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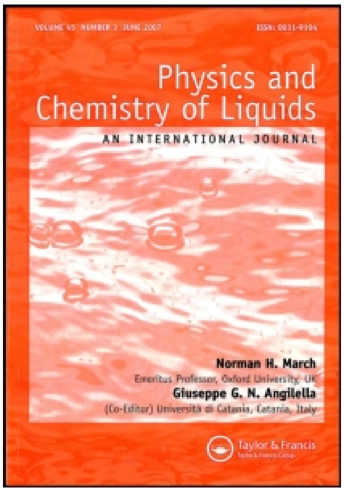

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^{1}H NMR RELAXATION STUDIES ON GLYCERINE-WATER AND DIOXAN-WATER WITH PARAMAGNETIC IONS

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The Proton magnetic Resonance (PMR) spin-lattice and spin-spin relaxation times (T_1 and T_2) were measured in highly viscous (glycerine-water) and less viscous (dioxan-water) systems at different temperatures. The values of relaxation times increase with increasing the temperature. This result is interpreted as due to the combined effect of viscosity and temperature in these solutions. The relaxation times were also measured in these solutions containing paramagnetic ions (PMI). The results indicate that the possibility of an anti-parallel bonding of the paramagnetic ions is higher in highly viscous solutions as compared to low viscous systems and the association in the above mixtures appears to be weak.

Keywords: NMR; paramagnetic ions; molecular association and viscosity

INTRODUCTION

The presence of paramagnetic substances in a liquid reduces the relaxation times (T_1) and (T_2) of nuclei of the solvent. This effect was first demonstrated by Bloch, Hansen and Packard [1] for protons in aqueous solutions of Fe^{3+} ions. This effect was further studied by Bloembergen, Purcell and Pound [2] in aqueous solutions of

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paramagnetic ions such as Cu^{++} and Fe^{+++}. 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 the different molecules. Bloembergen *et al.* [2] attributed the reduction in the values of relaxation times is due to diffusional Brownian motion of the water molecules in the vicinity of paramagnetic ions. According to Bernheim *et al.* [3] 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 spheres 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 [4–6]. Gutowsky and Ravikind [7, 8] were the first to study the effect of free radicals on NMR relaxation times in certain non-viscous solvents. Modak *et al.* [9] 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. Since the relaxation times in the above study are not absolute measurements, it is considered worthwhile to repeat the measurements in highly viscous

(Glycerine – water) and less viscous (Dioxan – water) using more sophisticated low resolution pulsed NMR spectrometer.

In the present study, Dioxan can be chosen as a less viscous system since Dioxan mixes freely in all proportions with water, has almost identical density and many studies of physical properties of the mixtures were already carried out [12, 13]. Further infrared and NMR studies [14 – 16] indicate that molecules of water and dioxan interact strongly. Hence it is considered worthwhile to study the relaxation measurements in these mixtures with and without paramagnetic ions. The paramagnetic ions are likely to be more mobile in these mixtures (as compared to glycerine – water mixtures) and this should reveal some interesting information on the nature of molecular interactions.

MATERIALS AND METHODS

In the present study, the PMR relaxation times were measured in the solutions of glycerine – water mixtures of volume proportions 90% glycerine and 10% water (solution A), 80% glycerine and 20% water (solution B), 70% glycerine and 30% water (solution C) and 60% glycerine and 40% water (solution D). Solution (1.0 M) of copper and chromium nitrates are formed by dissolving it in double distilled water. The solutions were added in different amounts to glycerine and the proportion of glycerine to water is brought to the desired value by further addition of the required amount of water. The concentration is expressed as number of particles/cc and the range is from 0.1×10^{-20} ions/cc to 0.5×10^{-20} ions/cc.

Dioxan – water mixtures were prepared in volume ratio 9 : 1 (solution D), 8 : 2 (solution E), 7 : 3 (solution F). The paramagnetic ions used are copper nitrate and chromium nitrate. In these paramagnetic ions, copper ions are weakly paramagnetic whereas chromium ions are strongly paramagnetic. One molar solutions of copper nitrate, chromium nitrate were prepared by dissolving in different amounts to dioxan and desired concentration value is obtained by further addition of the required amount to water. The concentration is expressed as number of ions per m^3 and the range is from 0.1×10^{-20} ions/cc to 0.5×10^{-20} ions/cc.

The spin-lattice and spin–spin relaxation times (T_1 and T_2) in these solutions in the above concentrations were measured at different temperatures of 30°, 40°, 50°, 60°C using Bruker PC 20 NMR process analyzer at a RF frequency of 20 MHz. Saturation recovery technique was used for the measurement of (T_1) and CPMG pulse sequence was carried for the measurement of (T_2). Temperature variation was carried out by circulating water from a thermostatically controlled water bath to an accuracy of ± 1°C. Viscosity and density measurements were carried out using Ostwald's viscometer and Pyknometer at a temperature of 30°C.

