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A Raman study of concentrated ethanol–LiCl solid solutions

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Abstract. Raman spectra were measured for ethanol solid solutions of LiCl of various concentrations between 5 and 77 K. With increasing LiCl concentration, the O–H stretching and the intermolecular vibrational bands changed abruptly from broad bands to sharp peaks at a mole ratio $n \simeq 8$ of EtOH to LiCl. This spectral change is explained by a phase transition from glass to a crystalline hydrate-like cluster. For the solutions at $n \leq 8$, a marked spectral change was observed, at temperatures around 68 K, in the O–H stretching bands, and was ascribed to a lowering of the symmetry of the crystal structure due to thermal contraction on decreasing temperature. Other solid solutions of alkali halides also showed similar spectral changes with alkali halide concentration, except for methanol solutions, but none of them showed any spectral changes on decreasing temperature. These results imply that crystallization commonly takes place in rapidly cooled concentrated solutions of alkali halides, and that the ethanol solid solution of LiCl has a unique crystal structure which causes the spectral change with temperature.

1. Introduction

Solvation of electrolyte ions in alcohol and aqueous solutions has been studied by various experimental methods. Neutron diffraction experiments have revealed that the solvation numbers, which represent the number of solvent molecules coordinated to an electrolyte ion, decrease with increasing electrolyte concentration in liquid [1] and solid [2] states. This is interpreted as resulting from a situation where most solvent molecules are coordinated to both cation and anion, and are shared between two solvation shells in concentrated solutions. When rapidly cooled, a dilute solution of electrolyte is expected to freeze into a solid with almost the same solvation shell structure as in the liquid state. It should be noted, however, that a phase separation is apt to occur in concentrated solid solutions [3, 4].

Infrared [5] and Raman [6–9] studies have shown spectral changes in the O–H stretching bands with electrolyte concentration and temperature. One can expect the infrared and Raman bands of solutions to be more clearly resolved in the solid state at low temperatures than in the liquid state. Strauss and Symons [5] reported the infrared spectra of methanol solutions of electrolytes. They observed three bands in the O–H stretching region for concentrated solid solutions of lithium halides and assigned them as ‘bulk band shifted by cation’, ‘anion solvate band’ and ‘solvent–shared ion pair band’, in order of increasing wavenumbers. The solvent–shared ion pair is ascribed to the O–H group that are hydrogen bonded to both an anion and a cation.

Similar spectral features were also reported for the alcohol solid solutions of alkali halides by means of Raman spectroscopy by Yamauchi and Kanno [8, 9]. They ascribed the three bands in the O–H stretching region to ‘bulk band’, ‘solvent–shared ion pair band’ and

'anion band', in order of increasing wavenumbers, on the basis of the cation dependence of the bands. Their assignments are not in agreement with those of Strauss and Symons [5].

Recently Hase *et al* [10] reported the Raman spectra of pure ethanol glass and ethanol solid solutions of lithium chloride ($\text{LiCl}\cdot n\text{EtOH}$). They confined their study to the solutions whose mole ratio n of ethanol to LiCl is above nine. For pure ethanol glass they revealed that the O-H stretching region consists of two bands of different polarizations. For solid solutions of $\text{LiCl}\cdot n\text{EtOH}$ at $n > 9$, they showed that in spite of the apparent decrease of the low-frequency band and the concomitant growth of the middle band with increasing electrolyte concentration, the intensity ratio between the two bands was constant at $n > 9$. They assigned both of the two broad bands as bulk solvent bands affected by anions or cations, because the frequencies and depolarization ratios of the two bands corresponded to those for pure ethanol glass. The high-frequency narrow band was ascribed to solvent-shared ion pairs because its peak wavenumber and full width at half maximum (FWHM) value was independent of electrolyte concentration. They also measured Raman spectra in the low-frequency region, where intermolecular vibrations appear. The peaks at ~ 200 – 300 cm^{-1} were assigned as the hydrogen bond stretching band.

