Raman spectroscopic study of glassy aqueous zinc halide solutions

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Raman Spectroscopic Study of Glassy Aqueous Zinc Halide Solutions

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Raman spectra of aqueous zinc halide solutions are obtained in both liquid and glassy states. It is shown that the detection and characterization of weak low frequency Raman bands in aqueous solutions is much easier in the Raman spectrum for the glassy state than for the liquid state. Comparison of the spectra shows that the tetrahedral ZnX_4^{2-} ions are the most stable ionic entities in the glassy state.

INTRODUCTION

Although Raman spectroscopy has been extensively used for elucidating the structural characteristics of ionic entities in aqueous solutions,[1-3] the strong Rayleigh scattering wing, which extends over to $300 \, cm^{-1}$ or more, often prohibits diffused low frequency Raman bands from a clear observation, thus reducing the effectiveness of Raman spectroscopy. To circumvent this difficulty, difference Raman spectroscopy has been developed,[4-6] and the subtraction of the Rayleigh scattering wing with appropriate assumptions is also frequently made to obtain the baseline-corrected Raman bands.[7,8]

In the previous paper[9] we showed that the Rayleigh scattering wing can be effectively reduced to a negligible level by taking a Raman spectrum of a glassy aqueous solution. Therefore, the unambiguous identification of low frequency Raman bands, which are hidden or obscured by the strong Rayleigh scattering wing in a Raman spectrum of the liquid state, becomes possible in a Raman spectrum of the glassy state.

In this paper we report the Raman spectra of the glassy aqueous solutions of zinc halides to show the full advantage of Raman spectroscopy of the glassy state over that of the liquid state for an identification of feeble low frequency Raman bands in aqueous solutions. New structural information is also obtained from the comparison of the spectra for both liquid and glassy states.

EXPERIMENTAL

Aqueous solutions of $ZnCl_2$, $ZnBr_2$ and ZnI_2 were prepared by dissolving the required amount of anhydrous salt in distilled water. To see the effect of added halide ions on the Raman bands, lithium halides (LiCl, $LiBr \cdot H_2O$ and $LiI \cdot H_2O$) were used to increase the halide-to-zinc ratio of certain solutions.

Glassification of the aqueous solution was made by immersing a sample of the solution (~0.2 ml) contained in a 5 mm inner diameter Pyrex glass tube into liquid nitrogen. Overall cooling rate was usually about $4 \times$ $10^2 \, K \, min^{-1}$. As the best Raman spectrum is obtainable when a glassy sample has no cracks, several attempts were made to minimize cracks in the glassy sample, e.g. by slow cooling or thermal annealing near the glass transition temperature of the glassy sample.

Raman spectra were measured with a JASCO R-800 spectrophotometer using 500–600 mW of the 514.5 nm line of a CR-8 argon ion laser as an exciting source. The signal-to-noise ratio was enhanced by multiscan averaging. The glassy sample was kept at liquid nitrogen temperature during Raman measurements by employing a transparent Dewar vessel. The spectral resolution was $2 \, cm^{-1}$ in this study. Room temperature measurements were also made for spectral comparison.

RESULTS AND DISCUSSION

Raman spectra of the glassy aqueous solutions ($R = 10$, R = mols of water/mols of salt) of $ZnCl_2$, $ZnBr_2$ and ZnI_2 are shown in Figs. 1, 2 and 3 together with those at room temperature. As seen in these figures, low
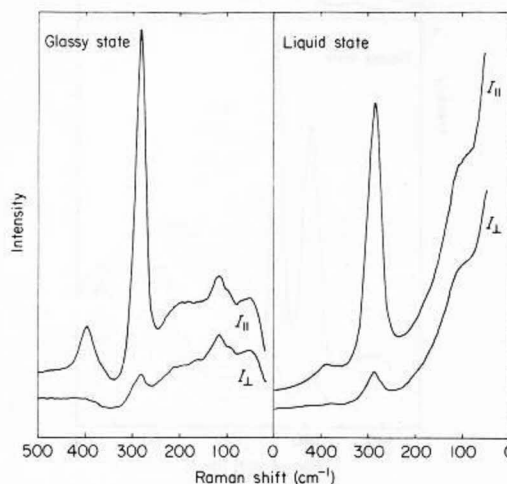

