Raman spectroscopic study of lithium and sodium perchlorate association in propylene carbonate–water mixed solvents

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Raman spectra of 1 M solutions of LiClO$_4$ and NaClO$_4$ in propylene carbonate (PC) with different amounts of water added (H$_2$O/cation mole ratio = 0–55.5) were recorded in the spectral region 880–980 cm^{-1}. Principal component analysis, a statistical method and deconvolution were applied in investigating the association in these solutions. The results indicate the existence of a band at the high-wavenumber side of the ν_1 band of free perchlorate anion. As established by deconvolution, the position of the band is at 938–940 cm^{-1}. This band is attributed to monodentate contact ion pairs and is present in the solutions of perchlorates in pure PC and with a minimum amount of water added. The presence of monodentate contact ion pairs was established by deconvolution of the Raman spectrum of a 1 M solution of Mg(ClO$_4$)$_2$ in pure PC, but at very low concentration. Copyright © 2000 John Wiley & Sons, Ltd.

INTRODUCTION

Perchlorate salts and propylene carbonate (PC), a cyclic ester of outstanding electrochemical and thermal stability and high dielectric permittivity (ε_r = 65 at 25 °C), are frequently used in electrolytes of advanced electrochemical devices, especially in secondary batteries.[1–6] The conductivity of electrolytes in batteries should be as high as possible. The strong ion–ion and ion–solvent interaction decreases the conductivity of these electrolytes by forming neutral species and by increasing the radius of the primary ion solvation shell, respectively. The studies of such interactions can help to increase the performance of electrolytes for electrochemical devices.

The splitting of PC bands and the appearance of new bands due to cation–PC and cation–ClO$_4^-$ interaction were observed by IR spectroscopy.[7,8] The absence of a ClO$_4^-$–PC interaction was evidenced and the cation–PC interaction was confirmed by proton NMR investigations.[7] The changes in the Raman spectra of the totally symmetric (ν_1) band of perchlorate anion in LiClO$_4$–PC solutions revealed the existence of different contact species, depending on the LiClO$_4$ concentration.[9] The presence of association was established much earlier by Raman spectroscopy of the same perchlorate band for LiClO$_4$ solutions in acetone[10] and diethyl ether.[11] A few years ago Chabanel and co-workers[12,13] extended Raman and IR spectroscopic investigations to solutions of alkali and alkaline earth metal perchlorates in various non-aqueous solvents. Also, they gave the correct assignment of association species.[12]

The high and low affinity of water in PC for alkali metal cations and perchlorate anion, respectively, was established in 1971 by proton NMR spectrocopy.[14] By Raman spectroscopy it was found that in solvating Li$^+$, water was preferred to ethylene carbonate and that there was no preference between ethylene carbonate and PC.[15]

In this work, 1 M solutions of perchlorates in PC were chosen because this is the most frequently used concentration for lithium secondary batteries.[1] Although water is strongly avoided in electrolytes for advanced electrochemical devices, its preference in solvating alkali metal and some other cations suppresses ion–ion and ion–organic solvent interactions and may be used in studying them. In an investigation previously conducted in our laboratories, the influence of water addition on ion–solvent and ion–ion interactions by IR spectroscopy of perchlorate solutions in PC was studied.[16] In this work, attention was directed towards the non-degenerate ν_1 band of perchlorate anion as the most sensitive to cation–ClO$_4^-$ interaction. To make the investigation more reliable, Raman spectra of 1 M solutions of LiClO$_4$ and NaClO$_4$ in PC and with different amounts of added water were statistically processed by factor analysis and deconvolution of the spectra was performed.

EXPERIMENTAL

PC and all perchlorate salts were of p.a. grade. PC was distilled twice under vacuum and both times the middle two-thirds fraction was collected.[17] LiClO$_4$ and NaClO$_4$ were dried at 120–140 °C and Mg(ClO$_4$)$_2$ at 200 °C under vacuum until constant mass was achieved. All perchlorate salt–PC solutions were degassed for at least 2 h prior to recording spectra or any water addition.

