How Conductivities and Viscosities of PC-DEC and PC-EC Solutions of LiBF$_4$, LiPF$_6$, LiBOB, Et$_4$NBF$_4$, and Et$_4$NPF$_6$ Differ and Why

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Electrolytes of LiBF$_4$, LiPF$_6$, LiBOB, Et$_4$NBF$_4$, and Et$_4$NPF$_6$ in propylene carbonate-diethyl carbonate (PC-DEC) and propylene carbonate-ethylene carbonate (PC-EC) binary solvents were compared for their electrolytic conductivity (κ) and viscosity (η) to assist their application to the batteries and capacitors and to understand the mechanisms underlying the differences in these properties. For η, the Li$^+$-salts resulted in considerably higher values than the Et$_4$N$^+$-salts, and the influence of an anion was such that the larger its size, the higher the η of the electrolyte. Correspondingly, κ of the Et$_4$N$^+$-electrolytes was substantially higher than the Li$^+$-electrolytes, and a larger anion was accompanied by a lower κ, except for electrolytes at the low-η end. Toward this end, the order of κ tended to be in reverse: the κ of an electrolyte with a larger anion rose relative to one with a smaller anion. All evidence presented leads to the conclusion that the η, and thereby the κ, of the electrolytes are dominantly affected by the number of unassociated Li$^+$ ions through their solvation by the carbonate solvent molecules, the different anions of the Li-salts exerting their influence only through altering the number by their different powers for associating with the Li$^+$.

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To date, the most dominant form of electrolyte for lithium-ion batteries has been the liquid electrolyte composed of a mixed organic carbonate solvent and a lithium salt with a large and stable anion, and the most dominant members of the salts have been lithium hexafluorophosphate (LiPF$_6$), tetrafluoroborate (LiBF$_4$), and more recently, bis(oxalato)borate (LiBOB). For these reasons, electrolytic conductivities (κ) and viscosities (η) of PC-DEC and PC-EC solutions (PC: propylene carbonate; DEC: diethyl carbonate; EC: ethylene carbonate) of the three lithium salts have been systematically measured in wide ranges of mass fraction (w) of solvent composition, salt molality (m), and temperature (θ).[1-3] This report is aimed at bringing these individual studies together for a comparison of their κ and η for the purpose of highlighting the differences in the properties of these salts for the practical applications, understanding the mechanisms underlying these differences, and pointing out ways of using each salt judiciously according to particular application requirements.

To add clarity, two additional electrolyte systems, PC-DEC and PC-EC solutions of tetraethylammonium tetrafluoroborate (Et$_4$NBF$_4$) and hexafluorophosphate (Et$_4$NPF$_6$), were systematically and accurately measured for their κ and η, and the results were combined with those of the lithium salts for comparison and discussion. It was felt that the comparison of the lithium salts with the quaternary ammonium salts of the same anions could shed much light on the roles the cations, with their vastly different sizes, play in determining the η and κ. In addition, as these two solution systems are each themselves dominant electrolytes for nonaqueous electrochemical capacitors, the accurate measurement of their properties and the comparison of the results with each other and with the lithium electrolytes would provide much valuable information in this regard.[4-6] Note also that although the three carbonate solvent components studied here, EC, PC, and DEC, are far from exhausting all the carbonates available, most of the relationships observed and the conclusions drawn here with regard to the relative changes in the properties of the electrolytes with solvent composition is not expected to change much when DEC is replaced by EMC (ethyl methyl carbonate) or DMC (dimethyl carbonate), or when PC or EC by another cyclic carbonate.

Experimental

The experimental results of κ and η of the carbonate solutions of the three lithium salts used in the present discussion were from

previous studies.[1-3] The solutions of the two quaternary ammonium salts were measured in this study for their κ and η in the same way as for those of the three lithium salts.

More specifically, the Et$_4$NPF$_6$ and Et$_4$NBF$_4$ of both 99+% purity were purchased from Aldrich and Fluka, respectively, and the PC of 99.98% purity and DEC and EC both of 99.95% from Grant Chemical. These materials were used without further treatment. Starting solutions were prepared in an argon-filled dry box by mixing the Et$_4$N$^+$-salts to the solvents of PC, PC$_{0.8}$EC$_{0.2}$, PC$_{0.6}$EC$_{0.4}$, PC$_{0.4}$EC$_{0.6}$, PC$_{0.8}$DEC$_{0.2}$, PC$_{0.6}$DEC$_{0.4}$, PC$_{0.4}$DEC$_{0.6}$, and PC$_{0.3}$DEC$_{0.7}$, to concentrations near the saturation points of the salts. Measurement of κ on these solutions and their subsequent dilution for the next set of less concentrated solutions were carried out in a dry room. At the end of each measurement, a small amount of sample was taken from each electrolyte, on which the T_g was determined with a modulated differential scanning calorimeter (MDSC 2920, TA Instruments) cooled with liquid nitrogen. The κ of the solutions was measured with an impedance scan from 1 MHz to 20 Hz obtained with an HP 4284A precision LCR meter at selected
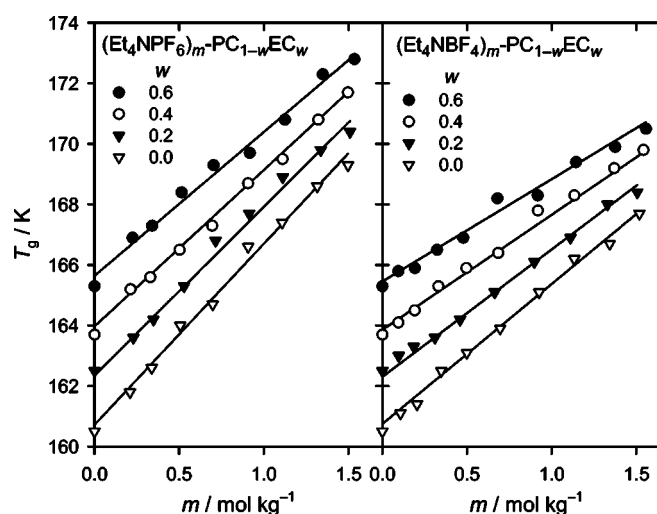
Figure 1. Change of glass transition temperature T_g with salt molality m at four values of solvent mass fraction w for the solutions (Et$_4$NPF$_6$)$_m$-PC$_{1-w}$EC$_w$ (left) and (Et$_4$NBF$_4$)$_m$-PC$_{1-w}$EC$_w$ (right), as indications for the changes in their viscosity.

