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Nonexistence of Hydration Number Change of Cd^{2+} Ions in Aqueous $Cd(NO_3)_2$ Solution

Hitoshi Kanno
Department of Chemistry, The National Defence Academy,
Hashirimizu, Yokosuka, Kanagawa 239

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Synopsis. Raman spectra for the Cd^{2+}-OH_2 stretching vibration (ν_1 band) were measured for aqueous $Cd(NO_3)_2$ solutions of R=15 and 40 (R: moles of water/moles of salt). Contrary to the results reported by Kuznetsov et al.,[5] it is concluded that the hydration number of Cd^{2+} ions does not change with salt concentration in the $Cd(NO_3)_2$ solution.

In recent years, inner-sphere hydration numbers have been determined by X-ray diffraction method for many metal cations in aqueous electrolyte solutions.[1-4] Most divalent cations are reported to have six water molecules in their inner-coordination spheres.[1,2] However, the recent X-ray diffraction study by Kuznetsov et al.[5] asserts that the hydration number of Cd^{2+} ions changes from four in an aqueous $Cd(NO_3)_2$ solution (R=40) to six in the R=25 solution where R is the molar ratio of water to salt in the solution. If this is the case, it should be the first experimental evidence for the hydration number change with variation of salt concentration for divalent cations and has a significant implication for our understanding of aqueous electrolyte solutions. Valeev et al.[6] have very recently reported that the Cd^{2+} ions in the R=10 solution are tetrahedrally coordinated with two water molecules and two nitrate ions. When ligands other than water molecules constitute a part of the coordination sphere, geometrical factors such as size and the manner of coordination (monodentate or bidentate) of the ligands have a large effect on the coordination number so that comparison between the coordination number of an all-aquated metal ion and that of a partially-aquated metal ion should be made with care.

On the other hand, Bol et al.[7] determined the coordination number of Cd^{2+} ions in aqueous $Cd(NO_3)_2$ solution ($R \simeq 55$) by X-ray diffraction method and reported that the hydration number of Cd^{2+} ions is six. The X-ray diffraction study by Ohtaki et al.[8] of aqueous $Cd(ClO_4)_2$ solution ($R \simeq 19$) also reports that it is about six. With these experimental data, it is evident that Cd^{2+} ions are octahedrally coordinated in concentrated Cd-salt solutions ($R \lesssim 25$). However, there is a clear discrepancy between the two reports by Kuznetsov et al.[5] and Bol et al.[7] in rather dilute $Cd(NO_3)_2$ concentration range (R=40—55). Therefore, it is important to determine whether the hydration number change really occurs with decreasing salt concentration in aqueous $Cd(NO_3)_3$ solution.

In this work, we examined the possibility of hydration number change of Cd^{2+} ions in aqueous $Cd(NO_3)_2$ solution by Raman spectroscopy. As a symmetric M-OH_2 stretching vibration (a ν_1 band) of aquated metal ions (M: metal cation) is sensitive in frequency to the constituents of the coordination spheres of the cations, it can serve as a sensitive probe for the hydration number change, if any, in aquated Cd^{2+} ions. We measured the ν_1 spectra for the aqueous $Cd(NO_3)_2$ solutions of R=15 and 40 and the ν_4 spectra of the NO_3^- ions in the solutions. Raman measurements were carried out in the same way as previously reported.[9]

Results and Discussion

The ν_1 spectra are shown in Fig. 1. We see only a small frequency change ($\Delta\nu_1 = 6 \pm 2\ cm^{-1}$) from the R=15 solution to the R=40 solution. From the ν_4 spectra shown in Fig. 2, we know that some nitrate ions are coordinated to cadmium ions in the R=15 solution because the coordinated NO_3^- ions give a higher ν_4 frequency (about 738 cm^{-1}) than 718 cm^{-1} (the ν_4 frequency for non-coordinated NO_3^- ions).[10] In the R=40 solution, the $\approx$738 cm^{-1} peak is much weaker than that in the R=15 solution, indicating that the inner-coordination sphere around a Cd^{2+} ion consists mostly of water molecules in the R=40 solu-

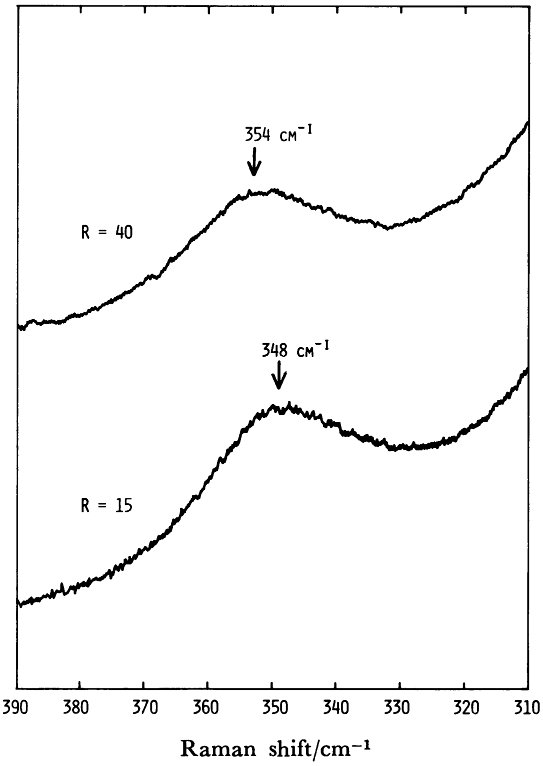

Fig. 1. Raman spectra of the Cd^{2+}–OH_2 stretching vibration for aqueous $Cd(NO_3)_2$ solutions of R=15 and 40.