Raman spectra were excited with 514.5 nm radiation from a Spectra-Physics Model 2020 argon ion laser at an effective power of 300 mW at the sample. Scattered radiation was analyzed using a Spex 1401 spectrometer interfaced to a 128 kbyte Apple IIe computer. The scans

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were acquired in steps of 1 cm^{-1} with a 2 s counting time, accumulating 10 scans per spectrum. The data were transferred to a personal computer for mathematical processing.

Data processing

Data processing was performed on spectra with a subtracted baseline and area normalized to unity. Smoothing procedures were not used. Data were processed by a factor analysis program written in our laboratory.[18] Deconvolution was performed with the Jandel Scientific Peakfit program, version 3.11B for DOS.

RESULTS AND DISCUSSION

In Fig. 1, the spectra of $LiClO_4$ and $NaClO_4$ solutions in PC, in the presence of different amounts of water, are shown. It is obvious that the variations of the bands in the
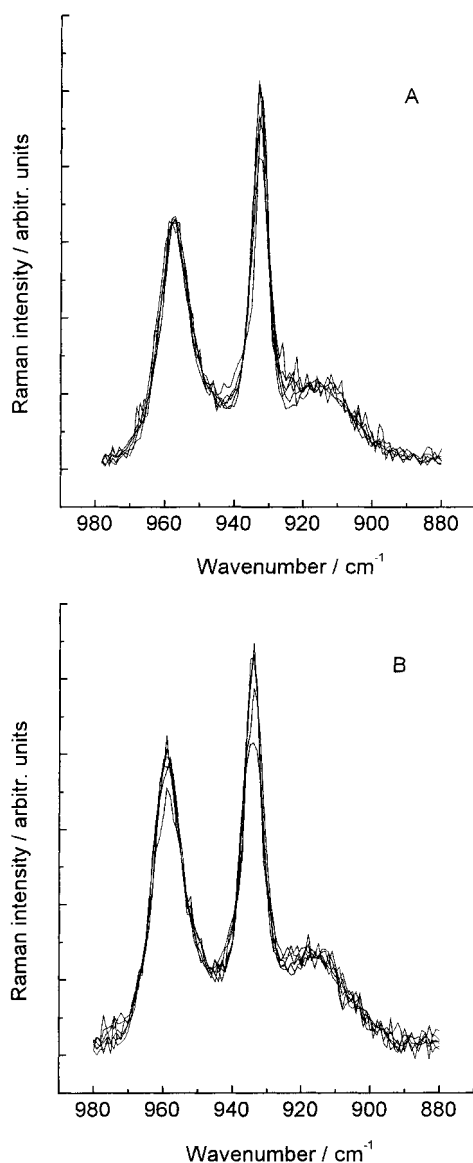
spectra of the perchlorates are very small, individually and if the spectra of $LiClO_4$ and $NaClO_4$ are compared.

