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Hydration properties of Na, K, Mg gluconates and gluconate/sucrose mixtures and their possible taste effect

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Abstract

Density and ultrasonic velocity were measured in aqueous solutions of sodium, potassium and magnesium gluconate as a function of increasing concentration. Apparent molar volume (AMV), apparent specific volume (ASV), isentropic apparent molar (IAMC) compressibility and hydration numbers were calculated from the experimental data. The results show that AMV and ASV increase as the concentration of gluconates is increased. This is interpreted on the basis of molecular interaction between solute and solvent molecules. These measurements were repeated by adding Na, K and Mg gluconates to 10 and 20% sucrose solution with the aim of understanding the influence of gluconates on water association in sucrose solutions. The results show that the values of IAMC decrease as the concentration is increased. Moreover, Mg gluconate shows more negative IAMC than Na and K gluconates. The observed results are explained on the basis of the hydration of gluconates in the sucrose-water system. NMR relaxation rates (R_1 and R_2) show an increase as the concentration of the gluconate is increased. On the other hand, the results of Na, K and Mg gluconate in 10 and 20% sucrose solutions demonstrated that the effect of Mg gluconate enhances the hydration properties of sucrose water mixtures more than Na and K gluconate. The overall results show the importance of water interactions with sapid molecules and this can lead to a better understanding of their tastes.

Keywords: NMR; Relaxation; Viscosity; Sugars; Density; Gluconic acid; Hydrogen bonding

1. Introduction

Taste is one of the chemical senses of man. In taste, water is important because no molecule can be tasted unless it is soluble and transportable to the receptors via oral fluids (Birch, 1976). When a substance dissolves in water a hydration shell is built and this hydration depends on the conformation of solute and configuration of the hydroxyl groups. Kabayama and Patterson (1958) have demonstrated that equatorial OH groups in β D-glucose for example are more readily hydrated than axial, and that this hydration proves to be a long-range hydration, which enhances water structure. Since it is the hydrated molecule, which diffuses to the receptor site, hydration is important in taste research. The hydration of sweet molecules in water in relation to their stereochemistry has been a subject of study over a long time (Birch, 1980; Crozier, 1934; Shallenberger, 1963). This behaviour can be understood, by spectroscopic techniques such as Nuclear Magnetic Resonance (NMR) (Arulmozhi & Srinivasa Rao, 1993; Suggett, 1976) or Raman (Mathlouthi, 1980), and volumetric methods such as viscosity (Mathlouthi et al., 1984) and apparent molar volume (Birch & Catsoulis, 1985). These methods have been used to demonstrate structurally determined hydration differences between solutes and the latter approach has been used in an attempt to explain chemoreceptor mechanisms (Birch & Shamil, 1988).

Apparent specific volumes reflect the packing of water molecules around the solute. Isentropic apparent molar compressibility, a measure of the compaction of the hydration layer around the molecules, takes into account the different attractive and repulsive forces exerted by the solutes on each other and on the structure of water. On the other hand, low resolution pulsed

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nuclear magnetic resonance (NMR) relaxation measurements could, in principal, provide more information pertinent to both the hydration and hydrogen bonding in solutions. Hertz et al. (1971) have reported the exchange rates of protons. These parameters are generally interpreted as indicators of "structure making" and "structure breaking" effects of salts on water. They indicate the way the salts disrupt water hydrogen bonds (Arulmozhi & Srinivasa Rao, 1993; Hertz, 1973). Recently, Birch, Grigor and Derby (1989) have used these parameters and precision densitometry to interpret the packing of the solutes (sugars and amino acids) among water molecules. They have also related them to their known sweetness properties.

Several studies have been made to explain the mechanism of sweet taste chemoreception through the above mentioned methods and well-established results have been published for the past two decades (Birch & Catsoulis, 1985; Mathlouthi & Hutteau, 1999; Suggett, 1976).

The main objective of the present work is to study the hydration properties of gluconates and gluconate/sucrose mixtures in aqueous solutions and to investigate whether there exists a relationship between these properties and taste.