Figure 1. Raman spectra of the $ZnCl_2 \cdot 10H_2O$ solution in both liquid and glassy states. The Raman band at ~60 cm^{-1} in the spectrum of the glassy state is a background spectrum common to chloride solutions.
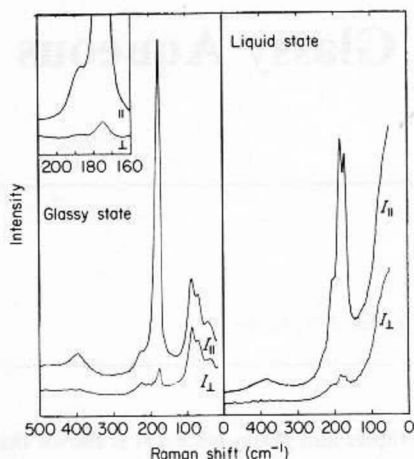
Figure 2. Raman spectra of the $ZnBr_2 \cdot 10H_2O$ solution in both liquid and glassy states. The inset shows the expanded view of the ν_1 band of the $ZnBr_4^{2-}$ ions, on which the ν_1 band of the $ZnBr_3^-$ ions is superimposed at 188 cm^{-1}. The Raman band at ~40 cm^{-1} is a background spectrum common to bromide solutions.

frequency Raman bands are clearly observed in the Raman spectra of the glassy samples in contrast to those at room temperature.

There has been a relatively large number of Raman studies of aqueous solutions of zinc halides at room temperature.[10-17] These studies coupled with other spectroscopic investigations have shown that the dominant zinc species in an aqueous solution of zinc halide with a large excess of halide ions are the tetrahedral ZnX_4^{2-} ions. Except for the ν_1 band, however, unambiguous observation of the other expected Raman bands (the ν_2, ν_3 and ν_4 modes) for the tetrahedral ZnX_4^{2-} ions in the aqueous solution has not been a
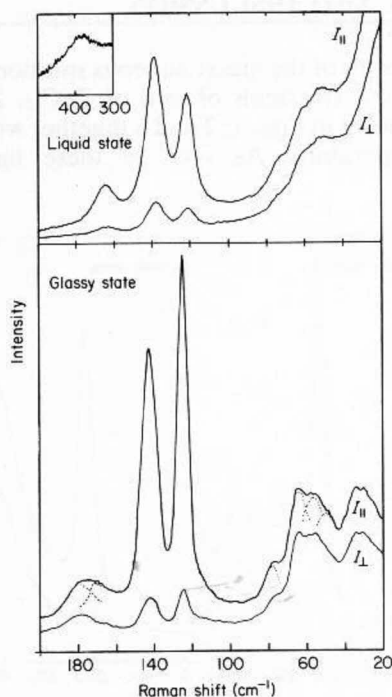
simple task for the reason mentioned above. The identification of weak low frequency Raman bands in aqueous solutions has usually been made by the decomposition of a broad Raman spectrum into several Gaussian components after the subtraction of the Rayleigh scattering wing[16] or by the observation of Raman spectra of organic extracts,[14] crystals or molten salts.[15] However, there is no guarantee that a structural configuration would not change in another, different environment. In fact, the tetrahedral $InCl_4^-$ species, the existence of which is well established in organic extracts from aqueous solutions,[18,19] molten salts[20] and solid,[21] is not observed in aqueous solutions, although the possibility is not ruled out completely that the species may exist in very low concentrations in aqueous solutions of very high chloride concentration.[22] Therefore, Raman band identification *in situ* is preferred.