The elementary step in factor analysis, principal component analysis (PCA),[19] was applied to reveal any systematic variation in a system of six spectra for both cations. After decomposition of an experimental matrix consisting of 600 points, the following eigenvalues were observed : 13.818, 0.041, 0.027, 0.011, 0.006 and 0.005 for $LiClO_4$ solutions and 19.145, 0.033, 0.021, 0.013, 0.013 and 0.009 for $NaClO_4$. As expected, almost all the data could be reproduced with high precision using only the first eigenvector. The rest of the eigenvectors explain only as little as 0.65% and 0.50% variance for $LiClO_4$ and $NaClO_4$ solutions, respectively. The analysis of these eigenvalues cannot reveal much. The loadings plot, however, is more useful. In Fig. 2 all eigenvectors are shown except for the first
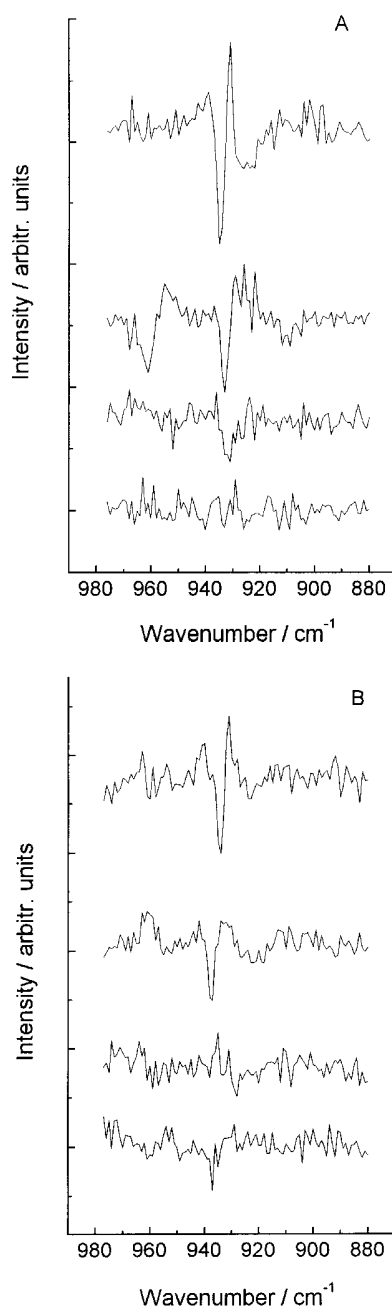

Figure 1. Experimental spectra of (A) $LiClO_4$ and (B) $NaClO_4$ in PC–H_2O mixed solvents (H_2O / cation mole ratio = 0, 2.77, 5.55, 11.1, 27.7 and 55.5).

Figure 2. Loadings plot for (A) $LiClO_4$ and (B) $NaClO_4$ spectral systems.

one, the shape of which is identical with the experimental spectra. In the spectral system of both cations the second eigenvector reveals important variations in the region of 925–945 cm⁻¹. The shape of the variation is very similar in both cases, with a downward peak at 935 cm⁻¹ and an upward peak at 931 cm⁻¹. The third eigenvector of both spectral systems also shows a downwards variation in the same region, whereas all other loading vectors in the LiClO₄ and NaClO₄ spectra do not show any change that could be regarded as different from noise. The shape of the second eigenvector for both alkali metal perchlorate spectra is typical of two-component systems and suggests that the band at ∼933 cm⁻¹ has a small shoulder at the higher wavenumber side in the solutions with a minimum water content. With increase in water content the shoulder disappears and the band at ∼933 cm⁻¹ becomes wider with a small intensity increase. These changes are slightly more distinct in the solutions of LiClO₄ in PC–H₂O mixed solvents, as the eigenvalues suggest.

Deconvolution of the spectra of LiClO₄ and NaClO₄ in pure PC as a solvent and in PC–H₂O mixed solvents with different amount of water (H₂O/cation mole ratio = 2.77, 5.55 and 11.1) was performed in the spectral region 980–880 cm⁻¹. The maximum water content was 11.1 water molecules per cation, corresponding approximately to the number of PC molecules per cation in a 1 M solution of perchlorates in PC. As water exhibits a much higher affinity towards alkali metal cations compared with PC, the association must be suppressed in solutions with such an amount of water.

A Gaussian–Lorentzian product function[20–22] was used for deconvolution:

$$GL(\tilde{v}) = A_0 \left\{ \exp\left[-\frac{(\tilde{v} - A_1)^2}{2\left(\frac{A_2}{1.46}\right)^2} \right] \right\} \left[1 + \frac{(\tilde{v} - A_1)^2}{\left(\frac{A_2}{1.46}\right)^2} \right]^{-1}$$

where A_0 is the maximum intensity of a band centered at wavenumber A_1 and A_2 is the width of a band at $A_0/2$.

