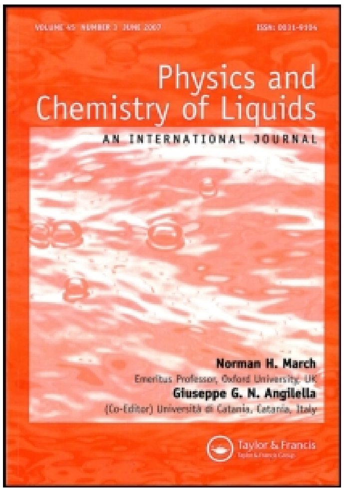

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PROTON MAGNETIC RESONANCE RELAXATION STUDIES IN AQUEOUS SOLUTIONS OF ALKALI HALIDES AND SUGARS

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The proton magnetic resonance (PMR) spin-lattice relaxation times (T1) were measured in aqueous solutions of glucose and sucrose. T1 was found to decrease with increase of sugar concentration. This result is interpreted as due to molecular association between sugar and water molecules. The relaxation times were also measured in aqueous solutions of alkali halides containing glucose and sucrose to study the influence of sugar on the relaxation times. The results are interpreted in terms of structure making and breaking properties of alkali ions.

KEY WORDS: Proton relaxation times (T1), glucose, sucrose, sodium chloride, potassium chloride.

INTRODUCTION

Carbohydrates play an important role in animal and plant life. Understanding the behaviour of these in dilute solutions is of considerable importance in medicine and biology. This behaviour can be understood, among others, by measuring thermodynamic properties in dilute solutions, like limiting apparent molal volume, adiabatic compressibilities, specific heat etc. The extent of hydration of carbohydrates depends on their conformation and configuration of their hydroxy group. Franks and coworkers[1] have demonstrated that equatorial hydroxy groups are more readily hydrated than axial, and differently hydrated solute molecules will differ in their compatibility with water structure. Several NMR studies in aqueous solutions of sugars have been reported and are used to demonstrate structurally determined hydration differences between solute and solvent molecules[1–5]. On the other hand influence of alkali halides on the physical properties of aqueous non electrolyte solutions have not been extensively studied in spite of their biological importance[6]. Recent ultrasonic velocity and absorption studies[7–9] in aqueous solutions of sugars containing alkali halides revealed interesting features on the nature of molecular interaction between constituents in these solutions. Proton magnetic resonance (PMR) relaxation studies[10] in aqueous solutions of sodium and potassium chlorides

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indicate that sodium ions are structure making in the sense that their effect on a solution of water molecules is a restriction of their overall motional freedom. The potassium ions are structure breaker implying that their effect in aqueous solutions is to increase the freedom of movement of water molecules. To obtain additional information on the nature of molecular processes in aqueous solutions of sugars such as glucose and sucrose, the proton magnetic resonance relaxation times (T1) were measured in the above solutions as the relaxation times are very sensitive to molecular environment.[11] The relaxation times were also measured in aqueous solutions of sodium and potassium chlorides containing glucose and sucrose. The results of the study are reported in this note.

EXPERIMENTAL DETAILS

The chemicals used in the present study were of AR/BDH quality and used without further purification. The solutions were prepared by taking known amounts of sugar and dissolving it in double distilled water so as to obtain solutions in the concentration range 2% and 5% by W/W ratio. This range of concentrations are normally used in the intravenous transfusion of fluids to the human body. Aqueous sodium and potassium chloride solutions were prepared in molar concentration ranging from 1 to 4. To these solutions glucose and sucrose are added so that the concentration of the sugar in the alkali halide solutions is 2% and 5%. The proton spin-lattice relaxation times (T1) in the above solutions were measured using a Bruker PC 120 NMR process analyser at a temperature of 40°C by circulating water from a thermostatically controlled water bath provided by Concord Instruments (P) Ltd. Bangalore with an accuracy better than ±0.1°C. 180-τ-90 pulse sequence was used for the measurement of T1. Five fold accumulation was used for the reduction of error, which is usually less than 2%. The error in the 3 parameter fitting of relaxation curve for T1 was less than 0.5%. The decay of magnetization in these samples is found to be mono exponential[12]. The density and viscosity in these solutions were measured at the same temperature of 40°C using Pyknometer and Ostwald's viscometer. The accuracy in the measurement of viscosity and density is of the order of 1%.

RESULTS AND DISCUSSION

Aqueous glucose and sucrose solutions

It can be seen from the Figures 1(a,b), 2(a,b) and from our earlier studies in other aqueous sugar solutions[6,12,13], the relaxation times T1 and T2 generally decreases as the sugar concentration increases. The decrease in the value of T1 generally indicates a greater association of the molecules in these solutions[6]. This result can be explained on the basis of two state fast exchange model[14]. This model assumes that when substances of large molecular weights are dissolved in water, a small