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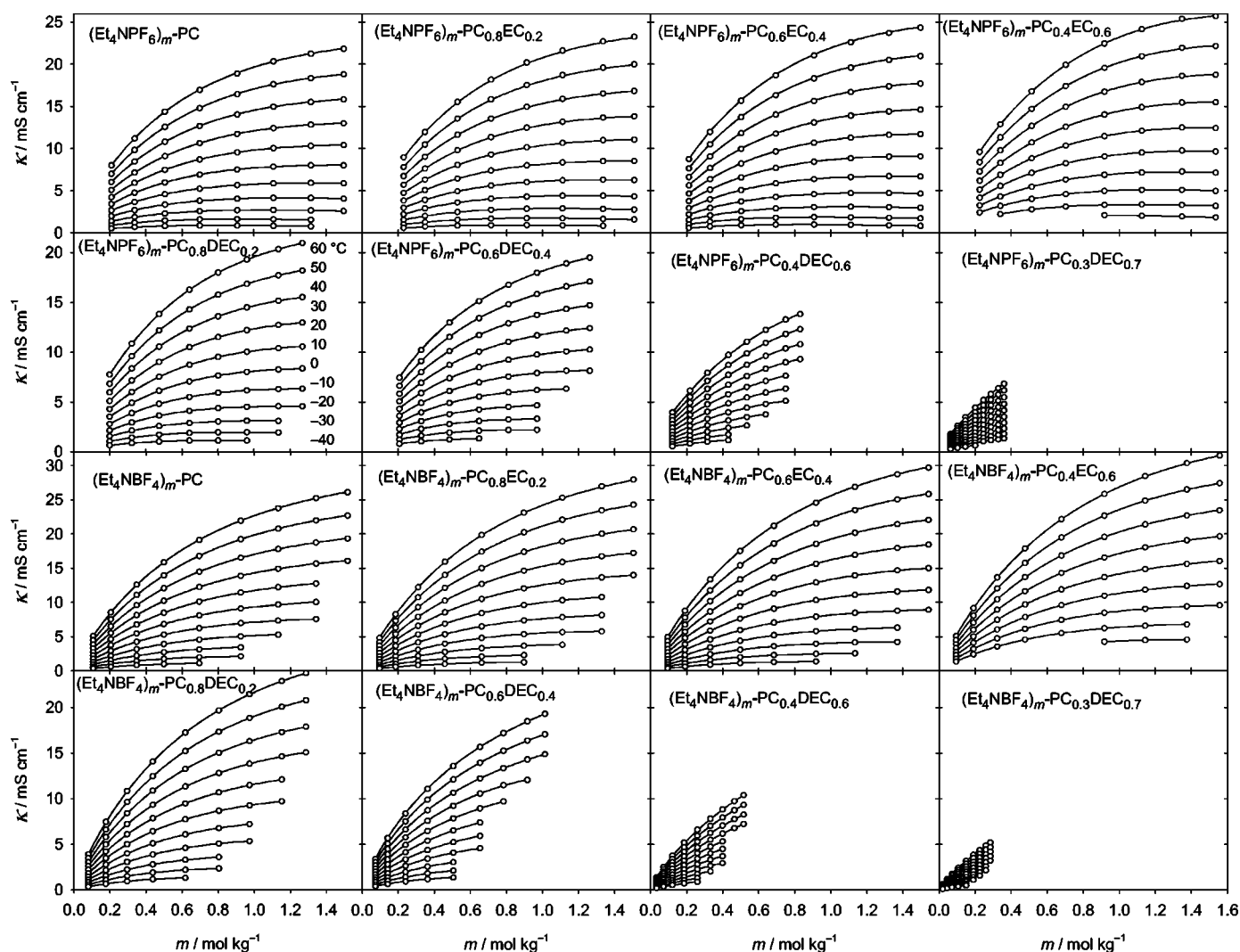
**Figure 2.** Change of electrolytic conductivity κ with salt molality *m* at temperatures from 60 to −40°C for the PC-EC solutions of Et₄NPF₆ (first two rows) and Et₄NBF₄ (last two rows) at various solvent compositions as indicated in the plots.

temperatures within a Tenney Jr. Environmental Chamber. The overall measurement error in κ was estimated to be below 0.5%. More experimental details on the determination of T_g and κ can be found elsewhere.[1,2,7]

Results
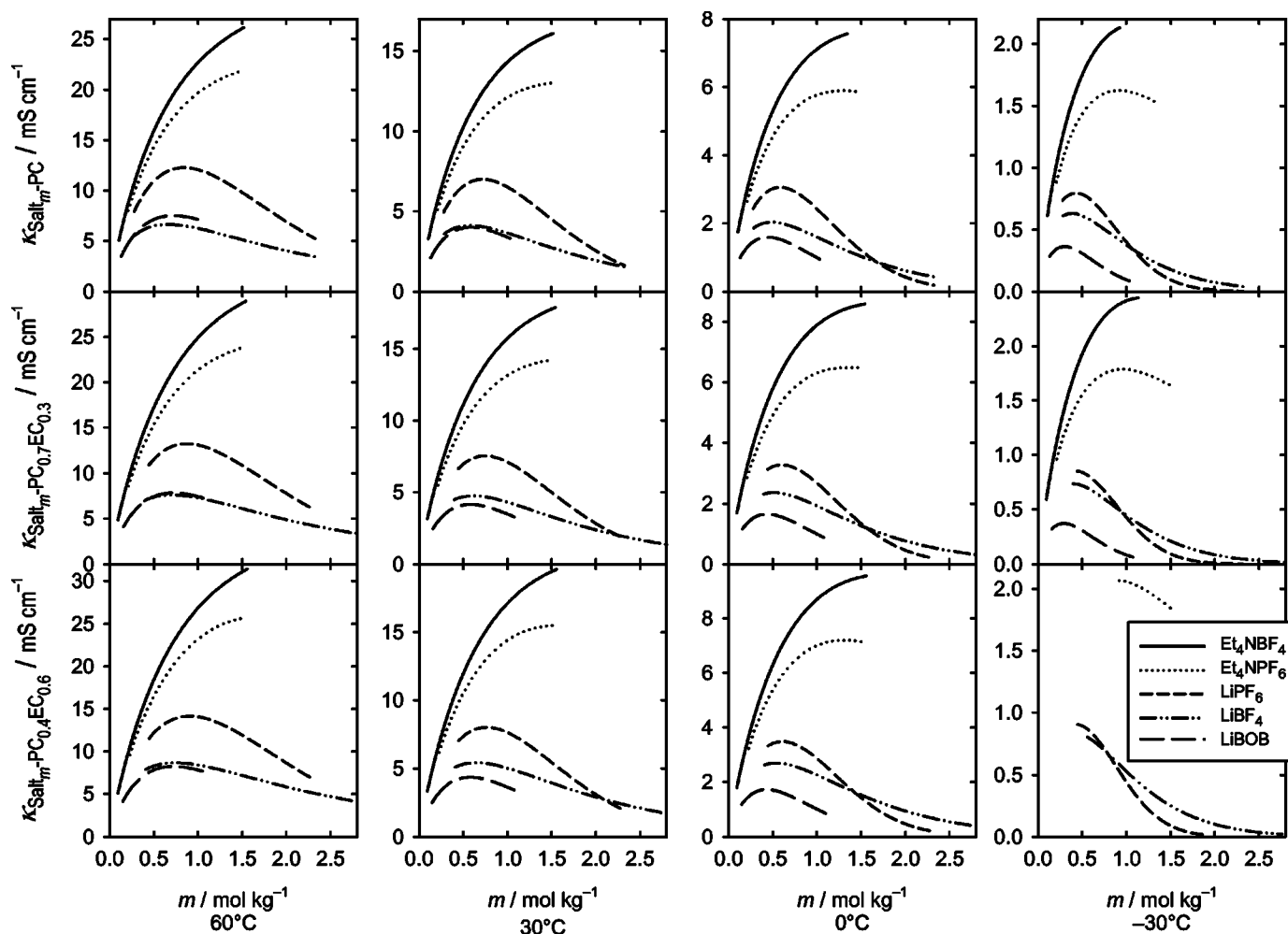
Viscosities of the PC-EC solutions of Et₄NPF₆ and of Et₄NBF₄.—As an indication for the change of η,[8] the experimental results of T_g measurement for the PC-EC solutions of Et₄NPF₆ and of Et₄NBF₄ are, respectively, plotted on the left and right of Fig. 1, together with their polynomial fitting functions. As shown, T_g of both solutions rises with *m* and with *w* of EC, just as that of the Li⁺-containing electrolytes. Also, for same values of *m*, T_g is higher for the PF₆⁻- than for the BF₄⁻-containing electrolytes, in accordance with the trend observed in the Li⁺-containing electrolytes.