$ZnCl_2$ solutions

Among three zinc halide solutions, the chloride solution has been most frequently subjected to Raman spectroscopy.[8,11,13-15] However, it seems that the structural characterization of the $ZnCl_4^{2-}$ ions in aqueous solution is not completely resolved. Recent studies of the Raman spectra for molten $CsZnCl_4$[15] and aqueous $ZnCl_2$ solutions[17] are interpreted in favour of a tetrahedral structure for the $ZnCl_4^{2-}$ ion. On the other hand, Irish *et al.*[13] proposed an octahedral structure for $ZnCl_4(H_2O)_2^{2-}$ with D_{4h} symmetry because of only two bands being observed. They argued that the two bending modes (ν_2 and ν_4) observed for $ZnBr_4^{2-}$ and ZnI_4^{2-} should have a larger separation for $ZnCl_4^{2-}$ than do the corresponding bands of $ZnBr_4^{2-}$ and ZnI_4^{2-} and therefore be readily observed. However, other experimental data from ion exchange,[23] electrochemical[24] and X-ray diffraction[25] measurements are all interpreted in favour of a tetrahedral structure for the $ZnCl_4^{2-}$ ion. Thus, it seems that the only problem to be resolved is either to seek the missing ν_2 (or ν_4) and ν_3 modes in a Raman spectrum for the $ZnCl_2$ solution, or to find out the reason why these Raman bands may not be observed in aqueous solutions.

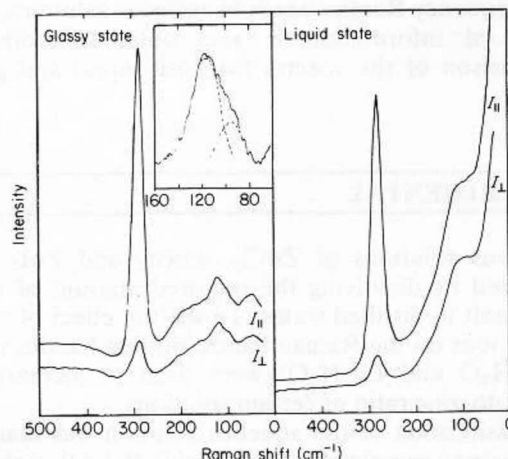In Fig. 4 the Raman spectrum of the glassy $ZnCl_2 \cdot 3LiCl \cdot 15H_2O$ solution is shown together with

Figure 3. Raman spectra of the $ZnI_2 \cdot 10H_2O$ solution in both liquid and glassy states. The inset shows the ν_1 band of the $Zn(H_2O)_6^{2+}$ ions in the liquid state. The Raman band at ~30 cm^{-1} is a background spectrum common to iodide solutions.

Figure 4. Raman spectra of the $ZnCl_2 \cdot 3LiCl \cdot 15H_2O$ solution in both liquid and glassy states.

that of the liquid state. One remarkable point is that the ν_2 and ν_4 modes of the tetrahedral $ZnCl_4^{2-}$ ion are perceptible in the spectrum of the glassy state although both are merged into nearly one envelope. Decomposition of the peak at $\sim110\,cm^{-1}$ into Gaussian components reveals that it consists of two Raman bands: a ν_4 mode at $117\,cm^{-1}$ and a ν_2 mode at $96\,cm^{-1}$. The band which should be slightly higher in frequency than the strongest ν_1 band is extremely difficult to recognize. However, our expanded scan of the spectrum and subsequent graphical decomposition of the strongest peak in the glassy $ZnCl_2 \cdot 3LiCl \cdot 15H_2O$ solution indicates that there is indeed a very weak ν_3 band at $305\,cm^{-1}$ on the foot of the overwhelmingly strong ν_1 band. Thus, we now safely conclude that the main ionic entity in the $ZnCl_2$ solution with excess chloride ions is tetrahedral $ZnCl_4^{2-}$ ions, in complete agreement with other experimental evidence.[15,25]

Comparison of the spectra for glassy $ZnCl_2 \cdot 10H_2O$ and glassy $ZnCl_2 \cdot 3LiCl \cdot 15H_2O$ solutions indicates that the main ionic species in the glassy $ZnCl_2 \cdot 10H_2O$ solution are tetrahedral $ZnCl_4^{2-}$ and octahedral $Zn(H_2O)_6^{2+}$ ions, the latter ions giving the symmetric stretching mode at $398\,cm^{-1}$ in the glassy state.