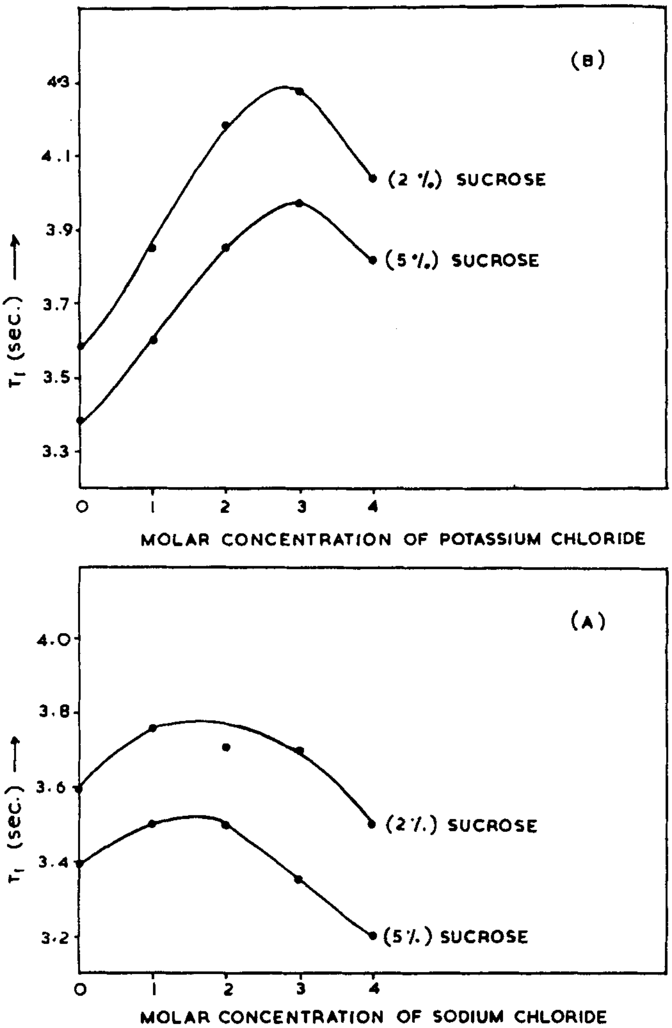

Figure 1 Variation of (T_1) with alkali halide concentration.

fraction of water is attached to the macromolecules and is highly immobilised. The rest of the water is like ordinary water (bulk water) and rapid exchange between these two fraction would yield average spin-lattice relaxation times (T1) weighted heavily by the small immobile fraction. If f is the fraction of water attached to the macromolecules, then spin-lattice relaxation T1s of the solution can be written as

$$\frac{1}{\mathrm{T1s}} = \frac{1-\mathrm{f}}{\mathrm{T1w}} + \frac{\mathrm{f}}{\mathrm{T1A}} \qquad (1)$$

where T1w is the relaxation time of the free water (bulk water) and T1A is the relaxation time of the slow fraction attached to the macromolecules, T1A being much

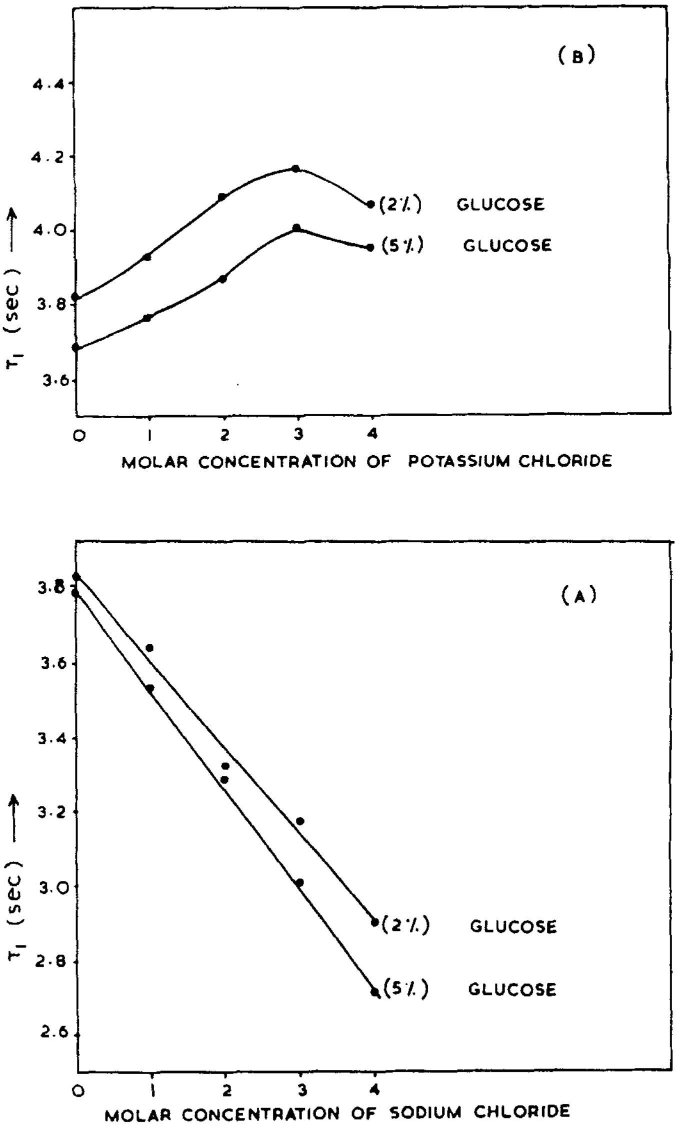

Figure 2 Variation of (T_1) with alkali halide concentration.

shorter than T1W. From the above equation, it can be seen that an increase in the value of f results in a decrease the value of T1s. The decrease in the value of spin-lattice relaxation time T1 in (pure) aqueous solutions of sugars with increase of solute concentration can be explained as due to the increase in the fraction "f" of water attached to sugar molecules due to molecular association[7]. This fraction f is likely to increase as the sugar concentration is increased which results in a further decrease of spin-lattice relaxation time (T1).