Conductivities of PC-DEC and PC-EC solutions of Et₄NBF₄ and Et₄NPF₆.—Figure 2 plots the results of κ measurement for the PC-DEC and PC-EC solutions of Et₄NPF₆ and Et₄NBF₄, together with their fitting functions κ = $f(m, w)$ in the θ-range of −40 to 60°C.[1,7] It can be seen that the κ initially rises with *m* and then starts to level off, the eventual fall being prevented only by the saturation of the solution. This situation was the result of the limited solubili-
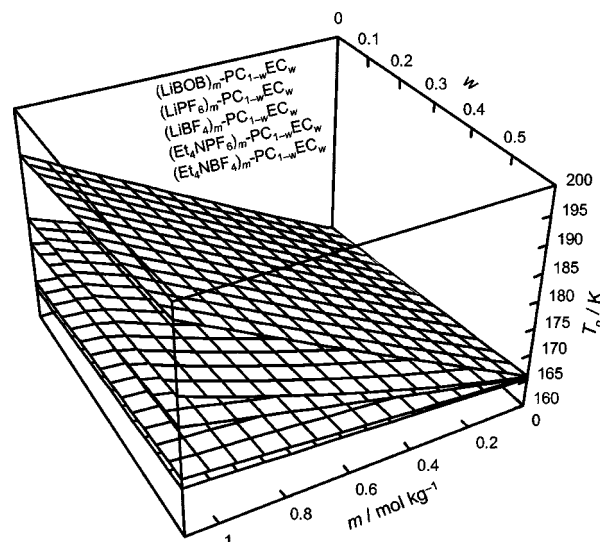
Figure 3. Comparison of surfaces of glass transition temperature T_g in the coordinates of salt molality *m* and solvent mass fraction *w* for the PC-EC solutions of LiBOB, LiPF₆, LiBF₄, Et₄NPF₆, Et₄NBF₄, as indications for the changes in their viscosity.

Figure 4. Comparison for the change of conductivity κ with salt molality *m* for the PC-EC solutions of Et₄NBF₄, Et₄NPF₆, LiPF₆, LiBF₄, and LiBOB at solvent compositions of 0 (top row), 0.3 (middle row), and 0.6 (bottom row) of EC mass fraction and at temperatures of 60 (first column), 30 (second column), 0 (third column), and −30°C (last column).

ties of the Et_4N^+-salts in combination with the high *m* values at which the κ would peak. General dependence of κ on *w* is such that the κ rises with *w* in the $PC_{1-w}EC_w$ solvent, as shown in the first- and third-row plots, and falls with *w* in the $PC_{1-w}DEC_w$ solvent, as shown in the first plot of the first-row plus the second-row plots and the first plot of the third-row plus the fourth-row plots. It is also seen that the solubility of the Et_4N^+-salts in the $PC_{1-w}DEC_w$ solvent diminishes rapidly with *w*. The results of κ in PC here agree with those by Ue in both the value and the observation of Et_4NBF_4 being more conductive than Et_4NPF_6.[5]

Discussion

What is known about the solvents, salts, and their solutions.— Because the η and ε of the solvents play major roles in determining the κ of the electrolytes through affecting the η of and the ion-association in the electrolytes, respectively, a summary is given here for what is already known on these properties of the solvents.[8] The ε of the solvents changes monotonically and smoothly with *w* and θ, falling with θ universally and falling with *w* in $PC_{1-w}DEC_w$ but rising in $PC_{1-w}EC_w$ (ε of DEC, PC, and EC at 40°C: 2.809, 61.43, and 89.78). From these results, Bjerrum critical distance has been calculated for univalent ions, which indicates that ion-association should be nearly independent of θ, rising only slightly with θ for high-ε solvents such as EC-rich mixtures of PC-EC and falling slightly for low-ε solvents such as DEC-rich mixtures of PC-DEC.

But it shows a strong dependency on *w*, rising steadily as ε falls with the change of *w*. The η of the solvents falls quickly with *w* in $PC_{1-w}DEC_w$ but rises slowly in $PC_{1-w}EC_w$ (η of DEC, PC, and EC at 40°C: 0.622, 1.91, and 1.93 mPa s).

