Raman Spectroscopic Evidence for Cation-Anion Contact in Molten Hydrates of Magnesium Chloride

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Raman spectra of molten hydrates of $MgCl_2$ were recorded for water contents between 4.0–8.0 mol/mol $MgCl_2$ and temperatures of 150–220 °C. The low frequency range was characterized by two broad bands, one of which (335 cm^{-1}) was assigned to the $Mg(H_2O)_6^{2+}$ ion. From a comparison with the spectra of molten anhydrous $MgCl_2$/(KCl, RbCl, CsCl) mixtures, it was concluded that the second band at 208 cm^{-1} was caused by direct $Mg^{2+}-Cl^-$ contacts. The influence of KCl additions was investigated. Similarities to the behaviour of concentrated $ZnCl_2$ solutions are here pointed out.

The magnesium ion is known to form an octahedral hexaaquo ion in aqueous solutions,[1,2] in which the water molecules are relatively strongly bonded.[3] No spectroscopic evidence for cation-anion contacts exists in the literature for aqueous solutions of $MgCl_2$. According to Angell and Gruen,[4] the water in molten $MgCl_2 \cdot 6H_2O$ (m.p. = 117 °C) is so firmly bound to the magnesium ions that the melt can be described as an ionic liquid consisting of large, polarizable cations $Mg(H_2O)_6^{2+}$ and Cl^- anions. The thermodynamic behaviour of the system $MgCl_2$/KCl/H_2O indicates a coordination competition between H_2O and Cl^- around the magnesium ion, if the molar ratio H_2O:$MgCl_2$, R_H, is decreased to or below 7:1. Recent vapour pressure measurements[5] yielded enhanced activity coefficients of water, when KCl was added to molten $MgCl_2 \cdot 6H_2O$. Also, the increased solubility of KCl at $R_H < 7$ along the corresponding isotherms within this ternary system[6] supports the hypothesis of direct $Mg^{2+}-Cl^-$ interaction.

Within the concentration range of molten hydrates, vibrational spectroscopy has been applied to magnesium nitrate only. No splitting of the v_4 mode of the nitrate ion was observed if $R_H > 6$.[7,8]

Therefore, it was concluded that, under these conditions, no direct $Mg^{2+}-ONO_2^-$ contact occurs. Recently, this conclusion was questioned from a band component analysis of the v_1 nitrate Raman band at 1050 cm^{-1}. These results indicated contact ion pairs already in solutions with concentrations above two molal.[9] Unfortunately, the $Mg-O$ vibration of $Mg^{2+}-ONO_2^-$ pairs has such a low molar scattering efficiency that it is not even detectable in the Raman spectrum of anhydrous molten $Mg(NO_3)_2$/$NaNO_3$.[7] On the other hand, well defined vibrations of the $MgCl_4^{2-}$ complex ion have been reported for molten mixtures of $MgCl_2$/(KCl, RbCl,CsCl), as well as bands of dimeric species $Mg_2Cl_n^{4-n}$ at lowered alkali chloride contents.[10] Therefore, one can expect the occurence of direct $Mg^{2+}-Cl^-$ contacts within the hydrated melts of magnesium chloride to give rise to bands in the appropriate wave number range 250–150 cm^{-1}.

Experimental

All the chemicals were of reagent grade. Magnesium chloride was recrystallized twice and dried over a period of several weeks at a temperature of 80 °C. Two different hydrate samples were used as starting material, the composition of which was $MgCl_2$ + 3.93(1)H_2O and $MgCl_2$ +

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4.01(1)H_2O determined independently by means of Karl Fischer (H_2O), argentometric (Cl^-) and complexometric (Mg^{2+}) titrations. The required compositions were prepared by direct weighing of appropriate amounts of salt and water (~15 g) into the Raman cell. Small amounts of HCl (0.001–0.02 mol HCl/mol $MgCl_2$) were added to remove traces of hydroxide during the drying of the magnesium chloride.

Rasotherm glass tubes, 10 mm I.D.×200 mm, were used as Raman cells. They were stoppered with pressure-tight teflon seals. The cells were placed in a 300 mm long furnace, connected with an Eurotherm® proportional controller having a temperature gradient below 5 K over the whole length. The temperature was measured outside the Raman cell with a chromel-alumel thermo-couple positioned near the laser beam entrance into the cell.

A Dilor RT30 triple monochromator Raman spectrometer interfaced with a Bruker Aspect® 2000 minicomputer was employed. The spectrometer had a cooled photomultiplier and slits having 4 and 5 cm^{-1} spectral resolution were used. The melts were illuminated in the 90° mode and the polarization was directed with a half wave plate. Photon counting times between 0.5 and 4.0 s were employed within steps of 0.5 and 1.0 cm^{-1}. Argon ion lasers from Spectra Physics (model 2000) and from Coherent (model 52G) were used for excitation, using the 514.5 and 488.0 nm lines, respectively, with powers of 1.0–0.5 W.