First the deconvolution of PC spectra was performed. Three bands were obtained (Fig. 3), which served as a starting basis for the deconvolution of the spectra of perchlorates. The results of deconvolution for LiClO₄ solution are shown in Fig. 4 and Table 1 and for NaClO₄
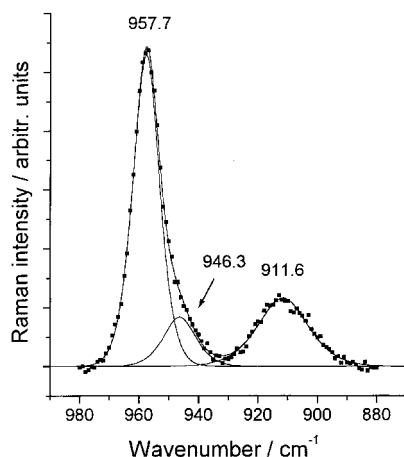

Figure 4. Deconvolution and band fitting in the Raman spectra of LiClO₄ in PC–H₂O mixed solvents in the region of the v_1 band of perchlorate anion.

Figure 3. Deconvolution and band fitting in the Raman spectrum of PC in the spectral range 980–880 cm⁻¹. The correlation coefficient of the fit is $r^2 = 0.9974$.
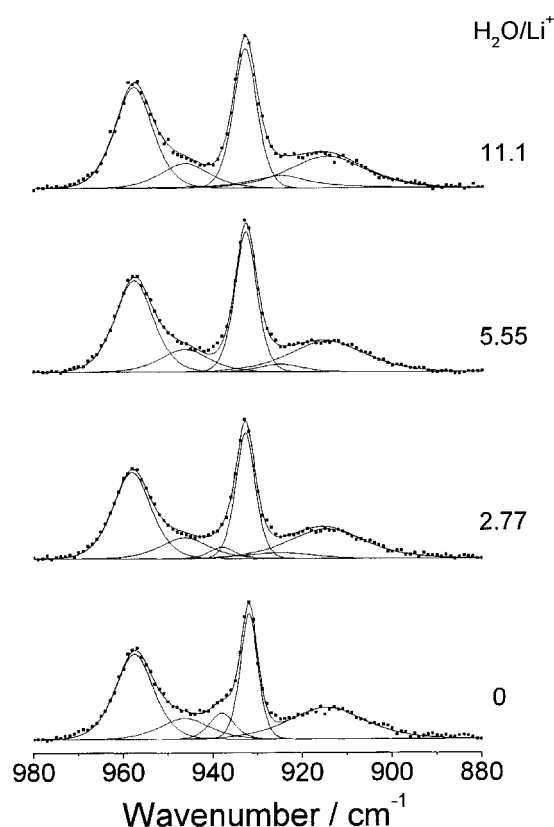
solutions in Fig. 5 and Table 2. The parameters of the PC bands next to the v_1 perchlorate band envelope were fixed during band fitting. The PC band at the low-wavenumber side of the v_1 band envelope is moved slightly to higher wavenumbers compared with its position in pure PC (911.6 cm⁻¹) (Fig. 3), being moved more in the case of NaClO₄ than LiClO₄ solution in PC. The position of this PC band was fixed at 914.6 and 916.3 cm⁻¹ for all LiClO₄ and NaClO₄ solutions, respectively (Tables 1 and 2), as obtained from deconvolution of water-free solutions. The shift is most likely due to the existence of low-intensity v_2 overtone bands of perchlorates, which have been observed earlier for aprotic solvents.[23] In band fitting of spectra of the solutions with different amounts of water added, a band at 925 cm⁻¹ had to be added, which was done in accordance with band component analysis of lithium and sodium perchlorate solutions in water by Frost et al.[24] and Miller and Macklin.[23] The parameters of the 925 cm⁻¹ band were determined from the solutions with maximum water content (H₂O/cation mole ratio = 11.1) and all of them were kept constant except for intensity, which decreased with lowering of the amount of water added. We believe that this band is due to the overtone of the v_2 perchlorate band in solutions containing water.[23]

The band fitting analysis revealed one or two components under the v_1 perchlorate band envelope, depending on the amount of water added (Figs 4 and 5). The first band of high intensity is certainly due to a free perchlorate anion, and is present in all perchlorate solutions. At the high-wavenumber side of this band a band at 938.1 cm⁻¹ in LiClO₄ and at 940.0 cm⁻¹ in NaClO₄ solution in PC were obtained. The intensity of this band is low, but