In addition to the above specific solvents and their solutions of lithium salts to be compared and discussed, other electrolytes of lithium salts in carbonates, esters, and other aprotic solvents have been measured or estimated for their properties. In particular, many anions commonly used as a counterion to Li^+ in making Li^+ electrolytes have been estimated through calculation for their ionic volumes, which include BF_4^- (51 Å³), ClO_4^- (56 Å³), PF_6^- (69 Å³), AsF_6^- (73 Å³), BOB^- (119 Å³), to mention just a few relevant to this study.[9,10] In related studies, strength of ion association of these anions with Li^+ has been estimated to follow the order of the anionic volume, *i.e.*, $BF_4^- > ClO_4^- > PF_6^- > AsF_6^-$ in PC-γBL (γ-butyrolactone) and PC-EMC solutions.[9,11] In a separate study, electrolytic conductivities of PC-DEC solutions of $LiBF_4$, $LiClO_4$, $LiPF_6$, and $LiAsF_6$ have been measured as functions of *m* and *w*, and shown to increase in the order of increasing anionic size and peak in *w* as well as in *m*, at θ's around room temperature.[12] The increase of κ with anionic size has also been found for $LiBF_4$, $LiClO_4$, and $LiAsF_6$ in γBL-DME (1,2-dimethoxyethane) binary solvent in other studies, in which it was also found through calculation that the cyclic carbonates and esters have their rings puckered for their most stable conformations.[13,14] In contrast, κ of $LiClO_4$ in
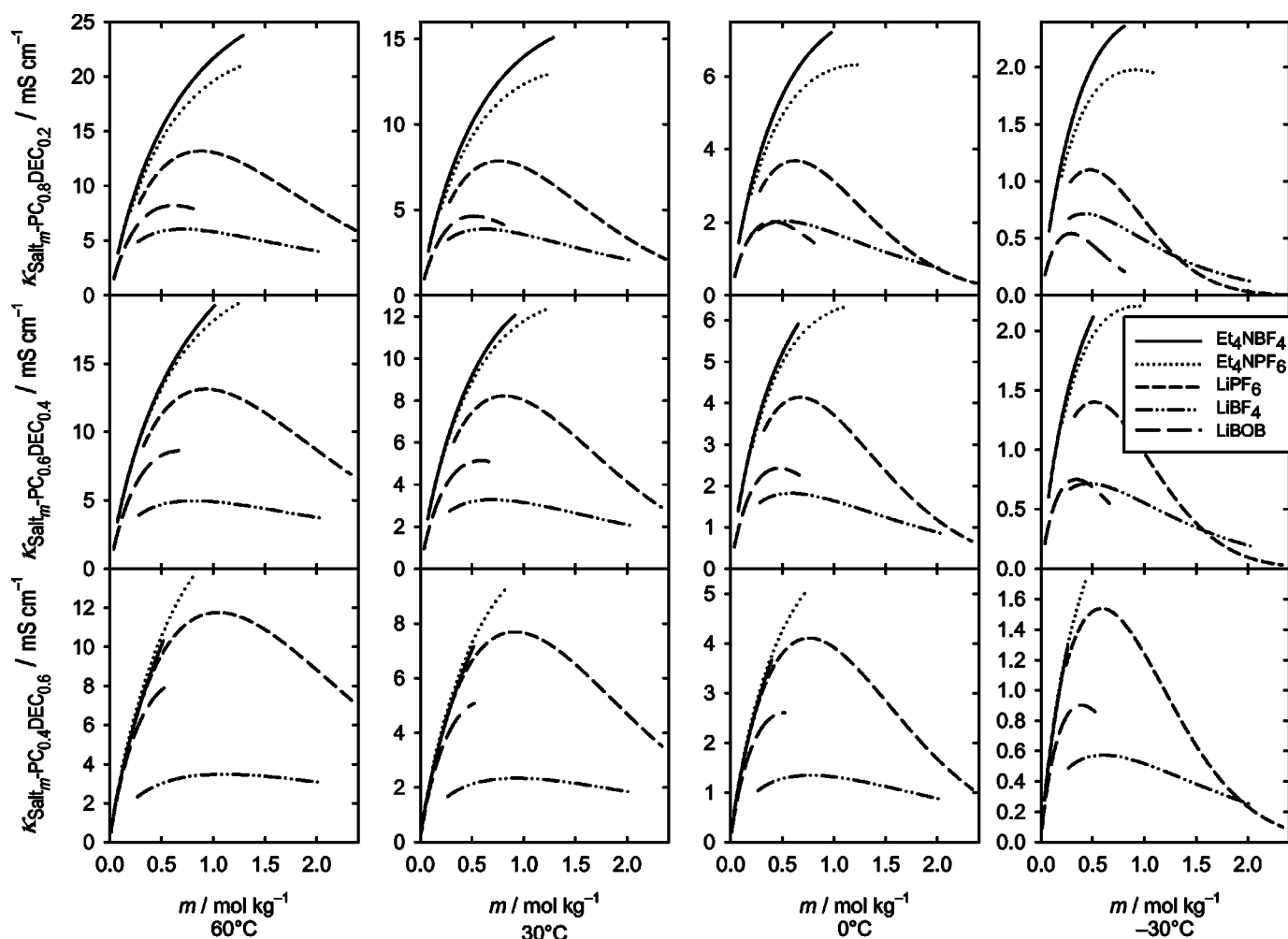
Figure 5. Comparison for the change of conductivity κ with salt molality m for the PC-DEC solutions of Et_4NBF_4, Et_4NPF_6, $LiPF_6$, $LiBF_4$, and LiBOB at solvent compositions of 0.2 (top row), 0.4 (middle row), and 0.6 (bottom row) of DEC mass fraction and at temperatures of 60 (first column), 30 (second column), 0 (third column), and $-30°C$ (last column).

PC-AN (acetonitrile) binary solvent has been found to peak in m but keep increasing with AN-content in the solvent, with the maximum κ and the corresponding m falling on a straight line.[15] The latter correlation has also been found among solutions of different salts in PC.[16]

Solvation and ion association have also been studied for lithium salts in carbonates, esters, and other similar aprotic solvents. The focus of the solvation has always been on the solvation of Li^+ by these solvent molecules, their solvation of anions being assumed nearly nonexistent due to their having a concentrated and well-exposed center of negative charge on their carbonyl oxygen but no comparable positive center.[17] The ability of such solvation of a cation as a Lewis acid by a solvent as a Lewis base is empirically measured by the donicity of the solvent,[18] of which the values for EC, PC, DEC, and DMC (dimethyl carbonate) are, respectively, 16.4, 15.1, 16.0, and 15.1 kcal/mol^{-1}.[19,20] The narrow spread of these numbers indicate that the carbonates have roughly the same propensity for solvating a cation irrespective of their cyclicity (baring the effects of steric hindrance), consistent with the carbonates having an identical carbonyl group that is solely responsible for their donicity. Through the means of spectroscopy, computation, and transport property measurement, it is found that Li^+ ions are always solvated by the carbonate or ester solvents, with the most likely solvation number around 4 at low salt concentrations.[20-27] At high salt concentrations, this solvation number is generally believed to drop due to ion association and the lack of

available solvent molecules;[24,26,27] for example, the most stable solvation number of Li^+ when paired with a ClO_4^- has been calculated to be between 1 and 2.[26] This trop of solvation number, however, has some times been contradicted.[21] It is generally accepted, with strong supporting evidence, that Li^+ ions will associate with their counterions in concentrated solutions or in solvents of a low ϵ.[1,2,3,8,9,11,22,24,25,27]