RESULT

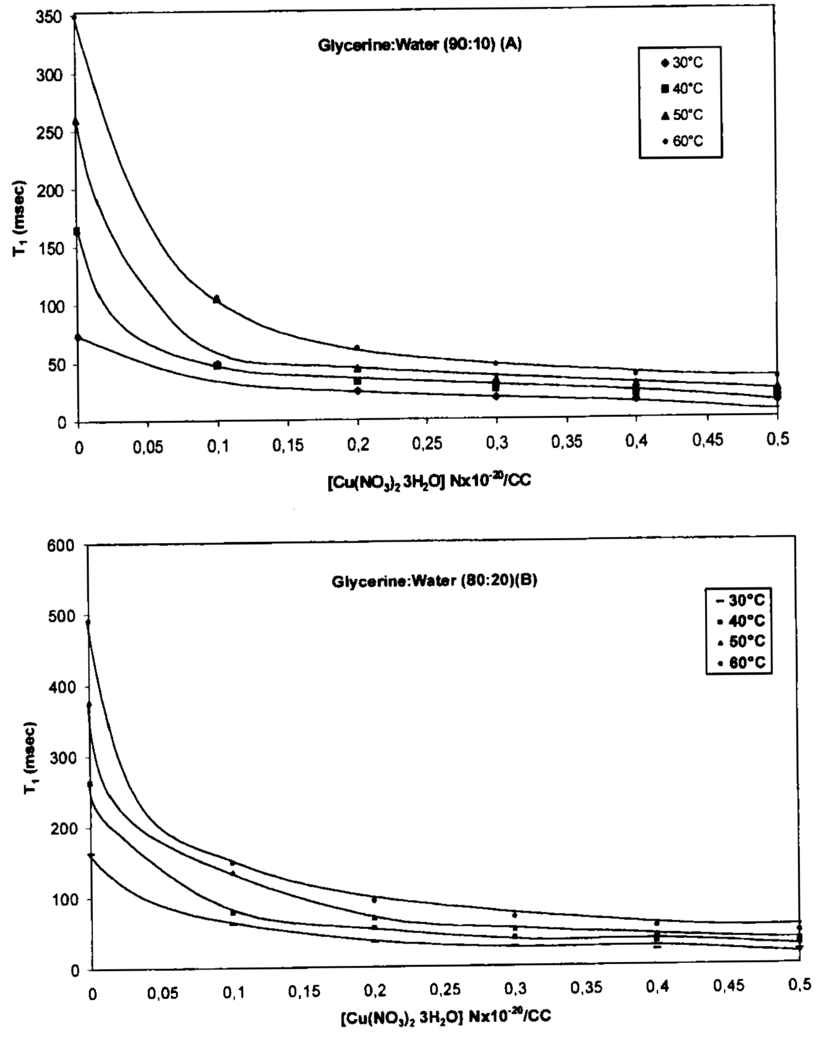
Copper Ions

The variation of spin-lattice relaxation times (T_1) and spin–spin relaxation time (T_2) in glycerine–water solution (A–D) with paramagnetic ions (PMI) (Cu^{++}) at different concentration and different temperatures are shown in Figures 1(A–D) and Figures 2(A–D).

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 0.1×10^{-20} ions/cc for all the solutions studied. Further increase of PMI concentration decreases the relaxation times gradually. Similar behavior is also seen for all the solutions at higher temperature. The influence of viscosity remains fairly constant for all the PMIs studied.

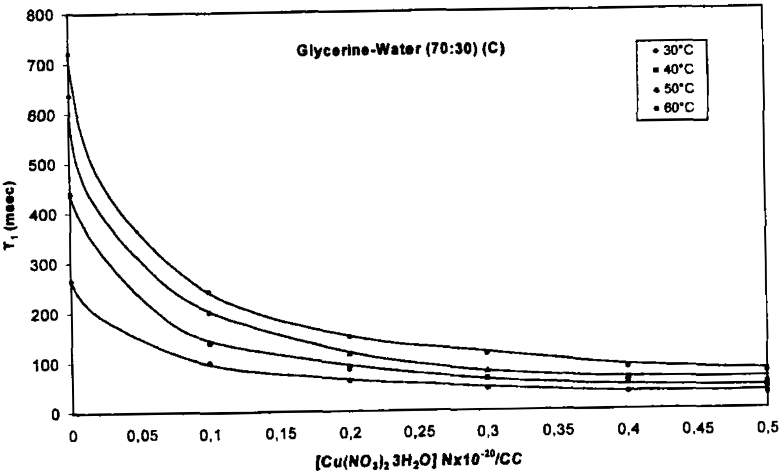
Chromium Ions

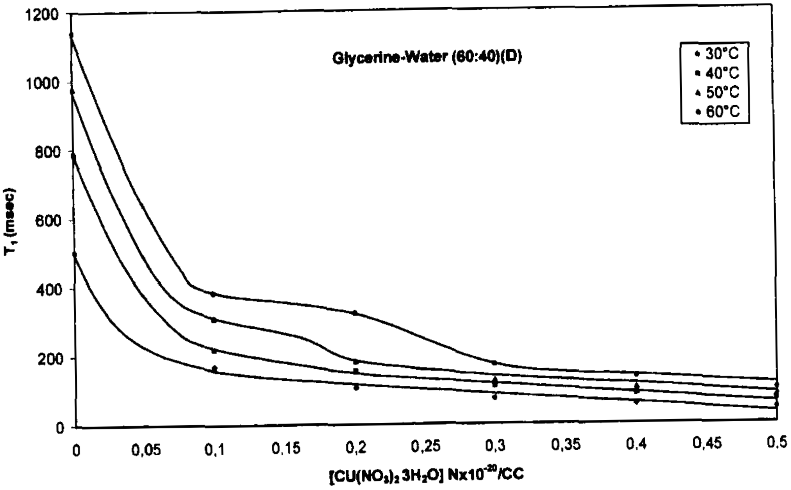
The results of spin-lattice relaxation times (T_1) with different compositions of glycerine–water mixtures with paramagnetic ions (Cr^{++}) and at different temperatures are shown in Figures 3(A–D). The variation of viscosity against different proportions of glycerine–water mixtures with added paramagnetic ions such as copper nitrate and chromium nitrate at a temperature of 30°C are shown in Figures 4, 5. The decay of magnetization was checked for each sample and it is found to be



FIGURES 1(A–D) Spin-lattice relaxation time (T_1) as a function of increasing Copper Nitrate Concentration in the different proportions of glycerine–water mixtures at different temperatures. The relaxation times were measured in these solutions using Bruker PC 120 NMR process analyser as described in the experimental section.

mono-exponential (Fig. 6). The results obtained for Cr^{++} solution is similar to the results obtained for Cu^{++}. The addition of Cr^{++} in glycerine–water mixture does not change the viscosity drastically.

