Variation of Absorption Spectra of Aqueous DMSO Solutions Measured by the Ultraviolet–Attenuated-Total-Reflection Method

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Dimethyl sulfoxide (DMSO) is a famous solvent for biologists and organic chemists. It is well known that DMSO is miscible with water and has cryoprotection effect. Hydration structure of the aqueous DMSO solution changes greatly with the concentration. In the dilute region, DMSO works as a structure maker of water, but as the concentration increases, it behaves as a structure breaker [1]. The hydration structure has been discussed with various methods [2–4]. The UV absorption spectroscopy can be a good method to reveal the electronic structure of hydrated DMSO. However, large absorption of DMSO in the UV region makes it difficult to measure spectra with conventional methods. To prevent this problem, we employ the ultraviolet–attenuated-total-reflection method. In this study, we measure a series of absorption spectra of aqueous DMSO solutions with a systematic change of the concentration.

The experiments were performed on the beamline for vacuum-ultraviolet circular dichroism spectroscopy, BL-12. We nearly made a housing for a prism with two wings for suppressing stray light. The prism for this study was made of synthetic fused silica and inserted in the housing box in an inverted triangular manner. The box was then placed along the light axis so as to satisfy the total reflection conditions. The samples were dropped on the top face of the prism. Finally, a cover glass was placed on the sample, and the box was closed with a lid. The sample chamber was purged with nitrogen gas. The wavelength range for the measurements was 180–280 nm, and the spectrum of liquid water was used as a reference. The sample of aqueous DMSO solutions was prepared with molar fraction of DMSO ranging from 0.01 to 0.10. The reagent DMSO was obtained commercially from FUJIFILM Wako Pure Chemical Corp., Japan.

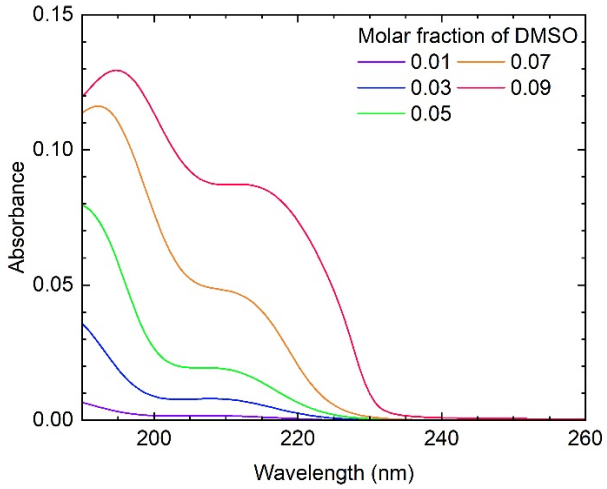

FIGURE 1. Ultraviolet–ATR absorption spectra of aqueous DMSO solutions measured for a series of molar fraction of DMSO.

The obtained spectra have strongly concentration-dependent, as shown in Fig. 1. Two peaks of absorption bands shift to the longer wavelength side in a non-linear way. The spectrum for $x_D = 0.09$ is apparently

different from the others.

Quantitative analysis of spectra is carried out by the principal component analysis (PCA). For analysis, data in the range $x_D < 0.09$, where the intensity of spectra increases monotonically, is used. The results of PCA are shown in Fig. 2. The measured spectra are well explained by three components (PC1–PC3). The primary component (PC1) of the vector resembles the spectrum for $x_D = 0.07$. The score of PC1 would be in a straight line as expected by Beer's law, but the line deviates upward. In fact, the score is proportional to the square of the molar concentration of DMSO. This indicates the existence of the DNSO dimer.

Based on the behavior of the scores, the hydration structure can be divided into three regions. The first region covers the dilute solution under 1.96 mol/L. The second region ranges from 1.96 to 2.81 mol/L. The higher concentration solutions form the third region. The boundaries are in accord with the change in hydration structure reported by Refs. [2–4].

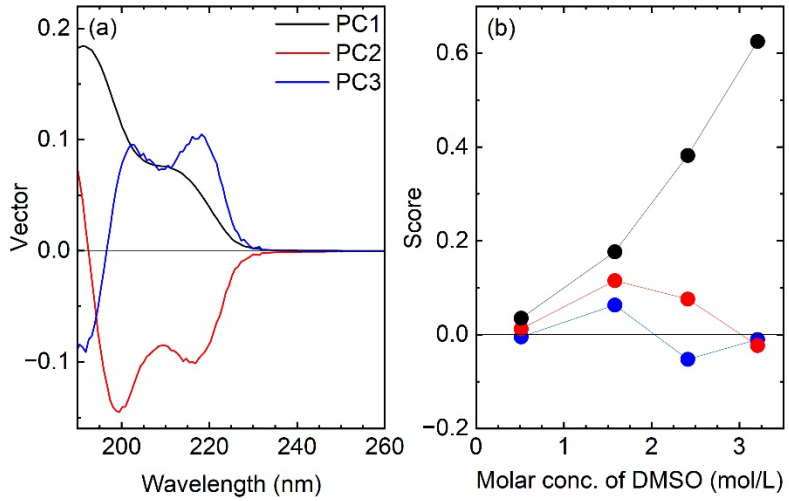

FIGURE 2. Spectral components (a) and scores (b) obtained by PCA for the UV absorption spectral data shown in Fig. 1. The explained variance ratio of PC1–PC3 are 96.2, 2.9 and 0.8%, respectively.

REFERENCES

1. I. I. Vaisman and M. L. Berkowitz, *J. Am. Chem. Soc.* **114**, 7889–7896 (1992).
2. K. Mizuno, S. Imafuji, T. Ochi, T. Ohta and S. Maeda, *J. Phys. Chem. B* **104**, 11001–11005 (2000).
3. D. N. Shin, J. W. Wijnen, J. B. F. N. Engberts and A. Wakisaka, *J. Phys. Chem. B* **105**, 6759–6762 (2001).
4. S. Roy, S. Banerjee, N. Biyani, B. Jana and B. Bagchi, *J. Phys. Chem. B* **115**, 685–692 (2011).
5. K. Matsuo, T. Fukuyama, R. Yonehara, H. Namatame, M. Taniguchi and K. Gekko, *J. Electron Spectrosc. Relat. Phenom.* **144–147**, 1023–1025 (2005).