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

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ABSTRACT

The proton magnetic resonance (PMR) spin-lattice relaxation times (T_1) were measured in aqueous solution of fructose. T_1 was found to decrease with increase of fructose concentration. This result is interpreted as due to molecular association between the fructose and water molecules. The relaxation times T_1 were also measured in aqueous solutions of alkali halides containing the sugar fructose to study the influence of this sugar on the relaxation times. The results are interpreted in terms of structure making and breaking properties of alkali ions.

INTRODUCTION

Recent ultrasonic velocity studies (ref. 1) 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 (ref. 2) in aqueous solutions of sodium and potassium chlorides 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 termed as structure breaking implying that their effect in aqueous solutions is to increase the freedom of movement of water molecules. To obtain additional information on the molecular processes in aqueous solutions of fructose, the proton magnetic resonance spin-lattice relaxation times T_1 were measured in the above solutions as relaxation times (T_1) are very sensitive to molecular environment. The spin-lattice relaxation times T_1 were also measured in aqueous solutions of sodium and potassium chlorides containing fructose. The results of the study are reported in this paper.

EXPERIMENTAL

The chemicals used in the present study were of AR/BDH quality and used without further purification. The fructose solutions were prepared by dissolving a known amount of substance in double distilled water to obtain 2%, 6% and 10% concentration of the solute. 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 concentrations ranging from 1 to 4. To these solutions, fructose is added so that the concentration of the sugar in the alkali halide solutions is 2%, 6% and 10%. The proton spin-lattice relaxation times T_1 in the above solutions were measured using a Bruker PC 120 NMR process analyser at a temperature of 40°C. 180- τ -90 pulse sequences were used for the measurements of T_1 at an RF frequency of 20 MHz. The error in the measured values of T_1 are of the order of 0.3%. The decay of magnetization in this samples is found to be mono-exponential. The spin-lattice relaxation times T_1 in aqueous sodium chloride solutions containing several concentrations of fructose are shown in Table 1, whereas Table 2 contains the values obtained for aqueous potassium chloride solutions containing fructose. The variations of T_1 as a function of sodium chloride concentration for 2%, 6% and 10% fructose concentrations are shown in Fig. 1 and the values of T_1 as a function of KCl concentration for the three fructose concentrations are plotted in Fig. 2.

TABLE 1
PMR spin-lattice relaxation times (T_1) in aqueous solutions of sodium chloride containing fructose.

Concentration of NaCl mol/lit	Proton spin-lattice relaxation times T_1 (sec)		
	Concentration of fructose		
	2%	6%	10%
0.0	3.52	3.15	2.88
1.0	3.44	2.98	2.85
2.0	3.23	2.91	2.58
3.0	3.02	2.71	2.47
4.0	2.81	2.58	2.29

TABLE 2
PMR spin-lattice relaxation times (T_1) in aqueous solutions of potassium chloride containing fructose¹.

Concentration of NaCl mol/lit	Proton spin-lattice relaxation times T_1 (sec)		
	Concentration of fructose		
	2%	6%	10%
1.0	3.50	3.04	2.79
2.0	3.51	3.31	3.05
3.0	3.18	3.01	2.95
4.0	3.55	3.04	2.76

AQUEOUS FRUCTOSE SOLUTIONS

It can be seen from Table 1, that in pure aqueous solutions, the relaxation time T_1 decreases with increase of fructose concentration. This result can be explained on the basis of two fraction fast exchange model (Ref. 3). This model assumes that when substances of large molecular weights are dissolved in water, a small fraction of water is attached to macromolecules and is

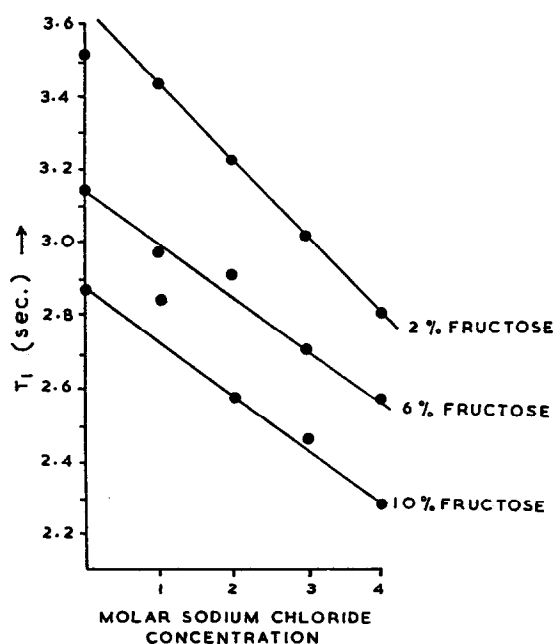


Fig. 1. Variation of T_1 with sodium chloride concentration.

highly immobilised. The rest of the water is like ordinary water (called bulk water) and rapid exchange between these two fractions would yield reduced average spin-lattice relaxation time T_1 weighted heavily by the small immobile fraction. If f is the fraction of water attached to the macromolecules, then the spin-lattice relaxation T_{1s} of the solution can be written as

$$\frac{1}{T_{1s}} = \frac{1-f}{T_{1w}} + \frac{f}{T_{1A}} \quad (1)$$

where T_{1w} is the relaxation time of the free water (bulk water) and T_{1A} is the relaxation time of the slow fraction attached to the macromolecules, T_{1A} being much shorter than T_{1w} . From the above equation, it can be seen that an increase in the value of f results in a decrease value of T_{1s} .

