their practical values. These ranges were from 0.4 to 1.8 mol kg⁻¹ for the salt content, 0.23 to 0.54 mol fraction of EC for the solvent composition, and -40 to 60°C for the temperature. We then fitted these data with a trivariate polynomial function of conductivity as a function of these variables. As we were able to obtain a good fit using only a fourth degree polynomial, the resulting function traced the experimental data closely and smoothly. When plotted in the space of salt content and solvent composition at specific temperatures, this function revealed the way conductivity changed with the simultaneous changes of salt content and solvent composition, thus pointing out the direction for the optimization of the electrolytes through adjustment of these variables. Further, comparison of the plots of different temperatures showed how temperature affected the conductivity change, and therefore how the variables should be adjusted according to particular temperature needs. We also discuss and interpret in qualitative terms the trends found in the change of conductivity with the three variables, based on the dependency on the same variables of these three factors: the number of dissociated ions in the electrolyte, the dielectric constant of the solvent, and the viscosity of the electrolyte.

Experimental

Sample preparation.—For brevity, we use, whenever appropriate, the symbols κ , m , and η to, respectively, denote the electrolytic conductivity, the molal salt concentration, and the viscosity of the electrolyte, x and ϵ , the mole fraction of EC and the dielectric constant of the solvent, and T the temperature of the sample. For sample preparation, we obtained for the binary solvents EC and EMC with their respective purities of 99.95 and 99.9% from Grant Chemical and EM Industries, Inc., and for the salt LiPF₆ of purity 99.9% from Stella Chemifa Co. All the handling and preparation of the solvents and electrolytes was done in a dry glove box filled with argon. The

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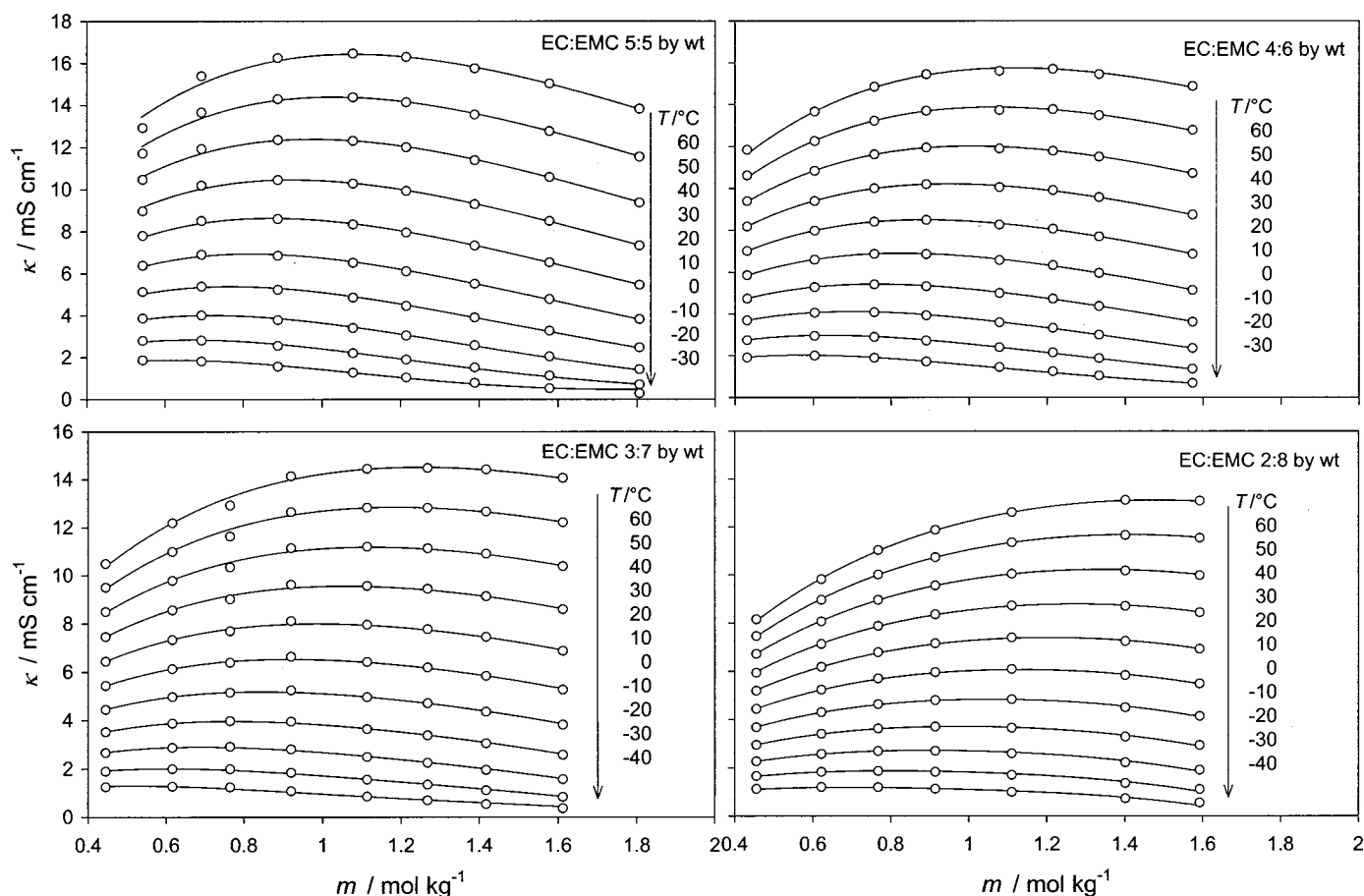


Figure 1. Change of conductivity κ with salt content m at different temperatures T and solvent compositions EC:EMC for electrolytes of LiPF_6 in EC-EMC. The dots represent experimental data and the curves plot the fitting function of Eq. 4.

four binary solvents of different compositions were made by mixing EC and EMC in the weight ratios of 5:5, 4:6, 3:7, and 2:8 for EC:EMC, which corresponded, respectively, to 0.542, 0.441, 0.336, and 0.228 for x . Out of each of these, seven to eight electrolyte samples were prepared by dissolving LiPF_6 salt to values of m from 0.4 to 1.8 mol kg^{-1} .

Conductivity measurement.—We measured the electrolytic conductivities of the electrolytes using an HP 4284A precision LCR meter.¹⁶ Temperature of the samples was controlled with a Tenney Jr. Environmental Chamber. The dip-type conductivity cells were made of a Pyrex glass body and a pair of electrodes of a platinum-iridium alloy, with a cell constant of about 0.1 cm^{-1} calibrated with a standard KCl solution. On the cell body was connected a glass tube with a ground-glass opening, by which the electrolyte could be put into the cell and then sealed with a ground-glass stopper. Each measurement of conductivity for a particular temperature was carried out after the samples had been kept at that temperature for 1 h for a full thermal equilibration. The temperature range for the measurement was typically from -40 to 60°C with 5°C increments. For a determination of conductivity, impedance of the sample was scanned from 1 MHz to 20 Hz, from which a Nyquist impedance curve was subsequently made. The conductivity was then evaluated on the real axis at the intersection or at the closest approach the impedance curve made with the real axis. The frequency for such an occurrence was typically around 20 kHz.

