

Conductivity, viscosity and IR spectra of Li, Na and Mg perchlorate solutions in propylene carbonate/water mixed solvents

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The influence of water addition on the electric conductivity, viscosity and IR spectra of Mg, Li and Na perchlorate solutions in propylene carbonate (PC) was examined. Conductivity and viscosity data pointed out ion–solvent and ion–ion associations that were most pronounced in $\text{Mg}(\text{ClO}_4)_2$ solutions. IR investigations were directed towards the spectral region $1000\text{--}600\text{ cm}^{-1}$. The changes of the ν_4 band of the perchlorate anion at 624 cm^{-1} and the changes of solvent bands in the spectral region $980\text{--}890\text{ cm}^{-1}$ caused by water addition to 1 M solutions indicated the formation of contact ion pairs. The appearance and increase in intensity of the otherwise IR-inactive perchlorate band at 931 cm^{-1} , upon water addition, was attributed to cation– $\text{H}_2\text{O}\text{--}\text{ClO}_4^-$ solvent shared ion pairs.

Introduction

An appreciable electrochemical and thermal stability, as well as the high relative permittivity ($\epsilon_r = 65$ at 25°C) of propylene carbonate (PC) enable this cyclic ester to be applied as a solvent in different electrochemical devices.^{1–4} Owing to their good solubility in PC, perchlorate salts, especially LiClO_4 , are frequently used in the composition of PC-based solutions, particularly in the development of secondary lithium batteries.¹

In the papers published to date, the association in perchlorate salt–PC solutions has been investigated mostly through the conductivity of diluted solutions.^{5,6} The existence of ion pairs with rather small formation constants was established, but the answer to the question as to whether one deals with the contact or solvent shared ion pairs depended upon the theoretical model used to interpret the conductivity data.⁶ Ion–solvent and ion–ion interactions in perchlorate salts–PC solutions have also been investigated by vibrational spectroscopy methods.^{7–9} By IR spectroscopy of concentrated solutions, the ion–PC interactions were evidenced on the basis of both the splitting of existing PC bands and the appearance of the new bands.^{7,8} The existence of cation–PC interactions, and the absence of anion–PC interactions was evidenced by IR and proton NMR investigations of perchlorate/PC solutions.⁷ The concentration and temperature dependence of the shape of the ν_4 band of the perchlorate anion pointed to the presence of contact ion pairs.⁸ Analysis of the ν_1 band of perchlorate anion in Raman spectra showed the existence of different contact species when the concentration of LiClO_4 in PC was varied.⁹ One can find the correct assignation of the bands of alkali and alkaline-earth metal perchlorates in the papers by Chabanel *et al.*^{10,11}

The ability of alkali metal cations to bind water in aprotic solutions had been established far earlier by proton NMR.¹² That affinity was demonstrated to be very pronounced and almost negligible for Li^+ cation and perchlorate anion, respectively.¹² By Raman spectroscopy it was found that in solutions of LiClO_4 in ethylene carbonate ($\epsilon_r = 95.3$ at 25°C)–water mixed solvents, the lithium cation is solvated

preferably by water. When, instead of water, the second solvent was PC, no selective solvation was observed.¹³

In this article we have tried to draw some conclusions about the association in solutions of perchlorate salts in PC by investigating the influence of water addition on electric conductivity, viscosity and IR spectra. In addition to the LiClO_4 salt we also investigated $\text{Mg}(\text{ClO}_4)_2$ and NaClO_4 . The Mg^{2+} ion has a crystallographic ionic radius equal to that of Li^+ , but its charge is twice as large, and the Na^+ ion has a crystallographic ionic radius larger than that of Li^+ . For these reasons differences in both ion–ion and ion–solvent interactions in the solutions of these salts may be expected. 1 M concentration was chosen as this concentration is in the range used most frequently in applied electrochemistry.

