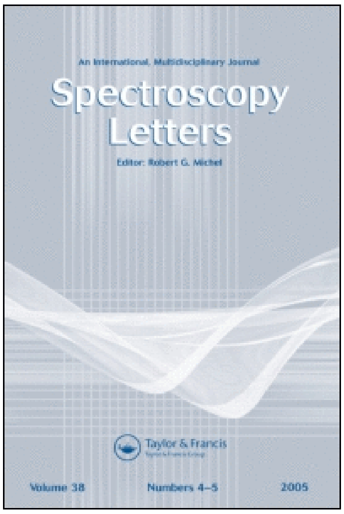

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The Calculation of Correlation Time (τ) for T_1 Spin–Lattice and T_2 Spin–Spin Relaxation Times in Agar Solutions

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ABSTRACT

In this study, solvent proton spin–lattice (T_1) and spin–spin (T_2) relaxation times in agar solutions vs. increasing agar concentrations were measured by a FT-NMR. Each of $1/T_1$ and $1/T_2$ rates was linearly proportional to the agar concentration. The relations between the relaxation rates and agar concentrations correspond to the formulas representing the fast chemical exchange of water protons between free water and water bound to agar. The present results suggest that the ratio of relaxation rates in bound phase (T_{2b}/T_{1b}) is equal to the ratio of the slopes in the relations (K_2/K_1), and the τ can be calculated from the equality of these ratios.

Key Words: NMR; Agar; Water structure; T_1; T_2; Correlation time (τ).

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INTRODUCTION

Nuclear magnetic resonance spectrocopy (NMR) studies on agar gels are carried out for several purposes. Since the water content of gel is close to that of biological tissues, agar gels are proposed as a basic reference material to measure relaxation times and imaging parameters[1,2] and they are also used as a agar diffusion assay for the determination of antibacterial activity.[3,4] In addition, the antimicrobial activity of some pharmacological compounds has been determined by agar dilution method.[5–7] Furthermore, agar was studied by NMR as a compound of polysaccharides and other materials.[8–16]

The $1/T_1$ and $1/T_2$ relaxation rates in agar solutions have been studied by many authors.[2,14,17–19] In these studies, the correlation time (τ) is numerically calculated by considering a combined use of NMR spectroscopy and T_1 spin–lattice and T_2 spin–spin relaxation times. However, there is a controversy on the determined τ values. In some studies, a single τ was used for calculation, while multi τ were used in the others. Therefore, the calculation of the τ value in agar solutions is still of a scientific interest.

It is known that relaxation mechanism in agar solution is caused by the fast chemical exchange of protons between free water and water bound to agar.[2] Taking into account this matter, the present study aims to fit the concentration dependences of the $1/T_1$ and $1/T_2$ rates in agar solutions to the fast chemical exchange formulas. This study also aims to calculate a τ value by using the results derived from the fitting.

EXPERIMENTAL METHOD

In the present work, agar solutions at various concentrations (0.5–2%), obtained by mixing each agar solution for 5 min at 100°C, were introduced to NMR tubes. Then, T_1 and T_2 relaxation times of each tube were measured by using a proton FT-NMR spectrometer operating at 60 MHz. The T_1 and T_2 relaxation times were measured by inversion recovery and spin-echo techniques, respectively. The pulse delays at inversion recovery were changed from 0.5 to 1 sec. Pulse repetition time was set at 10 sec. In spin-echo technique, echo times were changed from 20 to 160 msec. The temperature of the probe was kept at (20°C $\pm$ 0.5°C) by JNM-VT-3C automatic temperature controller unit. Experimental errors were estimated as ± 0.03 sec for T_1 and ± 0.07 sec for T_2 measurements.

RESULTS AND DISCUSSION

The dependences of $1/T_1$ and $1/T_2$ rates on agar concentrations are shown in Figs. 1 and 2. It is seen that the plot of each relaxation rate vs. increasing amounts of agar gives a straightline. The relations concerning these lines can be rearranged as

$$\frac{1}{T_1} = 0.28 + 0.037C \quad \text{and} \quad \frac{1}{T_2} = 0.76 + 4.88C \tag{1}$$

where C replaces x and denotes concentration of agar. The intercepts (0.28 and 0.76) show the relaxation rates of agar-free water, whereas 0.037 and 4.88 denote the slopes of the lines.