Figures for comparison and discussion.—For comparison and discussion, and for reference for those interested in knowing the relative values and changes in κ and η of the carbonate solutions of $LiPF_6$, $LiBF_4$, LiBOB, Et_4NPF_6, and Et_4NBF_4, in Fig. 3 through 9 are plotted the results of the Et_4NPF_6 and Et_4NBF_4 just presented combined with the earlier ones for the $LiBF_4$, $LiPF_6$, and LiBOB in the same solvents of PC-DEC and PC-EC. Figure 3 plots the T_g of the solutions as surfaces in the coordinates of m and w to indicate the change of η for the solutions. Figure 4 plots κ as a function of m for the $PC_{1-w}EC_w$ solutions of the five salts for w values of 0, 0.3, and 0.6 and θ values of 60, 30, 0, and $-30°C$, and Fig. 5 does the same for the $PC_{1-w}DEC_w$ solutions except for a different set of w values of 0.2, 0.4, and 06. Note that the first row of plots in Fig. 4 for the PC solutions of the salts serves as the starting row for both the PC-EC solutions of Fig. 4 and the PC-DEC solutions of Fig. 5, for the observation of change with w in the $\kappa(m)$ curves. These curves are the extended Casteel-Amis $\kappa(m, w)$ functions that have
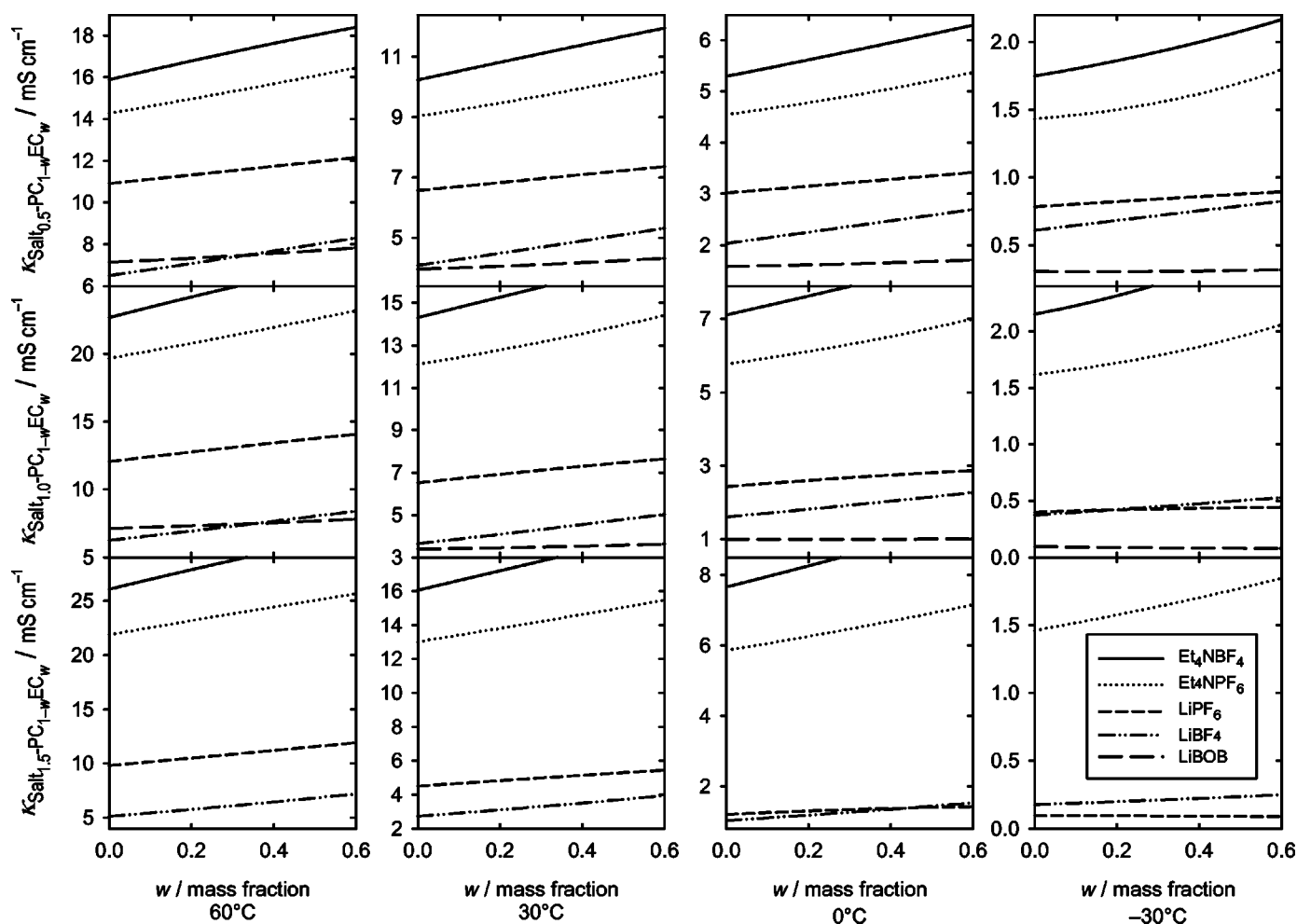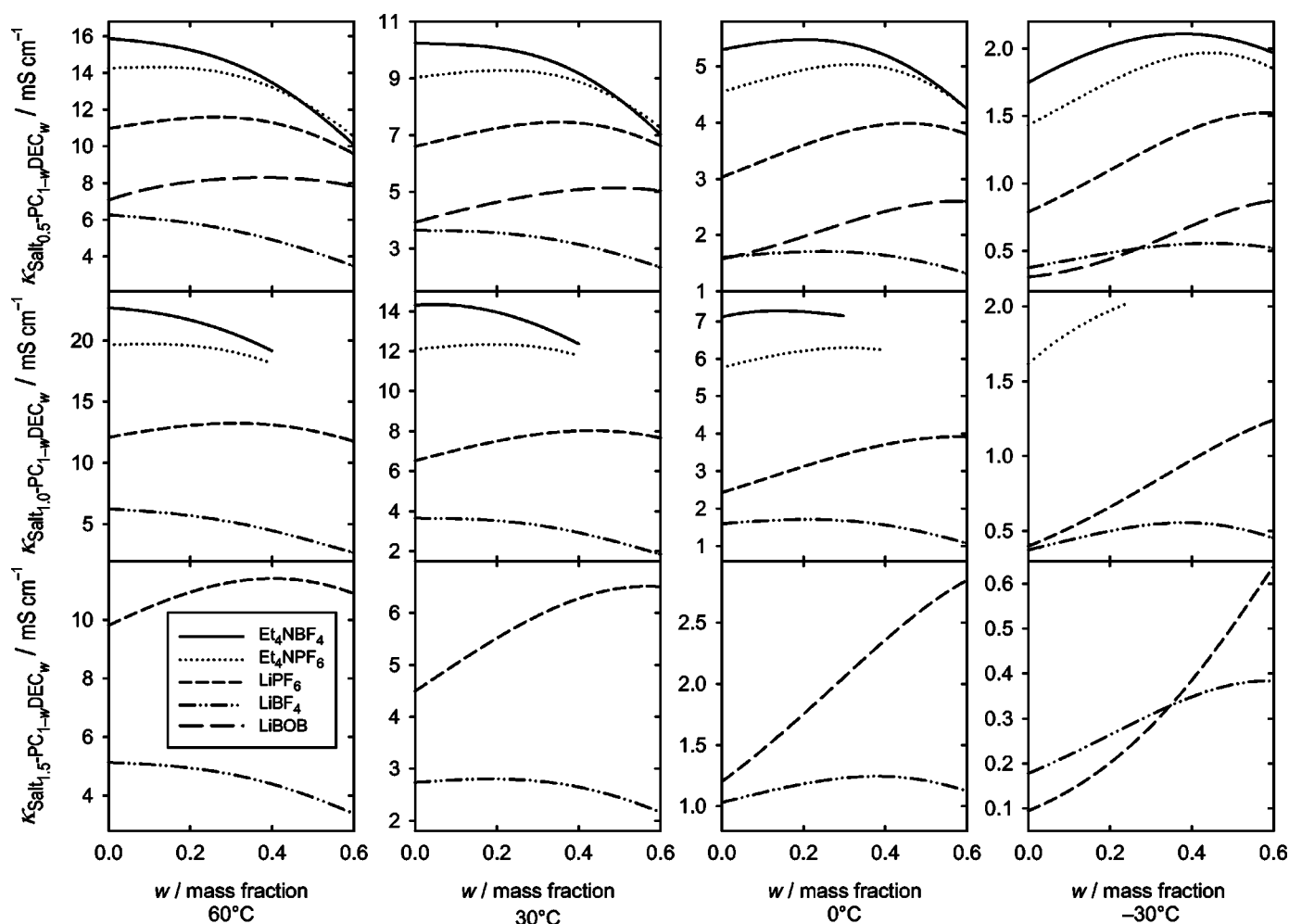
Figure 6. Comparison for the change of conductivity κ with solvent mass fraction w of EC for the PC-EC solutions of Et_4NBF_4, Et_4NPF_6, $LiPF_6$, $LiBF_4$, and LiBOB at salt molalities of 0.5 (top row), 1.0 (middle row), and 1.5 mol kg^{-1} (bottom row) and at temperatures of 60 (first column), 30 (second column), 0 (third column), and −30°C (last column).

