Raman Spectroscopic Study for Dimethylsulfoxide Solution of $\text{Zn}(\text{SCN})_2$ under High Pressure

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Raman spectra of $\text{Zn}(\text{SCN})_2 \cdot 30\text{DMSO} \cdot 4\text{NaSCN}$ solution (DMSO=dimethylsulfoxide) were measured at high pressures and room temperature. The effect of pressure on the interactions between Zn^{2+} ions and SCN^- ions and the solution structures were examined. The relative intensity of the symmetric C-N stretching vibration due to SCN^- ions decreases with increasing pressure. Peak frequencies of both symmetric (in-phase) and asymmetric (out-of-phase) C-N stretching vibrations decrease up to 100 MPa as the pressure increases. The self-association of DMSO molecules in this solution increases with increasing pressure. With these results, it is suggested that $[\text{Zn}(\text{NCS})_4]^{2-}$ complexes form the solvent-separated complex pairs at higher pressures.

[Raman spectroscopy, zinc thiocyanato complex, dimethylsulfoxide, high pressure, self-association]

1. Introduction

Many studies of the interaction of thiocyanate ion with metal cations have been performed[1-8]. Raman and X-ray studies of zinc thiocyanato complexes in a dimethylsulfoxide(DMSO) solution have shown the dominant structure of $[\text{Zn}(\text{NCS})_4]^{2-}$ [7]. In the complex $[\text{Zn}(\text{NCS})_4]^{2-}$ of the hard acceptor Zn^{2+} , the thiocyanate ions coordinate to Zn^{2+} ions *via* N atom in a regular tetrahedral arrangement with an angle $\text{Zn}-\text{NCS}=180^\circ$ [8].

On the other hand, there are many investigations on the structure of liquid DMSO and its binary solutions by various experimental techniques [9-14]. From these results, DMSO is known to be a highly associated liquid. However, the structure of the liquid is still controversial in the literature. Several liquid structures of DMSO have been suggested. For example, DMSO in solution can form less polar cyclic dimers[9] or more polar chain polymers[13] or a mixture of cyclic aggregates and linear chain like dimers[14]. In view of these observations, it is very interesting to see the effect of pressure on the interactions between Zn^{2+} ions and SCN^- ions and the solution structures.

In the present study, Raman spectra of $\text{Zn}(\text{SCN})_2 \cdot 30\text{DMSO} \cdot 4\text{NaSCN}$ solution were measured up to 300 MPa at room temperature. We mainly examined the C-N stretching vibrational bands of thiocyanate ions and S-O stretching vibrational bands of DMSO molecules.

2. Experimental

DMSO (Wako Pure Chemicals) was dried with type 3A1/8 molecular sieves. $\text{Zn}(\text{SCN})_2$ and NaSCN (Wako Pure Chemicals) were dried under a reduced pressure before use. Raman spectra were measured with a JASCO NR-1100 spectrophotometer. The spectra were obtained using ca. 300 mW of the 514.5 nm line of an NEC argon-ion laser as an exciting source. The spectral resolution in this study was 1 cm^{-1} . The high pressure Raman cell was of the type described

previously[15]. We used a pyrex glass internal sample cell to avoid corrosion of the pressure vessel by the sample solution. The pressure was measured using a Heise gauge with an accuracy of ± 5 bar.

3. Results and Discussion

Raman spectra of the C-N stretching vibrational band for the $\text{Zn}(\text{SCN})_2 \cdot 30\text{DMSO} \cdot 4\text{NaSCN}$ solution at various pressures are shown in Fig. 1. At 0.1 MPa, the Raman spectrum has three peaks (2111, 2083, 2063 cm^{-1}) due to SCN^- ions. The peaks of 2111, 2083 cm^{-1} are ascribed to the symmetric (in-phase) and asymmetric (out-of-phase) C-N stretching vibrational bands of SCN^- ion coordinating to Zn^{2+} ions, respectively[3]. The lowest frequency peak is due to the solvated free SCN^- ion. It is found in this study that the relative intensity of the symmetric C-N stretching vibrational band decreases with increasing pressure. The respective peak frequencies of the C-N stretching bands are plotted as a function of pressure in Fig. 2. Peak frequencies of both symmetric and asymmetric stretching vibrations initially decrease up to ~ 100 MPa. These initial decreases in the frequencies indicate that the interactions between Zn^{2+} ions and SCN^- ions seem to be getting weaker with increasing pressure at lower pressures. On the other hand, the frequency of the solvated free SCN^- ions shifts to higher frequency as the pressure increases.

As far as authors know, Raman spectroscopic measurement of pure liquid DMSO itself under high pressure has not been reported yet. Thus, we have checked the pressure dependence of the Raman spectrum of DMSO. Fig. 3 shows the Raman spectral change of the S-O stretching vibrational band for DMSO at various pressures. At 0.1 MPa, this band consists of the peaks due to the S-O stretching vibrations of the self-associated ($\sim 1048\text{ cm}^{-1}$) and unassociated (1058 cm^{-1}) molecules of DMSO and the overlapping peaks due to the rocking vibrations of the

Fig. 1. Raman C-N stretching vibrational spectra for the $\text{Zn}(\text{SCN})_2 \cdot 30\text{DMSO} \cdot 4\text{NaSCN}$ solution at various pressures.