Salts of gluconic acid are chosen for the present study, since it is a mild organic acid, non-corrosive and has excellent complexing ability. It occurs naturally in plants and foodstuffs, is non-toxic and is fully utilized in the body, like carbohydrates. This molecule has an interesting character as it has AH,B sites (Shallenberger & Acree, 1971), which means a sweet character. However, bitterness may be conferred by the C=O bond. Moreover, this molecule has the ability to mask bitterness. Sucrose can be taken as a parent solution since sucrose serves as a reference standard for all sweet substances.

2. Materials and methods

Sodium, potassium, magnesium gluconates and sucrose were reagent grade chemicals obtained from Sigma chemicals (France). The chemicals were dried to constant weight at 40°C over phosphoric pentoxide prior to dissolution. Water used for all the experiments was HPLC grade. Solutions were made up w/w and all measurements were carried out at 20°C. Analyses were repeated until constant values were obtained.

2.1. Density and sound velocity measurements

The density and sound velocity values for sucrose and sucrose/gluconates mixtures were determined using an Anton–Parr density sound analyzer (DSA 48) from Parr Scientific Ltd, Raynes Park, London, UK. The temperature was maintained at 20±0.1°C. The density of the samples was measured from the period of oscillation of an oscillating U-tube. The sound velocity was calculated from the propagation speed of ultrasonic pulses in a known distance within the sample in the measuring cell. The instrument was calibrated using air and distilled water. Density and sound velocity measurements were accurate to $\pm 1\times10^{-4}$ g/cm^3 and ±1 m/s respectively. The partial molar volume (ϕ_v cm^3/mol), apparent specific volume (ASV cm^3/g), isentropic apparent molar compressibilities [$K\phi(s)$ cm^3/mol bar] and hydration numbers (n_h) are calculated from the experimental values of density and sound velocity. All other calculation details are adequately described elsewhere (Parke & Birch, 1999).

2.2. NMR relaxation measurements

^{1}H NMR measurements were carried out using an Oxford QP20$^+$ NMR Process Analyzer at a frequency of 20 MHz, until constant values were obtained at 298 K. The inversion recovery sequence, 180–τ–90° was used for (T_1) measurements. The proton transverse (T_2) magnetization decay curve was determined by sampling up to 250 echoes stemming from the Carr–Purcell–Meiboom–Gill pulse sequence (CPMG) with an interpulse delay of 1.5 ms. The experiments were also repeated using a series of CPMG pulse sequences with variable 90–180° interpulse spacing (τ); an identical total duration and 250 points in common was used. For each measurement the magnetic fields were checked and the relaxation times were measured. The temperature was controlled with accuracy better than 25±1°C by circulating a fluorinated solvent in a Dewar vessel around the NMR probe. No attempt has been made to de-gas the samples, since the dissolved O_2 does not cause any change in the values of relaxation. This was checked by our earlier NMR studies on pulse spacing experiments on amino acids (Arulmozhi & Rutledge, 2000). The relaxation curves were decomposed into sums of exponential with a non-linear regression program based on a Marquardt algorithm and it was found to be monoexponential for all the solutions (Rutledge, 1996). The decay of the signal was also monitored using a dual beam storage oscilloscope.

3. Results and discussion

3.1. Apparent molar volume and compressibility

In the present study, the measured values of density, sound velocity and calculated values of apparent molar volume, apparent specific volume, isoentropic apparent molar compressibility and hydration numbers for pure potassium, magnesium and sodium gluconates with increasing molality concentrations are given in Tables 1–3.