The Zn–Cl stretching vibration appears at $284\,cm^{-1}$ in the $ZnCl_2 \cdot 10H_2O$ solution at room temperature, which is very close to the ν_1 band of $ZnCl_4^{2-}$. However, the X-ray diffraction study[25] has shown that the average zinc species in the $ZnCl_2$ solution of $R = 5.3$ can be described as $ZnCl_2(H_2O)_2$ with a pseudo-tetrahedral configuration. Therefore, the band at $284\,cm^{-1}$ presumably consists of several symmetric stretching modes ascribable to $ZnCl_2$, $ZnCl_3^-$ and $ZnCl_4^{2-}$ species. This is supported by the asymmetry of the band shape and the slightly higher peak position ($284\,cm^{-1}$) as compared to the corresponding peak position ($282\,cm^{-1}$) in the $ZnCl_2 \cdot 3LiCl \cdot 15H_2O$ solution at room temperature. This is in parallel to the observations for the $ZnBr_2$ and ZnI_2 solutions, as will be shown later. As no attempt was made to decompose the Raman bands at $284\,cm^{-1}$ into several Gaussian components, frequency assignment of the stretching band for the $ZnCl_2$ species was not made in this study.

ZnBr$_2$ solutions

Drastic changes are observed for the Raman spectrum of the $ZnBr_2 \cdot 10H_2O$ solution on going from the liquid state to the glassy state, indicating the composition changes of the main zinc species with this process. In the $ZnBr_2 \cdot 10H_2O$ solution at room temperature the strongest polarized peak consists of three Raman bands of comparable intensities, their frequencies being approximately 208, 183 and $172\,cm^{-1}$. The Raman bands at 208 and $183\,cm^{-1}$ have usually been assigned to the symmetric stretching modes of $ZnBr_2$ and $ZnBr_3^-$ species, respectively.[14] Although they have comparable intensities to the Raman band at $172\,cm^{-1}$, which is the ν_1 mode of a $ZnBr_4^{2-}$ ion, in the $ZnBr_2 \cdot 10H_2O$ solution at room temperature, both decrease considerably in their intensities in the Raman spectrum of the glassy state, indicating that both species are transformed into more stable species of $ZnBr_4^{2-}$ and $Zn(H_2O)_6^{2+}$ ions at low temperatures. A very weak depolarized Raman
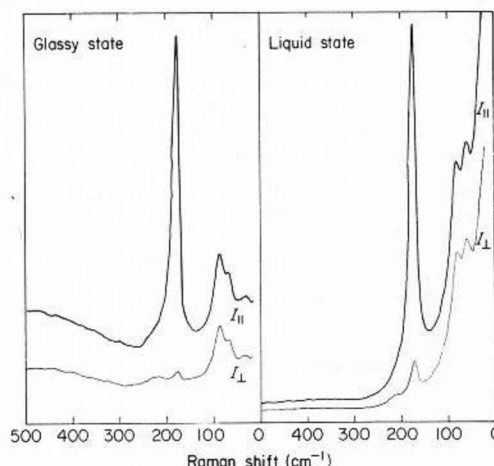

Figure 5. Raman spectra of the $ZnBr_2 \cdot 3LiBr \cdot 15H_2O$ solution in both liquid and glassy states.

band is observed at $223\,cm^{-1}$ in the spectra of glassy $ZnBr_2 \cdot 10H_2O$ and $ZnBr_2 \cdot 3LiBr \cdot 15H_2O$ solutions and is assigned to the ν_3 mode of $ZnBr_4^{2-}$ ions. The Raman spectra of both liquid and glassy states of the $ZnBr_2 \cdot 3LiBr \cdot 15H_2O$ solution (Fig. 5) show that most zinc species exist as $ZnBr_4^{2-}$ ions with other species being negligibly small when there are excess bromide ions in the solution.

The assignment of the ν_2 and ν_4 modes of tetrahedral $ZnBr_4^{2-}$ ions is straightforward from the comparison of the spectra for the $ZnBr_2 \cdot 10H_2O$ and $ZnBr_2 \cdot 3LiBr \cdot 15H_2O$ solutions. A Raman peak at $400\,cm^{-1}$ in the glassy $ZnBr_2 \cdot 10H_2O$ solution is assigned to the ν_1 mode of $Zn(H_2O)_6^{2+}$ ions, although there may be minor contributions from other intermediate complexes such as $ZnBr_p(H_2O)_q^{(2-p)+}$ species ($p \leqslant 3$). This is supported by the same frequency of the Zn—O stretching band in both $ZnCl_2 \cdot 10H_2O$ and $ZnBr_2 \cdot 10H_2O$ solutions.