It is well known that relaxation rates in agar solutions are averaged by population-weighted rapid chemical exchange of water protons between free and bound states. This can be expressed as follows;[2,17,19]

$$\frac{1}{T_i} = \frac{P_\mathrm{f}}{T_{i\mathrm{f}}} + \frac{P_\mathrm{b}}{T_{i\mathrm{b}}} \qquad i = 1,\ 2, \ldots \tag{2}$$

where P_f, P_b, $1/T_{i\mathrm{f}}$, and $1/T_{i\mathrm{b}}$ refer to the fractions and the relaxation rates of free and bound water, respectively. Inserting $P_\mathrm{f} = (1 - P_\mathrm{b})$ into Eq. (2) gives

$$\frac{1}{T_i} = \frac{1}{T_{i\mathrm{f}}} + \left(\frac{1}{T_{i\mathrm{b}}} - \frac{1}{T_{i\mathrm{f}}}\right) P_\mathrm{b} \tag{3}$$

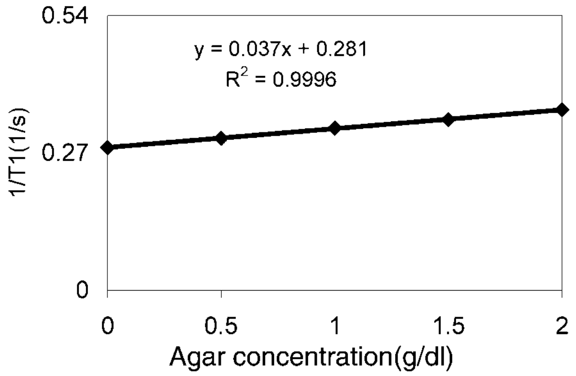

Figure 1. Dependence of the $1/T_1$ on agar concentration.

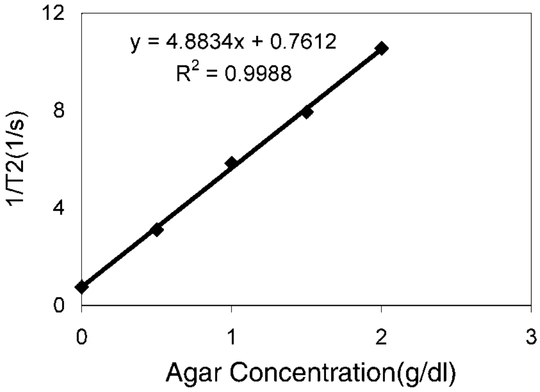

Figure 2. Dependence of the $1/T_2$ on agar concentration.

since $1/T_{if} \ll 1/T_{ib}$,[20] Eq. (3) reduces to Eq. (4)

$$\frac{1}{T_i} = \frac{1}{T_{if}} + \frac{P_b}{T_{ib}} \tag{4}$$

Equation (4) can be derived in a different way; since $P_b \ll P_f$ in agar solution,[17,19] P_f can be nearly taken as 1 and then Eq. (2) becomes identical to Eq. (4). On the other hand, the fraction of bound water is proportional to the protein content. Therefore P_b can be written as $P_b = LC$, where L is proportionality constant. Then, Eq. (4) can be written as

$$\frac{1}{T_i} = \frac{1}{T_{if}} + \frac{L}{T_{ib}}C \tag{5}$$

if we define L/T_{ib} as K_i, Eq. (5) becomes as

$$\frac{1}{T_1} = \frac{1}{T_{1f}} + K_1 C \quad \text{and} \quad \frac{1}{T_2} = \frac{1}{T_{2f}} + K_2 C \tag{6}$$

Equation (6) is identical to the relations in Eq. (1), and the K_1 and K_2 correspond to the slopes in Eq. (1). Equation (6) can be arranged as

$$\frac{1}{T_1} - \frac{1}{T_{1f}} = \frac{L}{T_{1b}}C = K_1 C \quad \text{and} \quad \frac{1}{T_2} - \frac{1}{T_{2f}} = \frac{L}{T_{2b}}C = K_2 C$$

then

$$\frac{1/T_{2\mathrm{b}}}{1/T_{1\mathrm{b}}} = \frac{1/T_2 - 1/T_{2\mathrm{f}}}{1/T_1 - 1/T_{1\mathrm{f}}} = \frac{K_2}{K_1} \tag{7}$$

since K_2/K_1 is measurable, thus $T_{2\mathrm{b}}/T_{1\mathrm{b}}$ can be determined.

