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Effect of the Transition Metal Elements on the Relaxation Times in the Agar Solutions

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In this study, the relaxation times of T_1 spin-lattice and T_2 spin-spin are measured by adding the ions such as Mn^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+} and Cu^{2+} in various concentrations to the different concentration of agar solution. The measurement are carried out by using a FT-NMR spectrometer working at the proton resonance 60 MHz at the room temperature. T_1-measurement is realized by the technique of the Inversion Recovery (IR) and the T_2-measurement by that of the Spin-Echo (SE). It is found that the variation of the $1/T_1$ and $1/T_2$ with respect to the ion concentration is linear for each agar concentration. Furthermore, the effect of the each ion in favour of the contribution to the relaxation is evaluated depending on ε, the relaxation-enhancement parameter of the proton added to a solution.

Key Words: NMR, Agar, T_1, T_2, Transition metals, Relaxivity.

INTRODUCTION

It is well known the MR-technique have been used in the examination of the biological liquids and in the diagnosis of the diseases[1]. The quality of the MR-image used for the diagnosis depends on the T_1 and T_2-ratio in addition to the other factors[2]. On the other hand, the states of the water in the agar solutions exhibit a parallelism to the states of the tissue-water. For this reason, the agar solutions are recommended as an important test material for the calibration of the quality of MR-image[3,4]. Although the tissue T_1 is shorter than the agar-T_1 and the relaxation ratios in the tissues exhibit a broad distribution, the agar can be made a perfect tissue-equivalent material by bringing the agar-tissue parallelism to a better situation[5,6]. But, the number of the paramagnetic ions examined for this purpose is limited and does not include all the transition elements[7]. Hence, the effect of the other transition elements on the agar-T_1 and T_2 is assumed to be interesting[8,9].

In this study, the T_1 and T_2 relaxation times are measured by adding the ions such as Mn^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+} and Cu^{2+} in various concentrations to the agar solution having 0.5 % concentration. Furthermore, the experiments are repeated for the agar solutions of 1, 1.5 and 2 % and the effect of the each ion in favour of the contribution to the relaxation are explained *via* the proton relaxivity (enhancement in relaxation ratio per unit concentration).

EXPERIMENTAL

The agar used in this study is a difco-bacto agar in the shape of fine gramiler and made by Difco Laboratory (Michigan, U.S.A).

Preparation of the stock solutions: The stock solutions of the various paramagnetic ions such as Mn^{2+}, Cr^{3+}, Fe^{3+}, Cu^{2+} and Ni^{2+} are obtained by solving the manganese chloride ($MnCl_2·4H_2O$), chromium chloride ($CrCl_3·6H_2O$), ferric nitrate ($Fe(NO_3)_3·3H_2O$), copper sulfate ($CuSO_4·5H_2O$) and nickel chloride ($NiCl_2·6H_2O$) prepared in a proper way into the distilled water kept in a volumetric flask of 250 mL separately.

Preparation of the agar solutions containing paramagnetic ion: The agar solutions containing paramagnetic ion are obtained by adding the ions extracted in a proper way from the stock solutions by using the automatic pipettes to the agar solutions prepared as the weight per cent (in the limits of 0.5, 1, 1.5 and 2 %). These solutions are then boiled for 5 to 10 min at 100ºC on a heater having a magnetic stirer in such a way that an agar sole is obtained. During this process, in order to prevent the changing of the concentration by the vaporisation, system with a back-cooling is used. Then, the sole obtained in this way is transferred into NMR tubes heated before, which have a diameter of 10 mm and after a reasonable time the sole become a rigid-shaped gel.

T_1 and T_2 measurements: The T_1 and T_2 measurements are accomplished at the room temperature by using a FT-NMR spectrometer working at the proton resonance of 60 MHz. The T_1 measurements are accompolished by the Inversion Recovery(IR) technique and the T_2 measurements are accompolished according to the Spin-Echo (SE) technique. In the inversion recovery, the pulse interval is between 0.05 and 10 s. The duration of the pulse repeating is taken to be 20 s. In the SE technique, the echo-times are varied from 20 to 160 ms in the laps of 20 ms.

Determination of the relaxivity: In order to understand the effect of the ions in favour of the contribition to the relaxation, the ions such as Mn^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+} and Cu^{2+} in various concentration are added to the agar solutions in various concentrations. Then, $1/T_1$-ratios measured are plotted *vs.* the concentration. The values of the relaxivity are found from the slope of this curve. This slope is corresponding to the following equation:

$$R = (1/T_{1b} - 1/T_{1a})/C \qquad (1)$$

where, $1/T_{1b}$ and $1/T_{1a}$ are the relaxation ratios before and after the addition of the ion, respectively. C is the ion concentration and R is the proton relaxivity of the ion into the agar solutions.