The solid solutions of $\text{LiCl}\cdot n\text{EtOH}$ look transparent at $n \geq 9$ as does pure ethanol glass, whereas they look waxy and opaque at $n < 9$, even when prepared at the same cooling rate. This difference in their appearance is expected to be attributable to the structural difference of the solid solutions. In this study we report Raman spectra for solid solutions of $\text{LiCl}\cdot n\text{EtOH}$ for several mole ratios at $n \leq 9$ which were measured at various temperatures. Raman spectra were also measured for concentrated solid solutions of $\text{Li}\cdot n\text{EtOH}$, $\text{LiCl}\cdot n\text{MeOH}$ and $\text{LiCl}\cdot n\text{H}_2\text{O}$ for comparison. In this report, the O-H stretching region of the Raman spectra is focused on and the intermolecular vibrational bands are also referred to briefly.

2. Experimental details

Reagent grade ethanol, ethanol- d_1 , methanol, water, anhydrous lithium chloride and lithium iodide were used to make solid solutions without further purification. Reagent grade monohydrate salt of $\text{LiCl}\cdot\text{H}_2\text{O}$ was also used and the Raman spectrum was measured for reference. Disc samples of solid solutions were made by rapidly cooling liquid solutions down to 77 K, as was described previously [10]. The cooling rate was about 4.8 K s^{-1} . The mole fraction of solvent to electrolyte in liquid solutions is used as the nominal mole fraction, n , of solid solutions. Saturated aqueous and methanol solid solutions of LiCl were made by using the transparent supernatant part of the saturated solutions which precipitated some amount of the solute. The solid solutions of $\text{LiCl}\cdot 9\text{EtOH}$, $\text{LiCl}\cdot 9\text{EtOD}$, $\text{Li}\cdot 10\text{EtOH}$, $\text{LiCl}\cdot 3\text{MeOH}$, $\text{LiCl}\cdot 4\text{H}_2\text{O}$ and the saturated methanol solution of LiCl were transparent and crack free, whereas $\text{LiCl}\cdot n\text{EtOH}$ and $\text{LiCl}\cdot n\text{EtOD}$ for $n \leq 8$, $\text{Li}\cdot 7\text{EtOH}$ and the saturated aqueous solution of LiCl appeared opaque and waxy.

The experimental set up used for measuring Raman spectra of solid solution samples at 77 K and 5 K has been described elsewhere [11]. The measurements at various temperatures between 5 and 77 K were carried out with the samples kept in cold helium gas. The 514.5 nm line of an NEC Ar ion laser with a typical output of 1000 mW was used as the exciting source for the Raman measurements. The wavenumber resolution with the slit condition used was about 5 cm^{-1} . The scattered light was detected by a Hamamatsu R-649 photomultiplier tube. Raman spectra were recorded with a Jasco NR-1100 spectrometer.

In our previous paper [10], the relative intensities of the Raman bands of $\text{LiCl}\cdot n\text{EtOH}$ at $n \geq 10$ were obtained by assuming the intensity of the C-C-O symmetric stretching

band of ethanol to be constant for different n values. In this study, we investigated more concentrated solutions of electrolytes, where the band shape of C–C–O symmetric stretching is quite different from those in dilute solutions. We doubted the validity of the assumption of the constant intensity of C–C–O stretching band in this concentration region and did not seek a quantitative analysis of the band intensity in this study.

3. Results and discussion

3.1. O–H stretching region

In figure 1 are shown typical Raman spectra in the O–H stretching region for LiCl. n EtOH for $n = 9, 8$ and 5 measured at 77 K and that for $n = 5$ at 5 K, together with those measured at room temperature. In both liquid and solid states, the high-frequency part of the bands increased while the low-frequency part decreased with increasing LiCl concentration. This implies that Li⁺ and/or Cl[−] ions break hydrogen bonds between ethanol molecules, and form more and more solvation shells around them. The broadness of the bands in the liquid state can be ascribed to the fast exchange of the OH groups between the first solvation shells and outside the shells. Their sharpness in the solid state indicates that the exchange rate becomes very low at low temperatures so that the configuration of ethanol molecules around an ion is almost frozen and fixed.