Table 1
Measured values of density, sound velocity and calculated values of apparent molar volume, apparent specific volume, isentropic apparent compressibility and hydration number of pure potassium gluconate

Molality	Density (g/cm^3)	Sound velocity	AMV (cm^3/mol)	ASV (cm^3/g)	Compr. coeff.	Ise. AMC (cm^3/mol bar)	nh	IASC (cm^3/g bar)
0.214	1.0231	1507	114.7	0.490	4.305E-05	−0.00661	14.4	−2.821E-05
0.427	1.0459	1530	116.9	0.499	4.087E-05	−0.00574	13.4	−2.453E-05
0.641	1.0678	1552	117.4	0.501	3.888E-05	−0.000521	12.7	−2.226E-05
0.854	1.0883	1574	118.1	0.504	3.710E-05	−0.00473	12.1	−2.019E-05
1.068	1.1076	1595	118.8	0.507	3.551E-05	−0.00429	11.5	−1.833E-05
1.281	1.1256	1615	119.5	0.511	3.407E-05	−0.00390	11.0	−1.666E-05

Table 2
Measured values of density, sound velocity and calculated values of apparent molar volume, apparent specific volume, isentropic apparent compressibility and hydration number of pure magnesium gluconate

Molality	Density (g/cm^3)	Sound velocity	AMV (cm^3/mol)	ASV (cm^3/g)	Compr. coeff.	Ise. AMC (cm^3/mol bar	nh	IASC (cm^3/g bar)
0.121	1.0229	1507	204.7	0.494	4.30E-05	−0.0116	25.5	−2.80E-05
0.241	1.0457	1529	207.8	0.501	4.09E-05	−0.0101	23.7	−2.43E-05
0.362	1.0670	1551	210.0	0.507	3.90E-05	−0.0089	22.2	−2.15E-05
0.482	1.0869	1572	212.0	0.511	3.73E-05	−0.0080	21.0	−1.92E-05
0.603	1.1062	1592	216.6	0.513	3.57E-05	−0.0073	20.0	−1.76E-05

Table 3
Measured values of density, sound velocity and calculated values of apparent molar volume, apparent volume, isentropic apparent compressibility and hydration number of pure sodium gluconate

Molality	Density (g/cm^3)	Sound velocity	AMV (cm^3/mol)	ASV (cm^3/g)	Compr. coeff.	Ise. AMC (cm^3/mol bar)	nh	IASC (cm^3/g bar)
0.229	1.0234	1510	105.5	0.484	4.28E-05	−0.007076	14.5	−3.24E-05
0.459	1.0469	1536	106.7	0.489	4.05E-05	−0.006285	13.5	−2.88E-05
0.688	1.0688	1516	107.8	0.494	3.84E-05	−0.005625	12.7	−2.58E-05
0.917	1.0894	1585	108.7	0.499	3.65E-05	−0.005076	12.0	−2.33E-05
1.146	1.1089	1609	109.4	0.502	3.48E-05	−0.004621	11.4	−2.12E-05
1.375	1.1269	1631	110.4	0.506	3.34E-05	−0.004197	10.8	−1.92E-05

From Tables 1–3, it can be observed that, in the case of pure gluconates, apparent molar volume (AMV) increases with increasing concentration. The values of AMV change from 204 to 216 cm^3/mol in the case of magnesium gluconate, 105 to 110 cm^3/mol for Na gluconate and 114 to 119 cm^3/mol for K gluconate with increasing molality. The values of ASV also increase as the concentration of the solute is increased. These results are in accordance with previous observations (Birch & Catsoulis, 1985; Birch & Shamil, 1986). Apparent molar volume is a measure of packing efficiency of solute molecules among solvent molecules and is therefore governed by the interaction of solute structure with water structure (Birch & Catsoulis, 1985). The values of AMV or ASV increase with increasing concentration of solute and this reflects the replacement of solute/solvent interaction by solute/solute interaction. Thus the less heavily hydrated solute molecules at higher concentration must disturb the water structure more, giving higher AMV. The present results of ASV/AMV indicate that the molecules of Na, K and Mg gluconate lie on the borderline of sour and sweet molecules. The salt Mg gluconate is more hydrated in water than K and Na gluconate. These parameters (ASV) are highly useful to predict taste quality and have already been correlated with some aspects of taste in the sugars (Birch & Catsoulis, 1985; Shamil et al., 1987).

Tables 1–3 show that the values of ultrasonic velocity also increase as the concentration of sugar is increased. Generally, increase in velocity indicates a greater association between solute and solvent molecules (Rao et al., 1990b; Smith & Winder, 1983). The calculated values of hydration number of pure gluconates show a decrease as the concentration of the solute increases.

