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Characterization of Solvents Soluble in Water by Oxygen-17 Nuclear Magnetic Resonance Spectroscopy

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The pH and concentration dependencies of proton and oxygen exchanges in water–solvent systems have been examined by oxygen-17 nuclear magnetic resonance (^{17}O-NMR) spectroscopy. A pH shift in a water–acetone system results in a coalescence of the ^{17}O water signal and an alteration in the intensities of the signals of water and acetone. The signal coalescence arises from proton exchange between water molecules and the signal alteration from oxygen exchange between water and solvent. On the other hand, dilution with solvent results in various patterns of ^{17}O water signals from singlet to triplet. Each water–solvent sample under diluted conditions gives a specific shape which reflects the intrinsic nature of the solvent. In this case, the proton exchange can be discussed by assuming a simplified reaction mechanism.

$$\text{solv}\cdots H_2O + H_3O^* \rightleftharpoons \text{solv}\cdots H_3O^* + H_2O$$

It is concluded that the F_i factor, which refers to a contribution arising from water–solvent interaction, can be taken as a good measure of proton exchange in water–solvent systems and is available for the characterization of solvents soluble in water.

Keywords——^{17}O-NMR; proton exchange mechanism; water–solvent interaction; solvent characterization

Introduction

Proton and oxygen exchanges between water and organic solvents have been studied with respect to dynamics.[1-15] Meiboom[1] investigated proton transfer in water by examining the pH dependency and discussed its dynamics on the basis of measurements of NMR relaxation. Greenzaid *et al.*[3,4,6] examined in detail the oxygen exchange in aldehyde– and ketone–water systems and studied the kinetics by oxygen-17 nuclear magnetic resonance (^{17}O-NMR) measurement. At the present stage, the general features in this field appears to be established. The pH and concentration dependencies of proton and oxygen exchanges in water–organic solvent systems are nevertheless further examined here by means of ^{17}O-NMR spectroscopy with the ultimate aim of characterizing various organic solvents soluble in water on the basis of their dynamics.

Experimental

Water (10% enriched $H_2{}^{17}O$) was obtained from The British Oxygen Co., Ltd. and solvents used in this experiment, acetone, acetonitrile, dioxane, methanol, pyridine, dimethylsulfoxide (DMSO), and tetrahydrofuran (THF analytical grade reagent), were all obtained from Wako Co., Ltd. They were all used without further purification, because purification did not affect the signal shapes and intensities. Various mixtures were prepared by adding weighed enriched water to weighed solvent. In the case of water–acetone samples, the molar fractions prepared were 0.145, 0.36, 0.58, 0.76, and 0.91. The desired pH of a sample was carefully obtained by the addition of a small amount of NaOD or DCl. ^{17}O-NMR measurements were performed on a Varian FT-80A spectrometer (10.783 MHz; sweepwidth, 8065; pulse width, 35 μs; data points, 323; acquisition time, 0.02 s; accumulations, 3000).

A rate equation was first set up for the reaction mechanism considered in the present paper. On the basis of the exchange mechanism, a rate constant (k) was calculated with the life time (τ) which was estimated by curve-fitting of various spectral shapes. The curve fitting was carried out by using a built-in DNMR3 routine program which is applicable for general chemical exchange. Calculations were performed on a HITAC M-200H computer, or sometimes a HITAC M-200H/M-280H/F-810 computer.

Results and Discussion

The ^{17}O-NMR spectra of the water–acetone mixture samples (molar fraction 0.145) are shown as a function of pH in Fig. 1. The spectrum at pH 7.4 (Fig. 1c) can be taken as that of a neutral solution to which neither acid nor base was added. A triplet on the high field side is due to water molecules, and the splitting of *ca.* 82 Hz arises from ^1H–^{17}O spin–spin interaction. A sharp single resonance line on the low field side is from acetone molecules.