Table 1. Band fitting results in the spectral range 980–880 cm^{-1} for LiClO$_4$ in PC–H$_2$O mixed solvents

H$_2$O/Li$^+$ mole ratio	GL1		GL2		GL3		GL4		GL5		GL6		
	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	r^2
0	914.6	19.9	—	—	932.0	4.5	938.1	6.5	946.3	12.8	957.6	10.0	0.9937
2.77	914.6	19.9	925.0	10.8	932.8	5.1	938.1	6.5	946.3	12.8	958.1	10.0	0.9958
5.55	914.6	19.9	925.0	10.8	932.7	5.7	—	—	946.3	12.8	957.7	10.0	0.9960
11.1	914.6	19.9	925.0	10.8	932.9	6.1	—	—	946.3	12.8	957.8	9.9	0.9948
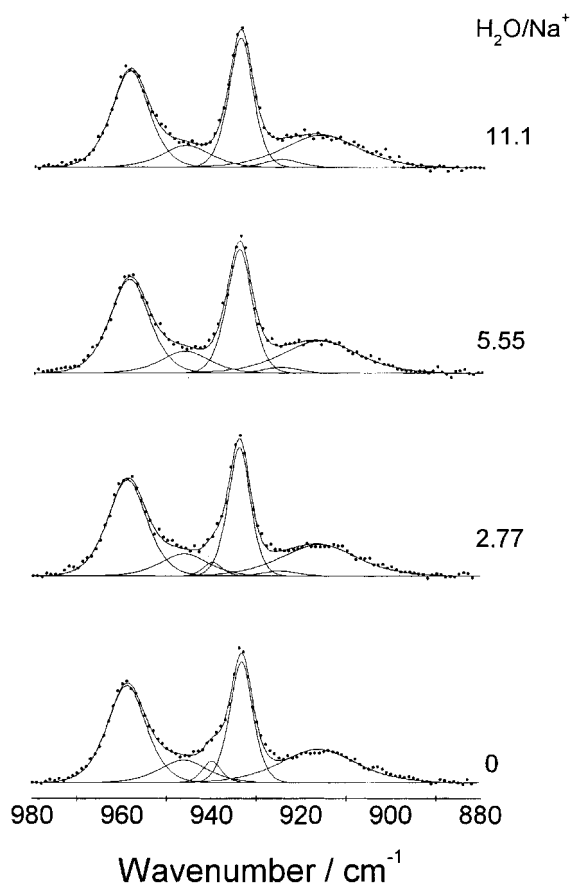
Figure 5. Deconvolution and band fitting in the Raman spectra of NaClO$_4$ in PC–H$_2$O mixed solvents in the region of the ν_1 band of perchlorate anion.

higher in the case of LiClO$_4$. When 2.77 molecules of water per cation are added, the intensity of the band at 938.1 cm^{-1}, i.e. 940.0 cm^{-1}, decreases, but it is still higher for LiClO$_4$. With larger amounts of water this band completely disappears in both salt solutions. In the case of LiClO$_4$ solutions in acetone, James and Mayes[10] earlier attributed the band at 939.3 cm^{-1} to solvent-separated (solvent-shared) ion pairs. Battisti *et al.*[9] in PC–LiClO$_4$ solution (10 : 1), which is close in concentration to our 1 M

solution of LiClO$_4$ in PC, obtained a band at 938 cm^{-1} by Lorentzian band fitting, which they also attributed to solvent-shared ion pairs. Chabanel *et al.*[12] and Alia *et al.*[25] gave the correct assignment of perchlorate association species. According to them, the solvent-shared ion pairs cannot give a separate anion spectral feature. Free or engaged in solvent-shared ion pairs, these anions are commonly designated as 'spectroscopically free' anions. According to this assignment, the bands at 938.1 and 940.0 cm^{-1} are due to contact ion pairs cation–ClO$_4$ in LiClO$_4$ and NaClO$_4$ solutions in PC, respectively. The fraction of contact ion pairs is higher for LiClO$_4$ than for NaClO$_4$ (Table 3). Raman spectra of perchlorates in PC–water mixed solvents additionally confirm this assignment : when water is present in the solution, cation–H$_2$O–ClO$_4^-$ solvent-shared ion pairs are formed.[16] An OH bridge between cation and perchlorate anion makes these entities much more stable than when a large PC molecule separates cation and ClO$_4^-$. In spite of this, there is no other spectral feature arising under the ν_1 band envelope after addition of water (Figs 4 and 5).

