Review Article

Speciation in Solutions of Lithium Salts in Dimethyl Sulfoxide, Propylene Carbonate, and Dimethyl Carbonate from Raman Data: A Minireview


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Our recent Raman studies of cation and anion solvation and ion pairing in solutions of lithium salts in dimethyl sulfoxide, propylene carbonate, and dimethyl carbonate are briefly overviewed. Special attention is paid to differences in our and existing data and concepts. As follows from our results, cation solvation numbers in solutions are low (∼2) and disagree with previous measurements. This discrepancy is shown to arise from correct accounting for dimerization, hydrogen bonding, and conformation equilibria in the solvents disregarded in early studies. Another disputable question touches upon the absence of free ions in solutions of lithium salts in carbonate solvents and the statement that the charge transfer in carbonate solutions is caused bySSIPs. Direct proofs of the nature of charge carriers in the solvents studied have been obtained by means of analyses of vibrational dynamics. It has been found that collision times for free anions are short and evidence weak interactions between anions and solvent molecules. In SSIPs, collision times are an order of magnitude longer thus signifying strong interactions between anions and cations. In CIPs, collision times become shorter than in SSIPs reflecting the transformation of the structure of concentrated solutions to that of molten salts.

1. Introduction

Due to its sensitivity to molecular interactions between functional groups of molecules and ions, vibration spectroscopy is perhaps the most powerful tool for studying speciation in nonaqueous solutions. This problem has been actively pursued in the past [1] and now is of great interest for nonaqueous electrolytes employed in lithium-ion batteries [2]. It is especially valuable to know the composition and structure of particles, that is, solvated cations, solvated anions, and various kinds of associates including solvent separated ion pairs (SSIPs), contact ion pairs (CIPs), and more complex aggregates present in solutions, because their formation and reactivity are considered to determine the creation of solid electrolyte interfaces emerging upon charge/discharge processes in batteries. In the case of battery electrolytes, experimentalists are deprived of opportunities to select simplest model solvents, so as to make the changes accompanying solvation more vivid, and are forced to operate with quite complex real systems. It should be mentioned that their own equilibria caused by hydrogen bonding, isomerisation, and so forth in the solvents employed in batteries are usually present. It makes spectroscopic studies of speciation in battery electrolytes a formidable task.

In our recent papers [3–7] we have described phase diagrams, conductivity, and Raman spectra of solutions of six lithium salts, namely, lithium tetrafluoroborate LiBF₄, perchlorate LiClO₄, bis(oxalato) borate LiB(C₂O₄)₂, trifluoromethylsulfonate LiCF₃SO₃, nitrate LiNO₃, and bis(trifluoromethylsulfonyl) imide LiN(CF₃SO₂)₂ in a concentration range from 0.05 to 0.25 mole fractions of a salt (from diluted solutions to the mixtures of molten LiX·4S solvates with LiX, where X is the anion) in three solvents, dimethyl sulfoxide, (CH₃)₂SO (DMSO), propylene carbonate, C₃H₆O₃ (PC), and dimethyl carbonate, C₃H₆O₃ (DMC). All these salts and solvents are employed in industrial and laboratory practice. Salt solutions in various mixtures of PC and DMC and DMC’s fluorinated variety are...
readily available on the market as the solvents for commercial lithium-ion batteries. DMSO is a prospective solvent for lithium-oxygen batteries [8–10]. Special attention has been paid to equilibria in the solvent studied. In DMSO [11,12] and DMC [13], these include dipole-dipole interactions between molecules. In PC, one should account for both dipole-dipole interactions and hydrogen bonding [14,15].

As far as speciation in DMSO solutions is concerned, signatures of cationic solvation have been characterized in precious studies [16–19] and up to four DMSO molecules have been found to form the solvation sphere of the Li\(^+\) ion interacting with it through the negatively charged oxygen atom of the S=O group. This solvation number might be corrected since DMSO is an ordered, associated liquid but dimerization equilibria have not been taken into account in solvation studies. In PC solutions, solvation is visible spectroscopically as an interaction of the Li\(^+\) ions with the oxygen atom of the C=O group [20, 21]. This leads to the decomposition of dimers existing in this associated and hydrogen bonded liquid [22]. The solvation number varies from 4 to 2 when the concentration of the solution grows [23–25]. Spectroscopic studies of solvation in DMC, which is considered neither ordered nor hydrogen bonded, have shown that solvation of the Li\(^+\) ions strongly influences conformation equilibria stabilizing the cis-trans conformer [26]. The solvation numbers determined by spectroscopic methods are equal to 4 [26].

