^{17}O-NMR Evidence on the Isolated Water Molecule in Hydrophobic Organic Solvents

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^{17}O-NMR spectra of $H_2{}^{17}O$ molecules in benzene, chloroform, ethylacetate, dimethylformamide, and 1-butanol were measured. For hydrophobic benzene and chloroform, the ^{17}O-NMR spectra give two peaks consisting of the triplet and singlet lines, which are assigned to the isolated monomeric and clustered water molecules, respectively. The observed triplet splitting due to the spin - spin coupling of $J_{^{17}\mathrm{O\text{-}H}}$ gives an evidence that the isolated water molecule can not exchange the protons between water molecules separated far away during the measurement time of NMR phenomenon.

Water is an important hydrogen-bonding substance for the living, and so the nature of water forming hydrogen-bonding has been studied comprehensively.[1] The physical states of water in various environments are also an important research problem. Especially, it has been discussed whether the isolated monomeric (non-hydrogen bonding) water molecule exists or not in any state other than gaseous phase. Nakahara and Wakai measured the ^{1}H-NMR spectra of H_2O in organic solvents and reported that sparingly soluble water is monomeric in hydrophobic solvents and that some excess water beyond the miscible concentration is clustered at room temperature.[2] They deduced these results from the chemical shifts and the temperature dependence of ^{1}H-NMR spectra.

In this study, we investigate the physical state of water in hydrophobic organic solvents, to obtain more direct evidences for the existence of isolated water molecule, by applying ^{17}O-NMR spectroscopy, i.e., using the $H_2{}^{17}O$ (enriched 20.39% of ^{17}O isotope) as a probe. NMR spectra were measured with a Varian VXR-300 FT-NMR equipment at a fixed temperature of 25 ℃.

Figure 1 shows NMR spectra of $H_2{}^{17}O$ in benzene, chloroform, ethylacetate, dimethylformamide, and 1-butanol, in comparison with that of bulk water. Water contents are denoted also in the figure. Except the spectrum of $H_2{}^{17}O$ in chloroform, all show a single peak to be assigned to monomeric water. For the spectrum of $H_2{}^{17}O$ in chloroform, a peak at a high field should be assigned to the water monomer and another peak at a low field may be assigned to the clustered water according to the assignment of Nakahara and also from Figure 2. As solvents become more hydrophilic, the chemical shifts of the monomeric $H_2{}^{17}O$ molecules approach to the position of bulk water. This suggests that the interactions between solvents and water molecules and/or among water molecules increase with increasing of the hydrophobic nature of solvent. It is noted that the spectral peak of $H_2{}^{17}O$ in benzene and chloroform splits into the triplet. The observed splitting of 79 Hz is in close agreement with the published spin -spin coupling constant of $J_{^{17}\mathrm{O\text{-}H}}$ = 80 Hz.[3] This result implies that ^{17}O-NMR procedure is usefully applied for the study of the proton exchange reaction because of the large value of $J_{^{17}\mathrm{O\text{-}H}}$. This splitted structure is drastically affected with the rate of proton exchange among $H_2{}^{17}O$ molecules.[3] When the proton exchange is relatively slow, the triplet splitting is more clearly seen.[3-5] In the present spectra, this splitting becomes blurred in more hydrophilic solvent in which the proton-exchange reaction may be relatively fast so that the line is broadened. These facts suggest that $H_2{}^{17}O$ molecules within a content of 0.06 wt% in benzene exist in the isolated monomeric water state and can not exchange the protons with H_2O separated far away. The mean distance among water molecules in benzene is calculated to be 37 Å from the water content of 0.06 wt%. The proton exchange among water molecules separated 37 Å seems to be very slow. NMR spectra of $H_2{}^{17}O$ with water contents more than 0.06 wt% in benzene are shown in Figure 2. As can be seen from the figure , a new peak appears as a singlet at a lower field. Excess water beyond 0.06 wt%, therefore, becomes immiscible, and exists as the clustered water in

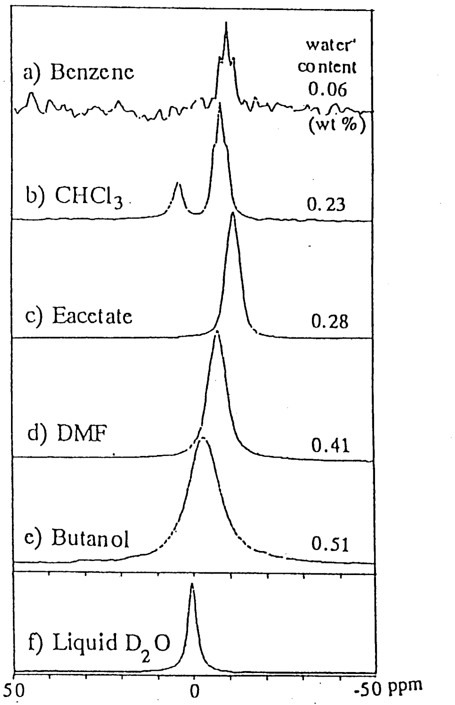

Figure 1. ^{17}O-NMR spectra of the ^{17}O enriched water in organic solvents.

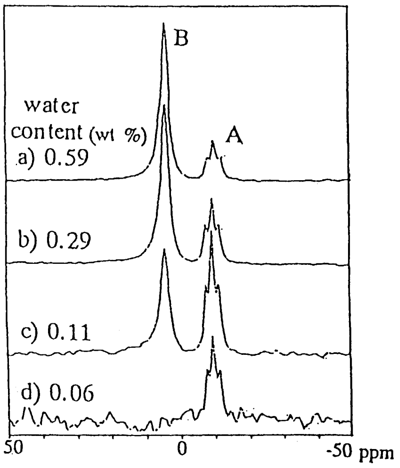

Figure 2. The variation of ^{17}O-NMR spectra of the ^{17}O enriched water in benzene with water contents

benzene. Water molecules in the cluster do not split into triplet due to the fast proton exchange similar to that in the bulk water.

In conclusion, the observed triplet splitting in ^{17}O-NMR spectra gives the more direct evidence on the presence of the isolated water molecule in hydrophobic organic solvents.

Moreover, it is interesting to see whether the triplet splitting of $H_2{}^{17}O$ is observable or not in the polar solvent with a low concentration comparable with that in benzene. If it is not obseved, intamolecular proton exchange may be possible in the solvent with proton acceptor sites. The author will investigate this point in a continued report.

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