As demonstrated in figure 1, Raman spectra in the solid state showed an abrupt change with LiCl concentration at around $n = 8$. This spectral change was characteristic of the solid state. The spectrum at $n = 9$ was very similar to those at $n \geq 10$, where the two broad bands at 3200 and 3305 cm^{−1} and the narrow peak at 3375 cm^{−1} were ascribed to ethanol molecules affected by anions or cations, and to solvent–shared ion pairs, respectively [10]. On the other hand, the spectra at $n \leq 8$ at 77 K showed three peaks at $3296, 3313$ and 3358 cm^{−1} and their contours resembled those of ethanol crystals [12] in respect of their small FWHM values. These features indicate that the solid solutions at $n \leq 8$ have a uniform and regular structure like a crystal, in contrast to the glassy solid solutions at $n \geq 9$. At $n \leq 8$, the wavenumbers and FWHM values of the peaks showed little dependence on LiCl concentration. Furthermore, the wavenumbers of the peaks at $n \leq 8$ are much closer to those of the solvent–shared ion pair of the solid solutions at $n \geq 9$. These results suggest that the crystalline solid solutions at $n \leq 8$ have configurations similar to the solvent–shared ion pairs consisting of ethanol molecules coordinated with both Li⁺ and Cl[−] ions. A tentative model of the local structure of the crystal is shown schematically in figure 2. Since ethanol molecules are embedded in it, the crystal structure can be regarded as a ‘hydrate-like cluster of LiCl with EtOH’. Judging from the Raman spectra, however, the crystallization does not necessarily propagate over the whole sample. The weak broad band beneath the sharp peaks for $n = 8$ implies that some glassy domains remain in the sample. The ratio of the glassy domains to the crystal domains in the sample is estimated by dividing the intensity of the broad band by the total intensity for $n = 10$, being about 0.5 for $n = 8$ and 0.2 for $n = 5$. It may be true that solid solutions of different structures can be obtained by preparing the samples at different cooling rates, but the dependence on the cooling rate was not studied here.

At $n > 9$, the O–H stretching bands of LiCl. n EtOH were not affected by the measurement temperature between 5 and 77 K, except for a small shift of the peak wavenumbers. For LiCl. n EtOH for $n \leq 8$, in contrast, the O–H stretching bands changed between 5 and 77 K. This is demonstrated in figure 1, curve D. The spectrum at 5 K consisted

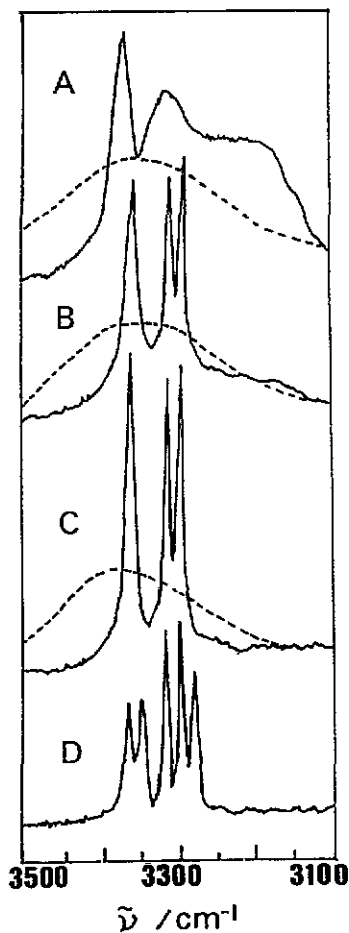


Figure 1. Raman spectra of the O-H stretching region for LiCl.9EtOH (curves A), LiCl.8EtOH (curves B) and LiCl.5EtOH (curves C) at 77 K and LiCl.5EtOH (curves D) at 5 K (full curves) and at room temperature (broken curves). The scattering intensity scale is arbitrary.