A pH shift of the neutral sample in an acidic or basic direction brings about pronounced alterations in the signal shape and intensity. The ^{17}O triplet resonance line of water is observed to coalesce gradually with a pH shift from neutral. This can be explained as follows. The proton exchange between water molecules is accelerated by the pH shift and therefore, the spin–spin splitting appearing in the ^{17}O water signal is averaged out by the fast proton exchange, leading to the coalescence behavior. Assuming that the exchange mechanism of this

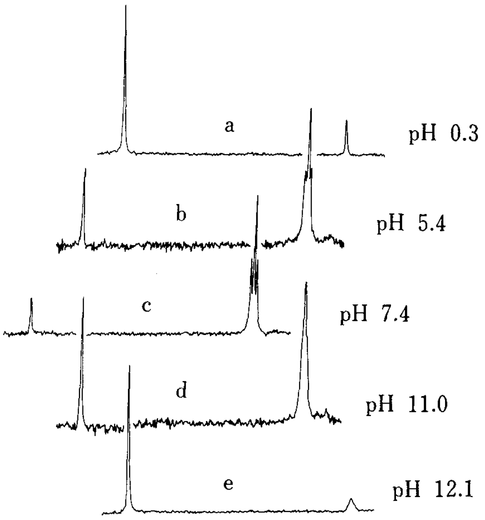


Fig. 1. ^{17}O-NMR Spectra of Water–Acetone Mixture Samples (molar fraction $\alpha=0.145$) as a Function of pH

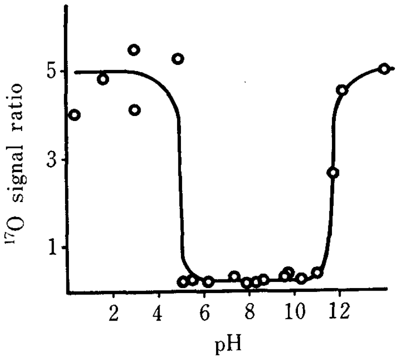
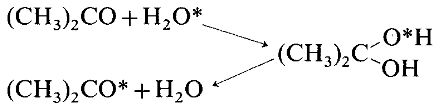


Fig. 2. Plots of the Acetone–Water Signal Ratio in the ^{17}O-NMR Spectrum in Water–Acetone Samples (molar fraction $\alpha=0.145$) as a Function of pH

system is based on an acid–base catalysis reaction mechanism, a rate constant (k) for the proton exchange can be obtained from a plot of life time (τ) against pH, where τ is easily estimated by a routine curve-fitting programme for the signal shape of each pH solution. The estimated rate constant, therefore, is of the order of 10^9 $l \cdot mol^{-1} \cdot s^{-1}$, which is in good agreement with the result reported by Meiboom.[1]

The intensity of the ^{17}O water resonance line was observed to decrease with a pH shift, whereas that of the acetone signal was found to increase (Fig. 1). Next, a more detailed examination was carried out (Fig. 2); the molar fractions are all 0.145. The acetone–water signal ratio in the pH region of 5 to 11 was unchanged at *ca.* 0.2, which is far smaller than the molar ratio (*ca.* 5.9) of each sample. On the other hand, the signal ratio in the pH region above 11 or below 5 is *ca.* 5, which coincides with the molar ratio (*ca.* 5.9) of each sample. This behavior seems to be due largely to the oxygen exchange between water and acetone, the reaction mechanism of which involves a hydration–dehydration process. The curve profile in Fig. 2 changes with time, so that this can be taken as a transient phenomenon. Since all of the observations shown in Fig. 2 are, in practice, carried out within 20 min of sample preparation, the samples in the pH region of 5 to 11 are still in a transient state because the exchange rate in this pH region is slow (of the order of 10^{-3} s^{-1}).[4] On the other hand, the samples in the pH region above 11 or below 5 have already reached exchange equilibrium because the exchange rate in this pH region is accelerated by addition of acid or base to the order of *ca.* $500\,M^{-1} \cdot s^{-1}$.[4] Therefore, as time passes, the transient state gradually transfers to the exchange equilibrium state. The above considerations on oxygen exchange do not conflict with the results of Greenzaid *et al.*[3,4,6]

The relationship between signal ratio and molar ratio in the pH regions above 11 and below 5 was examined in detail (Table I). There is a reasonably good linear relationship between the signal ratio and the molar ratio in the pH regions above 11 and below 5 (Fig. 3). This confirms that the state in these pH regions is governed by an accelerated oxygen exchange rate compared to that of the neutral samples. In this case, the oxygen exchange mechanism,[4] for example, can be written as



$$\begin{array}{l}(CH_3)_2CO + H_2O^* \searrow \\ \qquad\qquad (CH_3)_2C\begin{smallmatrix}O^*H\\ OH\end{smallmatrix} \\ (CH_3)_2CO^* + H_2O \swarrow\end{array}$$