Cation solvation is usually described in terms of electrostatic attraction, whereas anion solvation is considered to arise either from electrostatic attraction between positively charged hydrogen atoms of the methyl groups of a solvent and oxygen or fluoride atoms of an anion or from hydrogen bonding between them. Anion solvation in solutions of lithium salts in DMSO manifests itself in Raman spectra in the region of stretching CH\(^3\)-vibrations as an upshift and broadening of respective lines signifying interactions between anions and solvent molecules [18, 19, 27]. In PC solutions, signatures of anion solvation are less definite [22], and spectroscopic manifestations of anion solvation in DMC solutions have not been reported.

Ion pairing in electrolyte solutions is showing up as an uprise of extra lines in the region of stretching vibrations of anions. For example, upon adding LiClO\(_4\) and LiNO\(_3\) to DMSO, new lines appear on the high-frequency side of the lines corresponding to the totally symmetric \(v_1 (A_1)\) CI-O and \(v_1 (A_1')\) N-O vibrations of anions. For perchlorates, the line at 933 cm\(^{-1}\) is assigned to free, unperturbed ClO\(_4^-\) anions, the line at 938-939 cm\(^{-1}\) belongs to anions in SSIPs [28], and that at 944–946 cm\(^{-1}\) reflects the presence of CIPs where perturbations of the anion are the strongest [29, 30]. Line shifts for nitrates [16, 31, 32] and trifluoromethylsulfonates [17] are similar. The data on ion pairing of BF\(_4^-\) ions are much scarce [33, 34]. Bis(trifluoromethylsulfonyl) imide anion in solutions exists in the form of cis- and trans-conformers, the latter being more stable [35, 36]. The most intense Raman line at 740 cm\(^{-1}\) corresponds to the symmetric bending \(\delta_1 (A_1)\) CF\(_3\) vibrations and is convenient for studying ion pairing phenomena [37, 38]. For examining ion pairing phenomena in bis(oxalato) borates, the line at 724 cm\(^{-1}\) corresponding to the symmetric \(\delta_1 (A_1)\) O-B-O bending has been recommended [39].

Signatures of ion pairing in PC are recognized in systems containing ClO\(_4^-\) [20, 22], BF\(_4^-\) [24], N(SO\(_2\)CF\(_3\))\(_2\) [40], and CF\(_3\)SO\(_3^-\) [41] anions. Some of this data are controversial. In particular, Aroca and coworkers have shown that, in LiClO\(_4\)-PC solutions, the line at 933 cm\(^{-1}\) corresponds to free ClO\(_4^-\) anions, the line at 938 cm\(^{-1}\) belongs to SSIPs, and that at 944 cm\(^{-1}\) reflects the presence of CIPs. Brooksby and Fawcett disagree with this assignment considering that, in NaClO\(_4\)-PC solutions, the line corresponding to free ClO\(_4^-\) anions, SSIPs and CIPs manifest themselves at 930, 933, and 938 cm\(^{-1}\), respectively [22]. As far as DMC solutions are concerned, free anions, SSIPs, CIPs, and even more complex aggregates are detected in the LiAsF\(_6\)-DMC system [26].

In [3–7], speciation in DMSO, PC, and DMC solutions of lithium salts has been first described explicitly, with no arbitrary assumptions, in a single experiment. Solvated cations, anions, SSIPs, and CIPs have been detected, and their concentrations have been determined with due regard for equilibria existing in the solvents. In this paper, we briefly overview this data with special emphasis on differences in our and existing concepts. Specifically, we put forward an explanation of low cation solvation numbers in solutions and emphasize that they originate from correct accounting for association processes in the solvents studied. Secondly, we show that differences in the concentrations of CIPs in solutions of different salts can be understood in terms of ion pairs dissociation energy obtained by means of quantum chemical calculations. Finally, we suggest that solvation equilibria in solutions are significantly determined by the donor numbers of solvents.