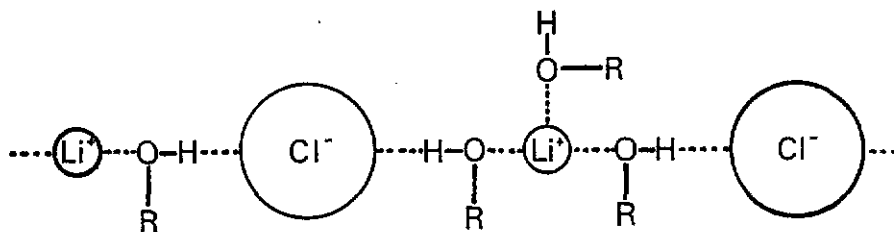


Figure 2. Schematic structure of a tentative model for the hydrate-like cluster of LiCl with EtOH.

of five sharp peaks at 3285, 3303, 3321, 3353 and 3371 cm^{-1} . The spectral change was completely reversible between 5 and 77 K, and was not gradual but abrupt around 68 K, in

such a way that three new peaks grew while five peaks diminished on warming from 5 K. This implies that the splitting of the peaks cannot be ascribed to a mere reduction of the distribution of the O–H stretching energy owing to lower temperatures. It is inferred that a thermal contraction of hydrogen bonds between ethanol molecules and electrolyte ions on lowering the temperature leads to a lowering of the symmetry of the crystal structure, so that the splitting of the O–H stretching bands that were degenerate above 70 K takes place.

Very similar changes with electrolyte concentration and temperature were observed in the O–D stretching spectra of solid solutions of LiCl.*n*EtOD. LiCl.*n*EtOD at $n \leq 8$ had three sharp peaks at 2450, 2463 and 2492 cm^{-1} at 77 K and five peaks at 2444, 2456, 2468, 2490 and 2500 cm^{-1} at 5 K. The ratio between the peak wavenumbers of the O–D stretching bands and the corresponding O–H stretching bands was 0.742–0.744, in approximate agreement with the theoretical value of 0.728. It is evident from these results that the solid solutions of LiCl.*n*EtOD at $n \leq 8$ have the same crystal structure as those of LiCl.*n*EtOH, which consists of hydrate-like clusters of LiCl with EtOD.

Raman spectra of other solid solutions of alkali halides were measured. The spectrum for LiI.10EtOH showed a broad band at 3370 cm^{-1} accompanied by a shoulder at 3260 cm^{-1} , whereas the LiI.7EtOH spectrum showed two sharp peaks at 3415 and 3438 cm^{-1} . The peak wavenumbers of LiI.7EtOH were higher than those for LiCl.*n*EtOH, which implies a weaker hydrogen bond between I^- and the OH group of ethanol than between Cl^- and the OH group. The O–H stretching spectra for LiCl.*n*H₂O also showed a remarkable change with LiCl concentration: for LiCl.4H₂O a broad band at 3430 cm^{-1} with a shoulder at 3279 cm^{-1} , and for the saturated solution, four sharp peaks at 3353, 3368, 3411 and 3528 cm^{-1} . These spectral changes with LiCl concentration were similar to that for LiCl.*n*EtOH and LiCl.*n*EtOD, and lead us to conclude that crystallization of hydrate and hydrate-like clusters is very common in solid solutions of alkali halide which are made by rapidly cooling very concentrated liquid solutions. The O–H stretching spectra of the monohydrate salt of LiCl.H₂O, which was measured for reference, has two sharp peaks at 3365 and 3381 cm^{-1} which are quite close to two of the four for the saturated aqueous solution of LiCl. This coincidence of the wavenumbers implies that the saturated solid solution has, at least partly, a crystal structure similar to that of the monohydrate salt. The solvation numbers of Cl^- and I^- ions for EtOH are ~ 4 –5 and ~ 2 –3, respectively, whereas those of Cl^- for H₂O are ~ 4 –6 [1, 2]. It seems that the greater the solvation number around an anion, the greater the number of sharp peaks which appear in the O–H stretching spectra at 77 K. In other words, the solvation around anions plays an important role in crystallization in concentrated solid solutions. We did not study the role of cations in this study because of the small solubility of cations other than Li^+ for ethanol. A detailed knowledge of the crystal structure of the hydrate-like clusters in the solid solutions will only be obtained if x-ray and/or neutron diffraction experiments are carried out.