Attribution of cation–ClO$_4$ contact ion pairs to monodentate (C_{3V} symmetry) or bidentate (C_{2V} symmetry) coordination is based on the different splittings of degenerate bands, mainly the ν_2 band, of perchlorate anion (T_d symmetry) due to symmetry lowering.[12,13,23,26] Simultaneously with splitting of the ν_2 band, in the case of bidentate coordination, the appearance of a new band at the low-wavenumber side of the ν_1 fundamental was observed.[13,25] An opposite shift was proposed for

Table 3. Band fitting results of the ν_1 band envelope of ClO$_4^-$ anion

M$^+$	H$_2$O/M$^+$ mole ratio	Position/cm^{-1}		Half-width/cm^{-1}		Area (%)	
		Free	Paired	Free	Paired	Free	Paired
Li$^+$	0	932.0	938.1	4.5	6.5	77.0	23.0
	2.77	932.8	938.1	5.1	6.5	89.6	10.4
	5.55	932.7	—	5.7	—	100.0	—
	11.1	932.9	—	6.1	—	100.0	—
Na$^+$	0	933.5	940.0	6.0	4.8	87.4	12.6
	2.77	934.1	940.0	5.8	4.8	91.6	8.4
	5.55	934.3	—	6.6	—	100.0	—
	11.1	934.3	—	6.3	—	100.0	—

Table 2. Band fitting results in the spectral range 980–880 cm^{-1} for NaClO$_4$ in PC–H$_2$O mixed solvents

H$_2$O/Li$^+$ mole ratio	GL1		GL2		GL3		GL4		GL5		GL6		
	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	A_1 $\bar{\nu}$/cm^{-1}	A_2 $\bar{\nu}$/cm^{-1}	r^2
0	916.3	19.9	—	—	933.5	6.0	940.0	4.8	946.3	12.8	959.0	10.1	0.9926
2.77	916.3	19.9	925.0	9.0	934.1	5.8	940.0	4.8	946.3	12.8	959.1	10.2	0.9926
5.55	916.3	19.9	925.0	9.0	934.3	6.6	—	—	946.3	12.8	958.8	10.3	0.9915
11.1	916.3	19.9	925.0	9.0	934.3	6.3	—	—	946.3	12.8	958.9	9.7	0.9931

monodentate geometry.[12,25] Hence, it seems that the band at 938–940 cm^{-1}, obtained in this work by deconvolution and attributed to contact ion pairs, is due to monodentate coordination of perchlorate anion. The characteristic of NaClO$_4$ in aprotic solvents is bidentate coordination of perchlorate anion with a band which should appear at 926 cm^{-1}.[12] PCA applied to the system of NaClO$_4$ spectra did not suggest the existence of any variation at the low-wavenumber side of the ν_1 band. In our previous investigation it was found, by IR spectroscopy, that even the formation of contact ion pairs in a 1 M solution of NaClO$_4$ in PC was not observable on the basis of the ν_4 band.[16] The region of the ν_3 band was blurred by PC bands.[27] Therefore, Raman spectra of the ν_2 band of both perchlorates in PC (with no water added) were additionally recorded in the spectral region 400–500 cm^{-1}. The spectra were very similar, but unfortunately they were of low quality and in addition they were overlapped by the PC band at 455 cm^{-1}, thus making the deconvolution unsuccessful. These results together with the deconvolution results suggest that there are no bidentate contact ion pairs, at least not in any significant concentration, in a 1 M solution of NaClO$_4$ in PC.