Data fitting.—We used Mathematica 4 from Wolfram Research for fitting mathematical functions to the experimental data and for some of the graphical presentations of the resulting functions. To observe the change of κ with simultaneous changes of m , x , and T ,

the most convenient and suitable way was to find a trivariate polynomial function $\kappa = f(m, x, T)$ that would faithfully represent the experimental data and yet would not contain terms of excessively high degrees, and to subsequently plot out the function for the observation. To find such a function, we first determined the proper degree for each of the individual variables in the following way.

To determine the proper degree for m , we first fitted a polynomial $\kappa = f(m)$ of degree three to the experimental κ - m data at constant values of x and T , and observed the value of R^2 . Here, we have used f to denote a polynomial function with positive powers for its variable(s); thus, $f(m)$ of degree three would be $a_0 + a_1m + a_2m^2 + a_3m^3$, where the a 's are the constants to be evaluated through fitting. To judge the quality of a fit, we mainly relied on the value of R^2 generated at the end of the fit. R^2 here is called the coefficient of determination, and a value of it close to unity can be interpreted for the present application as indicating that the experimental data would be faithfully represented by the polynomial function to which it refers.²² We then incremented the degree of $f(m)$ to four and repeated the fitting process, and found R^2 to be closer to unity. Values of R^2 at this stage were already higher than 0.999. Expectedly, further incrementing $f(m)$ to higher degrees was found not to improve R^2 significantly. We therefore deemed degree four to be proper for m . For comparison, we also fitted the same data with the equation

$$\kappa = m^a \exp(bm^2 + cm + d) \quad [1]$$

where a , b , c , and d are the constants to be determined through fitting.²³ This empirical equation has been widely used for fitting

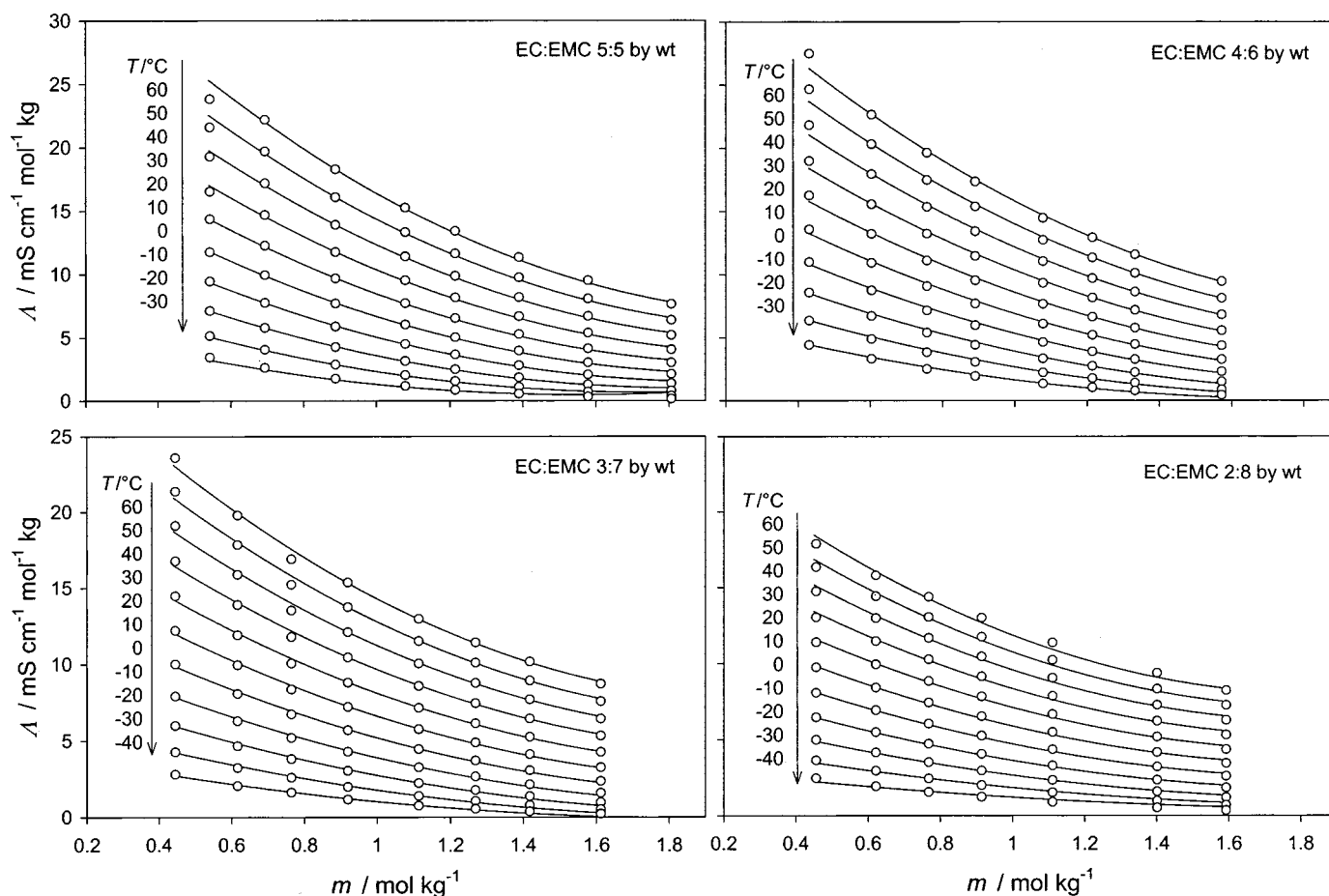


Figure 2. Change of molal conductivity Λ with salt content m at different temperatures T and solvent compositions EC:EMC for electrolytes of LiPF_6 in EC-EMC. The dots represent experimental data and the curves plot a trivariate polynomial fitting function.

conductivities of electrolytes of practical concentrations.^{4,8,24} Fitting of this equation produced fits that were inferior to $\kappa = f(m)$ of degree four but better than of degree three, judging by their values of R^2 .

Following the same procedure, we found degree three to be proper for the variable T by fitting polynomial functions $\kappa = f(T)$ to our experimental κ - T data at constant values of m and x . These fits were further compared with those produced by fitting the commonly used equation

$$\ln \kappa = a + bT^{-1} + cT^{-2} \quad [2]$$

to the same data, where a , b , and c are the constants to be determined by fitting.^{24,25} The comparison showed better fits for $\kappa = f(T)$ of degree three than for Eq. 2.