Results and discussion

Representative spectra of molten magnesium chloride hexa- and tetrahydrate are shown in Fig. 1. In recordings of the extended range 2500–50 cm^{-1}, no new bands were found other than the known librational and bending modes of water at 850–450 cm^{-1} and 1645 cm^{-1}, respectively. The spectrum of the hexahydrate (Fig. 1A) showed two polarized bands with maxima at 335(10) cm^{-1} and 208(10) cm^{-1}. Fig. 1A and Fig. 1B demonstrate that a temperature variation of about 30 K has negligible effect on the spectrum. At a water content of 4 mol H_2O/mol $MgCl_2$ the 335 cm^{-1} band nearly vanished, while the low frequency band was not significantly changed.

In aqueous solutions of $Mg(NO_3)_2$, (1–3 molal), the magnesium-water vibration of the hexa-
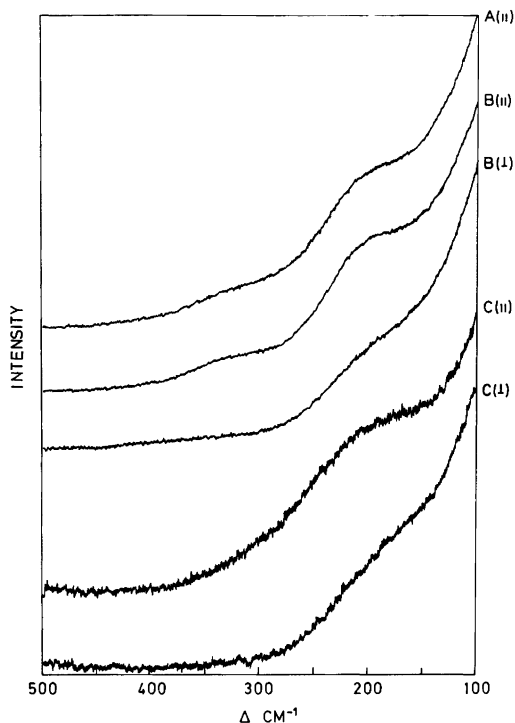

Fig. 1. Raman spectra of molten magnesium chloride hydrates between 500–100 cm^{-1}, A – ($MgCl_2$ + 6.1 H_2O), T = 150 °C, B – ($MgCl_2$ + 6.1 H_2O), T = 180 °C, C – ($MgCl_2$ + 4.0 H_2O), T = 218 °C.

aquo cation has been reported at 354 cm^{-1} at temperatures around 100 °C.[7,11] The frequency of this peak decreases with increasing temperature[11] or decreasing water content.[7,8] This band was observed below 340 cm^{-1} at $R_H < 6$ in the system $Mg(NO_3)_2$–H_2O.[7] Taking the much higher temperature and the influence of another anion (Cl^-) into account, an assignment of the band at 335 cm^{-1} to the hexaaquo ion of magnesium in the present system agreed well with the literature.

The broad band between 270–150 cm^{-1} in Fig. 1 is obviously caused by Mg–Cl vibrations. Molten anhydrous magnesium chloride shows a broad band within the same frequency range.[12,13] Huang and Brooker[13] emphasized the presence of a shoulder around 244 cm^{-1} and resolved the band into three peaks with maxima at 130, 194 and 244 cm^{-1}. The peak at 244 cm^{-1} was identified as the v_1 mode of the complex ion $MgCl_4^{2-}$, while the low frequency peaks were attributed to

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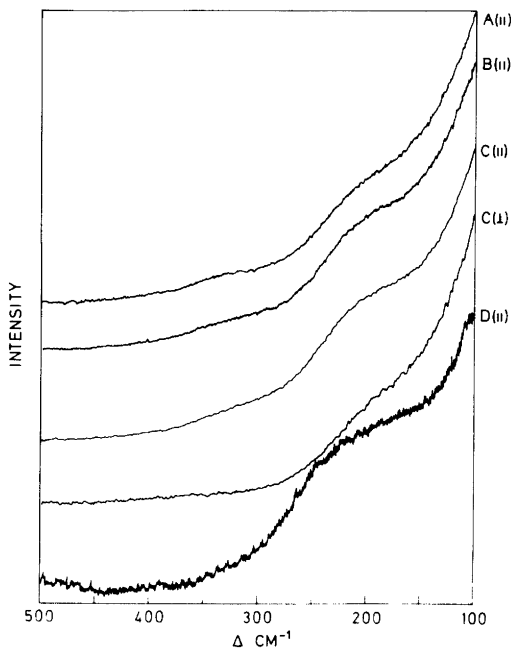
Fig. 2. Raman spectra of molten magnesium chloride hydrates in the presence of KCl A − (MgCl$_2$ + 7.95 H$_2$O + 0.4 KCl), T = 170 °C, B − (MgCl$_2$ + 7.0 H$_2$O + 0.3 KCl), T = 190 °C, C − (MgCl$_2$ + 6.1 H$_2$O + 0.3 KCl), T = 190 °C, D − (MgCl$_2$ + 3.9 H$_2$O + 0.4 KCl), T = 207 °C.

dimeric species.[13] Additions of alkali chloride, MCl (M = K, Rb, Cs) presumably cause shifts toward higher wave numbers accompanied by a decrease in the half-band width.[10,14] Only for molar