2. Experimental Details

Lithium salts and solvents, preliminary operations with them, their quality control, and the preparation of solutions are described in [4]. Raman spectra were excited by the 532 nm line of a solid state (Nd:YAG) laser and registered at Analytical Center of Common Access, Dagestan Scientific Center of the Russian Academy of Sciences, Makhachkala, on a confocal Raman microscope (Senterra, Bruker, Germany) with a 20x camera lens, the slit of 50 × 100 mkm, and resolution of 3 cm\(^{-1}\). At least 20 scans were accumulated at polarized (\(I_{VV}\)) and depolarized (\(I_{VH}\)) scattering geometries with the integration time of 20 s. The first and the second letters in subscripts denote the state of polarization of the incident and scattered radiation, respectively; \(V\) stands for vertical and \(H\) for horizontal. Knowing \(I_{VV}(\nu)\) and \(I_{VH}(\nu)\), where \(\nu\) is the running wavenumber, the so-called isotropic and anisotropic line profiles were calculated as

\[
I_{iso}(\nu) = I_{VV}(\nu) - \frac{4}{3} I_{VH}(\nu),
\]

\[
I_{aniso}(\nu) = I_{VH}(\nu).
\]

Since all the lines studied are sharply polarized only isotropic spectra are presented in what follows.
Solvation phenomena and ion pairing perturb the molecules of solvents and anions are showing up in Raman spectra as appearance of new lines corresponding to vibrations of new structural entities. These new lines are situated in a close proximity to the lines of unperturbed particles resulting in composite lines. Their decomposition has been performed by a method described in [42] where experimental spectra are modelled by the sum of the following expressions:

\[ I(\nu) = \frac{2\pi c}{x} \exp\left(\frac{\tau_1/\tau_2}{(\tau_1^2 + \tau_2^2)^{1/2}}\right) K_n(x), \]

where \( x = \frac{4\pi^2c^2(v - \nu_0)^2 + 1/\tau_2^2}{n}, n = 2 \) if \( \nu_0 = 0 \) and \( n = 1 \) if \( \nu_0 \neq 0 \), \( c \) is the speed of light, \( \nu_0 \) is the wavenumber of the line maximum, \( \tau_1 \) and \( \tau_2 \) are certain parameters, and \( K_n(x) \) is the modified Bessel function of the second kind. This expression is more flexible than the commonly used Voigt function and is widely used for the decomposition of overlap lines [43]. In order to find the dependence of the amount of particles present in solutions on the concentration of lithium salts, \( \xi_i = f(c_{\text{salt}}) \), it was considered that \( \xi_i \) values are proportional to integrated intensities of isotropic lines. As no data exist regarding scattering abilities of particles in the free state, solvation sphere, SSIPs, and CLPs, their possible differences at the present state of our knowledge were disregarded.

We skip any detailed description of the vibrational spectra of pure DMSO, PC, and DMC; it can be found in [44–46]. In all spectra processing procedures, we account for the presence of all lines in the investigated regions. For the sake of simplicity, in figures, we give calculation results for the lines directly involved in interparticle interactions (see explanations below) and do not talk over changing parameters of other lines visible in selected spectral windows.

### 3. Results and Discussion

#### 3.1. Spectroscopic Signatures of Solvation.

On adding lithium salts the Raman spectra of solvents undergo changes, namely, the shift and broadening of the lines studied occur, and saltsthe Ramanspectra of solvents undergo changes, namely, (A) CH stretching vibration gives two component lines. Concentration dependence of their intensities reveals that the high-frequency component (\( \sim 2919 \text{ cm}^{-1} \)) corresponds to the nonbonded DMSO molecules, whereas the low-frequency one (\( \sim 2913 \text{ cm}^{-1} \)) belongs to the solvent molecules entering the solvation sphere of the anion and hydrogen bonded to them.

Upon adding the salt, the overall PC line corresponding to \( \nu_{14} \) (A) CH stretching vibrations is changing insignificantly. However, the concentration dependence of data fits reveals that, on rising concentration, clear redistribution of intensity between the low- and high-frequency components takes place. As the high-frequency component (\( \sim 2941 \text{ cm}^{-1} \)) increases and the low-frequency component (\( \sim 2930 \text{ cm}^{-1} \)) decreases in intensity one can be confident that the former belongs to the PC molecules entering the solvation sphere of the anion and hydrogen bonded to them, whereas the latter reflects the presence of the nonbonded solvent molecules.