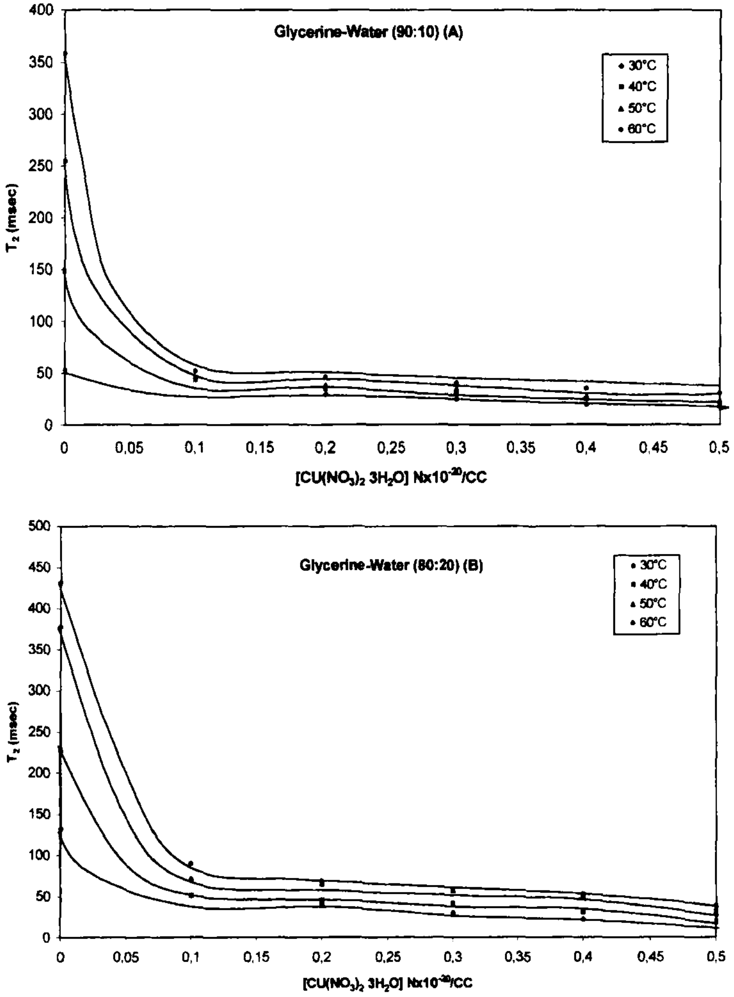




FIGURES 1(A–D) (Continued).

DISCUSSION

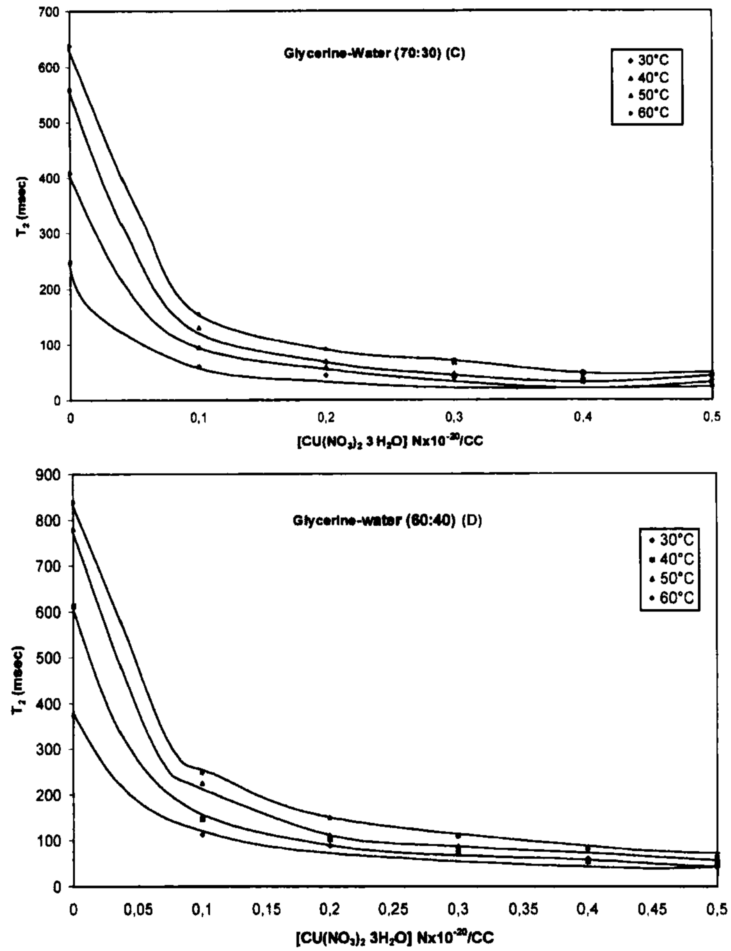
It will be appropriate to discuss the results obtained in glycerine–water mixture without paramagnetic ions first and then assess the influence of paramagnetic ions on highly viscous systems. Since the relaxation times (T_1) and (T_2) are approximately equal in these



FIGURES 2(A – D) Spin – spin relaxation time (T_2) as a function of increasing Copper Nitrate Concentration in the different proportions of glycerine – water mixtures at different temperatures. The relaxation times were measured in these solutions using Bruker PC 120 NMR process analyser as described in the experimental section.

mixtures, it can be concluded that dipole – dipole interaction is a dominant relaxation mechanisms.

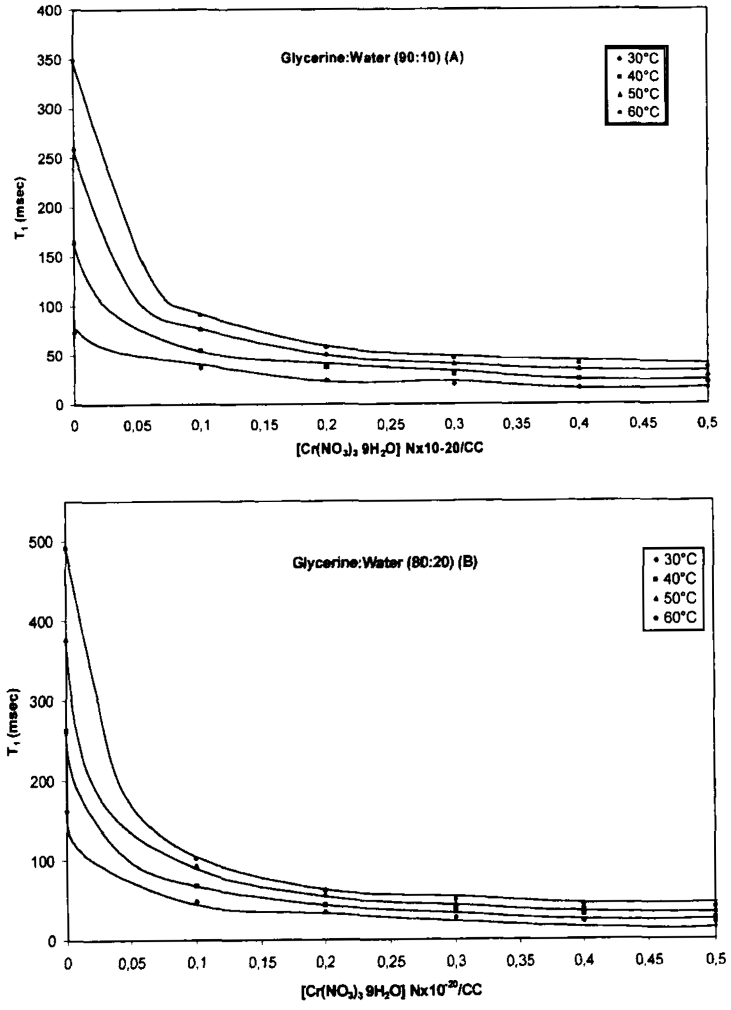
Relaxation times were measured for the volume proportions of glycerine – water solutions, which cover a wide range of viscosity at a temperature of 303°K. From the figures, it can be observed that



FIGURES 2(A–D) (Continued).