Hydration numbers (n_h) are indicative of the number of water molecules that are disturbed by the presence of solute in solution. The values of calculated hydration numbers for gluconates are in good agreement with the literature data (Parke, 1997).

Hydration numbers (molecules of water in the first shell of hydration) vary from 2.7 to 11 for D-glucose, and from 5 to 21 for sucrose depending on the technique of investigation (Allen et al., 1974; Suggett, 1976). In general, the larger the compressibility hydration number, the higher the number of water molecules disturbed, but better is the packing of the solute within the hydrogen-bonded structure of water. As the concentration of solute is increased, solute–solute interaction replaces solute–solvent interaction, leading to a decrease in the number of water molecules disturbed and, hence, a corresponding decrease in the compressibility hydration numbers. In other words, at low solute concentration, molecules, being heavily hydrated, are more compatible with water structure and cause little disturbance to it, thus giving lower ASV. At high solute concentration the molecules are less hydrated and less compatible with water structure and have higher ASV. However, the present study (Tables 1–3) shows that K and Na gluconate are more compatible with water structure and the hydration layer is less disturbed compared to aqueous solutions of Mg gluconate (Galema & Hoiland, 1991). This is further strengthened by the results reported by Parke and Birch (1999) on some artificial sweeteners.

Another interesting parameter is the compactness of water in the layer of hydration around the solute; this is the isentropic apparent molar compressibility (IAMC) (Galema & Hoiland, 1991). Fig. 1 illustrates the relationship between isentropic apparent molar compressibility [$K_{\theta(s)}$] and molality of pure Na, K, and Mg gluconates. From Fig. 1 it can be seen that the IAMC increases as concentration of salt is increased. The limiting values of compressibilities directly give insight into the compressibility of the hydration layer compared to that of pure water. As suggested by Galema and Hoiland (1991) the more negative the partial molar compressibility, the more will the hydration layer be disturbed compared to pure water. The present study clearly shows that Mg gluconate has a greater hydration number as compared to Na and K gluconates.

The present study is also extended by adding 0.1 to 0.6 g of Na, K or Mg gluconate to a fixed 10 or 20% (wt.%) sucrose solution to investigate the influence of salts on the hydration of sucrose. The measured values of density, sound velocity and calculated values of apparent molar volume, apparent specific volume, isentropic apparent molar compressibility and hydration numbers of 10 and 20% sucrose solutions containing gluconates are given in Tables 4–6.

From Tables 4–6, it can be observed that the values of AMV and ASV are decreased as the concentration of salt is increased in both 10 and 20% sucrose solution. To explain this phenomenon, the formation of 'icebergs' of water around the solute molecules has been postulated (Frank & Evans, 1945); the icebergs have an open structure formed near hydrophobic solutes; the solute hence fills interstitial cavities that would normally be formed. The loss of free space during hydrophobic hydration is larger than the increase in volume accompanying the increase in ice-likeness; as a consequence a net decrease in volume occurs (see Tables 4–6).