Fig. 2. Frequency variations of the C-N stretching bands for the $\text{Zn}(\text{SCN})_2 \cdot 30\text{DMSO} \cdot 4\text{NaSCN}$ solution as a function of pressure.

○: in-phase, △: out-of-phase,
□: free solvated SCN^- ion

methyl groups[9]. As seen in Fig. 3, another peak at $\sim 1025 \text{ cm}^{-1}$ appears at 50 MPa. It is noteworthy that above 50 MPa the higher peak at $\sim 1048 \text{ cm}^{-1}$ completely disappeared and only lower sharp peak at $\sim 1020 \text{ cm}^{-1}$ remains. It is also found that liquid DMSO freezes above 50 MPa by an application of pressure. Thus, the lower peak at 1020 cm^{-1} is ascribed to the S-O stretching vibration of the solid crystal of DMSO. This result indicates that the interaction between DMSO molecules is getting stronger and the self-association of liquid DMSO increases with increasing pressure. Recent data [9, 10, 12] have persisted that the molecular arrangement in the liquid DMSO is similar to that in the solid state. That is, DMSO molecules associate in an antiparallel way rather than in a chain-like way. Considering above our results, it is suggested that DMSO in the liquid state favors the structure of more compact solid-like cyclic dimers rather than that of linear chain-like polymers. Therefore, DMSO are easily crystallized by compression.

Raman spectra of the S-O stretching vibrational band for the $\text{Zn}(\text{SCN})_2 \cdot 30\text{DMSO} \cdot 4\text{NaSCN}$ solution

Fig. 3. Raman S-O stretching vibrational spectra for DMSO liquid at various pressures.

at various pressures are shown in Fig. 4. At 0.1 MPa, a single broad peak was observed. As the pressure increases, the peak at $\sim 1048 \text{ cm}^{-1}$ appears at 50 MPa. This peak may be ascribed to the self-associates of DMSO molecules in the $\text{Zn}(\text{SCN})_2 \cdot 30\text{DMSO} \cdot 4\text{NaSCN}$ solution[9]. As shown in Fig. 4, the frequency of this peak decreases with increasing pressure. As just described above, the downward frequency shift of this

peak indicates that the interaction between DMSO molecules in the solution is getting stronger with increasing pressure, because the solid crystal of DMSO has a sharp peak at $\sim 1020\text{ cm}^{-1}$ in the S-O stretching vibrational region. Above 50 MPa, the spectrum becomes rather complicated and it has many shoulders. This spectral change is emphasized with increasing pressure. The assignments of the respective peaks are difficult at this moment. Fine structure seems to appear as the freezing pressure is getting near. It should be noted that the solution crystallizes at the pressure of about 275 MPa.

Fig. 4. Raman S-O stretching vibrational spectra for the $\text{Zn}(\text{SCN})_2 \cdot 30\text{DMSO} \cdot 4\text{NaSCN}$ solution at various pressures.

In these observations, our results are explained in the following way, though it is rather speculative. As discussed above, self-association of DMSO molecules in the solution increases with increasing pressure. On the other hand, Zn^{2+} ion coordinates to thiocyanate ion strongly and the complex $[\text{Zn}(\text{NCS})_4]^{2-}$ is finally formed in the solution, most probably in a tetrahedral configuration[7,8]. It is expected that the average distance between the SCN^- ions in the $[\text{Zn}(\text{NCS})_4]^{2-}$ complexes and other neighboring molecules or species becomes shorter as the pressure increases. Therefore, the interactions of the S atoms of SCN^- ions in the complexes with the adjacent species would be getting stronger, and relatively the coordination of N atoms of SCN^- ions to a Zn^{2+} ion in the complex may be getting weaker. Thus, the initial decreases (up to $\sim 100\text{ MPa}$) of the peak frequencies for the symmetric and asymmetric C-N stretching vibrations are ascribed to

this pressure effect. The upward shifts of these frequencies above 100 MPa are correspond to the restriction on the movement of these molecules by further compression. As the pressure approaches to the point ($\sim 275\text{ MPa}$) at which the solution crystallizes by compression, some $[\text{Zn}(\text{NCS})_4]^{2-}$ complexes probably form the solvent-separated complex pairs one another. The amount of the solvent-separated pairs increases with increasing pressure. The reason is that the self-association of DMSO molecules in the solution prevails with increasing pressure and the $[\text{Zn}(\text{NCS})_4]^{2-}$ complexes are short of sufficient solvent molecules to interact. Thus, the cosphere overlaps, that is, solvent-separated complex pairs necessarily become more dominant at higher pressures. However, there is little possibility that the contact pairs of complexes by using the SCN^- ion of one of the pair exist in the solution, because the C-N stretching band for bridging thiocyanato complex ($\text{M}-\text{NCS}-\text{M}$; M=metal) usually occurs at a fairly higher frequency than that for isothiocyanato complex ($\text{M}-\text{NCS}$)[16]. Consequently, it is ascribed to the above mentioned structural change under high pressure that the relative intensity of the symmetric C-N stretching vibration band decreases with increasing pressure.

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