RESULTS AND DISCUSSION

In the solutions prepared in the various agar concentrations the variation of $1/T_1$ and $1/T_2$ with respect to the added ion concentrations for Mn^{2+} are shown in Figs. 1 and 2, respectively. In order to prevent the repetition the T_1 and T_2 data are not given. It can be seen from these figures the variation of $1/T_1$ and $1/T_2$ with respect to the ion concentration is linear. This result is valid for the other ions and is consistent with the previous findings[10].

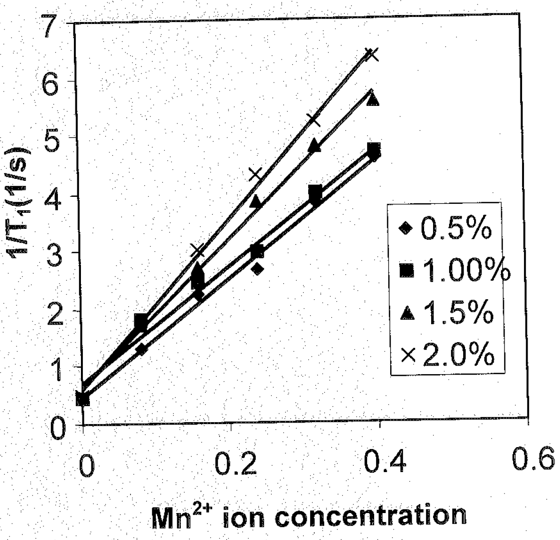

Fig. 1. Behaviour of Mn^{2+} ions against $1/T_1$ in different agar concentration

The values of the relaxivity obtained from the slopes of the curves showing the relaxation ratios *vs.* the ion concentrations are given in Table-1. Therefore the T_1 and T_2 relaxivity of Mn^{2+} into the agar is greater than that into water, the relaxivities for the other ions into the agar are getting smaller. These findings are in agreement with those obtained before[11,12].

On the other hand, the enhanced relaxation added to a solution is defined as

$$\varepsilon = [1/T_{1a+ion} - 1/T_{1a}]/[1/T_{1w+ion} - 1/T_{1w}] \quad (2)$$

If the numerator and the denominator of this relation is divided by the concentration C, one has

$$\varepsilon = [1/T_{1a+ion} - 1/T_{1a}]C^{-1}/[1/T_{1w+ion} - 1/T_{1w}]C^{-1} = R_{agar}/R_{water} \quad (3)$$

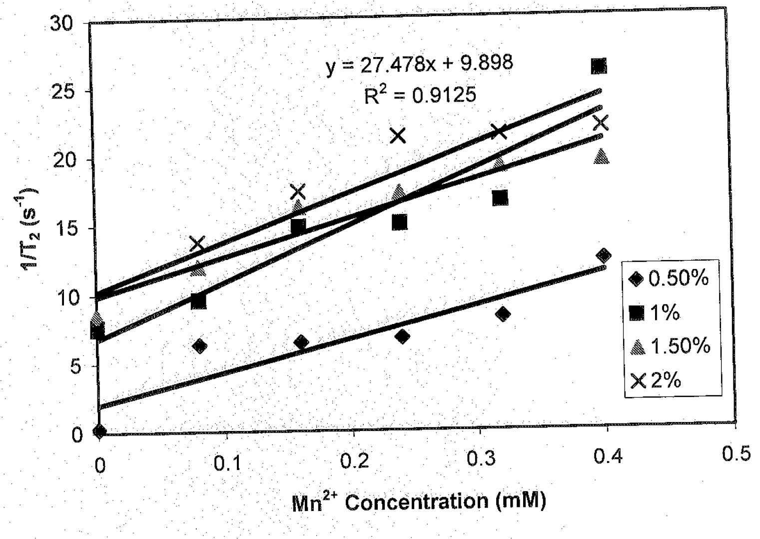

Fig. 2. Behaviour of Mn^{2+} ions against $1/T_2$ in different agar concentration

TABLE-1

VALUES OF THE RELAXAVITY OF THE IONS SUCH AS Mn^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+} AND Cu^{2+} IN THE INCREASED AGAR CONCENTRATIONS