We note that only LiCl.*n*MeOH solid solutions had no remarkable spectral change in the most concentrated region. This result is expected from the transparent appearance of the concentrated solid solution, and implies that the solvation number around an anion is not the only factor to decide the O–H stretching band shape, as the solvation number of Cl^- in methanol is four. The infrared study [5] reported the solvent-shared ion pair band in a concentrated LiCl.*n*MeOH solution, and a Raman band corresponding to it was observed at 3391 cm^{-1} in this study also. In methanol solution, ions break the bonding between methanol molecules and orient the OH groups towards them, but do not contribute to the formation of long-range order. It should be taken into consideration that pure methanol forms a crystal when rapidly cooled, while pure ethanol forms a glass. This difference may be responsible for different structures between the most concentrated methanol and ethanol

solid solutions of LiCl.

It is noted that none of the solid solutions except $\text{LiCl}\cdot n\text{EtOH}$ and $\text{LiCl}\cdot n\text{EtOD}$ showed any marked spectral changes with temperature. This implies that crystalline $\text{LiCl}\cdot n\text{EtOH}$ and $\text{LiCl}\cdot n\text{EtOD}$ are quite unique in their structure. Since the crystal structure is determined by interactions between the solvent molecules and electrolyte ions, it is probable that only $\text{LiCl}\cdot n\text{EtOH}$ and $\text{LiCl}\cdot n\text{EtOD}$ at $n \leq 8$ have such a symmetry as is lowered by thermal contraction.

3.2. Intermolecular vibrational region

Remarkable spectral changes with changing electrolyte concentration were also observed in the intermolecular vibrational bands, which appeared below 350 cm^{-1} . Figure 3 shows the intermolecular spectra for the solid solutions whose O-H spectra were studied above. For $\text{LiCl}\cdot n\text{EtOH}$, (figure 3(a)), the spectra at $n \geq 10$ had a few broad bands at $\sim 200\text{--}300\text{ cm}^{-1}$, whose contours were similar to those of pure ethanol glass. They were ascribed in the previous paper [10] to the stretching of hydrogen bonds between ethanol molecules affected by electrolyte ions. These bands underwent narrowing of their width and splitting with increasing LiCl concentration at around $n = 8$ (figure 3(b)). New peaks were observed at 138 and 195 cm^{-1} at $n \leq 8$. These bands can be ascribed to the stretching of weaker hydrogen bonds which are additionally formed between electrolyte ions and ethanol molecules, or alternatively to a longitudinal acoustic mode (LAM) which is caused by the long-range ordering.

All the other solid solutions showed similar changes in the intermolecular bands accompanied by the abrupt change in the O-H stretching bands, except methanol solutions which showed no remarkable change in the O-H spectra. These results imply that the energy distribution of each intermolecular vibrational mode becomes more uniform with increasing electrolyte concentration, and give evidence for the occurrence of crystallization.