Experimental

All chemicals used were of p.a. purity. PC was distilled twice under vacuum, and both times the middle $\frac{2}{3}$ fraction was collected.¹⁴ LiClO_4 and NaClO_4 were dried at $120\text{--}140^\circ\text{C}$ and $\text{Mg}(\text{ClO}_4)_2$ at 200°C under vacuum until constant mass was achieved. Electrical conductivity was measured by a Wayne Kerr B 224 bridge at a fixed bridge frequency (1592 Hz) using a cell with platinized platinum electrodes. Density was measured by a pycnometer. The measurements of viscosity were performed with a rotation viscosimeter MLW Rheotest 2, using a cylindrical cell 10 ml in volume. The presented viscosity data are average values obtained from three measurements at different rotating speeds. All measurements were performed at 25°C . A dispersive spectrophotometer, Perkin Elmer 983G, with KRS5 windows (with 0.023 mm spacer) were used to record IR spectra. Spectra were recorded with nominal resolution 3 cm^{-1} (or better). The solutions were kept safe of contamination by atmospheric gases.

Results and discussion

1. Conductivity and viscosity

In Fig. 1 the dependence of the specific conductivity on dilution is presented for solutions of magnesium, lithium and

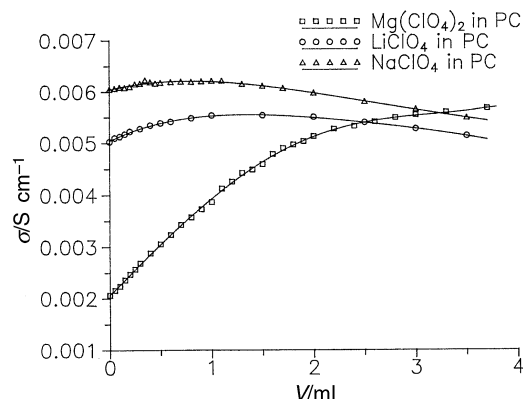


Fig. 1 The effect of solvent addition (dilution) on the specific conductivity of perchlorate solutions in PC at 25 °C. The starting volume is 3.25 ml.

sodium perchlorates in PC. The starting volume and starting concentration of all three perchlorate solutions were 3.25 ml and 1 M, respectively. Ignoring the change in density, one can assume that the salt concentration decreases from 1 M to *ca.* 0.5 M along the abscissa. The curves pass through a maximum for solutions of LiClO₄ and NaClO₄, while for the Mg(ClO₄)₂ solution the maximum is expected to appear at higher dilution. Such a course of specific conductivity *vs.* dilution curves is known from earlier work on concentrated LiClO₄ solutions in PC.¹⁵ The presence of a maxima indicates that ion association is characteristic of all three solutions. The positions of the maxima indicate that association is most pronounced in Mg(ClO₄)₂ solution, and is somewhat more pronounced in LiClO₄ than in NaClO₄ solution. Specific conductivity of 1 M Mg(ClO₄)₂ solution, although its charge concentration is four times larger, is 2.5–3 times lower than that of 1 M alkali perchlorate solutions. In comparison with the two other perchlorate solutions under investigation, the behavior of Mg-perchlorate solution favors the conclusion that the ion association dominates, and that the associates most probably involve very large particles.

Fig. 2 and 3 present the change of specific conductivity and viscosity of 1 M solutions of lithium, sodium and magnesium perchlorate in PC, induced by addition of water. In each diagram, one can see that the increase of the water-to-salt mole ratio causes the increase in specific conductivity, and simultaneously, the decrease in viscosity. The LiClO₄ and NaClO₄ solutions show a similar dependence of viscosity on the amount of water added, the viscosity of LiClO₄ being always slightly higher. On the other hand, the specific conductivity of NaClO₄ solutions is somewhat higher in comparison