Another frequently used equation for fitting κ - T data of electrolytes, especially at low temperatures, is the Vogel-Tammann-Fulcher (VTF) equation²⁶

$$\kappa = AT^{-1/2} \exp[-B/R(T - T_0)] \quad [3]$$

where R is the gas constant, and A , B , and T_0 are the constants to be determined through fitting. By the position it occupies in the equation, T_0 is the temperature at which conductivity would completely vanish, and thus is sometimes called the vanishing conductivity temperature.^{1,11,27-29} This equation, when fitted to our κ - T data, produced slightly better fits than $\kappa = f(T)$ of degree three.

Finding a proper degree for x in the same way was not possible because of the lack of constancy in m for the experimental κ - x data by the way we had prepared the samples. Instead, we used the fourth

degree $\kappa = f(m)$ that had been fitted to the experimental κ - m data as described above to calculate κ at a series of selected values of m for each of the four experimental values of x . The values of κ thus obtained were then paired up with the values of x , forming four pairs of κ - x data for each of the selected m . These κ - x data were then used to fit polynomial functions $\kappa = f(x)$, and the proper degree for x was thereby found to be three.

For the final trivariate polynomial function $\kappa = f(m, x, T)$, we generated its component terms by multiplying together $f(m)$ of degree four and $f(x)$ and $f(T)$ of degree three. From all the terms of the product $f(m)f(x)f(T)$, we retained all those with an overall power equal to or less than four, the highest degree of the individual polynomials, i.e., terms of $m^a x^b T^c$ where $a + b + c \leq 4$. This was to ensure that the effects on κ of the simultaneous changes of the variables were properly represented by the cross-product terms and no unwarranted irregularities would be introduced by terms of excessively high overall powers. With these as its component terms, $\kappa = f(m, x, T)$ was fitted to the experimental κ - (m, x, T) data to determine the coefficients of the terms and the value of R^2 . This approach of finding $\kappa = f(m, x, T)$ seemed to be an appropriate one as the function so found always yielded values of R^2 very close to unity and the fitted function when plotted never showed overly irregular changes, as we show.

Results and Discussion

Change of conductivity with salt content.—We plotted in Fig. 1 half of the experimental data (open dots) in the form of κ vs. m ; the other half with temperatures in between those indicated in the plots

were left out for clarity of the plots. From fitting the complete set of experimental data of $\kappa(m, x, T)$ with a fourth degree trivariate polynomial $\kappa = f(m, x, T)$, whose component terms were formed as described in the last section, we obtained, with a value of 0.99975 for R^2 , the equation

$$\begin{aligned} \kappa = & -3.37115 + 12.5608m - 7.89593m^2 + 3.51922m^3 \\ & - 1.15471m^4 + 18.1863x - 6.22756mx - 13.6916m^2x \\ & + 8.43904m^3x - 7.83732x^2 + 19.607mx^2 - 18.4529m^2x^2 \\ & - 30.6369x^3 + 29.2mx^3 - 0.0429918T + 0.180877mT \\ & - 0.0836202m^2T + 0.0230098m^3T + 0.195946Tx \\ & + 0.0676686mTx - 0.14134m^2Tx + 0.147429Tx^2 \\ & + 0.173059mTx^2 - 0.51634Tx^3 - 0.000223097T^2 \\ & + 0.00011233mT^2 + 0.0000495286m^2T^2 \\ & + 0.000952777T^2x + 0.00117334mT^2x \\ & - 0.000619157T^2x^2 - 3.46897 \times 10^{-7}T^3 - 2.75041 \\ & \times 10^{-6}mT^3 - 5.57653 \times 10^{-6}T^3x \end{aligned} \quad [4]$$

Here, the quantities κ , m , x , and T have the units of mS cm^{-1} , mol kg^{-1} , mole fraction of EC, and $^{\circ}\text{C}$, respectively. We provide this equation here to assist those who may want to evaluate the conductivities of particular electrolytes in this electrolyte system. This equation is represented with the κ - m curves in Fig. 1 by taking x and T in the equation to the desired values.

The behavior of κ of the current electrolyte system with changes of m , x , and T can be satisfactorily explained by the following three factors and their dependency on m , x , and T . The first is the number factor, *i.e.*, the number of dissociated ions per unit volume of the electrolyte solution. Since these ions respond freely to the applied electrical fields, the higher the number is, other variables being equal, the higher will be the conductivity of the electrolyte. Notice that this number is not always proportional to the salt content m . When the latter becomes too high, especially in a solvent of low dielectric constant, ions of opposite charges can actually become associated, or paired, and thereby cease to contribute to the overall conductivity. Then, an increase in m of an electrolyte actually lowers its conductivity by reducing the number of dissociated ions. Furthermore, an increase in temperature favors dissociation of the ions due to the added thermal agitation.³⁰

The second factor is the dielectric constant of the solvent, ϵ . A solvent of a high dielectric constant shields the ions of one charge from the attraction of those of the opposite charge, thus preventing ion association in the electrolyte. Dependency of ϵ on x can be approximated as linear for a binary carbonate solvent, *i.e.*, $\epsilon = x\epsilon_{\text{EC}} + (1-x)\epsilon_{\text{EMC}}$.^{14,30-34} (More correctly, x as appears in this equation is a fraction in volume rather than in moles, but the difference is not large enough to alter the discussion here.) Furthermore, ϵ generally becomes smaller with rising T , as the added thermal energy disrupts the alignment of the solvent molecules to the applied electrical field.³⁴⁻³⁷ It is important to note that while a rise in T lowers the value of ϵ of the solvent, the added thermal agitation also weakens the ion pairing. However, it seemed that for the present case, the former factor dominated the latter, and ion association became stronger as T rose. The same dominance causes the conductivities of many electrolytes to peak as their T rises to high values.²⁶

The third major factor determining the conductivity of an electrolyte is the viscosity of the electrolyte, η . Other conditions being equal, an electrolyte of a lower η will have a higher conductivity, as the charge carriers move more easily in such an electrolyte in response to an applied field. Dependency of η on T is universal; η increases with lowering T , following a relation similar to Eq.