In DMC solutions, the behavior of \( \nu_{14} \) (A) CH stretching vibration in the salt solutions in DMC is similar to that of CH-vibration in DMSO solutions. Splitting of the line occurs and, in accord with concentration dependence, the split lines can be assigned to the low-frequency component (\( \sim 2919 \text{ cm}^{-1} \)) corresponding to the nonbonded DMC molecules and the high-frequency one (\( \sim 2931 \text{ cm}^{-1} \)) belonging to the solvent molecules, which enter the solvation sphere of the anion and are hydrogen bonded to them.

Intensity measurements enable one to find the dependence of the amount of particles present in solutions on the concentration of lithium salts LiX, \( \xi_i = f(c_{\text{salt}}) \). Using these concentration dependencies one can calculate \( \overline{\nu}_i \), the mean number of the solvent molecules bonded to cations and anions (solvation number, coordination number, or the so-called Bjerrum function), as

\[ \overline{\nu}_i = \frac{\xi_i}{c_{\text{salt}}}, \]

where \( \xi_i \) is the equilibrium concentration of the solvent molecules bonded to \( i \) th ion and \( c_{\text{salt}} \) is the total concentration of the salt. It appears that, for cations, \( \overline{\nu}_i \) values are almost independent on concentration being equal to ca. 2 (Figure 3). This value is much less than that usually obtained in other works. The reason for such discrepancy lies in the fact that, in previous investigations [17, 19], no equilibria in the solvents, dimerization equilibrium on the first place, have been taken into account. In this case, Raman spectra similar to that shown in Figure 1 are decomposed into two lines instead of three lines in our works; that is, the solvent spectrum is modelled with two lines corresponding to nonsolvating and solvating molecules. Differences in fits with three and two lines under the envelope of a composite line have been analyzed in [4]. Representative data are shown in Figure 4. Differences between experimental and calculated intensities (Figure 4, lower panels) visually signify that the three-line fit better reflects reality. Respective statistics (Table 1) support this statement. This means that disregarding possible equilibria in solvents may lead to a significant increase in the
3.2. Spectroscopic Signatures of Ion Pairing. Signatures of ion pairing in solutions are showing up first of all as extra lines appearing in the vicinity of intense lines corresponding to nondegenerated vibrations of anions. For example, adding LiBF$_4$ to DMSO splits $v_1$ line of BF$_4^-$ into three components at 760, 763, and 768 cm$^{-1}$, which can be assigned to anions in the free state, in SSIPs, and in CIPs, respectively (Figure 6). Evolution of the integrated intensities of the component lines enabling one to find the concentrations of free anions and ion pairs in all solutions studied is shown in Figure 7. The data for nitrate solutions are not presented because the spectra

estimated concentration of solvated ions and hence to higher (i.e., mistaken) solvation number values.

Unlike cations, the mean coordination number of anions significantly depends on concentration and varies within wide limits (Figure 5).

Figure 1: Raman spectra of DMSO, PC, and DMC solutions containing 0.15 mole fractions of LiClO$_4$ in regions sensitive to cation solvation effects.

Figure 2: Raman spectra of DMSO, PC, and DMC solutions containing 0.15 mole fractions of LiClO$_4$ in the region sensitive to anion solvation effects.
Figure 3: Concentration dependence of the amounts of monomeric, dimeric, and solvating molecules of the solvent and mean number of the solvent molecules bonded to cations in ionic solutions of DMSO, PC, and DMC.

of NO$_3^-$ and the solvent overlap severely and cannot be decomposed.

As follows from the data presented in Figure 7, the concentration of CIPs in DMSO solutions of lithium salts decreases in the following order of anions: $\text{BF}_4^- > \text{ClO}_4^- \approx \text{CF}_3\text{SO}_3^- > \text{N}($SO$_3$CF$_3$)$_2 = \text{B}($C$_2\text{O}_4$)$_2 = 0$. Interestingly, dissociation energies of ion pairs Li$^+$A$^-$ obtained by means of quantum chemical calculations (B3LYP/6-31+G$^*$ method) can be arranged in the same order (Table 2). This means that a minimal potential energy of pairwise interactions exists (580 kJ mol$^{-1}$), below which contact ion pairs in DMSO solutions of lithium salts cannot be formed, and the amount of CIPs in solutions of salts in DMSO is determined by the dissociation energy of contact ion pairs. If these
Table 1: Computation results obtained with (three lines) and without (two lines) distinguishing between monomeric and dimeric molecules of the solvent in the DMSO solution containing 0.15 mole fractions of LiClO$_4$.