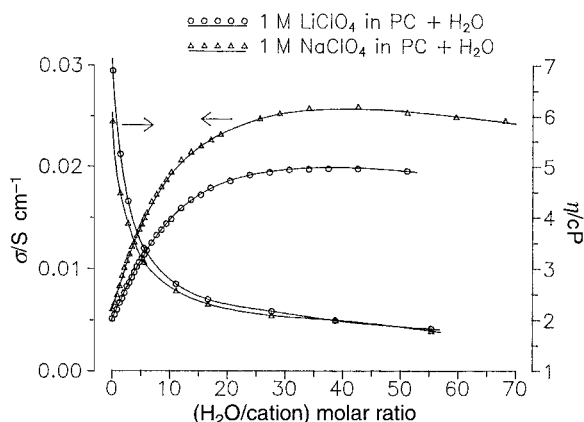


Fig. 2 Specific conductivity and viscosity *vs.* H₂O/cation mole ratio for LiClO₄ and NaClO₄ solutions in PC + H₂O at 25 °C. The starting solution is 1 M perchlorate salt in PC.

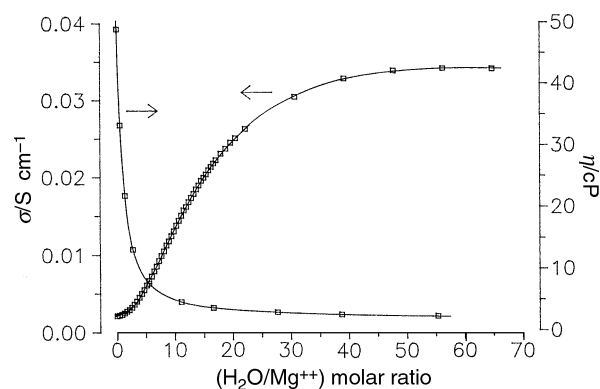


Fig. 3 Specific conductivity and viscosity *vs.* H₂O/Mg²⁺ mole ratio for Mg(ClO₄)₂ solutions in PC + H₂O at 25 °C. The starting solution is 1 M Mg(ClO₄)₂ in PC.

with that of LiClO₄ solutions (Fig. 2). The Mg(ClO₄)₂ solution shows very interesting behavior: the viscosity of this solution is seven times higher than that of LiClO₄ solution, and more than eight times higher than the viscosity of NaClO₄ solution. The addition of a small amount of water, corresponding to the mole ratio H₂O/Mg²⁺ = 1–2, lowers abruptly the viscosity, while the specific conductivity undergoes only a minor change (Fig. 3). A rather high water-to-cation mole ratio is required for this solution to reach the molar conductivity of the other solutions. Namely, a mole ratio H₂O/cation of 11–12 and 17–18 is required to equal the molar conductivity of Mg(ClO₄)₂ solution for LiClO₄ and NaClO₄ solution, respectively (Fig. 4). A particular behavior of Mg(ClO₄)₂ solution is also visible in Fig. 5, which presents Walden's product, λ*η*, *vs.* water-to-cation mole ratio. For Mg(ClO₄)₂ solution only, Walden's product passes through a minimum, while for LiClO₄ and NaClO₄ solutions it shows a permanent increase with dilution by water.

The addition of water to 1 M LiClO₄ and NaClO₄ solutions does not drastically change Walden's product values, contrary to the case of Mg(ClO₄)₂ solution, (Fig. 5). The slow increase in Walden's product with gradual water addition is typical of a transition from organic to water solutions.¹⁶ A small jump which occurs at H₂O/Na⁺ mole ratios between 2 and 3, which is obviously due to a faster increase in conductivity, but also due to a somewhat slower decrease of viscosity of NaClO₄ solution relative to that of LiClO₄ solution. It is plausible that there is a notable decrease in solvated Na⁺ ion radius at the transition of H₂O/Na⁺ mole ratio from 2 to 3. Probably for that reason, the conductivity curve of NaClO₄ is slightly shifted towards higher conductivity values, showing a

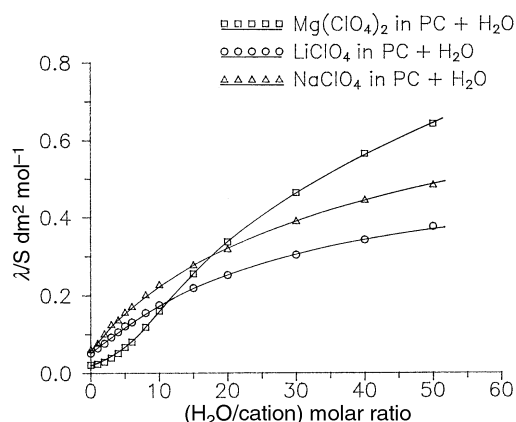


Fig. 4 Molar conductivity *vs.* H₂O/cation mole ratio for Mg(ClO₄)₂, LiClO₄ and NaClO₄ solutions in PC + H₂O at 25 °C. The starting solutions are 1 M salts in PC.