Of all the solid solutions studied, only $\text{LiCl}\cdot n\text{EtOH}$ and $\text{LiCl}\cdot n\text{EtOD}$ at $n \leq 8$ gave intermolecular spectra which changed remarkably on lowering temperature: several sharp peaks appeared below 150 cm^{-1} when measured at 5 K and the spectral change was reversible between 5 and 77 K . Note that similar peaks were observed for pure ethanol crystals at 5 K in this frequency region, and were assigned as translational, librational, and torsional vibration of the lattice [12]. For $\text{LiCl}\cdot n\text{EtOH}$ at $n \leq 8$, the low wavenumbers of the peaks and the small FWHM values lead us to assign them as long-range intermolecular vibrations. The existence of such vibrations is strong evidence for crystallization in the solid solutions. The spectrum of the saturated aqueous solid solution of LiCl shows peaks at very low frequencies at 77 K as well as 5 K . This may be due to crystallization which is more uniform than in ethanol solid solutions.

4. Summary

We have reported the Raman spectra in $\text{LiCl}\cdot n\text{EtOH}$ and other solid solutions, varying the electrolyte concentration and temperature. With increasing electrolyte concentration, all the solid solutions studied except the methanol solution showed abrupt spectral changes, which were attributed to the phase transition to the crystalline hydrate-like cluster. The remarkable spectral change on lowering the temperature was unique to $\text{LiCl}\cdot n\text{EtOH}$ and $\text{LiCl}\cdot n\text{EtOD}$ at $n \leq 8$, and it was tentatively interpreted as the result of a change of the symmetry group of the crystal structure, probably due to a thermal contraction of intermolecular bonds.

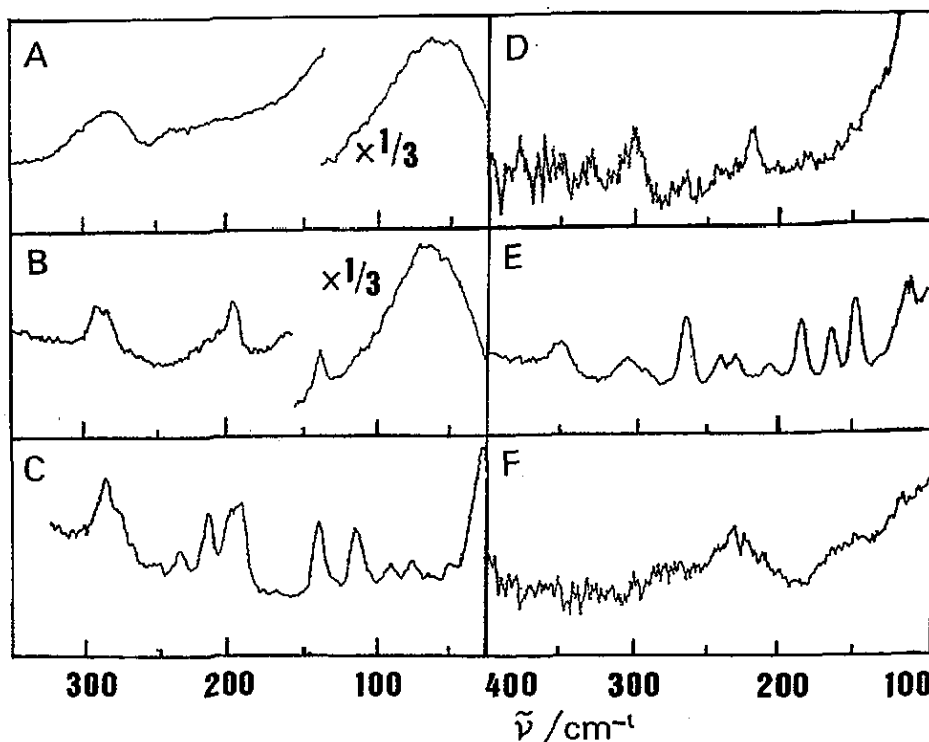


Figure 3. Raman spectra of the intermolecular vibrational region for LiCl.10EtOH (a) and LiCl.5EtOH (b) at 77 K and LiCl.5EtOH at 5 K (c) and LiCl.7EtOH (d) and saturated aqueous (e) and methanol (f) solutions of LiCl at 77 K. The scattering intensity scale is arbitrary.

The spectral changes observed in the intermolecular vibrational bands may support this hypothesis.

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