Aqueous sucrose solution containing KCL

It can be seen from Figure 1(b) that the PMR spin-lattice relaxation time T1 in aqueous sucrose solutions containing KCl generally increases with increase of KCl concentration and shows a maximum at 3.0 molar concentration. This increase could be explained as due to the structure breaking effect of K^+ ions[6]. The decrease in the value of T1 when KCl concentration exceeds 3 molar can be understood by noting that the increased degree of motional freedom which may increase the probability of molecular association between water and sucrose molecules. This association should result in an increase in the value of f which results in shortening of T1 observed in both 2% and 5% aqueous sucrose solutions.

Aqueous sucrose solution containing NaCl

In aqueous sodium chloride solutions containing 2%, 5% sucrose, the PMR relaxation time T1 shows a maximum at 1 molar concentration, but on further addition of NaCl it generally decreases (Figure 1a). The initial increase may be due to the fact that the macromolecules water complex might have been disturbed by the introduction of Na^+ ions and thereby shedding some water molecules which result in increase in T1 value. But on further addition of NaCl, the complex could have adjusted to the alkali enviornment and the structure making effect of Na^+ ions are likely to be dominant and resulting in a characteristic decrease in T1 value.

Aqueous glucose containing sodium and potassium chloride

It can be seen from Figure 2(a), that PMR relaxation time T1 in 2% and 5% aqueous glucose solution decreases with increase of sodium chloride concentration. This is to be expected because sodium ions are structure makers and their effect is to restrict the overall motional freedom of solute water molecules. This restriction results in a decrease of bulk water fraction (increase in the value of f) which may be responsible for the decrease in the value of T1 with increase in sodium chloride for any sugar concentration (Eq. 1). The decrease in the value of T1 with increase in glucose for any NaCl concentration has been already discussed.

The measured values of T1 in the present case in aqueous glucose solutions have been explained on the basis of two state fast exchange model Eq. 1 however has to be modified for aqueous solutions of sodium chloride containing glucose. Another term f1/T1Na may have to be added to the righthand side of the Eq. 1 where f1 is the fraction immobilised by sodium ions and T1Na is the relaxation time of this fraction. In the absence of accurate values of T1Na and T1A is not possible to calculate the values of f and f1.

From the Figure (2b), it can be seen that the PMR relaxation time T1 in both the two systems (2% and 5% glucose solutions) increases with increase in the KCl concentration up to 3 molar but on further addition of KCl the T1 value begins to decrease. This behaviour is similar to that as for sucrose and the explanation proposed for sucrose solution may also hold for the present case.

It is also interesting to note that from the figures and our earlier NMR studies in aqueous solutions of other sugars[6], the relaxation times T1 are found to decrease as the concentration of sugars is increased. However T1 values are found to be lower in sucrose solutions than in glucose solutions for any particular solute concentration. The decrease in the value of T1 in any solution generally indicates a greater association of the molecules in them[6,7]. The greater association may be brought either by the ionic hydration of the solute[17,18] or through hydrogen bonding between the solute and solvent molecules[19]. In the present case, the increased cohesion between the molecules in the solution appears to be due to later effect. The glucose and sucrose have different number of hydroxy groups which may form hydrogen bonds with water molecules. The conductivity studies of sucrose solution[19] also suggestive of the formation of hydrogen bonds between sucrose and water molecules. This results from a structuring of water molecules caused by hydrogen bond formation between OH groups of sugars and oxygen of water. Hydrogen bonds then create a microscopic or molecular resistance to movement. The sucrose have nearly double the number of OH groups than the glucose molecules. Hence it is not unreasonable to expect a greater association in sucrose solution as compared to glucose solution. The greater association in sucrose molecule will lead to lower T1 values as compared to glucose solution for any particular solute concentration. From the figures it is observed that the T1 values in pure sucrose solutions are lower than pure glucose solution. The possibility of greater association in sucrose solutions through hydrogen bonding is also supported by the ionic conductivity studies[16] in aqueous sugar solutions. The viscosity measurements in the above systems indicate that the viscosity is higher in aqueous solutions of sugar containing NaCl as compared to solution containing KCl. This is to be expected because the sodium ions are water structure maker and potassium ions are breakers. The increased cohesion brought about by NaCl may be responsible for the higher value of viscosity.

The present NMR studies in the aqueous solutions of sugars have generally established the usefulness of the two fraction fast exchange model of water molecules in interpreting the structure making and breaking properties of alkali halides containing sugars

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