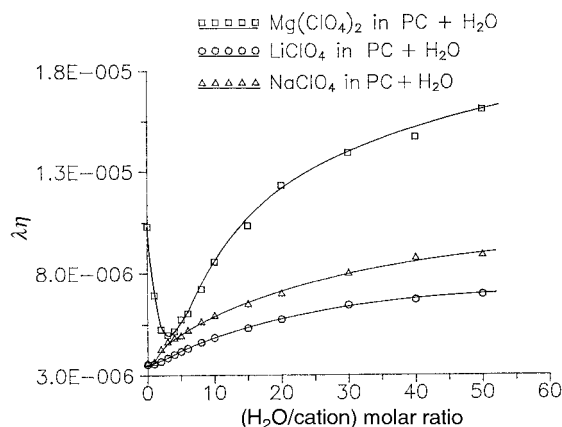


Fig. 5 Walden's product *vs.* $\text{H}_2\text{O}/\text{cation}$ mole ratio for $\text{Mg}(\text{ClO}_4)_2$, LiClO_4 and NaClO_4 solutions in $\text{PC} + \text{H}_2\text{O}$ at 25°C . The starting solutions are 1 M salts in PC. $[\lambda\eta] = \text{S m mol}^{-1} \text{ kg s}^{-1}$.

different trend in comparison to the conductivity curve of LiClO_4 , which is, namely, a straight line in the low water concentration range (Fig. 4).

In a previous paper, by adding water to a 1 M solution of $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile, Berman *et al.*¹⁷ established that Walden's product remains constant up to the mole ratio $\text{H}_2\text{O}/\text{Mg}^{2+} = 3\text{--}4$ and steeply increases with further increases in water content. Comparing their results to the results obtained by ^{35}Cl NMR,¹⁷ these authors stated that, upon addition of small quantities of water, contact ion pairs transformed themselves into solvent shared ion pairs.

The general behavior of conductivity and viscosity of the solutions under investigation indicate, in dry solutions, either strong ion-solvent or strong ion-ion interactions, or both. This is especially owing to the facts relating to the 1 M $\text{Mg}(\text{ClO}_4)_2$ solution, such as: low conductivity in comparison with that of 1 M LiClO_4 and 1 M NaClO_4 solutions (Fig. 1); the negligible change of conductivity and significant change of viscosity with addition of small amounts of H_2O (Fig. 3), by reason of which Walden's product passes through minimum and exceeds its initial value with a large amount of added water (Fig. 5) and, finally, its higher specific conductivity in comparison with that of LiClO_4 and NaClO_4 solutions at high water contents. In all solutions one can suppose the existence of highly solvated cations, involving, in the case of Mg cation, perhaps more than one solvation shell (responsible for high viscosity) as well as another species, for instance contact ion pairs, dimers, solvent shared ion pairs *etc.*, which are responsible for low conductivity of dry solutions, especially in Mg-perchlorate solution. One can interpret the consequences of water addition as follows: in the early stages of water addition, the decomposition of ion-solvent agglomerations is primarily responsible for the radical decrease in viscosity, causing no remarkable increase in conductivity. Enlargement of the water content gradually diminishes the ion-ion interactions. Consequently, at a large enough water concentration, the conductivity of $\text{Mg}(\text{ClO}_4)_2$ solution is much greater than that of LiClO_4 and NaClO_4 solutions, thanks to its two times higher concentration of ClO_4^- ions and two times higher cation charge.

2 IR spectra

To get a more complete picture about associations in the solutions under investigation, the influence of water addition was observed by means of IR spectroscopy.