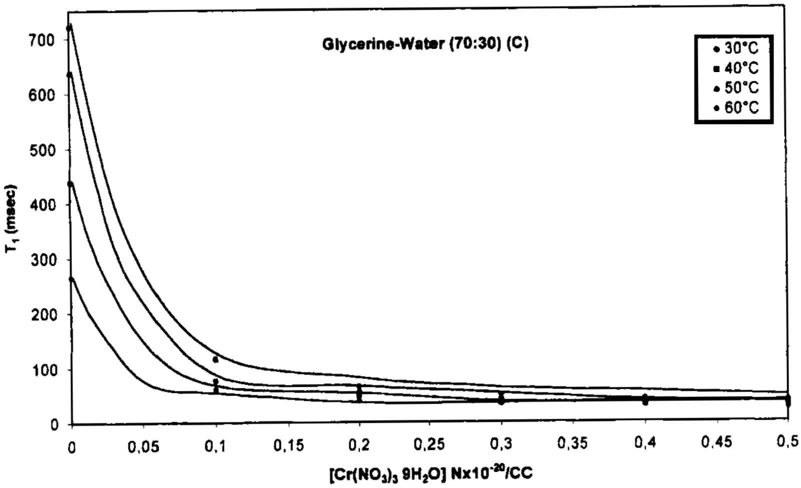
the exact proportionality between ($1/T_1$) and η is not perhaps to be expected, since the progressive change of concentration must bring with it a change in the environment of each protons [10].

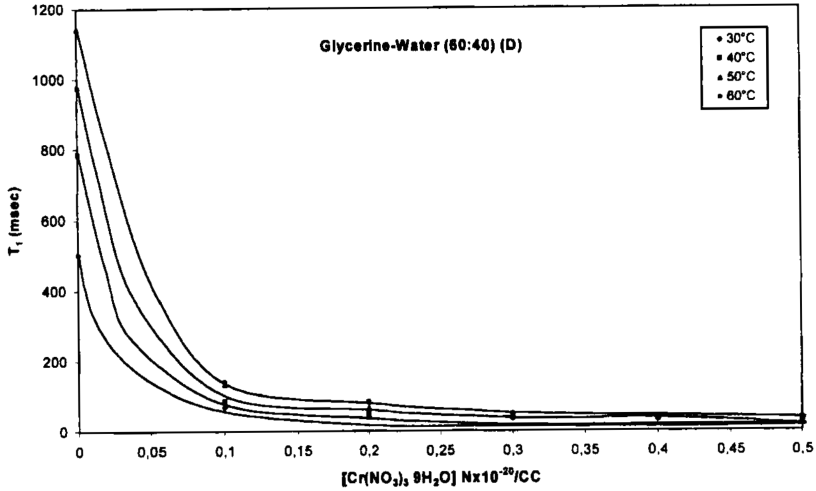
It may also seen from Figure 1 that the relaxation time (T_1) changes from 74–349 msec as the temperature is increased from 30–60°C for solution (A) with zero PMI concentration. This effect may be entirely due to the change in the viscosity (η) as viscosity in glycerol decreases from 612 cp to 81 cp [11] in this temperature range. Since ($1/T_1$) is



FIGURES 3(A–D) Spin-lattice relaxation time (T_1) as a function of increasing Chromium Nitrate Concentration in the different proportions of glycerine–water mixtures at different temperatures.

inversely proportional to η/T [10], it can be inferred that the large change observed in the value of (T_1) with increase of temperature may be due to the combined effect of change in viscosity and temperature. Similar effect is also observed for the variation of (T_2) with temperature in the above solutions.





FIGURES 3(A–D) (Continued).

Glycerine–Water with Paramagnetic Ions

According to Bernheim *et al.* [3], the longitudinal relaxation time (T_1) for protons in the presence of paramagnetic ions is given by

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

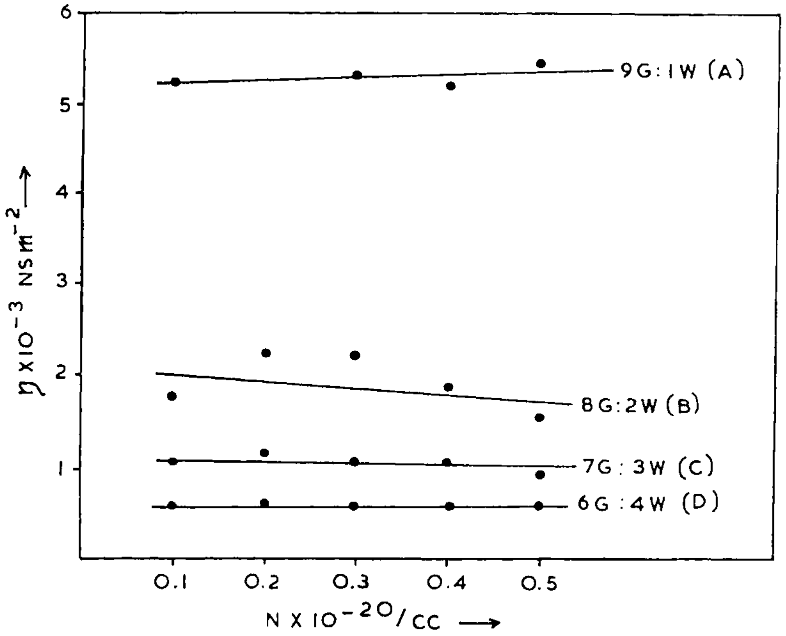


FIGURE 4 Viscosity *versus* concentration of copper nitrate in glycerine–water mixture.