Coalescence of a ^{17}O water triplet in water–acetone neutral solutions as a function of solvent composition is shown in Fig. 4. As the acetone concentration increases, ^1H–^{17}O spin–spin splitting appears in the spectrum. On the other hand, as the acetone concentration decreases, the ^{17}O water triplet coalesces gradually, finally becoming a sharp singlet. Since the samples used in this case are all neutral, the observed coalescence behavior must be governed

Table I. Relationship between ^{17}O Signal Ratio in Acetone–Water Mixtures and the Molar Ratio

Molar ratio	^{17}O signal ratio of Neutral sample (pH 7.4)	 Acidic sample (pH)	 Basic sample (pH)
5.90	11.2×10^{-2}	3.96 (0.3)	4.48 (12.1)
1.78	2.96×10^{-2}	1.31 (1.2)	1.41 (12.4)
0.72	1.35×10^{-2}	0.533 (1.6)	0.486 (11.7)
0.32	1.03×10^{-2}	0.217 (1.8)	0.234 (10.8)
0.10	0.95×10^{-2}	0.0734 (1.9)	0.056 (10.0)

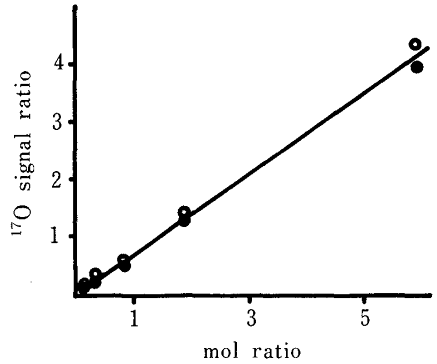


Fig. 3. Relationship between ^{17}O-NMR Signal Ratio and Molar Ratio in Acetone–Water Solutions

○, basic samples; ●, acidic samples.

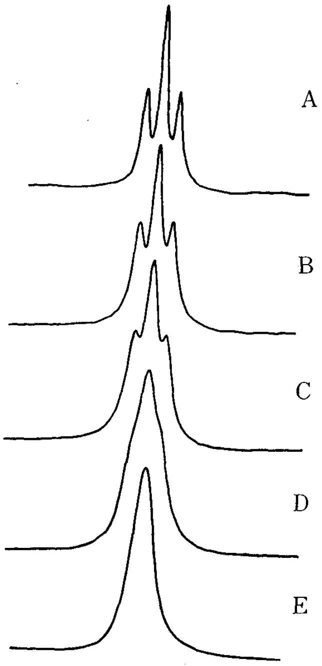


Fig. 4. ^{17}O-NMR Spectra of Water in Neutral Water–Acetone Solutions as a Function of Concentration

A, $\alpha=0.14$; B, $\alpha=0.36$; C, $\alpha=0.58$; D, $\alpha=0.76$; E, $\alpha=0.91$.

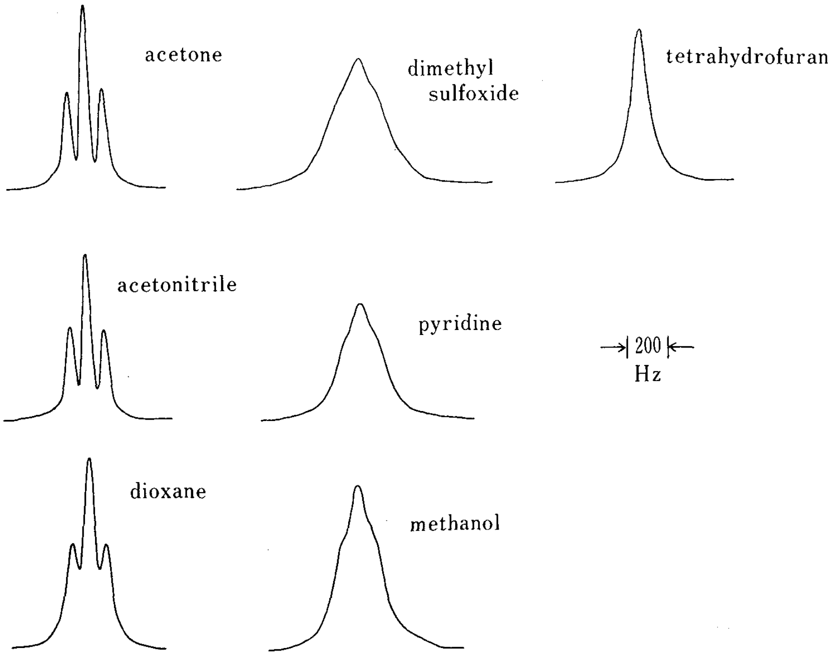


Fig. 5. ^{17}O-NMR Spectra of Water in Neutral Water–Solvent Solutions under Diluted Conditions