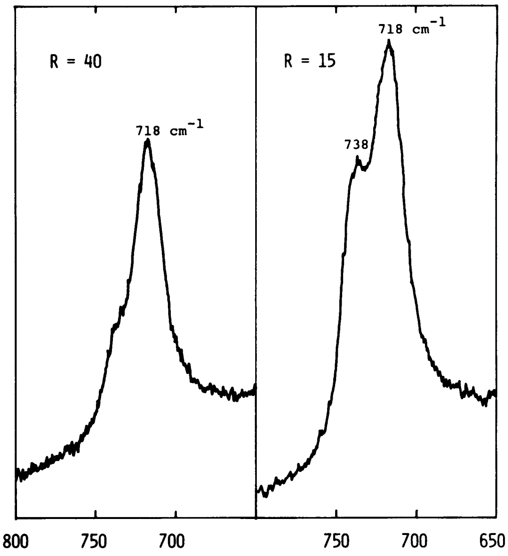

Fig. 2. Raman spectra of the ν_4 band of the NO_3^- ions in aqueous $Cd(NO_3)_2$ solutions of $R=15$ and 40.

tion. It is a well-known fact that a ligand other than water molecules enters into an inner-coordination sphere of an aquated cation, the frequency of a ν_1 band gets lower than that for all-aquated cations.[10,11] In other words, the overall effects of increasing in mole fraction of a aquated Cd^{2+} ions partially substituted with nitrate ion(s) such as $[Cd(NO_3)(OH_2)_n]^+$ ion are a steady decrease in the total ν_1 frequency. Therefore, the frequency change $\Delta_{\nu 1}=6\pm2$ cm^{-1} between the $R=15$ and 40 solutions is mainly ascribable to the difference of the average constituents of the innersphere coordinations: The mole fraction of nitrate ions complexed to Cd^{2+} ions is larger in the $R=15$ solution than in the $R=40$ solution. In the Raman study by Davis and Plane,[12] it is reported that the nitrate ions coordinated to Cd^{2+} ions are acting as a monodentate ligand and that no evidence for complex species higher than $[Cd(NO_3)(OH_2)_n]^+$ was found. The smallness of the ν_1 frequency change from $R=40$ to $R=15$ indicates that the mole fraction of nitrate ions coordinatig to Cd^{2+} ions is not large. This is also confirmed by the Raman ν_4 spectrum for the $R=15$ solution.

There have been a few examples[13,14] which can be a guide for the estimation of the frequency change when the hydration number change really takes place in aqueous $Cd(NO_3)_2$ solution. The conversion from an octahedral to a tetrahedral configuration of a metal halide gives rise to an increase in the frequency of the symmetric stretching vibrations (a ν_1 band): e.g.,

$$[InCl_6]^{3-}(\nu_1\text{: } 275\text{ cm}^{-1}) \longrightarrow [InCl_4]^-(\nu_1\text{: } 366\text{ cm}^{-1})$$

and

$$[SnCl_6]^{2-}(\nu_1\text{: } 301\text{ cm}^{-1}) \longrightarrow [SnCl_4](\nu_1\text{: } 360\text{ cm}^{-1}).^{13)}$$

Hydration number change of rare earth ions from 9 to 8 results in the ν_1 frequency change of about 25 cm^{-1}, e.g., $[Eu(OH_2)_9]^{3+}(\nu_1$: 369 cm^{-1})→$[Eu(OH_2)_8]^{3+}(\nu_1$: 394 cm^{-1}).[14] Thus, the hydration number change, if it really occurs in an aqueous $Cd(NO_3)_2$ solution between $R=15$ and 40, should give rise to a ν_1 frequency change of more than 30 cm^{-1}. However, the observed ν_1 frequency shift is much smaller than the one expected from the hydration number change. Accordingly, we conclude that the hydration number change, at least the one proposed by Kuznetsov et al.,[5] does not takes place in aqueous $Cd(NO_3)_2$ solution between $R=15$ and 40. From the ν_1 results shown in Fig. 1 and the X-ray diffraction results by Bol et al.,[7] it is considered that the coordination number of all-aquated Cd^{2+} ions in an aqueous $Cd(NO_3)_2$ solution remains six in all concentration ranges ($15\lesssim R\lesssim 55$). This is supported by the observation[15] that the ν_1 band is at 356 ± 3 cm^{-1} in an aqueous $Cd(ClO_4)_2$ solution ($R=15$), in which all Cd^{2+} ion are octahedrally hydrated according to the X-ray diffraction study by Ohtaki et al.[8]

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