Where 'N' is the concentration of paramagnetic ions, μ_{eff}^2 is their effective magnetic moment and 'τ_c' is the correlation time for the rotation of the molecules containing protons as well as paramagnetic ions

$$\tau_c = 4\pi\eta a^3/\mathrm{K}T \qquad (2)$$

Where 'K' is the Boltzmanns constant, 'T' is the absolute temperature, 'a' is the molecular radius of the complex and 'η' is the co-efficient of viscosity. Combining Eqs. (1) and (2) at constant temperature we get

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

From the above equation and Figures 7, 8, that $(1/T_1)$ increases linearly for the solutions of C and D containing Cu^{++} ions, whereas for solutions A and B that $1/T_1$ increases linearly up to PMI concentration of 0.3×10^{-20} ions/cc and for higher PMI concentration there is deviation from linearity. The linear increase of $(1/T_1)$ observed

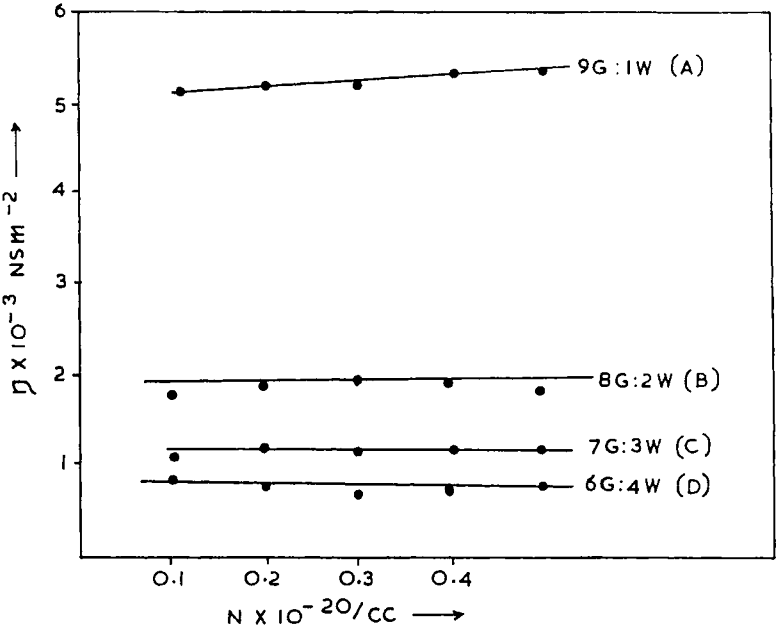


FIGURE 5 Viscosity *versus* concentration of chromium nitrate in glycerine–water mixture.

with increase of PMI concentration indicate that the molecular radius '*a*' does not change appreciably in these solutions thereby indicating that the complex formation in these solution is rather weak. Solutions A (90G + 10W) and B (80G + 20W) are highly viscous systems as compared to C (70G + 30W) and D, the mobility of the ions is restricted and this may increase the probability of anti parallel bonding of the paramagnetic ions. This anti parallel bonding reduces the value of μ_{eff} and $(1/T_1)$ decreases with increase of PMI concentration. The variation of spin–spin relaxation time (T_2) is similar to the variation of (T_1) with increasing PMI concentration and the explanation proposed above may also holdgood for (T_2).

Dioxan – Water Mixture with Paramagnetic Ions

In continuation of the above work, the present investigation is undertaken to understand the influence of addition of paramagnetic

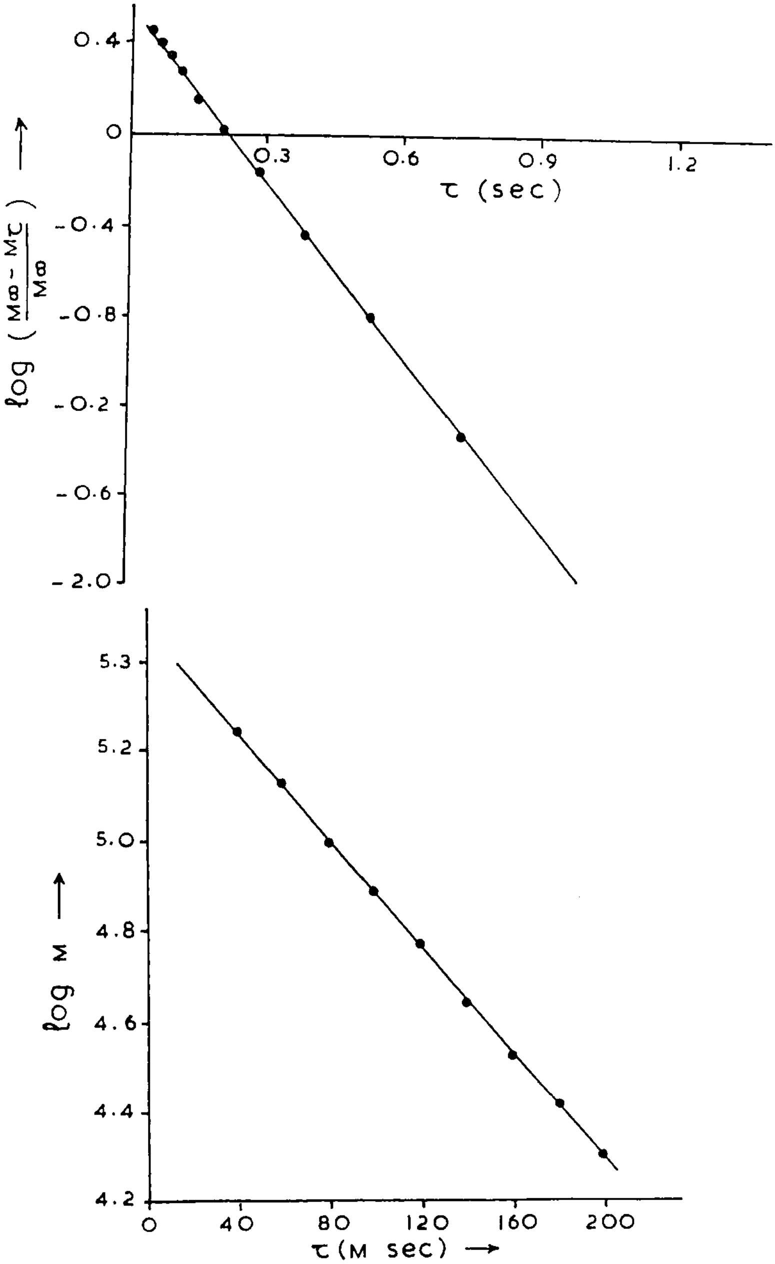


FIGURE 6 Log M *versus* τ of solution D (80% glycerine and 20% water).