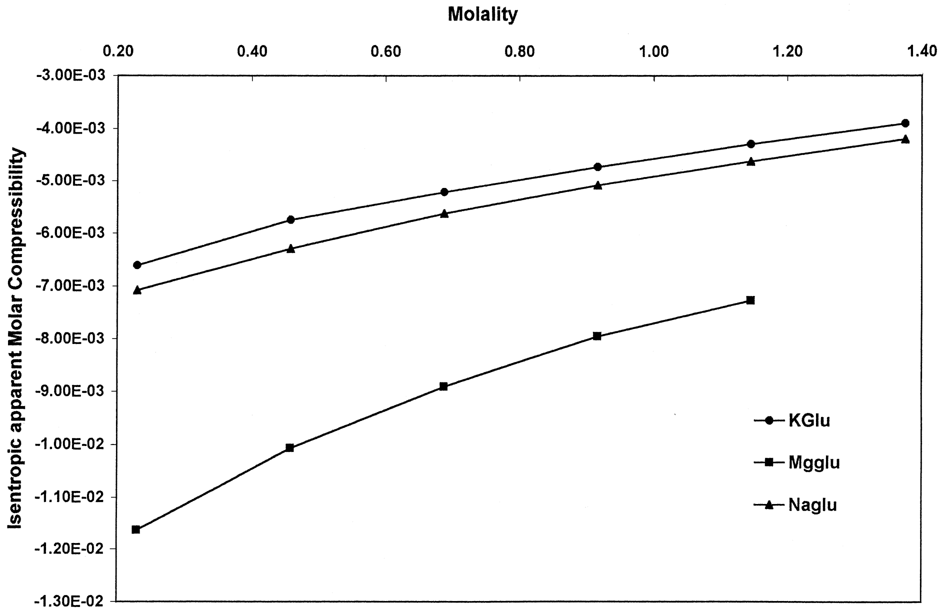

Fig. 1. Plot of isentropic apparent molar compressibility against molality of pure Mg, K and Na gluconates.

Table 4
Measured values of density, sound velocity and calculated values of apparent molar volume,apparent specific volume, isentropic apparent specifc compressibility and hydration number in water + sucrose + gluconate system

Total molality	Molality K Glu	Density (g/cm^3)	Sound velocity	AMV (cm^3/mol)	ASV (cm^3/g)	Compr. coeff.	Ise. AMC (cm^3/mol bar)	Ise. ASC (cm^3/g bar)	Hydration number
Sucrose (10%) + Potassium gluconate									
0.313	0.021	1.0367	1513	204.4	0.610	4.22E-05	−0.00185	−5.52E-06	13.2
0.335	0.042	1.0391	1515	198.4	0.604	4.19E-05	−0.00213	−6.49E-06	13.2
0.356	0.064	1.0414	1518	193.4	0.599	4.17E-05	−0.00236	−7.30E-06	13.2
0.378	0.085	1.0435	1520	189.4	0.596	4.15E-05	−0.00248	−7.79E-06	13.1
0.399	0.107	1.0457	1522	185.6	0.592	4.13E-05	−0.00261	−8.34E-06	13.1
0.420	0.128	1.0479	1524	182.1	0.589	4.11E-05	−0.00274	−8.86E-06	13.1
Sucrose (20%) + potassium gluconate									
0.606	0.021	1.0681	1539	208.7	0.616	3.95E-05	−0.00110	−3.26E-06	12.2
0.627	0.042	1.0706	1542	204.8	0.611	3.93E-05	−0.00131	−3.90E-06	12.2
0.648	0.064	1.0726	1544	202.0	0.609	3.91E-05	−0.00141	−4.25E-06	12.2
0.670	0.085	1.0747	1547	199.2	0.606	3.89E-05	−0.00151	−4.60E-06	12.1
0.691	0.107	1.0767	1549	196.7	0.604	3.87E-05	−0.00160	−4.90E-06	12.1
0.712	0.128	1.0787	1551	194.4	0.602	3.85E-05	−0.00168	−5.19E-06	12.1

Table 5
Measured values of density, sound velocity and calculated values of apparent molar volume,apparent specific volume, isentropic apparent specifc compressibility and hydration number in water + sucrose + gluconate system