only by the stoichiometry of this system. On the other hand, the coalescence behavior should be due essentially to proton exchange. Accordingly, the mechanism of proton exchange can be correlated to the stoichiometry of the system. It is well known that water has ice-like cluster structures linked by hydrogen bonds. As acetone is added to water, the water structure is slightly broken up, and a structure of water bound to acetone appears. Assuming that the proton exchange reaction occurs throughout all hydrogen bond intermediates, the bond-breaking effect on the water structure induced by the solvent must influence the proton exchange. This influence, therefore, results in the change of the signal shape from a singlet to a triplet, because the proton exchange averages out the spin–spin coupling J_{O-H} which is responsible for the triplet signal.

The ^{17}O water signal in other water–organic solvent systems under diluted conditions (less than 5% v/v) do not always show the triplet as in the case of the water–acetone system. Rather, they show intrinsic signal profiles ranging from triplet to singlet according to the species of solvent (Fig. 5). The signal shapes for acetone, acetonitrile and dioxane show distinct triplets. On the basis of an acid–base catalysis reaction mechanism, a rate constant (k) of *ca.* $10^5\,l\cdot mol^{-1}\cdot s^{-1}$ can be easily obtained based on a life time (τ) of 0.01 s estimated by the routine curve-fitting procedure for the signal shapes. The signal shapes for methanol, pyridine and DMSO show broader lines with a shoulder. A rate constant of *ca.* 10^7 was obtained by the same procedure. The signal shape for THF is a coalesced sharp singlet resembling a proton-irradiated spectrum. In this case, the estimated rate constant is of the order of 10^9.

For the purpose of characterizing various organic solvents, it appears to be convenient to set up a simplified, common reaction mechanism for these systems, rather than the acid–base catalysis reaction mechanism which is applicable to a system with a pH shift. The reaction mechanism, for example, can be written as,

$$\mathrm{solv}\cdots H_2O + H_3O^* \rightleftharpoons \mathrm{solv}\cdots H_3O^* + H_2O$$

Then, $\tau^{-1} = k[H_3O^*][H_2O]/[\mathrm{solv}\cdots H_2O] = k[H_3O^*]\cdot F^{-1}$ where τ^{-1} is an exchange rate, k is a rate constant, and F is $[\mathrm{solv}\cdots H_2O]/[H_2O]$. Then, the rate constant can be expressed solely in terms of F, because τ and $[H_3O^*]$ can be estimated by NMR curve fitting and pH measurement of the sample, respectively. The term $[\mathrm{solv}\cdots H_2O]$ ($\simeq[\mathrm{solv}\cdots H_3O^*]$) can be taken as the reduced concentration of a solvent, and so contains not only a stoichiometric contribution but also a contribution induced by water–solvent interactions. Accordingly, the F value can be divided into two terms; F_f from the stoichiometric contribution, and F_i from the water–solvent interaction.

$$F = F_f + F_i$$

None of the spectra shown in Fig. 5 change with further dilution. The F_f values are *ca.* 5. Assuming that a water–acetone system, which shows typical signal coalescence behavior on dilution, can be taken as a standard case for the F factor, F values in other systems can be easily estimated by extrapolating each signal shape to the corresponding signal shape in the standard case. Since F_f of each sample is known, the F_i value in each case can be easily estimated by subtracting F_f from F. According to the definition, the F_i value in the case of acetone should be near zero. The F value of methanol can be estimated to be about 2, because the signal shape nearly corresponds to that of $F\,(=F_f)$ in the standard case; therefore, F_i of *ca.* -3 is obtained. In the same way, the F value of THF is *ca.* 1 and F_f is *ca.* -4. Consequently, F_f takes negative values ranging from zero to *ca.* -5. As the negative value of F_i increases, the effect induced by the water–solvent interaction on proton exchange is reduced. On the other hand, as the negative value of F_i decreases, the effect of the water–solvent interaction on proton exchange increases. It may, therefore, be concluded that F_i can be taken as a good measure of proton exchange in water–solvent systems and is thus available to characterize solvents soluble in water.

In the present paper, the mechanistic outline of a method of solvent characterization has been presented. Further refinement of the method is in progress.

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