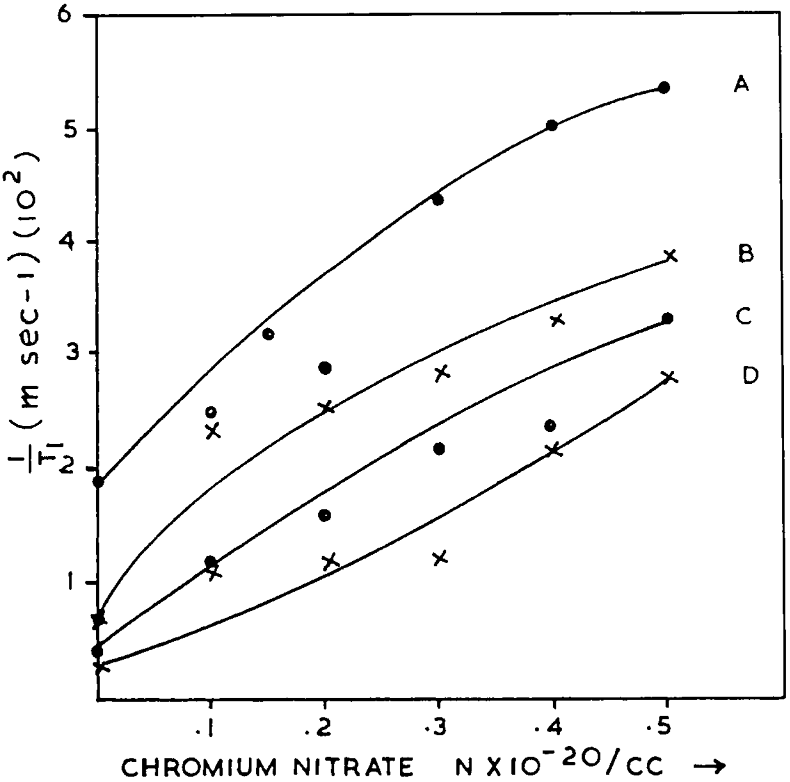


FIGURE 7 $(1/T_1)$ *vs.* ion concentration at several temperatures.

ions in less viscous medium of Dioxan rich, Dioxan–Water mixtures. The variation of spin-lattice relaxation times (T_1) and spin–spin relaxation times (T_2) in dioxan–water solutions with PMI concentrations of copper and chromium nitrates are shown in Figures 9 and 10.

It can be seen from figures that in all the three solutions (without paramagnetic ions) the relaxation times (T_1) and (T_2) is found to decrease with increase of concentration of water. The observed decrease in the relaxation times (T_1) and (T_2) may be attributed due to the strong hydrogen bond formation between dioxan with water molecules. Such strong hydrogen bond formation results in a decrease in the value of (T_1) and (T_2) as it is known that (T_1) decreases with increase in hydrogen bond energy [17].

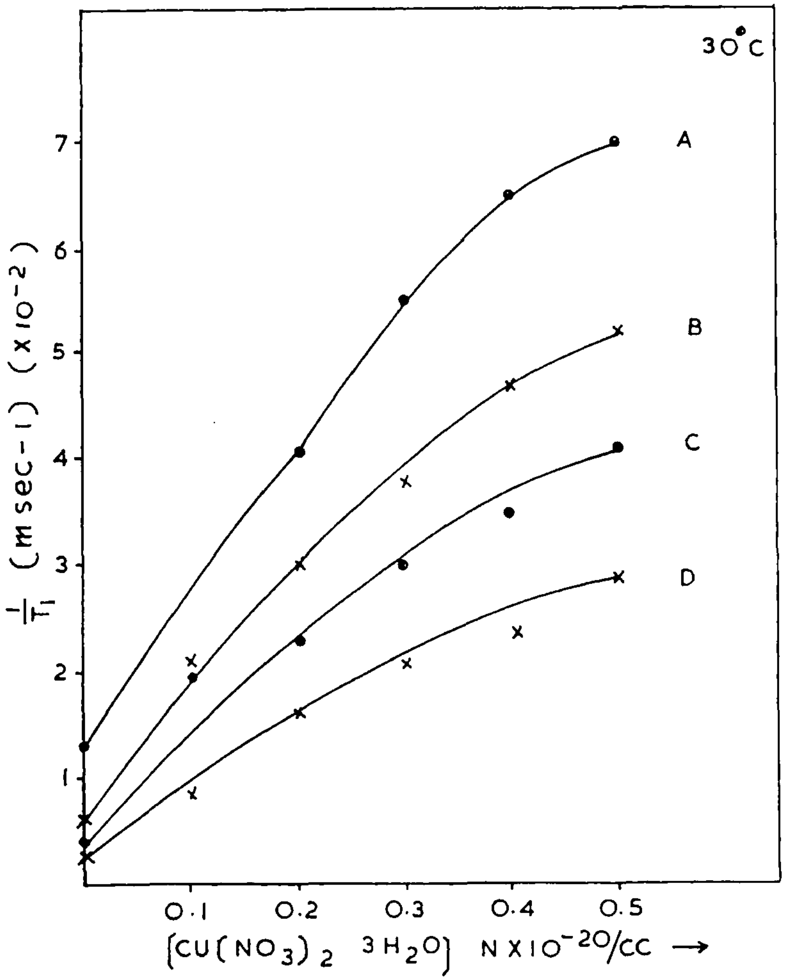


FIGURE 8 Variation of $(1/T_1)$ *versus* ion concentration of copper nitrate.

As discussed earlier, the addition of paramagnetic ions should decrease the relaxation times (Figs. 9, 10). The variations of $(1/T_1)$ against PMI concentrations were shown in Figure 11. From the figure, it can be observed that $(1/T_1)$ increase linearly for both copper and chromium nitrate for all the three solutions. It may be noticed that the plots of $(1/T_1)$ against PMI concentration (N) have a larger slope for Cr^{++} ion as compared to Cu^{++} ion in these solutions.