<table>
<thead>
<tr>
<th>Parameters of fits</th>
<th>Three lines</th>
<th>Two lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_1$</td>
<td>664.7</td>
<td>666.02</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>669.2</td>
<td></td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>674.3</td>
<td>673.73</td>
</tr>
<tr>
<td>Best weighted sum of squares</td>
<td>$3.6557 \times 10^3$</td>
<td>$1.0218 \times 10^4$</td>
</tr>
<tr>
<td>Weighted root mean square error</td>
<td>3.7212</td>
<td>6.2452</td>
</tr>
<tr>
<td>Weighted deviation fraction</td>
<td>$1.0756 \times 10^{-3}$</td>
<td>$3.6318 \times 10^{-3}$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99998</td>
<td>0.99996</td>
</tr>
</tbody>
</table>

Table 2: Ion pair Li$^+\cdot$A$^-$ dissociation energy obtained by means of quantum chemical calculations [50].

<table>
<thead>
<tr>
<th>Anion</th>
<th>Ion pair dissociation energy, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>653</td>
</tr>
<tr>
<td>BF$_4^-$</td>
<td>602</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>594</td>
</tr>
<tr>
<td>CF$_3$SO$_3^-$</td>
<td>594</td>
</tr>
<tr>
<td>N(SO$_3$CF$_3$)$_2^-$</td>
<td>580</td>
</tr>
<tr>
<td>B(C$_2$O$_4$)$_2^-$</td>
<td>521</td>
</tr>
</tbody>
</table>

Considerations are correct, nitrate solutions in DMSO can be suspected to contain the maximal concentration of CIPs.

In [5], significant efforts have been undertaken so as to understand the Raman spectra of solutions of LiClO$_4$ in DMSO, PC, and DMC. In [28–30], the lines at 929, 932, and 937 cm$^{-1}$ showing up in the LiClO$_4$-DMSO system are attributed to anions in free state, in SSIPs, and in CIPs, respectively. The similar treatment of the split lines for the NaClO$_4$-DMSO system has been made by Brooksby and Fawcett [22] and that for LiClO$_4$-H$_2$O nanodroplets has been made by Guo et al. [47]. In the carbonate solvents, data fits clearly reveal the presence of two types of ClO$_4^-$-containing particles with the lines at $\nu = 932.5$ and 937 cm$^{-1}$ in PC and at $\nu = 933$ and 942 cm$^{-1}$ in DMC. Comparing this finding with the results obtained for DMSO solutions, one may suppose that, in PC and DMC, free anions are absent, and only SSIPs and CIPs are showing up in Raman. On the other hand, Battisti and coworkers [20] preferred to assign the low-wavenumber lines to the free ClO$_4^-$ and the high-wavenumber lines to the anions in SSIPs.

In order to discern between these two assignments, the conductivity data [3] appear to be helpful. If one follows the assignment performed by Battisti and coworkers [20] and considers that the perchlorate lines at 932.5 and 937 cm$^{-1}$ in PC and at 933 and 942 cm$^{-1}$ in DMC correspond to the free anions and SSIPs, respectively (Assignment 1 in Figures 7(f) and 7(g)), the order of solvents for increasing concentration of free anions is PC < DMSO < DMC and that for decreasing concentration of SSIPs is PC > DMSO > DMC. Such orders have nothing to do with the order of solvents for increasing conductivity DMC < PC ≪ DMSO [3]. If one considers that the lines at 932.5 (PC) and 933 cm$^{-1}$ (DMC) belong to SSIPs and those at 937 (PC) and 942 cm$^{-1}$ (DMC) to CIPs (Assignment 2 in Figures 7(f) and 7(g)), the presence of free anions in PC and DMC should be excluded in the whole concentration range studied. Such consideration leads to the order of solvents for increasing concentration of free anions as PC = DMC(= 0) ≪ DMSO and that for decreasing...
concentration of SSIPs as DMC > PC > DMSO, which perfectly coincide with the order of solvents for increasing conductivity. It has been stressed in [5] that our conclusion is the first proof of the Fuoss theory [48], which states that SSIPs do contribute to conductance current.