Total molality	Molality Na glu	Density (g/cm^3)	Sound velocity	AMV (cm^3/mol)	ASV (cm^3/g)	Compr. coeff.	Isen. AMC (cm^3/mol bar)	Isen. ASC (cm^3/g bar)	Hydration number
Sucrose (10%) + sodium gluconate									
0.315	0.023	1.0368	1513	203.1	0.609	4.213E-05	−0.00195	−5.848E-06	13.3
0.338	0.046	1.0391	1516	196.5	0.604	4.189E-05	−0.00223	−6.863E-06	13.3
0.361	0.069	1.0415	1519	190.5	0.598	4.164E-05	−0.00251	−7.873E-06	13.3
0.384	0.092	1.0438	1521	185.5	0.593	4.140E-05	−0.00272	−8.702E-06	13.2
0.407	0.115	1.0461	1524	181.0	0.589	4.116E-05	−0.00291	−9.476E-06	13.2
0.430	0.138	1.0481	1527	177.7	0.587	4.095E-05	−0.00299	−9.869E-06	13.1
Sucrose (20%) + sodium gluconate									
0.607	0.023	1.0686	1540	207.2	0.614	3.946E-05	−0.00124	−3.662E-06	12.3
0.630	0.046	1.0706	1543	203.8	0.611	3.925E-05	−0.00136	−4.071E-06	12.2
0.653	0.069	1.0727	1545	200.4	0.609	3.904E-05	−0.00150	−4.554E-06	12.2
0.676	0.092	1.0749	1548	197.0	0.605	3.882E-05	−0.00164	−5.042E-06	12.2
0.699	0.115	1.0768	1551	194.3	0.604	3.862E-05	−0.00172	−5.333E-06	12.1
0.722	0.138	1.0794	1554	190.8	0.599	3.837E-05	−0.00191	−5.994E-06	12.1

Table 6
Measured values of density, sound velocity and calculated values of apparent molar volume,apparent specific volume, isentropic apparent specifc compressibility and hydration number in water + sucrose + gluconate system

Total molality	Molality Mg glu	Density (g/cm^3)	Sound velocity	AMV (cm^3/mol)	ASV (cm^3/g)	Compr. coeff.	Ise. AMC (cm^3/mol bar)	Ise. ASC (cm^3/g bar)	Hydration number
Sucrose (10%) + magnesium gluconate									
0.304	0.012	1.0368	1513	210.3	0.609	4.21E-05	−0.00197	−5.711E-06	13.7
0.316	0.024	1.0390	1515	210.4	0.605	4.19E-05	−0.00227	−6.526E-06	14.0
0.328	0.036	1.0413	1518	210.1	0.600	4.17E-05	−0.00257	−7.350E-06	14.4
0.340	0.048	1.0435	1520	210.1	0.596	4.15E-05	−0.00281	−7.960E-06	14.7
0.352	0.060	1.0458	1523	209.8	0.591	4.12E-05	−0.00307	8.658E-06	14.9
0.365	0.072	1.0481	1525	209.4	0.587	4.10E-05	−0.00331	−9.286E-06	15.3
Sucrose (20%) + magnesium gluconate									
0.596	0.012	1.0685	1540	211.2	0.614	3.95E-05	−0.00123	−3.572E-06	12.5
0.608	0.024	1.0706	1542	211.1	0.611	3.93E-05	−0.00138	−4.009E-06	12.6
0.620	0.036	1.0727	1545	210.9	0.609	3.91E-05	−0.00152	−4.394E-06	12.8
0.633	0.048	1.0745	1547	211.2	0.607	3.89E-05	−0.00161	−4.627E-06	12.9
0.645	0.060	1.0766	1549	211.0	0.605	3.87E-05	−0.00174	−4.985E-06	13.0
0.657	0.072	1.0784	1552	211.3	0.603	3.85E-05	−0.00181	−5.156E-06	13.1

Figs. 2 and 3 represent IAMC of Na, K, and Mg gluconate in 10 and 20% sucrose solution, respectively, as a function of molality. From Figs. 2 and 3, it is clear that the values of IAMC are higher for 20% sucrose solution containing gluconates than 10% sucrose. This may be due to the variation of hydration in these solutions whereas hydration is found to be more extensive in 10% sucrose solutions. Moreover, the IAMC is found to be greater for Mg gluconate than Na and K gluconate and can be interpreted as follows: when ions are introduced into a sucrose–water mixture they usually break the water structure. This depends on both the nature of ions and that of hydration. The water around the ions is less compressible than bulk water, leading to a large negative value (Galema & Hoiland, 1991). The hydration of sucrose in aqueous solution is found to be enhanced by the presence of Mg gluconate. This idea is further strengthened by the results of Isaacs (1981), showing that a solute exhibiting a large negative compressibility, has reduced water mobility in its vicinity.

