

## $^1\text{H}$ NMR Relaxation Studies in Ethanediol-Water with Paramagnetic Ion

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The proton magnetic resonance spin lattice relaxation time ( $T_1$ ) were measured in various volume proportions on ethanediol-water system at different temperatures. The values of relaxation time ( $T_1$ ) increase with increasing the temperature. The relaxation time was also measured in these solutions containing paramagnetic ion (PMI) such as copper nitrate. The results indicate that  $T_1$  decreased with increasing the copper nitrate.

**Key Words:** Relaxation studies, Ethanediol, Paramagnetic ion, Copper nitrate.

### INTRODUCTION

The presence of paramagnetic substances in a liquid reduces the relaxation times ( $T_1$ ) nuclei of the solvent. This effect was first demonstrated by Bloch, Hansen and Packard<sup>1</sup> for protons in aqueous solutions of  $\text{Fe}^{3+}$  ions. This effect was further studied by Bloembergen *et al.*<sup>2</sup> in aqueous solutions of paramagnetic ions such as  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ . An important mechanism towards decrease of ( $T_1$ ) is the modulation of nuclear magnetic dipolar interaction resulting from both the rotational as well as translational motion of different molecules. Bloembergen *et al.*<sup>2</sup> attributed the reduction in the values of relaxation times to the diffusional Brownian motion of the water molecules in the vicinity of paramagnetic ions. According to Bernheim *et al.*<sup>3</sup> the primary contribution towards the reduction of relaxation times ( $T_1$ ) in the presence of paramagnetic ions comes from rotational terms. The decrease in the value of relaxation times can also be interpreted in terms of some models. The ions are surrounded by a coordination sphere of solvent molecules. The nuclei in this salvation shell interact strongly with the unpaired electrons of the ion, the interaction having both magnetic dipole-dipole and hyperfine terms. For most iron-group ions dissolved in water, a rapid exchange of water molecules between free solvent hydration shell takes place and only a single proton resonance line is observed, which is the result of an averaging of the resonance of the free and bound molecules.

Several workers have reported the effect of paramagnetic ions on proton relaxation times<sup>4-6</sup>. Gutowsky<sup>7</sup> and Ravikind<sup>8</sup> were the first to study the effect of free radicals on NMR relaxation times in certain non-viscous solvents. Modak *et al.*<sup>9</sup> carried out NMR relaxation time ( $T_1$ ) measurements in glycerine-water mixtures by continuous wave technique by measuring the NMR signal heights. In their study, free radicals and paramagnetic ions were added to three different (glycerine rich) glycerine-water compositions. The results reveal that the free radicals increase the viscosity of these systems whereas there is no appreciable change in viscosity on the addition of paramagnetic ions (copper nitrate). Also the proton signal heights in these solutions showed an initial increase and a small decrease at higher concentration and also indicate that at a given concentration pair formation is more probable for free radicals than for paramagnetic ions. The initial increase in the signal height is attributed to the complex formation of the paramagnetic ions with water, glycerine and associated glycerine-water molecules.

In the present study, ethanediol can be chosen as a less viscous system since ethanediol mixes freely in all proportions with water. Hence, it is considered worthwhile to study the relaxation measurements in these mixtures with and without paramagnetic ions. The paramagnetic ion is likely to be more mobile in these mixtures and this should reveal some interesting information on the nature of molecular interactions.

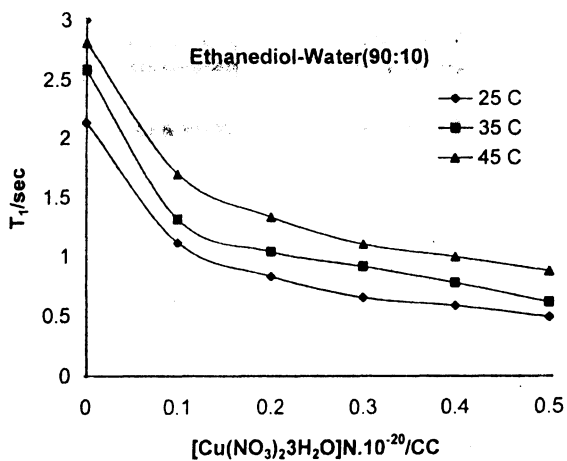
## EXPERIMENTAL

In the present study, the proton magnetic resonance (PMR) relaxation time was measured in the solutions of ethanediol-water mixtures of volume proportions 90% ethanediol and 10% water (solution A), 80% ethanediol and 20% water (solution B), 70% ethanediol and 30% water (solution C) and 60% ethanediol and 40% water (solution D). Solution (1.0 M) of copper nitrate prepared by dissolving it in double distilled water. The solutions were added in different amounts to ethanediol and the proportion of ethanediol to water brought to the desired value by further addition of the required amount of water. The concentration was expressed as the number of particles/cc and the range was 0.1 – 0.1 ions/cc. The paramagnetic ion used was copper nitrate.