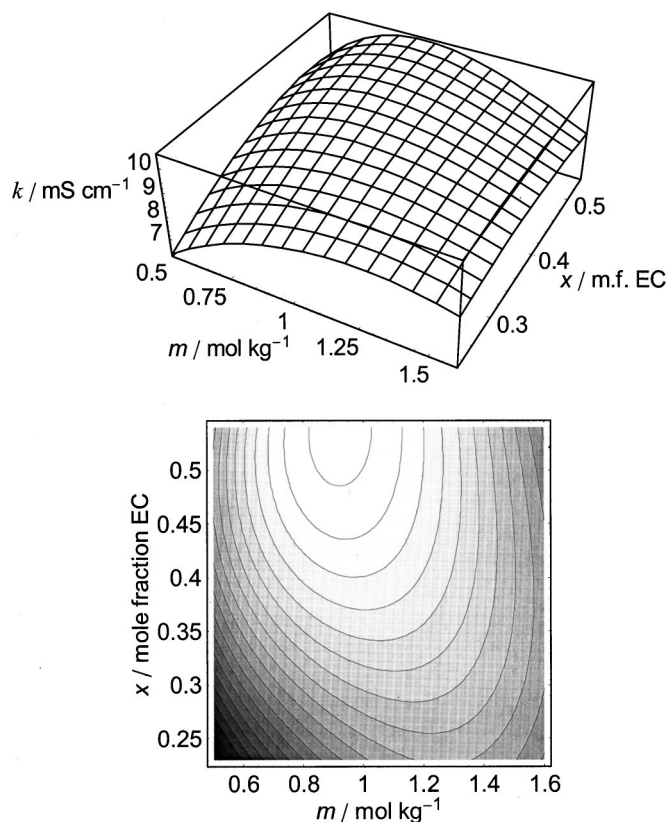


Figure 3. A detailed example of a double representation of Eq. 4 at 30°C with a surface plot (top) and a contour plot (bottom). The κ range of the surface plot is from 6.26 to 10.5 mS cm^{-1} , and the contour plot has a contour spacing of 0.2 mS cm^{-1} , and its highest contour at 10.4 mS cm^{-1} . Shading of the contour plot is such that the higher contour appears lighter.

3, 24-27, 33 Dependency of η on x can be approximated with the equation $\eta = \eta_{\text{EC}}^x \eta_{\text{EMC}}^{1-x}$, η thereby increasing monotonically with increasing EC content in the solvent.^{14,30-32} Finally, η increases with increasing m for a solution,^{25,38,39} which can be thought of, very roughly, as an extension of the rule just stated when the solution is viewed as a binary solution of the salt and the solvent.

Using these three factors and their changes with m , x , and T , we can consistently explain the change of κ with these three variables for the present electrolyte system. One prominent feature of Fig. 1 is that, as m increases from zero, κ initially increases but soon reaches a maximum (κ_{max}) at a particular value of m (m_{max}) and then decreases. Notice that κ_{max} here refers only to the maximum in κ with respect to change of m at fixed x . The initial stage of increasing κ manifests the dominance of the number factor, when an increase in m raises the number of dissociated ions and thereby makes the electrolyte more conductive. As m further increases, however, ion association and an increase in η become more dominant, offsetting the number effect, and κ first levels off and then falls. This trend of κ exhibiting a maximum at a certain m is a universal phenomenon for liquid electrolytes, which has been recorded for many other electrolytes of lithium salts.^{2,4,8,24,39} Practical implication of this is that control of m is an effective way of achieving maximum κ for an electrolyte. Of course, as m_{max} changes with x and T , as shown in Fig. 1, the control of m should be done accordingly.

We can eliminate the effect of m on the number factor by dividing κ by m . When this is done on the data of Fig. 1 and the resulting molal conductivity Λ plotted against m , we have Fig. 2. Now the molal conductivities decrease monotonically with increasing m , as would be expected since the number factor that would boost κ with increasing m has been taken out, and the remaining factors of vis-