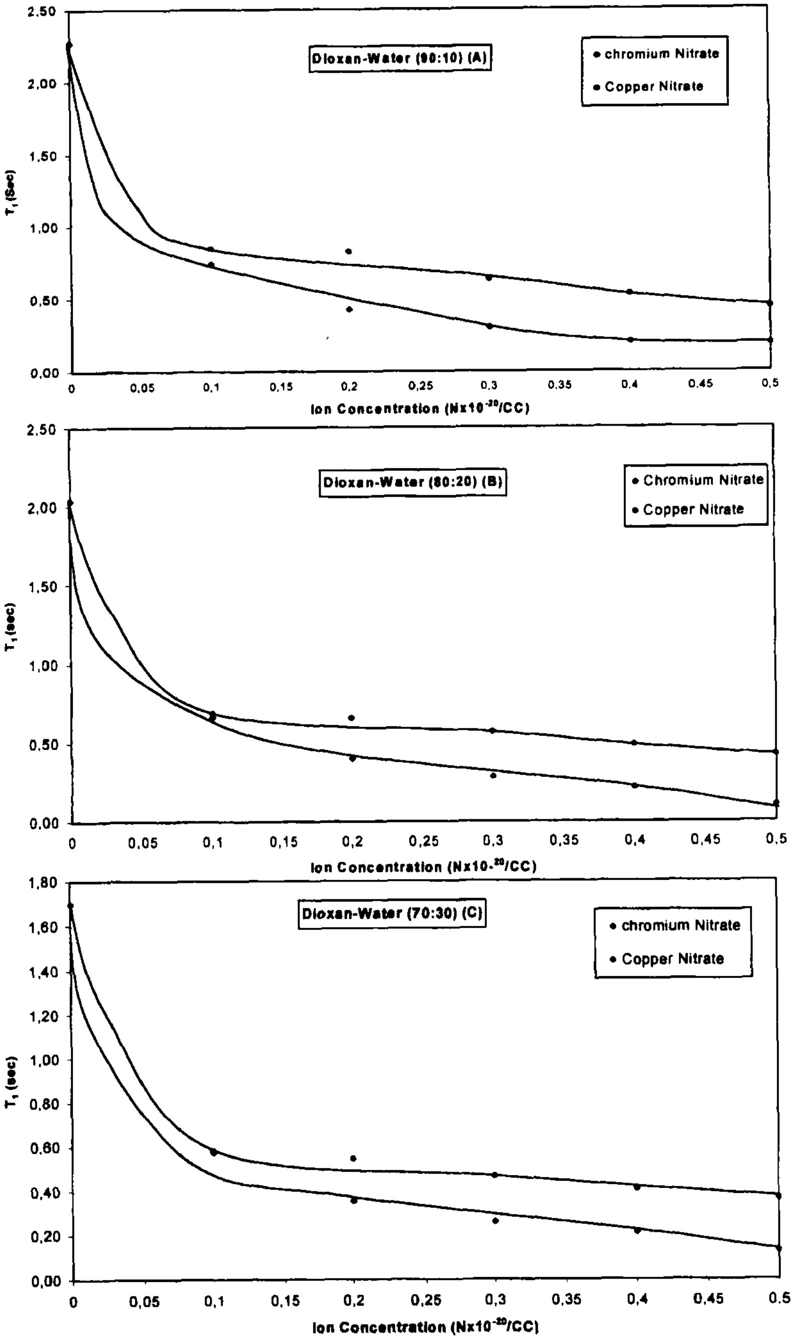


FIGURE 9 (A, B, C) represents (T_1) as a function of increasing chromium and copper Nitrate in the different proportions of dioxan–water mixtures.

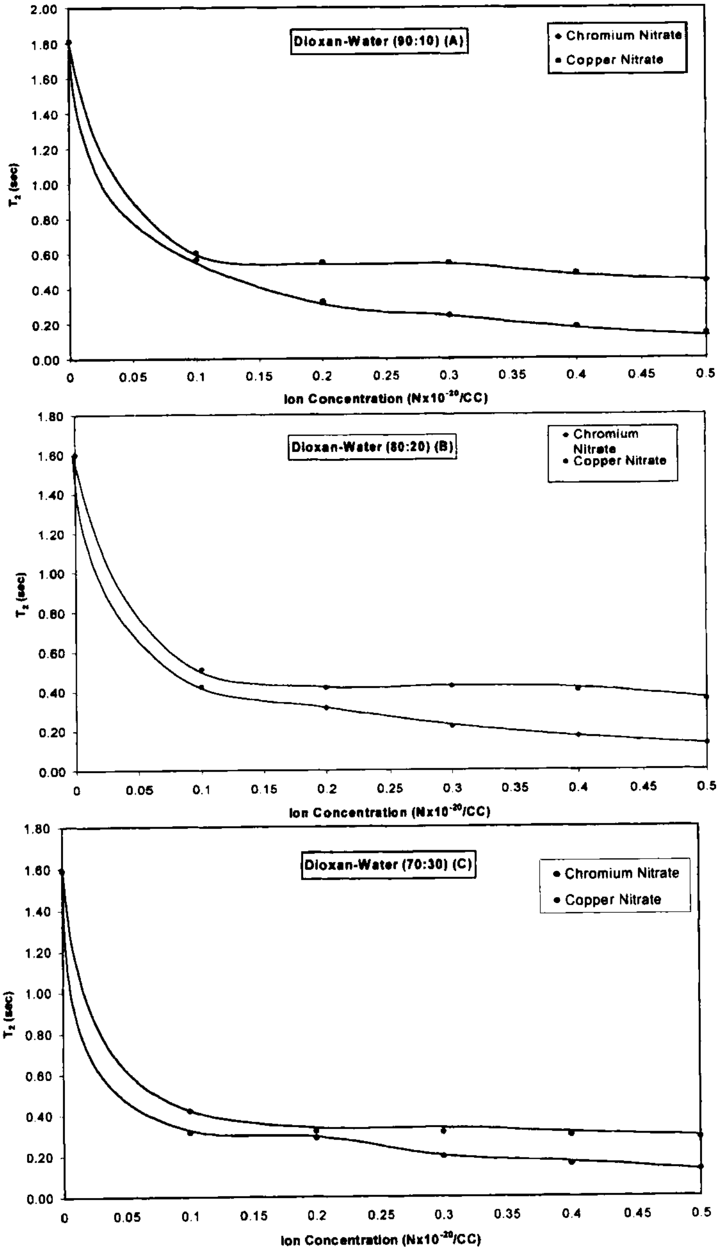


FIGURE 10 (A, B, C) represents (T_2) as a function of increasing chromium and copper nitrate in the different proportions of dioxan–water mixtures.