Table 1. Band parameters of Mg−Cl vibrations in hydrate melts of magnesium chloride

Composition*		v_{max}	Half-width	Temperature
(a)	(b)	cm^{-1}	cm^{-1}	°C
6.0	0	208(11)	84(2)	175
6.1	0	208(11)	85(10)	180
4.0	0	215(8)	91(10)	218
4.05	0	219(9)	101(2)	210
7.95	0.4	217(10)	72(7)	170
7.0	0.3	214(10)	63(8)	190
6.1	0.3	214(9)	82(6)	190
3.9	0.4	221(15)	120(10)	207

*(a) R$_H$ = mol H$_2$O/mol MgCl$_2$, (b) R$_K$ = mol KCl/mol MgCl$_2$.

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ratios MCl:MgCl$_2$ ≥ 2 the v_1 mode of the discrete MgCl$_4^{2-}$ complex appears as a single sharp peak.[10]

Raman spectra of the hydrated melts in the presence of KCl are presented in Fig. 2. Because of the limited solubility of KCl, and an upper limit of temperature, ~220 °C, due to vapour pressure increase, the molar KCl:MgCl$_2$ ratio reaches a value of only 0.4. When the Raman curves of Fig. 2 (MgCl$_2$ + H$_2$O + KCl melts) were compared with those of Fig. 1 (MgCl$_2$ + H$_2$O melts) it appeared that the general spectral features were the same. In order to detect small variations of the MgCl$_2$ hydrate melt spectra when KCl was added, difference curves were constructed. Hydrate melts with added KCl (Fig. 2) were compared with the pure hydrate melts (Fig. 1) of approximately the same R$_H$ ratio, although the temperatures did not match exactly. Thus, the difference curves 2C minus 1B (MgCl$_2$ + 6.1 H$_2$O) and 2D minus 1C (MgCl$_2$ + 4.0 H$_2$O) were constructed. Both of these curves were nearly horizontal with a small maximum at ca. 250 cm^{-1} and minima at 150 and 335 cm^{-1}. The intensity of the band between 270 and 150 cm^{-1}, ascribed to Mg−Cl vibrations, decreased with higher R$_H$ values. Even for R$_H$ = 8, this band is still present. In Table 1, the peak value and the half-band width of this band are listed for all the compositions investigated. They have been determined graphically and are means from a number of independent determinations. Except for the composition MgCl$_2$+4H$_2$O+0.4 KCl, all the variations of band positions are within the limit of uncertainty. However, the enhanced half-band width of the tetrahydrate melts (1C and 2D) is particularly significant since it was observed both in Fig. 1 and Fig. 2. Unfortunately, the band is too broad and without structure to attempt band convolution. Therefore, we can draw no further conclusions concerning the kind of "Mg−Cl" species present other than that there exists appreciable cation-anion contact.

The effect of KCl on the magnesium hexaaquo band becomes more pronounced at 335 cm^{-1}. Comparison between Figs. 1B and 2C reveals that, due to the added KCl, the Mg(H$_2$O)$_6^{2+}$ peak nearly vanishes, as was apparent from a minimum in the difference curve (see above). This gives further evidence for water-anion exchange within the coordination sphere of magnesium in the presence of excess chloride ions. At the higher water contents of R$_H$ equal to 7 and 8

(Figs. 2A and B) the hexaaquo ion appears again. The faint peak in the difference curves at *ca.* 250 cm^{-1} (see above) suggests an increased Raman signal at this wave number when KCl is added. The band may be attributed to the ν_1 mode of $MgCl_4^{2-}$, thus supporting the water-anion exchange in these melts when chloride ions are added.[13]

A similarity between the present $MgCl_2-H_2O$ and the $ZnCl_2-H_2O$ system should be pointed out. The high solubility of the $ZnCl_2$ allows investigations to be carried out down to $R_H \approx 2$ at room temperature. Thus, this system has been subject to intensive Raman spectroscopic studies.[15-18] The zinc ion is well known for its tendency toward complex formation with halide ions. The Raman spectrum of concentrated $ZnCl_2$ solutions is also characterized by a weak band due to $Zn(H_2O)_6^{2+}$ and by a much more intense and broad $Zn-Cl$ stretching band. The appearance of this spectrum is almost independent of the concentration.[19] The hexaaquo ion band loses intensity with increasing $ZnCl_2$ content, but is nevertheless detected[15] until 10 mol dm^{-3}. The addition of alkali chlorides or HCl causes disappearance of the $Zn(H_2O)_6^{2+}$ peak, while the $Zn-Cl$ band becomes more symmetrical.[15]

For water contents in the range $R_H = 4-10$, the spectroscopic features,[18] values for enthalpies of mixing,[20] and diffusion coefficients[19] can be consistently interpreted by an equilibrium of the species $Zn(H_2O)_6^{2+}/ZnCl_2(H_2O)_2/ZnCl_4^{2-}$. From the present work, the application of a corresponding model to the system $MgCl_2/H_2O$ seems reasonable; a firm conclusion depends upon more structural and thermodynamic information at low water contents.

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