As already known from spectrochemical data, the free perchlorate anion is of tetrahedral symmetry (T_d) and shows four fundamental vibrational bands, two of which only, $\nu_3 \approx 1102 \text{ cm}^{-1}$ and $\nu_4 \approx 624 \text{ cm}^{-1}$, are IR active. Both these bands are triply degenerate: the first is asymmetrical stretching, and the

second is asymmetrical bending. The other two bands, nondegenerate, $\nu_1 \approx 933 \text{ cm}^{-1}$ (symmetrical stretching), and double degenerate, $\nu_2 \approx 462 \text{ cm}^{-1}$ (symmetrical bending), are only Raman active. Since the band at 1102 cm^{-1} overlaps with the solvent bands, to consider ion-ion interactions by means of IR spectra only the ν_4 band at $\sim 624 \text{ cm}^{-1}$ remains available. Several solvent bands are also IR active. The band at 712 cm^{-1} corresponds to a symmetrical ring deformation, while the one at 958 cm^{-1} is a totally symmetric vibration,¹⁸ most probably symmetric "respiration" ring vibration.^{19,20} It has been established elsewhere^{8,9} that the band at 712 cm^{-1} is sensitive to PC interaction with Li^+ and Mg^{2+} .

From the above-mentioned reasons we focussed attention on the $1000\text{--}600 \text{ cm}^{-1}$ region only, because in this region the influence of water addition on both ion-solvent and ion-ion interactions can be observed.

In Figs. 6 and 7 the spectra marked with "0" correspond to a 1 M solution of perchlorate salts in pure PC. By observing the environment of the PC band at 712 cm^{-1} (Fig. 6, marked by vertical arrow), for Mg-perchlorate solution one can see a new intense band at 732 cm^{-1} (Fig. 6, slanted arrow), while for Li-perchlorate solution, only a weak shoulder at slightly higher wavenumbers appears (Fig. 7, slanted arrow). Regarding refs. 8 and 9 one deals with the splitting of the 712 cm^{-1} solvent band as a consequence of cation solvation. In Na-perchlorate solution, there are no visible features around the 712 cm^{-1} band which might be attributed to $\text{Na}^+\text{--PC}$ interaction. The preference of H_2O in cation solvation is evidenced by the gradual addition of H_2O to 1 M solutions of perchlorates. The band at 732 cm^{-1} and the shoulder at the high wavenumber side of the band at 712 cm^{-1} disappear (Figs. 6 and 7) due to the replacement of PC by water in the first solvation shell of Mg^{2+} and Li^+ . The interaction $\text{Mg}^{2+}\text{--PC}$ manifests itself at higher water concentrations than the $\text{Li}^+\text{--PC}$ one. Namely, at a mole ratio $\text{H}_2\text{O}/\text{Mg}^{2+} = 5.53$, a weak shoulder corresponding to the $\text{Mg}^{2+}\text{--PC}$ interaction still exists (Fig. 6), while at a considerably lower molar ratio, $\text{H}_2\text{O}/\text{Li}^+ = 2.77$, the interaction $\text{Li}^+\text{--PC}$ is manifest only by the asymmetry of the 712 cm^{-1} band (Fig. 7). By a rough estimation, using the method of peak surfaces, the solvent number was determined to be higher than seven for Mg^{2+} ion in a 1 M solution in PC. The uncertainty of this estimation