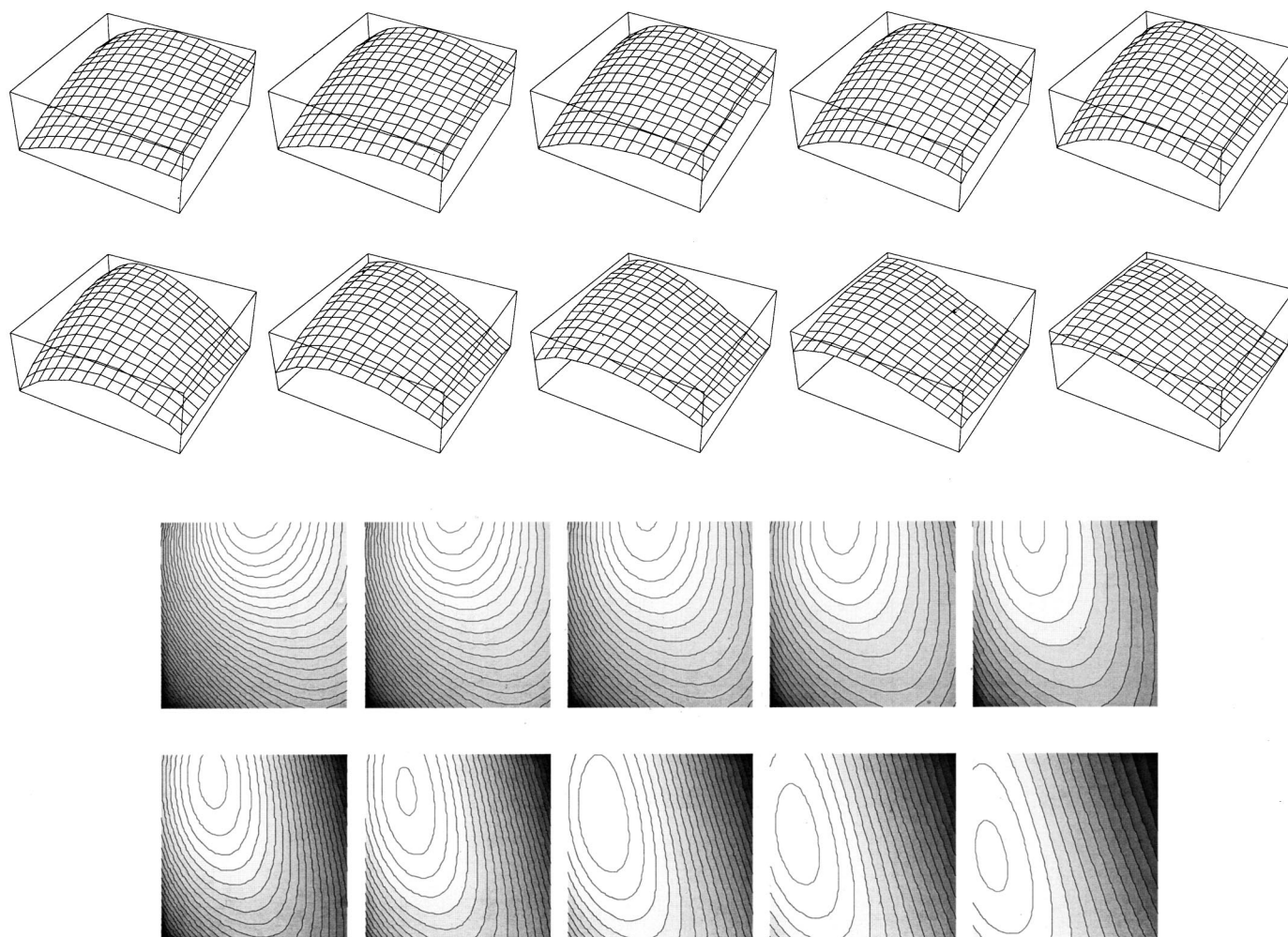


Figure 4. Change of conductivity with changes of salt content and solvent composition at different temperatures according to Eq. 4, each described by a surface plot (top rows) and a contour plot (bottom rows) in the corresponding positions. The orientations, titles, and units of the axes for the plots are the same as in Fig. 3. Temperatures for the figures are, in order of their appearance, from 60 to -30°C in 10°C decrement. The κ ranges for the surface plots are, in order of their appearance, (8.49, 16.7), (7.78, 14.6), (7.03, 12.6), (6.23, 10.6), (5.44, 8.70), (4.63, 7.00), (3.14, 5.47), (1.93, 4.14), (1.04, 3.00), and (0.46, 2.06) mS cm^{-1} . For the top row contour plots, the highest contours start at 16.4, 14.4, 12.4, 10.4, and 8.6 mS cm^{-1} from left to right and the contour spacing is 0.2 mS cm^{-1} ; for the bottom row, they start at 6.9, 5.4, 4.0, 2.9, and 2.0, and the spacing is 0.1.

cosity and ion association both work to decrease κ with increasing m .

Dependency of conductivity on simultaneous changes of salt content and solvent composition and its change with temperature.—For an electrolyte system of a salt dissolved in a mixed solvent, m and x can both be controlled and tailored in coordination to maximize the conductivity of the electrolyte according to the particular temperature needs. For this purpose, knowledge of the dependency of κ on simultaneous changes of m and x and in the change of this dependency with T becomes critical. Such knowledge can be readily acquired once we have a faithful mathematical representation of κ as a function of m , x , and T , such as Eq. 4. From such an equation, we can plot κ surfaces with m - x coordinates at a series of different temperatures and observe and compare the features of these surfaces. Such are the plots of Fig. 4, where we have placed ten pairs of surface and contour plots of κ according to Eq. 4 for successively lower temperatures. To provide more details on the abbreviated plots of Fig. 4, the pair of plots at 30°C has been enlarged, filled with axis titles and labels, and plotted in Fig. 3. The contour plots make their corresponding surface plots more quantitative as each contour represents a specific κ value indicated in the caption. They are also more revealing for locations of κ_{max} on the ridge of

the κ surface, which we designate as the κ_{max} line, along which are the optimal combinations of m and x for high κ values.

To more clearly show the change of the κ_{max} line with temperature, we determined such a line from each of the κ surfaces of Fig. 4 and plotted them together as m - x curves in Fig. 5. We also plotted these lines as κ - x curves in Fig. 6 to show their relative heights in κ . A prominent feature of Fig. 5 is that the κ_{max} lines move toward lower values of m with increasing x . The reason lies primarily in the increased viscosity as the solvent becomes more EC rich. This increase adds to the increase of viscosity due to increasing m , thus advancing m_{max} at which the overall viscosity starts to dominate the number effect. The same explanation also applies to the κ_{max} line shifting to the left with lowering T . The trend of smaller m_{max} at higher x , however, reverses itself at particularly high x and low T . A possible explanation for this is that under these high-viscosity conditions, the rate of further increase in η with increasing m would be slow, thus delaying the dominance of the viscosity over the number effect.

Another feature shown in Fig. 5 is the occurrence of an apex on each of the κ_{max} lines (the open dots; see also Fig. 6), which moves down to the right with decreasing T . Note that the apex thus defined is different from a κ_{max} , the κ maximum at a fixed m , whose exis-

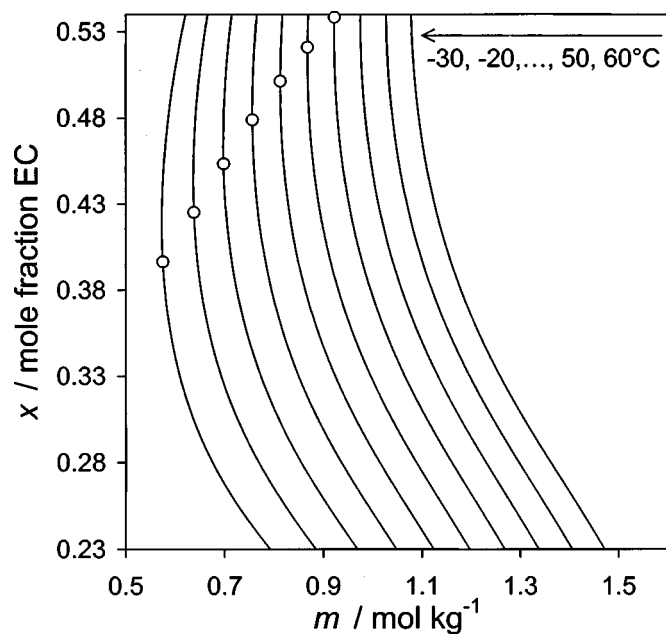


Figure 5. κ_{\max} lines and κ apexes (open circles) of the κ surfaces of Fig. 4 in the coordinates of salt content m and solvent composition x , demonstrating their change with temperature. Temperatures of the curves from right to left are from 60 to -30°C in 10°C decrement, as indicated in the figure.

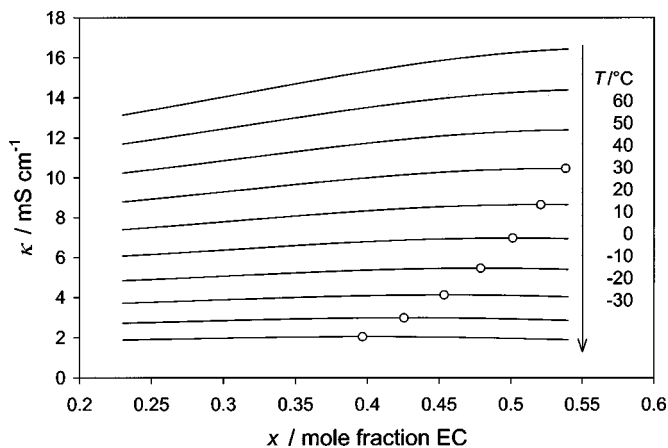


Figure 6. κ_{\max} lines and κ apexes (open circles) of the κ surfaces of Fig. 4 in the coordinates of solvent composition x and conductivity κ , demonstrating their change with temperature T .

tence does not guarantee the existence of an apex. The occurrence of an apex on a κ_{\max} line can be explained with the competing factors of ε and η . On the low x side of the apex, as x increases, ε of the solvent gets higher, which increases the number of dissociated ions in the electrolyte and hence its conductivity. On the high x side of