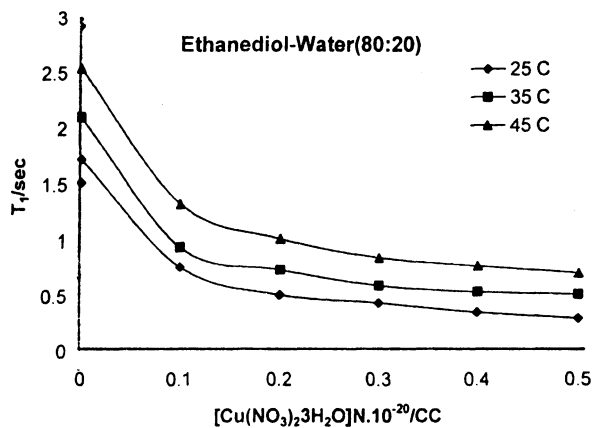
The spin-lattice relaxation times ( $T_1$ ) in these solutions in the above concentrations were measured at different temperatures of 30°, 25°, 135° and 45°C using Shimadzu-90 MHz NMR. Saturation recovery technique was used for the measurement of  $T_1$ . Temperature variation was carried out by circulating water in a thermostatically controlled water bath to an accuracy of  $\pm 1^\circ\text{C}$ . Density measurements were carried out using Ab pyknometer at a temperature of 25°C.

## RESULTS AND DISCUSSION

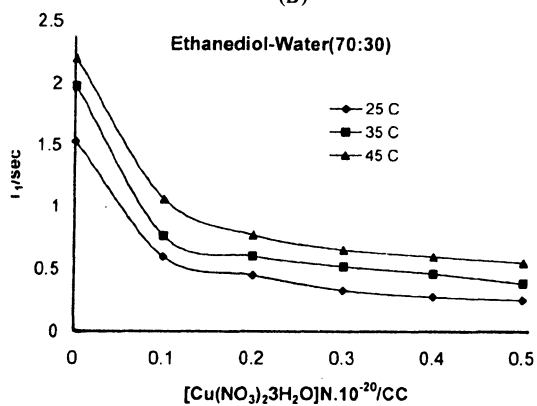
The variation of spin-lattice relaxation time ( $T_1$ ) in ethanediol-water solution (A–D) with paramagnetic ions (PMI) ( $\text{Cu}^{2+}$ ) at different concentrations and temperatures is shown in Fig. 1 (A–D).



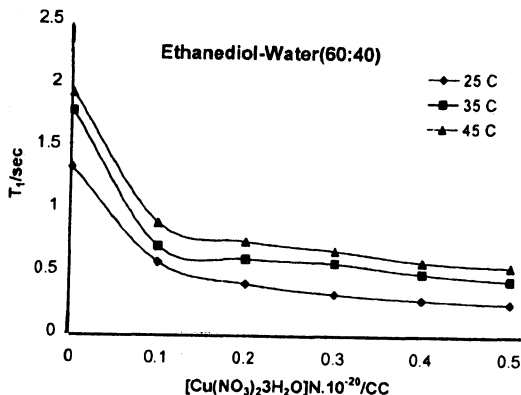
(A)



(B)



(C)



(D)

Fig. 1. Spin-lattice relaxation times as a functional of increasing copper nitrate concentration in the different proportions of ethanediol-water mixtures at different temperatures.

As can be observed from these figures, the relaxation times generally decrease with increase of PMI concentration. The initial decrease in the relaxation times is quite large up to PMI concentration of  $0.1 \times 10^{-20}$  ions/cc from all the solutions studied. Further, increase of PMI concentration decreases the relaxation times gradually. Similar behaviour is also seen for all the solutions at higher temperature. Results obtained are reported in Table-1.