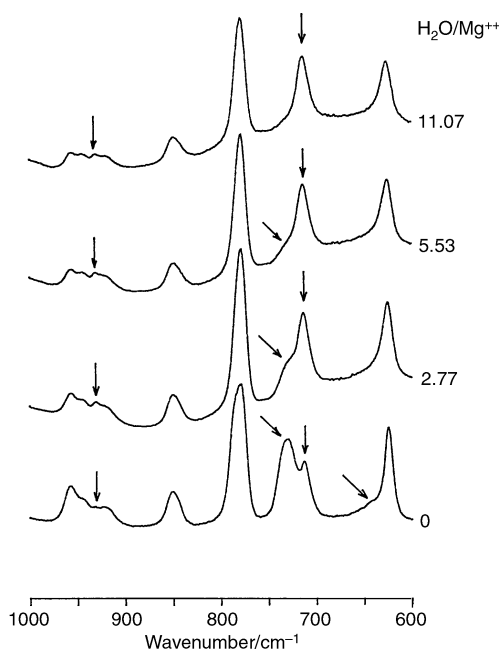


Fig. 6 Changes of IR spectra of 1 M $\text{Mg}(\text{ClO}_4)_2$ in PC with the addition of water. The $\text{H}_2\text{O}/\text{Mg}^{2+}$ mole ratio is presented at each spectrum.

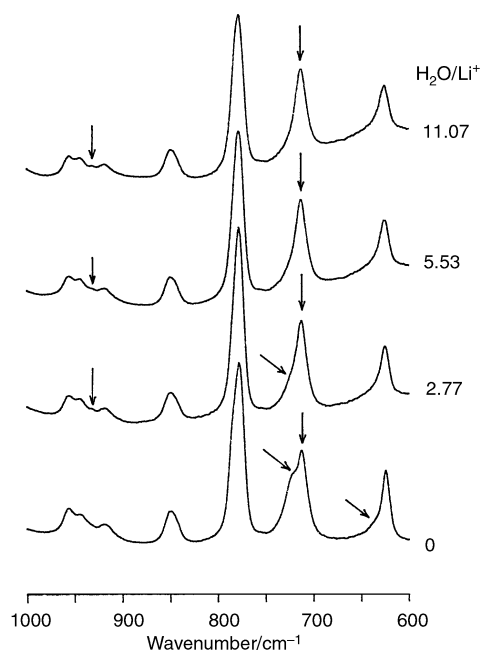


Fig. 7 Changes of IR spectra of 1 M LiClO_4 in PC with the addition of water. The $\text{H}_2\text{O}/\text{Li}^+$ mole ratio is presented at each spectrum.

originates from the fact that absorption coefficients of the bands at 712 and 732 cm^{-1} may be different.²¹

The ν_4 (624 cm^{-1}) band is naturally asymmetric on the low wavenumber side due to the presence of ^{37}Cl .¹⁰ In all 1 M solutions involving pure PC, at the high wavenumber side of the ν_4 one can observe a “wing”, Figs. 6 and 7 (slanted arrow) and Fig. 8. For the $\text{Mg}(\text{ClO}_4)_2$ solution it appears as a wide shoulder. For the LiClO_4 solution this feature is somewhat weaker, while in the case of the NaClO_4 solution only a slight asymmetry of the ν_4 band exists. By addition of water to a $\text{Mg}(\text{ClO}_4)_2$ solution, already at a mole ratio $\text{H}_2\text{O}/\text{Mg}^{2+} = 2.77$, the wide shoulder of the ν_4 band disappears, but asymmetry remains (Figs. 6 and 8). At the same $\text{H}_2\text{O}/\text{cation}$ mole ratio the shape of the high wavenumber side of the ν_4 band is changed for the LiClO_4 solution, but for NaClO_4 solution the shape remains unchanged in comparison with that in dry solution (Figs. 7 and 8). The change of the ν_4 band shape upon water addition is much more pronounced for more concentrated solutions. Namely, in the spectrum of 4 M LiClO_4 solution, the shoulder at the high wavenumber side of ν_4 band disappears completely upon addition of 2.77 H_2O molecules per Li^+ cation (Fig. 8). In the spectrum of 1.5 M $\text{Mg}(\text{ClO}_4)_2$ solution, after addition of 2.77 H_2O molecules per cation, the change in the ν_4 band shape is similar to that in the spectrum of 1 M solution; however, a new band at $\sim 640\text{ cm}^{-1}$ appears