been fitted to the measured $\kappa(m, w)$ data at the temperatures of measurement, sectioned at the plotting values of w. Figure 6 and 7 plot κ as a function of w for the PC-EC and PC-DEC solutions, respectively, for m values of 0.5, 1.0, and 1.5 mol kg^{-1} and θ values of 60, 30, 0, and −30°C. These $\kappa(w)$ curves are the same $\kappa(m, w)$ functions as used in Fig. 4 and 5 sectioned at the plotting values of m. Note that in these cases, many of the curves, in part or in whole, are absent from the plots of the more concentrated solutions due to the limited solubilities of Et_4NBF_4, Et_4NPF_6, and particularly, LiBOB. The last two figures, Fig. 8 and 9, plot as a function of w the ratio in κ of $Salt_m$-$PC_{1-w}EC_w$ over $Salt_m$-PC and of $Salt_m$-$PC_{1-w}DEC_w$ over $Salt_m$-PC, where Salt is one of the five salts. The purpose of these two figures was to demonstrate the effects of adding a second solvent component to PC on the κ of the resulting electrolytes. Of the two binary solvents, a rise of w in $PC_{1-w}EC_w$ primarily raises only the ε of the solvent and thereby weakens the ion-association, as EC is only slightly higher in η but substantially higher in ε than PC, while a rise of w in $PC_{1-w}DEC_w$ lowers both properties significantly. Another cause for a higher κ with a higher EC content in PC-EC is the tendency of EC replacing PC in the coordination shell around Li^+ and thus forming a smaller and more mobile solvated Li^+.[26] Aihara *et al.*[21] in their measurement of Li^+-salts in γ-BL found that the κ at 30°C followed the order $BOB^- < BF_4^- < PF_6^-$, in agreement with the present findings. Furthermore, the results here on $LiPF_6$ and $LiBF_4$ in PC-DEC as plotted in Fig. 4 through 7 agree with those of Ue and Mori on

the same salts in PC-EMC,[11] both in value for the PC-electrolytes and in the observation that the addition of a linear carbonate in PC predominantly raises the κ of $LiPF_6$ but lowers that of $LiBF_4$ (Fig. 7).

Dissociated Li^+ is the major cause for the high viscosity of an electrolyte.—The first theme of the dissociated Li^+ being the major cause for a high η of an electrolyte is clearly evident in the relative positions of the T_g surfaces of Fig. 3, which indicate that the carbonate electrolytes with Li^+ as a group are considerably more viscous than those with Et_4N^+. This is the result of the Li^+ ions, bearing an intense electrostatic surface field due to their small size, being strongly solvated by the carbonate solvent molecules. (Atomic volumes of Et_4N^+ and Li^+ have been estimated to be 170 and 1.8 $Å^3$, respectively.[9]) Such solvation would effectively immobilize the solvating solvent molecules thus preventing them from assisting the flow of the electrolyte and raising its η. It has even been suggested that at high salt concentrations, a carbonate (or an ester) molecule could solvate more than one Li^+ ions with its carbonyl and noncarbonyl oxygen atoms, thus forming an extended structure and increasing the η of the electrolyte even further.[24]

Anions of different sizes affect the viscosity of the electrolytes by their different degrees of association with Li^+.—This theme finds its experimental support in the changes of both the η and κ of the electrolytes. As seen in the changes of η of Fig. 3, the effect of the

Figure 7. Comparison for the change of conductivity κ with solvent mass fraction w of DEC for the PC-DEC solutions of Et_4NBF_4, Et_4NPF_6, $LiPF_6$, $LiBF_4$, and LiBOB at salt molalities of 0.5 (top row), 1.0 (middle row), and 1.5 mol kg^{-1} (bottom row) and at temperatures of 60 (first column), 30 (second column), 0 (third column), and $-30°C$ (last column).

different anions within the Li^+ group or Et_4N^+ group is such that a smaller anion is associated with a lower η. This can be explained by the stronger effective surface field on a smaller anion, which, by associating with an Li^+ more closely, would neutralize more of its positive charge and displace more solvent molecules from within the solvating shell into the free space.[24,26] Further evidence can been seen in the changes of κ shown in Fig. 8 and 9. Figure 8 shows that the smaller the anion, the more rapidly the κ of the $PC_{1-w}EC_w$ electrolytes rises with w, as a result of the rising ϵ of the solvent having a stronger effect in dissociating the paired ions of smaller sizes. With the $PC_{1-w}DEC_w$ electrolytes the opposite is true and is more pronounced, as is clearly shown in Fig. 9 where the κ of the Li^+ electrolytes with a small anion falls rather quickly with w and its accompanying decline in the ϵ of the solvent at higher values of θ.

Conductivity is dominantly determined by viscosity and ion-association in high- and low-viscosity situations, respectively.—The theme that η of an electrolyte dominates the change of its κ finds its support in Fig. 4 through 7. In Fig. 4 on the right side of the third and fourth columns of the plots, where the low θ and high m combine to make high-η situations, the κ of the electrolytes follows the order exactly opposite to that followed by their η. The same is true in Fig. 5, only this time it occurs at higher values of m because of

the lower η of the PC-DEC solvent than that of the PC-EC. The same occurs in the plots of Fig. 6 where θ is sufficiently low and m and w are sufficiently high.