The absence of solvated anions in LiClO$_4$-PC and LiClO$_4$-DMC systems, unlike LiClO$_4$-DMSO system, cannot be explained by the values of solvent dielectric permittivity, since DMSO and PC have a much higher dielectric permittivity than DMC (Table 3). Probably, donor numbers rule the game, since the donor number of DMSO is almost twice as much as those of PC and DMC (Table 3).

3.3. Spectroscopic Signatures of Ion Pairing: Vibrational Dynamics. An additional opportunity enabling one to explain...
the absence of free ions in solutions of lithium salts in carbonate solvents and to prove the statement that the charge transfer in carbonate solutions is caused by SSIPs is an analysis of vibrational dynamics in the systems studied. To do so one has to use an approach based on time-correlation functions (TCFs) of vibrational dephasing described in detail in [42, 43]. TCFs \( G(t) \) can be obtained by means of Fourier transforms of Raman spectra \( I(\nu) \):

\[
G(t) = \int_{-\infty}^{\infty} I(\nu) \exp\left(2\pi i c \nu t\right) d\nu, \tag{4}
\]

where \( c \) is the speed of light. It is usually considered that the main cause of line broadening in Raman is the so-called vibrational dephasing. Interactions of a particle with its environment (perturbations) lead to time-dependent changes (modulation) of the particle’s vibrational frequency \( \Delta \omega = f(t) \) and to vibrational phase shifts. If \( \omega \) is exponentially changing in time, \( G_\omega(t) = \exp(-t/\tau_\omega) \), where \( \tau_\omega \) is the modulation time, and the TCF of vibrational dephasing can be expressed by the Kubo equation

\[
G(t) = M_2^2 \tau_\omega^2 e^{-\left(1/\tau_\omega\right)^{-1} t/\tau_\omega}, \tag{5}
\]

where \( M_2 = \int \nu^2 I(\nu) d\nu/\int I(\nu) d\nu \) is the second vibrational moment (perturbation dispersion). As follows from existing theories (for details see [42, 43]), the modulation time is usually considered equal to the time between collisions in liquids, \( \tau_\omega = \tau_{BC} \). Depending on perturbations TCF and the spectrum are changing. If \( \tau_\omega \to 0 \) (moveable environment of a particle, weak perturbations, and nonspecific interactions) TCFs are exponential and the spectra are of Lorentzian form. If \( \tau_\omega \to \infty \) (interactions are strong, specific, and directed; molecule and its environment form a rigid quasi-lattice) TCFs and the spectra become Gaussian. Another parameter of the process is the dephasing time determined as the integral over \( G(t) \),

\[
\tau_V = \int G(t) dt.
\]

Calculations have been performed by the method suggested in [42, 43] according to which (2) can be Fourier transformed analytically giving \( G(t) \) in the following form:

\[
G(t) = \exp\left\{-\left(\frac{t^2 + \tau_1^2}{\tau_2^2}\right)^{1/2} - \frac{t^4}{\tau_2^4}\right\}. \tag{6}
\]

Once \( \tau_1 \) and \( \tau_2 \) are known, \( G(t) \) can be built, fit to Kubo equation (5), and analyzed. In Figure 8, representative TCFs for the free anions, SSIPs, and CIPs are shown. Their behavior is very characteristic. It appears that dephasing times in free anions are short. In SSIPs, \( \tau_V \) become longer, and respective TCFs “cover” the TCFs of free ions. In CIPs, \( \tau_V \) become shorter and respective TCFs remain under the envelope of the TCFs of SSIPs.

The analysis of modulation times appears even more straightforward (Table 4). In free anions, \( \tau_\omega \) are short and evidence weak interactions between anions and their environment (solvent molecules). In SSIPs, \( \tau_\omega \) are an order of magnitude longer thus signifying strong interactions between anions and cations. In CIPs showing up in more concentrated solutions, \( \tau_\omega \) become shorter than in SSIPs, probably
Figure 7: Concentrations of free anions and ion pairs in solutions of DMSO, PC, and DMC.

demonstrating that the structure of concentrated solutions acquires the features of molten salts, for which short \( \tau_w \) are quite obvious [49]. This proves our conjectures regarding the nature of charge carriers in carbonate solvents. A more detailed description of these results will be given in our forthcoming papers.