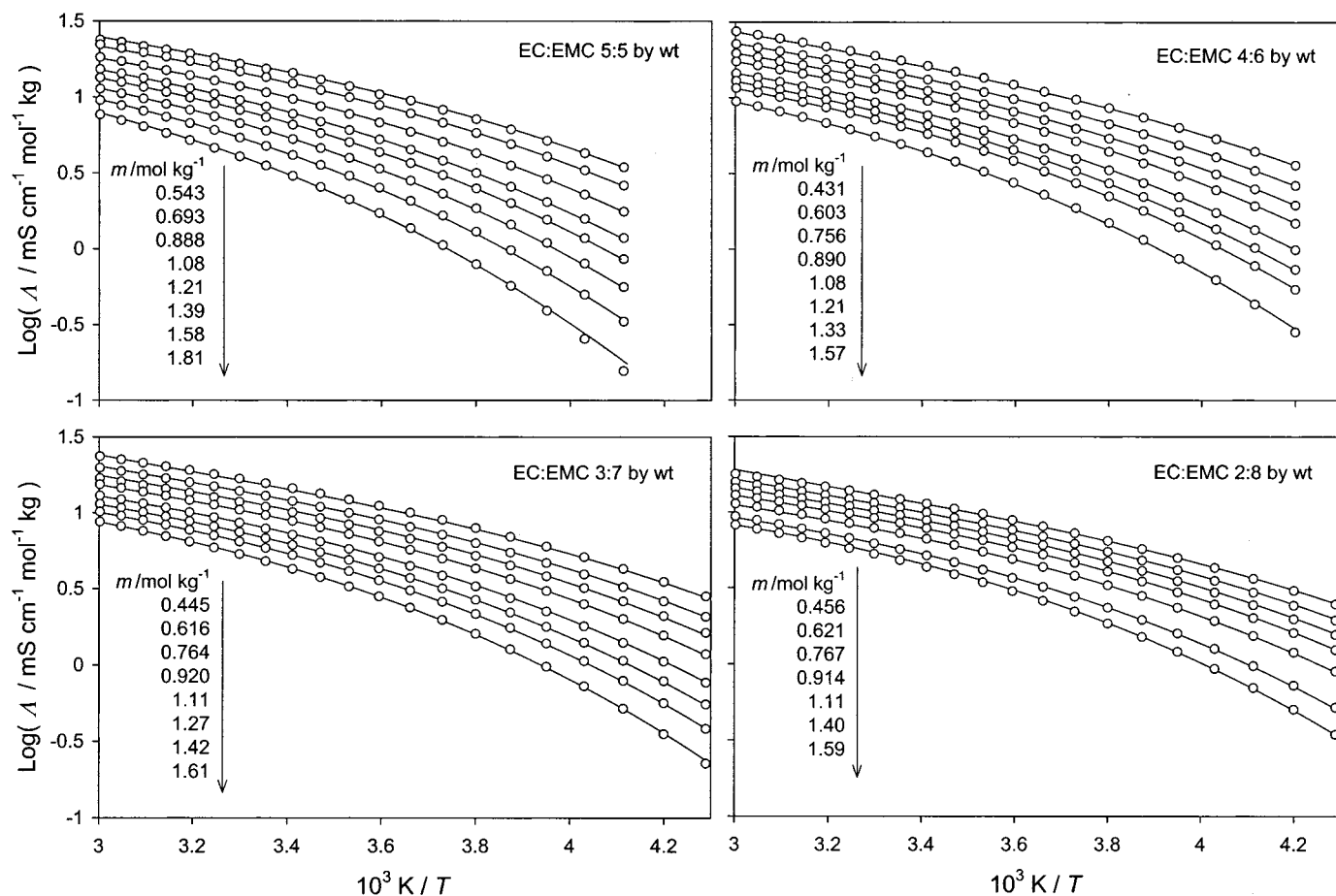


Figure 7. Change of logarithmic molal conductivity $\log \Lambda$ with the inverse of temperature $1/T$ at different salt contents m and solvent compositions EC:EMC for electrolytes of LiPF_6 in EC-EMC. The dots represent experimental data, and the curves plot a trivariate polynomial fitting function.

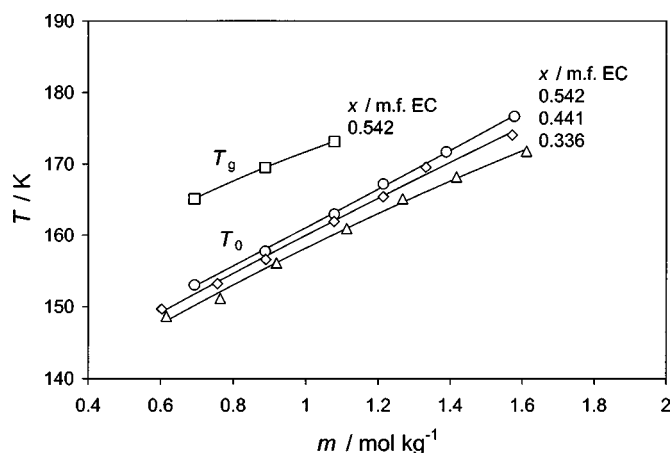


Figure 8. Comparison of the glass transition temperature T_g and the vanishing conductivity temperature T_0 of the VTF equation (Eq. 3) and their change with salt content m and solvent composition x . The values of T_g have been directly measured, and those of T_0 evaluated by fitting Eq. 3 to the experimental κ - T data.

the apex, on the other hand, increase in η with rising x has a stronger effect than the decrease in ion association, and conductivity falls. Further, by causing a rapid increase in η , a lowering T would bring on the dominance of η over ϵ at lower x and m , which explains the downward to the right movement of the apex in Fig. 5. The monotonic and substantial increase of η with lowering T is also manifested in the fall of the κ_{\max} line of Fig. 6 and the lowering height of the surfaces and contours of Fig. 4. Finally, it is interesting to note that as x increases on the low x side, the value of κ_{\max} on a κ_{\max} line rises (Fig. 6), while the line moves toward low m demonstrating the effect of viscosity increase (Fig. 5). This comes as a result of ion association setting in faster and earlier than the increase of viscosity as m increases from zero. Consequently, as x increases, weakening the ion association while raising the viscosity, κ increases with a faster rate as m increases from zero, resulting in a higher κ_{\max} even though the κ_{\max} occurs at lower m . A well-known case for the early setting in of the ion association as m increases from zero is that conductivities of even strong electrolytes start to depart from the Debye-Hückel relation at concentrations below 0.1 m .⁴⁰

Figures like Fig. 5 can be valuable tools for formulating electrolytes of high κ by mapping out the locations for the optimal combinations of m and x . If no restrictions applied to m and x , then an apex (an open dot of Fig. 5) on a κ_{\max} line of a particular T should be the aim for the optimal m - x combination for that T . If the movement of the apex with T were to be followed, both m and x would have to be lowered in value with lower T . If for some reason either m or x had to be at a particular value, then x or m could be adjusted so that the combination would fall on a κ_{\max} line at the desired T . In addition, departure from the apex or the κ_{\max} line should be allowed more for x than for m , as the value of κ is in general more sensitive to m than to x , and more so at lower T , as indicated by the narrowing of the κ ridge on the κ surfaces shown in Fig. 4. Finally, the trends found here should have a more general significance in suggesting how conductivities of other electrolyte systems with a similar constitution would change with the same variables, as the causes for these trends, as we have discussed, are not unique to the electrolytes of this experiment.