The clearest evidence of the ion-association dominating the change of κ of the electrolytes is seen on the right side of the first plot of Fig. 7, where the high θ and w and low m combine to make low-η situations. Here, as w increases and ϵ of the solvent steadily declines, the κ of Et_4NBF_4 goes from above to below that of Et_4NPF_6 at about 0.45 of w. For the same reason, the κ of $LiBF_4$ is much below that of $LiPF_6$ for all but the bottom-right plot, where the low θ and high m make a very high-η condition that favors a salt with strong ion-association. Looking from the left to the right plot in the first row, one can see the quick fall in the κ of $LiBF_4$ from being comparable to the κ of LiBOB to completely beneath it, a clear demonstration of a switch from viscosity control to ion-association control. Exactly the same situation can be seen in the first-row plots of Fig. 5. Other trends that can be observed in these figures can also be consistently explained in terms of the interplay of the viscosity and ion-association at different values of θ, m, and w.

A summary of practically useful observations.—The η of the electrolytes of lithium salts in carbonate solvents rises with the size of the anions counter to the Li^+ (Fig. 3). For an electrolyte made of a lithium salt and a cyclic carbonate solvent, it is crucial that a second noncyclic carbonate solvent be present in a significant pro-
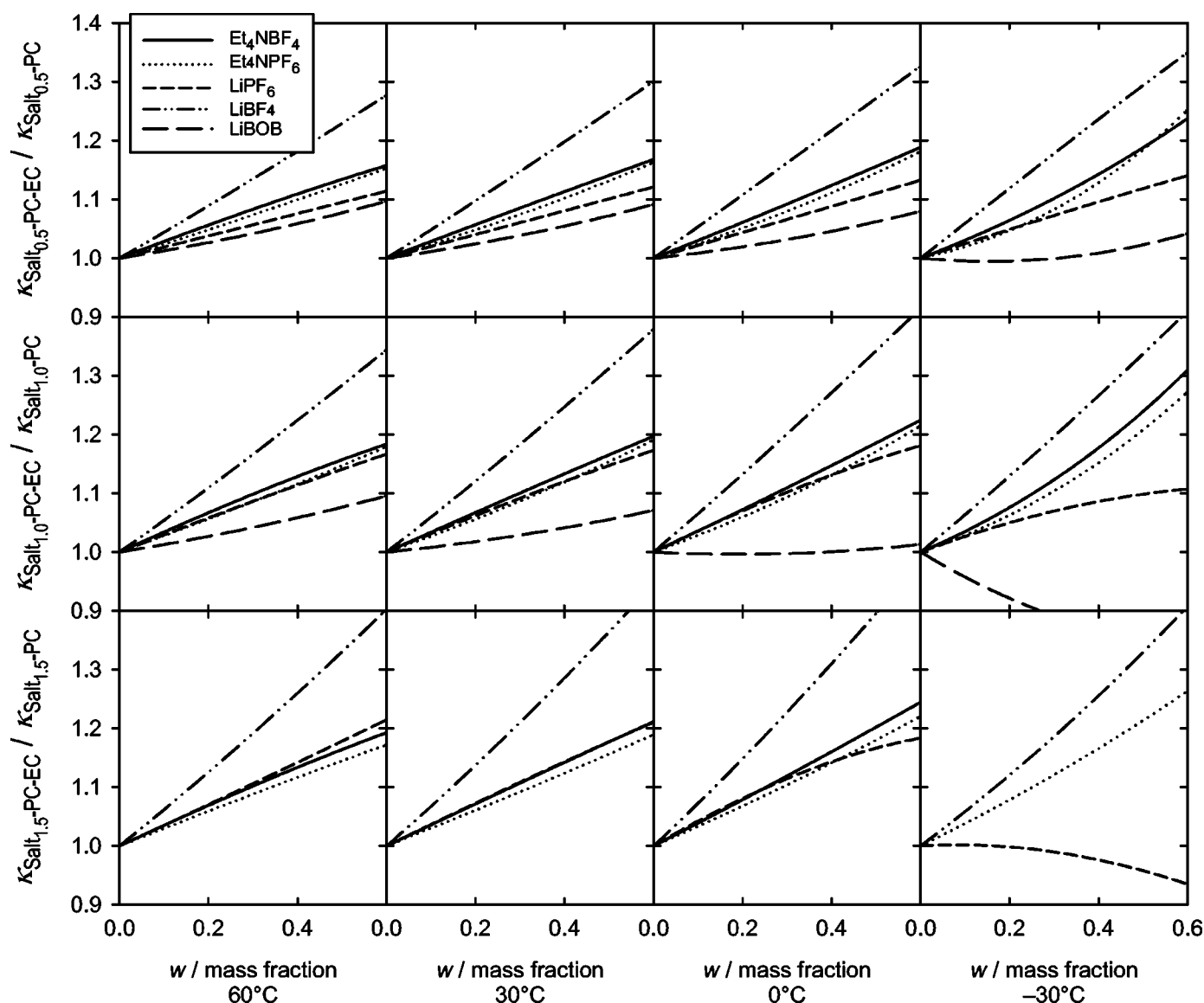
Figure 8. Comparison for the change with solvent mass fraction w of EC in the ratio of conductivity κ of Salt$_m$-PC-EC over Salt$_m$-PC for the PC-EC solutions of Et$_4$NBF$_4$, Et$_4$NPF$_6$, LiPF$_6$, LiBF$_4$, and LiBOB at salt molalities of 0.5 (top row), 1.0 (middle row), and 1.5 mol kg^{-1} (bottom row) and at temperatures of 60 (first column), 30 (second column), 0 (third column), and $-30°$C (last column).

portion for the electrolyte to have a decent conductivity, especially when the salt has a large anion and the electrolyte is intended for low-temperature operation (Fig. 9).

LiPF$_6$ electrolytes are more conductive than LiBOB electrolytes under all circumstances. They are mostly higher than LiBF$_4$ except under high-η conditions, accompanied by a low θ, high m, and a viscous solvent. Between LiBF$_4$ and LiBOB, the electrolytes of the former are more conductive under high-η situations and less conductive in low-η situations (Fig. 4 and 5). The behavior of the Li-BOB electrolytes is mostly governed by their high η and that of the LiBF$_4$ electrolytes by their strong ion-association, while that of LiPF$_6$ by both.

Using the solution Salt$_{0.7}$-PC$_{0.6}$DEC$_{0.4}$ at 30°C as a typical electrolyte for battery applications, κ of LiPF$_6$ is more than double that of LiBF$_4$, while that of LiBOB is about 50% higher than LiBF$_4$ (Fig. 5).