ZnI$_2$ solutions

Similar intensity changes as in the $ZnBr_2$ solution are observed for the Raman spectrum of the $ZnI_2 \cdot 10H_2O$ solution from liquid state at room temperature to glassy state. Comparison of the spectra for both the $ZnI_2 \cdot 10H_2O$ and $ZnI_2 \cdot 3LiI \cdot 15H_2O$ solutions gives the following assignments for the tetrahedral ZnI_4^{2-} ion: ν_1, $125\,cm^{-1}$; ν_2, $50\,cm^{-1}$; ν_3, $178\,cm^{-1}$; and ν_4, $66\,cm^{-1}$. These assignments are in good agreement with the previous reports for aqueous ZnI_2 solution with excess iodide ions,[11] and molten $CsZnI_3$ salt,[15] in which the predominant zinc species exists as the tetrahedral ZnI_4^{2-} ions. In the Raman spectrum of the glassy $ZnI_2 \cdot 10H_2O$ solution there are two Raman bands near 55 and $78\,cm^{-1}$, which disappear in the Raman spectrum of glassy $ZnI_2 \cdot 3LiI \cdot 15H_2O$ solution (Fig. 6). We ascribe these bands to the ZnI_3^- ions. From the structural studies on the corresponding zinc tribromide $ZnBr_3^-$ ion,[16] a pyramidal structure with C_{3v} symmetry is inferred for the structure of the ZnI_3^- ion. Our observation of two Raman bands (55 and $78\,cm^{-1}$) in the bending frequency region is compatible with the above inference. Failure to observe the antisymmetric stretching mode
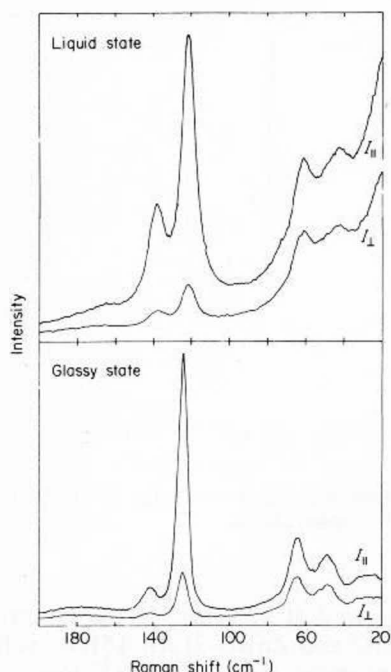
Figure 6. Raman spectra of the ZnI$_2$·3LiI·15H$_2$O solution in both liquid and glassy states.

Table 1. Observed frequencies of Raman bands (in cm^{-1}) and their assignments in the ZnX$_2$·10H$_2$O and ZnX$_2$·3LiX·15H$_2$O solutions.

Species		This work	Literature
Zn(H$_2$O)$_6^{2+}$	ν_1	398–400 (390 ± 5)	—
ZnCl$_3^-$	ν_1	298(—)	286^c
ZnCl$_4^{2-}$	ν_1	283 (282)	280^a, 278^b, 275^c
	ν_2	96 (—)	82–116^a, 110^b, 79^c
	ν_3	305 (—)	280^a, 278^b, 306^c
	ν_4	117 (—)	82–116^a, 110^b, 104^c
ZnBr$_2$	ν_1	— (208)	206^a, 208^c
ZnBr$_3^-$	ν_1	188 (183)	184^a, 182^c, 183^d
ZnBr$_4^{2-}$	ν_1	175 (172)	172^a, 172^c, 171^d
	ν_2	65 (62)	61^a, 66^c, 57^d
	ν_3	223 (212)	210^a, 208^c, 214^d
	ν_4	86 (84)	82^a, 88^c, 81^d
ZnI$_2$	ν_1	172 (165)	—
ZnI$_3^-$	ν_1	142 (138)	—
	ν_2	55 (—)	—
	ν_4	78 (74)	—
ZnI$_4^{2-}$	ν_1	125 (122)	122^a, 130^e
	ν_2	50 (43)	44^a, 60^e
	ν_3	178 (—)	170^a, 172^e
	ν_4	66 (61)	62^a, 70^e

^{a} Ref. 11. ^{b} Ref. 13. ^{c} Ref. 23. ^{d} Ref. 16. ^{e} Ref. 15.
Values in parentheses are of the liquid state at room temperature.