Change of conductivity with temperature.—As we have seen previously, conductivities of the electrolytes decrease monotonically with decreasing temperature. This is because, except for very high temperatures, where the κ of an electrolyte can actually fall with rising T due to the dominance of ϵ over η ,²⁶ the rise of η of an electrolyte with lowering T outweighs the increase of ϵ of the sol-

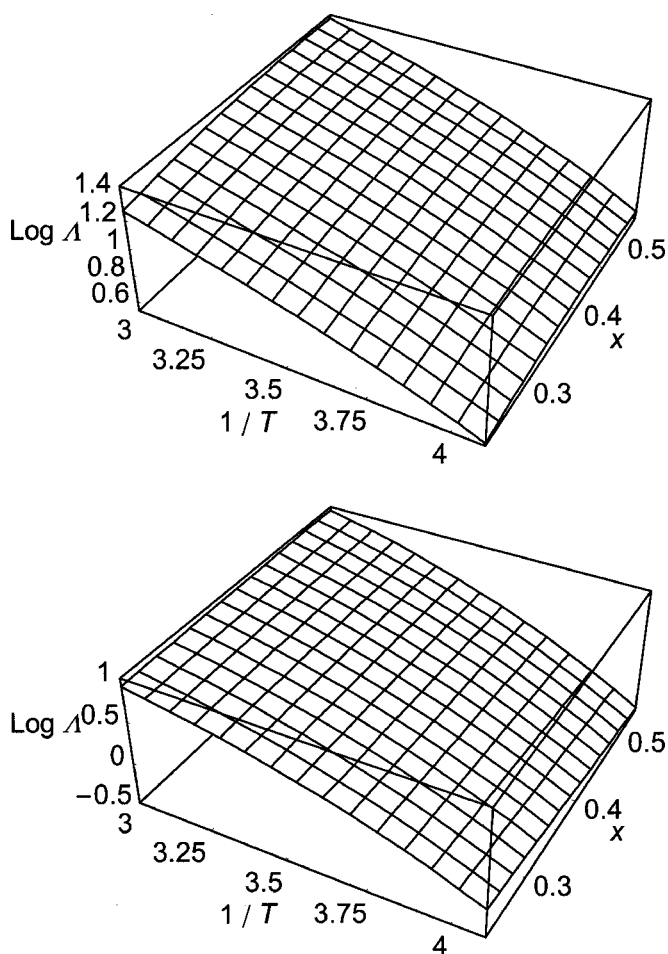


Figure 9. Change of logarithmic conductivity $\log \Lambda$ with the inverse of temperature $1/T$ and solvent composition x at salt contents of 0.5 (top) and 1.6 mol kg^{-1} (bottom). The complete titles of the axes are 10^3 K/T , $x/\text{mol kg}^{-1}$, and $\log(\Lambda/\text{mS cm}^{-1} \text{ mol}^{-1} \text{ kg})$. These surfaces have been produced with a trivariate polynomial that had been fitted to the experimental data of Fig. 7.

vent. To see more clearly the effect of temperature on conductivity, we have taken logarithmic molal conductivities for all the experimental data and plotted them against the inverse of temperature in Fig. 7. The resulting Arrhenius plots show, in addition to the monotonic change of conductivity with temperature, an increase in the rate of this change as T is lowered or as m is increased. These seem to point to a faster rate of change in η as η itself increases, as a lower T and a higher m both contribute to a higher η .

The κ - T data as plotted in Fig. 7 can be nicely fitted with Eq. 3. The result of the fitting is an evaluation for the constants of the equation, of which particularly interesting and meaningful is T_0 , the vanishing conductivity temperature. Values of T_0 so obtained for the three more EC-rich electrolytes are plotted in Fig. 8, along with several values of glass transition temperature (T_g) that we have directly measured for the most EC-rich electrolytes.¹⁶ T_g of a material is a characteristic temperature at which the material in the state of supercooled liquid changes its behavior from that of a liquid to a solid during cooling without undergoing crystallization, or conversely, from a vitreous solid to a liquid during heating. An example of such a switch of behavior would be in the thermal contraction of a supercooled liquid, which in cooling follows that of a liquid until T_g , when it breaks away from the liquid and starts a new trend characteristic of the material in its crystalline form. On the molecular level, as η of the liquid rises to as high as 10^{13} poise at T_g , the