4. Conclusion

In this paper, a brief overview of our Raman studies of cation and anion solvation and ion pairing in DMSO, PC, and DMC solutions of lithium salts, namely, tetrafluoroborate, perchlorate, nitrate, bis(oxalato) borate, trifluoromethylsulfonate, and bis(trifluoromethylsulfonyl) imide, is presented. Special attention is paid to differences in our and existing data and concepts. As indicated from our data, low cation solvation numbers (~2) in solutions disagree with previous measurements. This discrepancy is shown to arise from correct accounting for possible equilibria in the solvents studied, like dimerization (DMSO and PC), hydrogen bonding (PC), and conformation equilibria (DMC), disregarded in early studies. This unforeseen result has some analogies in molecular dynamics simulations of ionic solvation and probably calls for a reconsideration of existing data on solvation numbers. Another disputable question touches upon the absence of free ions in solutions of lithium salts in carbonate solvents and the statement that the charge transfer in carbonate solutions is caused by SSIPs. In order to support this conclusion, donor numbers have been analyzed, which in PC and DMC are as twice as high as those in DMSO. This means that solvation effects prevail in DMSO, whereas, in PC and DMC, ion pairing is being brought to the fore. Furthermore, differences in the concentrations of CIPs in solutions of different salts can be understood in terms of
Table 4: Relaxation $\tau_V$ and modulation $\tau_{\omega}$ times for Cl-O vibrations of ClO$_4^-$ anion in ionic solutions of DMSO, PC and DMC.

<table>
<thead>
<tr>
<th>c, m.f.</th>
<th>LiClO$_4$·DMSO</th>
<th>LiClO$_4$·DMC</th>
<th>LiClO$_4$·PC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_V$, ps</td>
<td>$\tau_{\omega}$, ps</td>
<td>$\tau_V$, ps</td>
</tr>
<tr>
<td>Free anion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>2.17$^a$</td>
<td>0.710$^b$</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>2.10$^a$</td>
<td>0.782$^b$</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>1.90$^a$</td>
<td>0.463$^b$</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>1.64$^a$</td>
<td>0.249$^b$</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>1.41$^a$</td>
<td>0.162$^b$</td>
<td></td>
</tr>
<tr>
<td>Anion in SSIP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>3.91$^a$</td>
<td>9.25$^b$</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>0.1</td>
<td>3.93$^a$</td>
<td>18.9$^b$</td>
<td>1.3 ± 0.2</td>
</tr>
<tr>
<td>0.15</td>
<td>3.53$^a$</td>
<td>10.8$^b$</td>
<td>1.3 ± 0.2</td>
</tr>
<tr>
<td>0.2</td>
<td>3.17$^a$</td>
<td>9.96$^b$</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>0.25</td>
<td>3.08$^a$</td>
<td>10.9$^b$</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>Anion in CIP</td>
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<tr>
<td>0.05</td>
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<td>2.1 ± 0.3</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>0.1</td>
<td>2.4 ± 0.1</td>
<td>7.3 ± 0.6</td>
<td>0.9 ± 0.1</td>
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<tr>
<td>0.15</td>
<td>1.75 ± 0.02</td>
<td>0.64 ± 0.09</td>
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<tr>
<td>0.2</td>
<td>1.37 ± 0.02</td>
<td>0.25 ± 0.04</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>0.25</td>
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</tbody>
</table>

$^a$Less than 1% uncertainty. $^b$Less than 2% uncertainty.

Figure 8: Representative time-correlation functions of dephasing of ClO$_4^-$ anion in free state, SSIP, and CIP in the DMSO solution containing 0.1 mole fractions of LiClO$_4$.

ion pair dissociation energies obtained by means of quantum chemical calculations. Even more direct proofs of the nature of charge carriers in carbonate solvents have been obtained by means of analyses of vibrational dynamics. It has been found that modulation (collision) times for free anions are short and evidence weak interactions between anions and solvent molecules. In SSIPs, $\tau_{\omega}$ are an order of magnitude longer thus signifying strong interactions between anions and cations. In CIPs, $\tau_{\omega}$ become shorter than in SSIPs reflecting the transformation of the structure of concentrated solutions to that of molten salts.

Competing Interests

The authors declare no conflict of interests.

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