According to Bernhein *et al.*<sup>3</sup>, the longitudinal relaxation time ( $T_1$ ) for profones in the presence of paramagnetic ions is given by

$$\frac{1}{T_1} = \text{constant } N/\mu_{\text{eff}}^2 \tau_c \quad (1)$$

where  $N$  is the concentration of paramagnetic ions,  $\mu_{\text{eff}}^2$  is their effective magnetic moment and  $\tau_c$  is the correlation time for the rotation of the molecules containing protons as well as paramagnetic ions.

$$\tau_c = 4\pi\eta a^3/KT \quad (2)$$

where  $K$  is the Boltzmann's constant,  $T$  is the absolute temperature,  $a$  is the molecular radius of the complex and  $\eta$  is the coefficient of viscosity. Combining Eqs. (1) and (2) at constant temperature, we get

$$\frac{1}{T_1} = \text{constant } N/\mu_{\text{eff}}^2 \eta a^3 \quad (3)$$

From the above equation and reported value in Table-2 and Fig. 2, that  $(1/T_1)$  increases linearly for the solutions of C and D containing  $\text{Cu}^{2+}$  ions, whereas for solutions A and B that  $(1/T_1)$  increases linearly up to PMI concentration of  $0.1 \times 10^{-20}$  ions/cc and for higher PMI concentration there is deviation from linearity. The linear increase of  $(1/T_1)$  observed with increase of PMI concentration indicates that the molecular radius  $a$  does not change appreciably in these solutions, thereby indicating that the complex formation in these solutions is rather weak.

TABLE-1  
RELAXATION TIME ( $T_1$ ) ON ETHANEDIOL-WATER SYSTEM IN THE PRESENCE  
OF COPPER NITRATE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Cu <sup>2+</sup> [Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O] (N × 10 <sup>-2</sup> /cc)	T <sub>1</sub>		
	25°	35°	45°
(A) Ethanediol-H <sub>2</sub> O (90 : 10)			
0.0	2.139	2.586	2.818
0.1	1.123	1.321	1.701
0.2	0.834	1.044	1.340
0.3	0.657	0.921	1.110
0.4	0.587	0.778	1.000
0.5	0.487	0.611	0.876
(B) Ethanediol-H <sub>2</sub> O (80 : 20)			
0.0	1.738	2.114	2.555
0.1	0.781	0.960	1.345
0.2	0.525	0.753	1.034
0.3	0.453	0.611	0.876
0.4	0.367	0.554	0.789
0.5	0.311	0.529	0.724
(C) Ethanediol-H <sub>2</sub> O (70 : 30)			
0.0	1.531	1.982	2.206
0.1	0.602	0.768	1.065
0.2	0.453	0.606	0.777
0.3	0.330	0.523	0.658
0.4	0.281	0.467	0.607
0.5	0.254	0.387	0.555
(D) Ethanediol-H <sub>2</sub> O (60 : 40)			
0.0	1.314	1.765	1.913
0.1	0.562	0.689	0.876
0.2	0.390	0.588	0.728
0.3	0.309	0.555	0.655
0.4	0.263	0.457	0.567
0.5	0.239	0.421	0.532

TABLE-2  
 VARIATION OF  $1/T_1$  vs. VARIOUS CONCENTRATION OF COPPER NITRATE ON SOLUTIONS (A-D) AT 25°C

$\text{Cu}^{2+}$ [ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ] ( $\text{N} \times 10^{-2}/\text{cc}$ )	$1/T_1$ ( $\text{s}^{-1}$ )			
	A	B	C	D
0.0	0.467	0.575	0.653	0.877
0.1	0.892	1.279	1.661	1.778
0.2	1.199	1.904	2.207	2.561
0.3	1.520	2.207	3.023	3.235
0.4	1.703	2.724	3.555	3.721
0.5	2.053	3.215	3.937	4.179

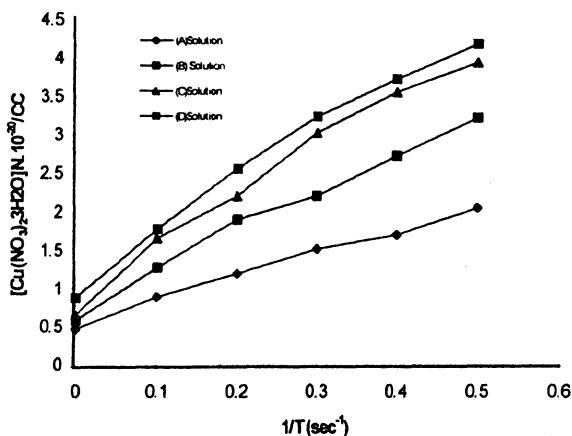


Fig. 2. Variation of spin-lattice rate vs. copper paramagnetic ion at 25°C.

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