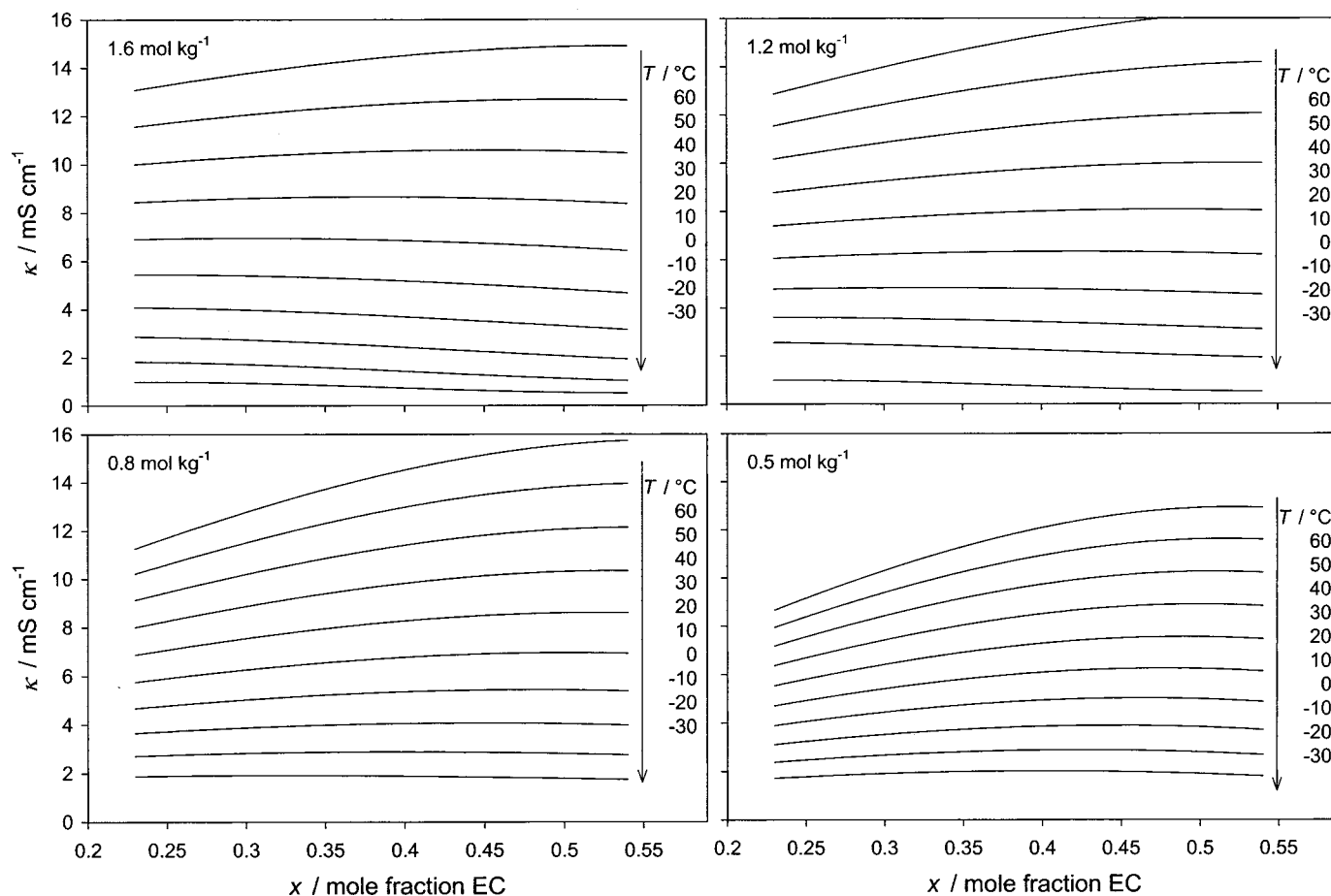


Figure 10. Change of conductivity κ with solvent composition x , according to Eq. 4, at different temperatures T and different salt contents as indicated in each of the plots.

molecules of the liquid are no longer able to rearrange themselves, rendering the further contraction of the material solid-like.⁴¹ It follows that the higher the viscosity of a liquid, the sooner it will reach this transition point in cooling, and the higher its T_g will be. As both a higher m and a higher x contribute to a higher η of an electrolyte, they would be expected also to raise the T_g of the electrolyte. That T_g indeed rises with higher m is demonstrated by the electrolytes of LiPF₆ in EC-EMC as shown in Fig. 8, and by many other solution systems.⁴² A case for the rise of T_g with higher x can be seen in the binary solvents of EMC-propylene carbonate (PC), where T_g of the solvent rises with its richness in PC, the more viscous of the two components.²⁰ Figure 8 also shows that T_0 rises with higher m and x just as T_g , but is lower than T_g by about 10°C. The similarity between T_g and T_0 is not surprising as T_g is the temperature at which the ions and the molecules of the electrolyte lose their mobilities, while T_0 is where the electrolyte loses its conductivity, which depends entirely on the movement of those same ions and molecules. The lower value of T_0 than T_g is also expected because while η of the electrolyte rises to a high but noninfinite value at T_g , its κ would vanish completely at T_0 (Eq. 3). Angell and Smith fitted their data of η and ϵ on several hydrogen-bonded molecular liquids at temperatures near their T_g 's with the VTF equation and obtained values of T_0 30 to 70°C below those of T_g .⁴³ Barthel *et al.* fitted their data of κ and η on a molten salt of trifluoromethanesulfonic acid monohydrate at temperatures far above its T_g , with nearly identical results for T_0 from the two sets of data.²⁷

Solvent composition also has a definitive though mild influence on the temperature dependency of conductivity of the electrolytes.

To observe this influence, we have fitted the experimental data of Fig. 7 with a trivariate polynomial and plotted in Fig. 9 two surfaces of this polynomial at salt contents of 0.5 and 1.6 mol kg⁻¹. It can be seen from both surfaces that the change of conductivity with temperature speeds up slightly as the solvent gets more EC-rich. However, comparison of these surfaces reveals that this accelerating change of κ with x is likely affected by two different mechanisms according to the salt content of the electrolytes. Along the low T edge of the bottom surface of Fig. 9 for 1.6 mol kg⁻¹ salt content, Λ falls with increasing x . This indicates that for concentrated solutions with high viscosities, conductivity is dominated by an increase of η with increasing x , although ion association also weakens as ϵ of the solvent increases. Also this high η situation is accentuated with a lowering of T . On the other hand, Λ rises with increasing x along the high T edge of the top surface of Fig. 9 for 0.5 mol kg⁻¹ salt content. The situation is therefore reversed for dilute solutions with low viscosities, where κ is dominated by the weakening ion association accompanying a rising ϵ as x rises. This low η situation is accentuated by an increase in T as η gets even lower and ion association stronger with the rise in x .

Change of conductivity with solvent composition.—Now that we have a faithful functional representation of the experimental conductivity data, we can easily obtain relationships between κ and x by taking m and T to desired values in the function. Such relationships would be difficult to obtain directly from experiments, as errors in the control of m during sample preparation would cause large uncertainties in these relationships because of the faster change of κ with m than with x . Some examples of the κ - x curves obtained from

Eq. 4 are plotted in Fig. 10. Compared to Fig. 1, we see that although the change of κ with x is generally slow, many of the κ - x curves still exhibit a maximum in κ . Such a maximum is a consequence of κ falling with x becoming either too small or too large, the former with weakened ion dissociation and the latter an increased viscosity in the electrolyte. The same maximum has been observed in many other electrolyte systems.^{2,14,32}

Conclusions

Electrolytic conductivity of the electrolyte system of LiPF₆ in EC-EMC measured at practical values of its salt content, solvent composition, and temperature could be faithfully fitted with a trivariate polynomial function. Such a function when plotted in the space of salt content and solvent composition at a series of temperatures showed how the conductivity changed with the simultaneous changes of salt content and solvent composition and how temperature affected this change. At 30°C, the conductivity reached a maximum of 10.5 mS cm⁻¹ at 0.92 mol kg⁻¹ for salt content and 0.54 mole fraction of EC for solvent composition. As the temperature was lowered, the values of these variables corresponding to the maximum conductivity also became smaller. In addition, change of conductivity was more rapid with salt content than with solvent composition, and more so at lower temperatures. Fitting the VTF equation to the experimental data resulted in an evaluation of T_0 , which was lower than the directly measured T_g of the same electrolytes and increased with salt concentration and EC content in the solvent. Finally, these observed trends in the change of conductivity with salt content, solvent composition, and temperature could be consistently explained based on the dependency on the same variables of these three factors: the number of dissociated ions in the electrolyte, the dielectric constant of the solvent, and the viscosity of the electrolyte. As these factors and how they affected the conductivity of the electrolytes were not unique to the electrolytes of this experiment, the trends found for them should have a more general significance in providing guidance on how conductivities of other electrolyte systems with a similar constitution would change with the same variables.

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