Ion	Relaxivity-T_1 (%)					Relaxivity-T_2 (%)				
	0	0.5	1.0	1.5	2.0	0	0.5	1.0	1.5	2.0
Mn^{2+}	7.10	10.30	11.45	12.83	14.59	41.60	47.3	50.0	53.4	60.1
Fe^{3+}	0.64	0.60	0.84	0.90	0.77	2.63	0.98	1.08	0.99	1.0
Cr^{3+}	4.80	1.074	0.95	1.010	1.065	10.01	2.45	2.08	1.62	1.0
Ni^{2+}	0.01	0.206	0.196	0.173	0.232	0.74	0.52	0.38	0.52	0.38
Cu^{2+}	0.65	0.718	0.646	0.696	0.692	0.98	1.06	0.95	1.05	0.77

where, R_{agar} and R_{water} in the proton relaxivity of Mn^{2+} into agar and water, respectively. The $\varepsilon > 1$ case shows that Mn^{2+} is bounded to an external region of the agar and the $\varepsilon < 1$ case shows that the other ions are bounded to a region, in which water cannot diffuse into the agar[13]. In fact, the relaxivities of Mn^{2+} shows a dependance on the concentration. These relaxivities increase with the increasing concentration (Figs. 1 and 2). This points out an intense bonding. The relaxivity does not exhibit any dependance on the concentration for the other ions. Accordingly, this situation does not mean that these ions are not bounded to the agar. If this is the case then ε = 1 should be obtained[14,15].

It is concluded that Mn^{2+} gives a dominant relaxivity relative to the other ones and that the neighbourhood of the ion (Fig. 3). Mn^{2+} is effected by the agar and hence, Mn^{2+} is bounded to the agar to a considerable extent.

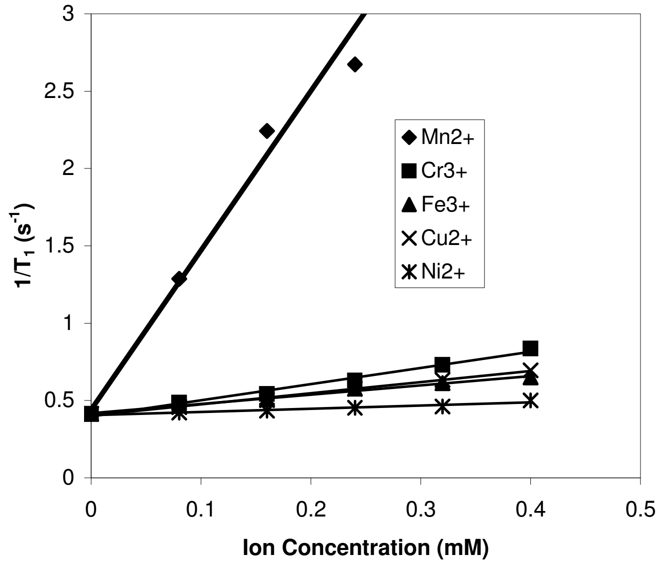

Fig. 3. Behaviour of different metal ions against $1/T_1$

The charge density of metal ions are changed by the interaction beetwen metal cation and oxygen atoms in the agar. As the charge of metal ions are increased the interaction beetwen agar and metal ions also increased. In this case the splitting in the *d*-orbitals of metal would be increased, therefore the relaxation time will be shorter. Mn^{2+} ions have small splitting due to d^5 system. Therefore, the relaxation time increases. This is due to the electrons passes through the e_g orbitals. The splittings of *d*-orbitals increases for Cr^{3+} and Fe^{3+} ions. Therefore, the high energy electrons return back in the short period of time[16]. So their relaxation times are short. In this two ions the electrons are in the t_{2g} orbitals level. In the case of Cu^{2+} and Ni^{2+} the electrons are in the e_g orbitals. However, due to Jahn-Teller effect, the energy of this orbitals are changed. Therefore, interaction with agar become stronger. In this case, the relaxation times for this two ions aret shorter, due to high energy state (Fig. 4).

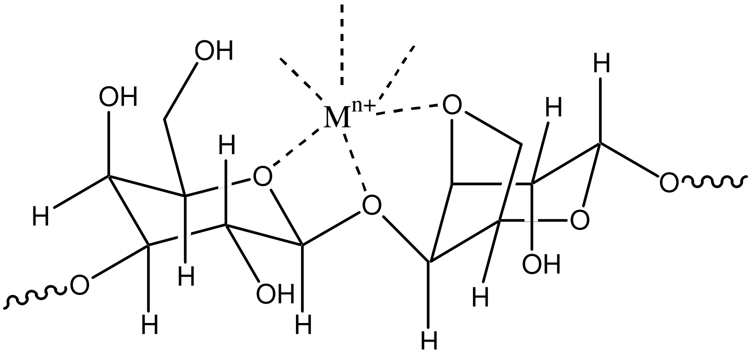

Fig. 4. Possible interactions between metal ions and oxygen atoms in agar

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