(ν_3) of the ZnI$_3^-$ ion is likely due to the weakness of the band and/or to the overlapping with other intense bands, leaving a slight ambiguity for the structural assignment. An appreciable amount of ZnI$_3^-$ ions remain even in the glassy ZnI$_2$·3LiI·15H$_2$O solution, in contrast to the corresponding glassy chloride and bromide solutions in which no detectable ZnX$_3^-$ (X = Cl or Br) are observed. The polarized Raman band near 400 cm^{-1} in the glassy ZnI$_2$·10H$_2$O solution is assigned to the ν_1 mode of the Zn(H$_2$O)$_6^{2+}$ ion, and it disappears completely in the ZnI$_2$·3LiI·15H$_2$O solution as do the corresponding solutions of the chloride and bromide.

Summing up these results and discussion, our assignments of the Raman bands for zinc halide solutions are given in Table 1, which also includes conclusions of other investigators for comparison.

General trends among three halide solutions

It would be worthwhile to see the general trends among these three aqueous solutions from liquid state to glassy state. The most significant feature is the increasing stability of the ZnX$_2$(H$_2$O)$_2$ and ZnX$_3$(H$_2$O)$^-$ species in the glassy state on going from chloride, bromide to iodide solutions. In fact, a Raman ν_1 band due to the ZnI$_3^-$ ions remains even in the glassy ZnI$_2$·3LiI·15H$_2$O solution whereas the corresponding band due to the ZnX$_3^-$ ions disappears completely in both chloride and bromide solutions with excess X$^-$ ions. This trend can be largely interpreted in terms of the steric effect by the increase of ionic radius. Equilibrium constants $K = [MX_4^{2-}]/[M^{2+}][X^-]^4$ for the equation $M^{2+} + 4X^- \rightleftarrows MX_4^{2-}$ at room temperature are of the order $K = 1, 10^{-1}$

and 10^{-2} for the chloride, bromide and iodide solutions, respectively.^{26} Though these values are obtained in more diluted solutions, they are in harmony with the observed trend.

The second point is the increasing population of the ZnX$_4^{2-}$ complex relative to other lower halide complexes, ZnX$_p^{(2-p)+}$ ($p = 1, 2, 3$), at low temperatures. This trend is clearly seen in the decrease in intensities or disappearance of Raman bands due to the ZnX$_p^{(2-p)+}$ complexes in the glassy solutions. In the aqueous solution of a stoichiometric halide-to-zinc ratio (i.e., X$^-$/Zn^{2+} = 2) the process may be given approximately by the reaction $2ZnX_2 + 6H_2O \rightarrow ZnX_4^{2-} + Zn(H_2O)_6^{2+}$. This trend is in marked contrast to aqueous gallium halide solutions in which the tetrahedral GaX$_4^-$ ions tend to be transformed into either octahedral Ga(H$_2$O)$_6^{3+}$ ions or lower halide complexes such as GaCl(H$_2$O)$_5^{2+}$ ions at low temperatures.^{9} The behaviour of the ZnX$_2$ solution is a kind of disproportionation and may be interpreted by the large difference in the thermal stabilities between ZnX$_4^{2-}$ and ZnX$_2$ species in aqueous solution at low temperatures.

Finally, it may be of some value to comment on the bandwidths between liquid state at room temperature and glassy state. The linewidth decreases with lowering temperature in all cases: the full half-bandwidth of the ν_1 band in the ZnX$_2$·3LiI·15H$_2$O solution is 25, 11.5 and 8.8 cm^{-1} in the liquid state at room temperature, and 18, 8.8 and 6.5 cm^{-1} in the glassy state for the chloride, bromide and iodide solutions, respectively. The ratio of the width in the glassy state to that in the liquid state is about 0.7 in all cases.

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