The relaxation rates of bound water in agar solutions are known to be caused by dipole–dipole interaction of protons and obey Solomon–Bloembergen equations for paired interaction.[17,19] The Solomon–Bloembergen equations can be written as

$$\frac{1}{T_{1\mathrm{b}}} = K\left(\frac{\tau}{1+\omega^2\tau^2} + \frac{4\tau}{1+\omega^2\tau^2}\right) \quad \text{and} \quad \frac{1}{T_{2\mathrm{b}}} = K\left(1.5\tau + \frac{2.5\tau}{1+\omega^2\tau^2} + \frac{\tau}{1+4\omega\tau^2}\right) \tag{8}$$

where ω is resonance frequency and τ is a correlation time, which describes the movement in the space of the dipole–dipole internuclear vector as the water–agar complex tumbling in the solution. The derivation of Eq. (8) is based on use of the same effective τ for both $1/T_1$ and $1/T_2$. This is reasonable since the perpendicular components of a fluctuating field caused by molecular motion lead to the relaxation. Assuming a single τ value and inserting Eq. (8) into Eq. (7) produces

$$\begin{aligned} \frac{T_{2\mathrm{b}}}{T_{1\mathrm{b}}} &= \frac{1.5\tau + \dfrac{2.5\tau}{1+\omega^2\tau^2} + \dfrac{\tau}{1+4\omega^2\tau^2}}{\dfrac{\tau}{1+\omega^2\tau^2} + \dfrac{4\tau_c}{1+\omega^2\tau^2}} = \frac{K_1}{K_2} = \frac{0.037}{4.883} \\ &= 7.577 \times 10^{-3} \end{aligned} \tag{9}$$

where ω is $2\pi\ \nu$ and ν is 60 MHz. Solving Eq. (9) yields nearly a value of 0.4×10^{-8} sec for effective τ.

It is known from literature that the presence of a single τ or multiple τ was assumed in calculation of correlation times in agar solutions.[2,17,19,21] A τ value of 3×10^{-8} sec was found when a single τ was assumed.[21] Also, a τ value of 0.6×10^{-8} or $1–2.10^{-8}$ sec was calculated if the distribution of correlation times is disregarded.[17,19] In addition, two distinct correlation times, corresponding to slow and relatively rapid motions, were noted in the studies assuming multiple τ.[17,19] The present effective τ (0.4×10^{-8} sec) is consistent with the τ related to relatively rapid motions (1.3×10^{-8} sec). This implies that the present τ may correspond to the τ value of relatively mobile protons in agar/water system, rather than firmly bound water. In fact, in the presence of two τ, the correlation function may be written as

$$\begin{aligned}\langle R_{ij}(t)R_{ij}(t+\tau)S_{ij}(t)S_{ij}(t)S_{ij}(t+\tau)\rangle &= R^2 \mathrm{e}^{-t/t_R} S^2 \mathrm{e}^{-t/\tau_S} \\ &= C\mathrm{e}^{-((1/\tau_R)+(1/\tau_S))\tau} = C\mathrm{e}^{-(\tau/\tau_{\mathrm{eff}})}\end{aligned} \tag{10}$$

where R and S denote rapid and slow motions, respectively. The effective τ, defined in Eq. (10), can be written as follows

$$\frac{1}{\tau_{\mathrm{eff}}} = \frac{1}{\tau_R} + \frac{1}{\tau_S}$$

In the studies assuming double τ, τ related to rapid motions (τ_R) is in order of 10^{-8} sec, whereas τ related to slow motions (τ_S) is of the order of 10^{-6} sec. That is, $\tau_S \gg \tau_R$ and $1/\tau_S \ll 1/\tau_R$. It implies that $1/\tau_{\mathrm{eff}} \approx 1/\tau_R$. Then $\tau_{\mathrm{eff}} \approx \tau_R$.

In conclusion, the relationships between the observed relaxation rates and agar concentrations correspond to the formulas representing fast chemical exchange of water protons between free and bound states. The present results suggest that T_{2b}/T_{1b} is equal to K_2/K_1, and the effective τ can be calculated from the equality of these ratios.

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