It is interesting to compare these results with theoretical calculations. SCF MO calculations for LiClO$_4$ by Klassen *et al.*[28] confirmed the low-wavenumber shift of the ν_1 band for a bidentate configuration and showed that the electron density for the Li$^+$—O bond in a monodentate is higher than in a tridentate structure. However, according to these calculations, carried out at the MP2 level, a bidentate structure is energetically favorable and has the highest Li$^+$—O bond electron density, unlike the suggested monodentate structure. The main reason for the possible partial discrepancy between experimental and theoretical results is the lack of solvent molecules in calculations. According to Gutmann[29] and Ohtaki and Radnai,[30] the steric hindrance becomes important when several large ligands are introduced to the coordination sphere of a small cation. In that case a structural change may occur. This has been confirmed recently by Blint,[31] who studied the competitive coordination of lithium ion also by an MO quantum mechanical approach. He showed that the energy of the contact ion pair Li$^+$–F$^-$ is changed (decreased) when a solvent molecule is added and suggested that the effect might be stronger for larger anions. In a 1 M solution of LiClO$_4$ in PC the solvation number of the lithium cation is four.[15] PC molecules are large and additionally have a considerable electron density on the ring oxygens.[7] Therefore, it becomes harder for perchlorate anion to direct two oxygens towards a small cation and monodentate geometry might become favorable.

The spectra of a 1 M solution of Mg(ClO$_4$)$_2$ in PC and PC–H$_2$O mixed solvents were also recorded, and the H$_2$O/Mg^{2+} mole ratio was the same as in the case of lithium and sodium perchlorates. Because of the very high viscosity of most of these solutions, background scattering
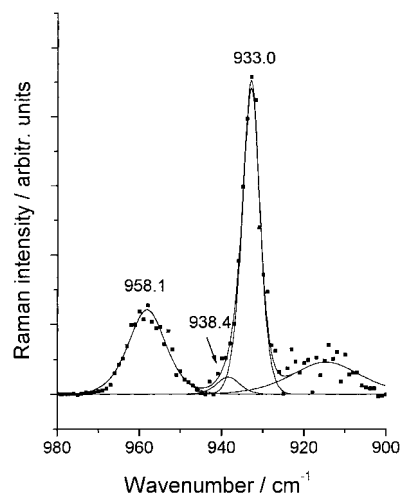

Figure 6. Deconvolution and band fitting in the Raman spectrum of a 1 M solution of Mg(ClO$_4$)$_2$ in PC. The correlation coefficient of the fit is $r^2 = 0.9738$.

was of very high intensity, and the spectra obtained were not good enough for PCA. We succeeded to a certain extent only in performing the deconvolution of the spectra of a 1 M solution of Mg(ClO$_4$)$_2$ in PC. As a result of a strong Mg^{2+}–PC interaction, the intensity of the totally symmetric PC band at ∼958 cm^{-1}[27] significantly decreased, and the band at 946.3 cm^{-1} completely disappeared (Fig. 6). The low-intensity band at 938.4 cm^{-1} is most probably due to contact ion pairs in monodentate coordination, which is in agreement with the results obtained for some other organic solvents.[13,25]

CONCLUSION

Two methods were used in the investigation of ion association in lithium and sodium perchlorate solutions in PC–H$_2$O mixed solvents with H$_2$O/cation mole ratio = 0–55.5. PCA was applied to six solutions with different amount of water. The second and third eigenvectors indicated the existence of systematic variations at the high-wavenumber side of the ν_1 perchlorate band. Deconvolution of spectra was performed in four solutions assuming that in a perchlorate solution with maximum water content (11.1 water molecules per cation) the association was suppressed. Deconvolution of the ν_1 envelope revealed a band at 938–940 cm^{-1} in a 1 M solution of both perchlorates in PC and in the solutions with a minimum amount of water added (H$_2$O/cation mole ratio = 2.77). This band was attributed to contact ion pairs in monodentate coordination.

The band deconvolution of the spectrum of a 1 M solution of Mg(ClO$_4$)$_2$ in PC also revealed a band at 938.4 cm^{-1} which was most probably due to monodentate contact ion pairs, present in a very small amount.

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