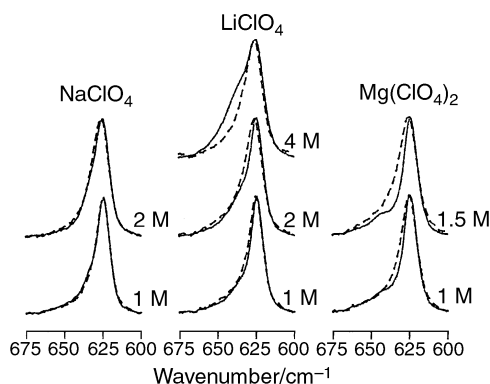


Fig. 8 IR spectra of ν_4 band of perchlorates. (—) in PC, (---) in PC/ H_2O mixed solvent ($\text{H}_2\text{O}/\text{cation}$ mole ratio = 2.77). Spectra are normalized to the same intensity.

(Fig. 8). In the spectrum of 2 M NaClO_4 solution, water addition causes only a slight broadening of the ν_4 band. In almost all cases, water addition makes asymmetry of ν_4 band more pronounced in the high frequency direction, most probably due to hydrogen bonding of perchlorate anion.

The changes in the ν_4 band shape with water addition and with salt concentration increase provide evidence that contact species are formed, since one expects that water, as a preferred solvent, entering in the first solvation shell, weakens the ion-ion interaction. Regarding both the Raman spectra published by Battisti *et al.*⁹ and the assignment published by Chabanel *et al.*,¹⁰ not only contact ion pairs but also dimers exist in 4 M LiClO_4 solution in dry PC. From Fig. 8, the existence of species larger than contact ion pairs, in this case dimers, might be also assumed, both from the spectral envelope shape of the ν_4 band of 4 M LiClO_4 solution and from its drastic change upon water addition, which can not be observed in other solutions. Therefore, in all other solutions, especially in those with a concentration that does not exceed 1 M, most probably only contact ion pairs are formed. In 1 M NaClO_4 solution, even the formation of contact ion pairs is not observable on the basis of the ν_4 band. The question as to which type of symmetry, C_{3v} or C_{2v} ,²² a perchlorate anion exhibits due to the contact ion pairs formation is hard to answer because there is not a complete removal of the degeneracy on account of symmetry lowering of ClO_4^- . Only in the case of magnesium perchlorate¹¹ may monodentate coordination (C_{3v} symmetry) be suggested in PC solutions, on the basis of the appearance of a new band at $\sim 640\text{ cm}^{-1}$ (Fig. 8).

Our results related to the ν_4 band agree with the results of Perelygin *et al.*⁸ and Petrucci *et al.*^{23–25} Namely, Perelygin *et al.*⁸ split the ν_4 band in PC solution by increasing either the temperature or perchlorate concentration. They explained the splitting as a consequence of symmetry lowering of ClO_4^- , caused by contact ion pairs formation. On the other hand, Petrucci *et al.*^{23–25} found similar behavior for the ν_4 band by IR spectroscopy of LiClO_4 solutions in different organic solvents. They explained the appearance of a pronounced “wing” by the existence of the satellite bands, the number of which depends on the type of contact species formed.

Along with the ν_4 band, changes in the spectral region $980\text{--}890\text{ cm}^{-1}$ were observed (Figs. 6, 7 and 9). After addition of water to 1 M LiClO_4 and $\text{Mg}(\text{ClO}_4)_2$ solutions, the band at $\sim 931\text{ cm}^{-1}$ becomes observable as a new one in the first solu-