The decrease in the value of spin-lattice relaxation time T_1 in aqueous solutions of fructose with increase of solute concentration can be explained as due to the increase in the fraction f of water attached to fructose molecules due to molecular association (Ref. 1). This fraction f is likely to increase as the fructose concentration is increased which results in a further decrease of spin-lattice relaxation time T_1 .

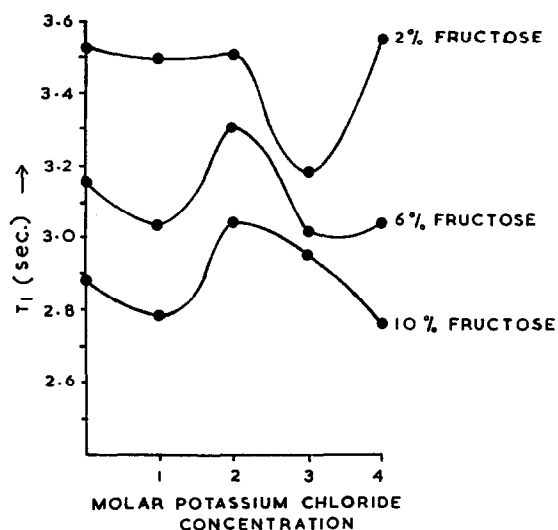


Fig. 2. Variation of T_1 with potassium chloride concentration.

AQUEOUS SODIUM CHLORIDE SOLUTIONS CONTAINING FRUCTOSE

It can be seen from Fig. 1, that the PMR spin-lattice relaxation time T_1 in all the three systems (containing 2%, 6% and 10% fructose) decreases with increase of sodium chloride concentration. This is to be expected because the 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 of T_1 (eqn. 1). The above argument explains the decrease in the value of T_1 with increase in sodium chloride for any fructose concentration. The decrease in the value of T_1 with increase in fructose for any sodium chloride concentration has already been described.

The measured values of T_1 in the present study in aqueous fructose solutions have been explained on the basis of two state fast exchange model (eqn. 1). Equation 1 however, has to be modified for aqueous solutions of sodium chloride containing fructose. Another term f_1/T_{1Na} may have to be added to the righthand side of the equation 1 where f_1 is the fraction immobilised by sodium ions and T_{1Na} is the relaxation time of this fraction. In the absence of accurate values of T_{1Na} and T_{1A} is not possible to calculate the values of f and f_1 .

AQUEOUS POTASSIUM CHLORIDE SOLUTIONS CONTAINING FRUCTOSE

In aqueous potassium chloride solutions containing 2% fructose, the PMR spin-lattice relaxation time T_1 remains fairly constant upto 2 molar concentration and then decreases and attains a minimum around 3 molar KCl concentration and then increases with further increase of KCl (Fig. 2). In 6% fructose solution, T_1 initially decreases with increase of KCl concentration attains a minimum around 1 molar concentration and then increases with further increase of KCl concentration. T_1 attains a maximum around 2 molar concentration of KCl. Further increase of KCl results in a decrease of the value of T_1 . The value of T_1 slightly increases between 3 and 4 molar concentrations of KCl. In 10% fructose solution, T_1 shows a similar trend as that of 6% fructose solution upto 2 molar KCl. T_1 decreases with increase of KCl in the range 2 to 4 molar concentrations.

The above results may be explained by nothing that potassium ions are structure breakers and structure breaking ions generally increase the degree of motional freedom of solute water molecules. This results in an increase of the bulk water. It can be inferred from equation 1, that the increase in bulk water fraction has a tendency to lengthen the value of T_1 . In 2% fructose solution, the structure breaking effect is predominantly observed when the KCl molar concentration exceeds 3 as T_1 is found increase with increase of KCl concentration. The decrease in the value of T_1 observed between 2 to 3 molar concentration of KCl can be understood by nothing that the increased degree of motional freedom may increase the probability of molecular association between water and fructose molecules. This association should result in an increase in the value of f which results in shortening of T_1 . Above 3 molar concentration, the effect of KCl dominates over that of fructose and hence there is an increase in the value of T_1 between 3 to 4 molar concentration of KCl.

As the concentration of fructose is increased to 6%, it can be seen from Fig. 2 that increase in the value of T_1 above 3 molar concentration of KCl is small as compared to 2% aqueous fructose solutions. This may be due to the increased number of fructose molecules on 6% solution. In 10% solution, T_1 decreases with increase of KCl concentration in the range 2 to 4 molar and this has to be attributed to the association of water molecules with fructose molecules which dominates over the structure breaking effect of potassium ions. The present NMR studies clearly establish the usefulness of the two fraction fast exchange model of water molecules in interpreting the structure making and breaking effects of alkali halides containing sugars.

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