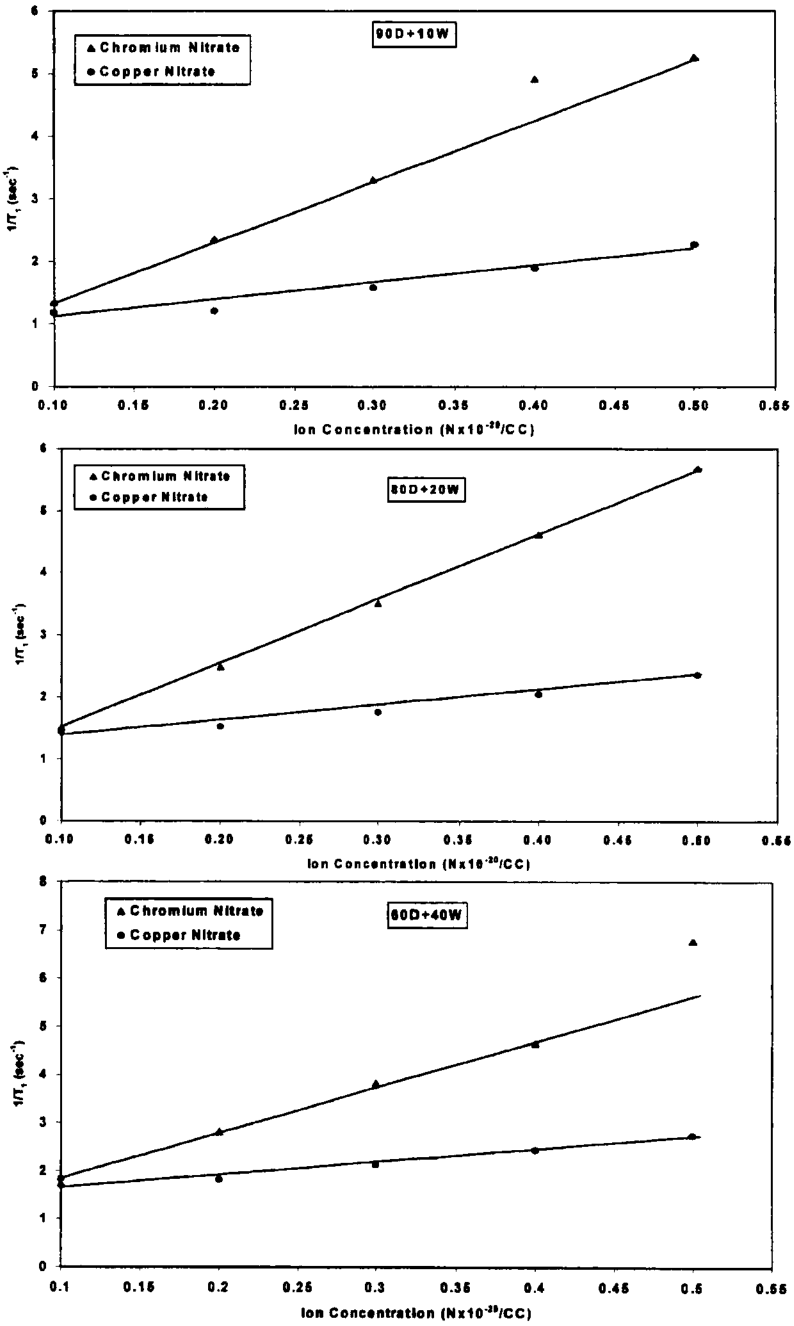


FIGURE 11 Variation of spin-lattice relaxation rate *versus* PMI concentrations.

The increase in the value of the slope may be attributed to the larger value of 'μ' for Cr^{++} ion [18]. The linearity of the plot $(1/T_1)$ *versus* PMI concentrations indicates the absence of anti parallel bonding of the paramagnetic ions in this low viscous system. This is to be expected because of the free mobility of the ions. The linear relationship between $(1/T_1)$ and PMI concentration also indicates that the molecular radius 'a' (Eq. (3)) is not significantly altered by the presence of paramagnetic ions.

In conclusion, it may be mentioned that the present study indicates the possibility of anti parallel bonding of the paramagnetic ions in highly viscous solutions as compared to low viscosity system. These results support the earlier ultrasonic studies in these solutions [19, 20].

Acknowledgement

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References

[1] Bloch, F., Hansen, W. W. and Packard, M. E. (1946). *Phys. Rev.*, **70**, 474.

[2] Bloembergen, N., Purcell, E. M. and Pound, R. V. (1948). *Phys. Rev.*, **73**, 679.

[3] Bernheim, R. A., Brwn, T. H., Gutowsky, H. S. and Woessner, D. E. (1959). *J. Chem. Phys.*, **30**, 950.

[4] Nolle, A. W. and Morgan, L. O. (1957). *J. Chem. Phys.*, **26**, 642.

[5] Bloembergen, N. (1957). *J. Chem. Phys.*, **28**, 572.

[6] Broersma, S. J. (1958). *J. Chem. Phys.*, **28**, 1158.

[7] Gutowsky, H. S. and Tai, J. C. (1963). *J. Chem Phys.*, **39**, 208.

[8] Rivkind, I. A. (1957). *Dokl. Akad. Nauk. USSR*, **117**, 448.

[9] Modak, S. G., Khare, P. L. and Mande, C. (1972). *Indian J. Pure and Applied Physics*, **10**, 293.

[10] Andrew, E. R. (1958). *Nuclear Magnetic Resonance*, Cambridge University Press.

[11] Charles, D. H., *Handbook of Physics and Chemistry*, Chemical Rubber Pub. Co., Cleavland (USA).

[12] Gordon, G., Hammes, N. and Knoche, N. (1966). *J. Chem. Phys.*, **45**, 4041.

[13] Atkinson, G., Rajagopalan, S. and Alkinson, B. L. (1980). *J. Chem. Phys.*, **72b**, 3511.

[14] Greinacker, E., Luttke, N. and Mecke, R. (1955). *Z. Electro. Chem.*, **59**, 23.

[15] Fratiello, A. and Miller, D. (1963). *J. Am. Chem. Soc.*, **85**, 3072.

[16] Fratiello, A. and Miller, D. (1965). *J. Chem. Phys.*, **42**, 796.

[17] Srinivasa Rao, A., Arulmozhi, V. and Rajalakshmi, S. (1993). *Bull. Soc. Chim. Belg.*, **102**(11 and 12), 693.

[18] Conger, R. L. and Selwood, P. W. (1952). *J. Chem. Phys.*, **20**(3), 383.

[19] Nambinarayanan, T. K. (1981). Ultrasonic studies on the nature of molecular interactions of some solutions, *Ph.D. Thesis*, University of Madras.

[20] Balasubramanian, V. (1988). Molecular Acoustical studies in some aqueous and non aqueous solutions, *Ph.D. Thesis*, University of Madras.