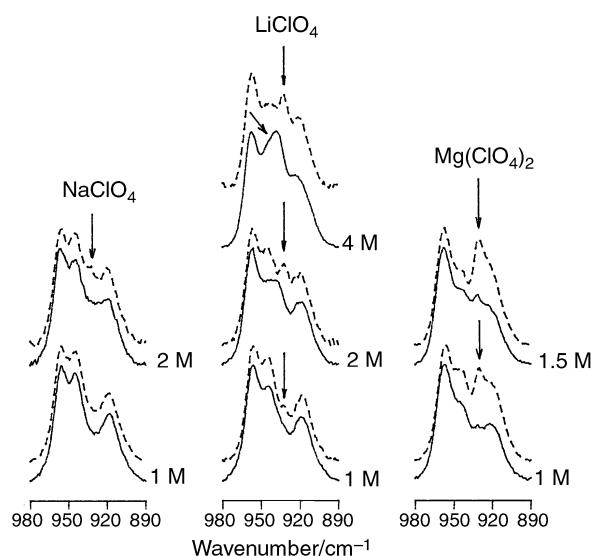


Fig. 9 IR spectra in $980\text{--}890\text{ cm}^{-1}$ spectral region. (—) spectra of perchlorates in PC, (---) spectra of perchlorates in PC/ H_2O mixed solvent ($\text{H}_2\text{O}/\text{cation}$ mole ratio = 2.77). Spectra are normalized to the same intensity.

tion, and becomes stronger in the second solution. The intensity of this band increases with the amount of water (Figs. 6 and 7, vertical arrow), but is very low. Simultaneously, the band at 958 cm^{-1} , which is due to a totally symmetric PC vibration,¹⁸ decreases. We suppose the second observation indicates the cation-PC interaction, which diminishes gradually with increasing water concentration. In the spectrum of 1 M NaClO_4 solution, in this wavenumber region, there are no changes caused by water addition (Fig. 9). The observed changes are in agreement with changes in the solvation band at 712 cm^{-1} described at the beginning of this section.

In more concentrated solutions, after addition of water, the appearance and rise of the band at $\sim 931\text{ cm}^{-1}$ is more emphasized. It appears with very low intensity when the water is added to 2 M NaClO_4 solution; however its intensity is especially high in the spectra of $\text{Mg}(\text{ClO}_4)_2$ solutions (Fig. 9). Given the possibility that the 931 cm^{-1} vibration is simply a partially visible IR-forbidden ClO_4^- vibration, our results relating to its intensity and its behavior under changing water concentration, suggest that it becomes IR active as a result of ion-solvent interactions, particularly due to the formation of solvent shared ion pairs, in which the solvent molecule is water. Namely, as known,¹⁰ the solvent shared ion pairs appear in the spectra at the same wavenumber as free perchlorate anion, whose vibrational band ν_1 is not IR active. Assuming a thin water shell, the cation may disturb tetrahedral symmetry of the perchlorate anion, enabling the appearance of the 931 cm^{-1} band. This is supported by the fact that its intensity depends on the cation field strength, since this band is the strongest in $\text{Mg}(\text{ClO}_4)_2$ solutions (Figs. 6 and 9, vertical arrow). These results are in agreement with Blint's study,²⁶ in which, by a computational approach, he showed that water presents the preferred solvent for solvent shared complexes.

Another band, having the maximum at $938\text{--}939\text{ cm}^{-1}$, can be observed in this spectral region but only when one deals with the 4 M LiClO_4 solution (Fig. 9, slanted arrow). Having in mind that dimers are evidenced in such a concentrated LiClO_4 solution,⁹ we suppose that the band at $938\text{--}939\text{ cm}^{-1}$ band is complex, originating from both contact ion pairs and dimers, the last of which otherwise show the band at $944\text{--}948\text{ cm}^{-1}$.¹⁰ This band disappears after addition of water, in accordance with the assumption that the water addition leads to the dissolution of corresponding species. No band of this kind is visible in other solutions. Therefore, these data permit the existence of only contact ion pairs and "free" ions in less concentrated solutions, especially in 1 M solutions of perchlorates in PC.

Conclusion

Taking into consideration the results of electrical conductivity and viscosity measurements, particularly those of $\text{Mg}(\text{ClO}_4)_2$ solutions in the early stage of water addition, the existence of big agglomerates is required in 1 M solutions. On the other hand, IR spectroscopy results permit that ion-ion interactions lead to agglomerates not larger than either contact ion pairs or solvent shared ion pairs, with preferred ion solvation by

water. Therefore, as the IR spectroscopy results do not oppose the assumption that ion solvation of any kind occurs, the high initial viscosity may be explained as a consequence of high solvation, even involving in the case of Mg^{2+} cation a multiple solvation shell.

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