LiBF$_4$ is favored for low-temperature applications because of the low η of its electrolytes. For example, for Salt$_m$-PC$_{0.6}$DEC$_{0.4}$ electrolytes at $-30°$C, the κ of LiBF$_4$ decreases with m much more slowly than that of LiPF$_6$, crossing over the latter at about 1.5 mol kg^{-1} of m (Fig. 5). The process becomes more extreme at lower temperatures or for more viscous solvents; for Salt$_m$-PC$_{0.4}$EC$_{0.6}$ at $-30°$C, for example, the crossover occurs when m is only 0.8 mol kg^{-1} (Fig. 4).

The low solubility of LiBOB in carbonate solvents with moderate values of η and ϵ and the high η of the LiBOB electrolytes would make it a difficult salt to work with for low-temperature applications.

The lithium salts seem to have considerably higher solubilities in the carbonate solvents than the quaternary ammonium salts (Fig. 4 and 5), most likely as a result of strong solvation of Li$^+$. However, an exception is seen in LiBOB, whose solubility is lower than the ammonium salts (Fig. 4 and 5), possibly due to a particularly strong bond between Li$^+$ and BOB$^-$ due to the irregular shape of BOB$^-$ and the small size of Li$^+$.

Between the lithium and quaternary ammonium salts, the latter when dissolved in carbonate solvents would result in much more conductive electrolytes. Between the BF$_4^-$ and PF$_6^-$ salts with a qua-
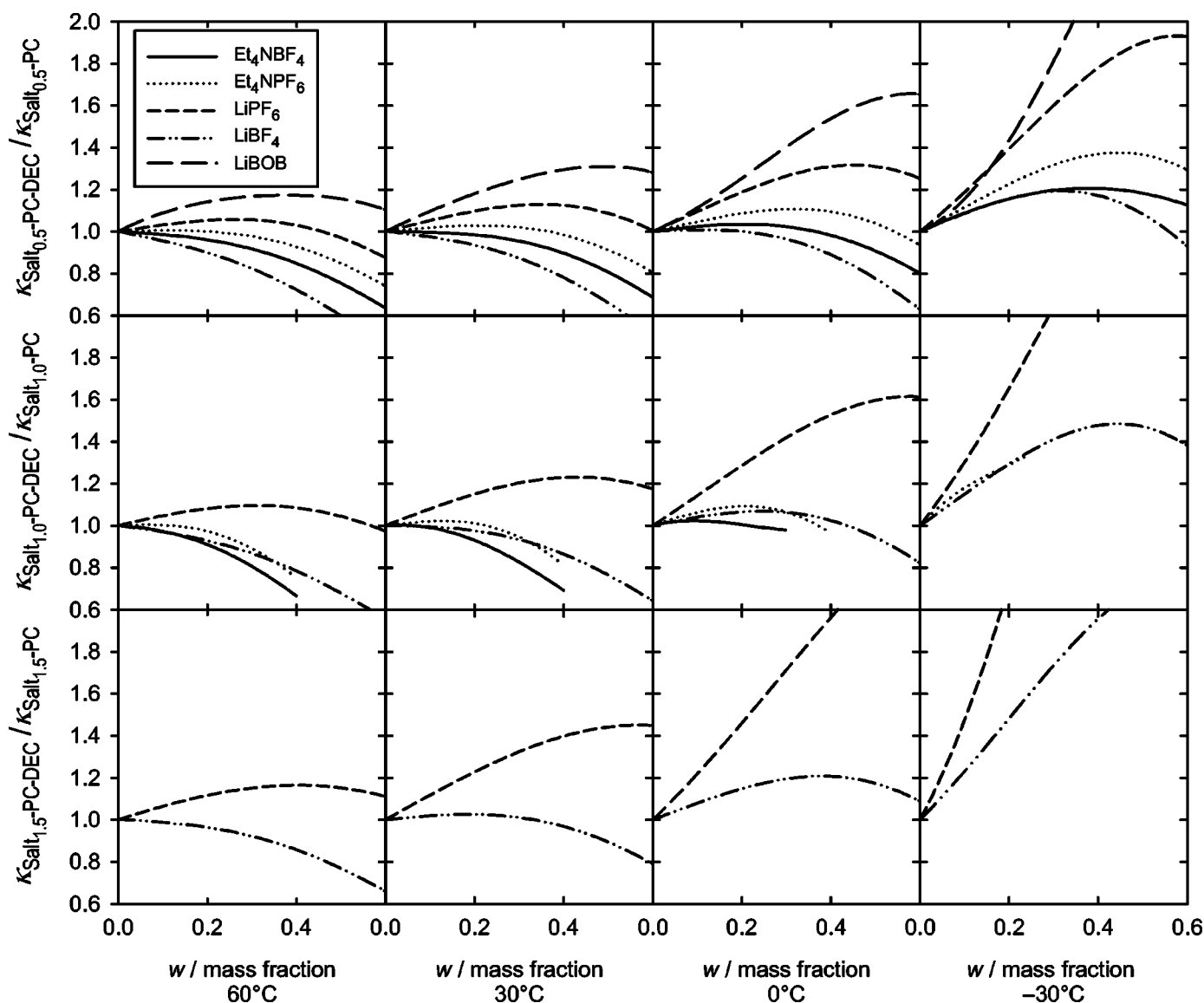
Figure 9. Comparison for the change with solvent mass fraction w of DEC in the ratio of conductivity κ of Salt$_m$-PC-DEC over Salt$_m$-PC for the PC-DEC solutions of Et$_4$NBF$_4$, Et$_4$NPF$_6$, LiPF$_6$, LiBF$_4$, and LiBOB at salt molalities of 0.5 (top row), 1.0 (middle row), and 1.5 mol kg^{-1} (bottom row) and at temperatures of 60 (first column), 30 (second column), 0 (third column), and $-30°C$ (last column).

ternary ammonium cation, the former would result in more conductive electrolytes than the latter, likely due to the stronger ion-association of the smaller BF$_4^-$ with the Et$_4$N$^+$ cations (Fig. 4 and 5), although the effect is much smaller than that among the Li$^+$ salts.

Conclusions

Viscosity η of Li$^+$-containing carbonate electrolytes was determined to be considerably higher than the corresponding Et$_4$N$^+$-containing electrolytes, and conductivity κ considerably lower. Among the Li$^+$-electrolytes, the influence of an anion was such that the larger its size, the higher the η of the electrolyte and the lower its conductivity κ under high-η conditions. For low-η situations, on the other hand, the order of κ was in reverse: the κ of an electrolyte with a larger anion rose up relatively to one with a smaller anion, as a result of stronger association of the smaller anion with Li$^+$. All the evidence leads to the conclusions that the η and thereby the κ of the electrolytes are dominantly affected by the number of unassociated Li$^+$ ions through their solvation by the carbonate solvent molecules, which, due to their molecular shape and charge distribution, strongly solvate only cations but not anions, and

the different anions of the Li$^+$-salts exert their influence only through altering the number of the dissociated Li$^+$ by their different propensities to associate with it.

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