3.2. Nuclear magnetic relaxation measurements

The results of NMR relaxation rates ($R_1 = 1/T_1$ and $R_2 = 1/T_2$) of pure Mg, Na and K gluconate in water at varied concentrations are shown in Figs. 4 and 5. The

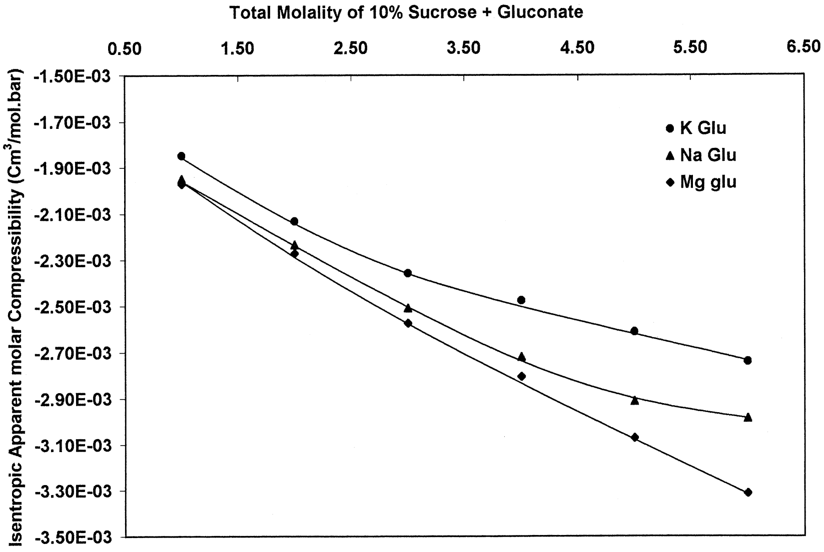

Fig. 2. Plot of IAMC against total molality of sucrose (10%) with gluconates.

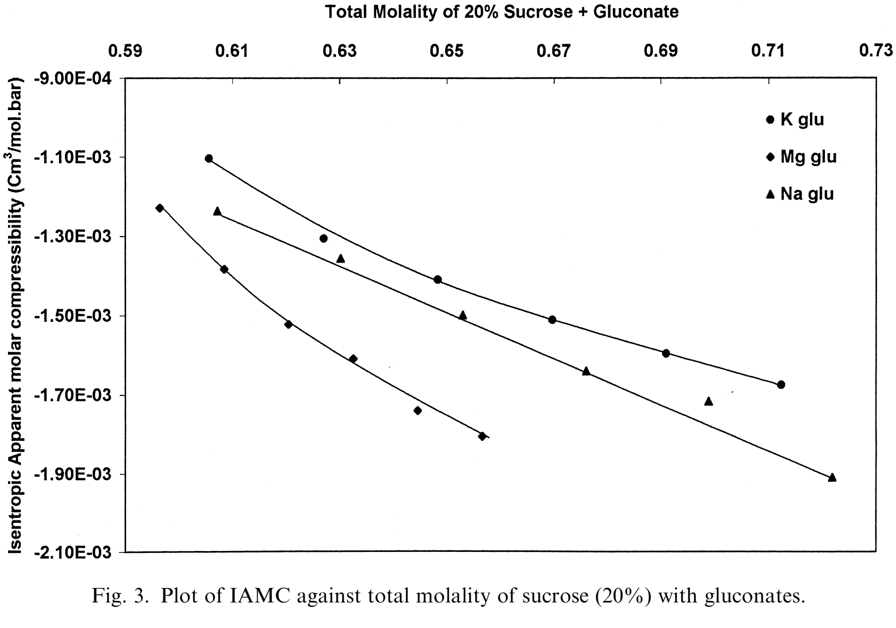

Fig. 3. Plot of IAMC against total molality of sucrose (20%) with gluconates.

decay of magnetization was checked for all the samples and it was found to be single exponential (Fig. 6). This indicates that the exchange between the free and bound water is fast, and the extreme narrowing condition is satisfied. From Figs. 5 and 6, it can be observed that the relaxation rates increase as the concentrations of the salts are increased. However, the increase is much more obvious for Mg than for Na and K gluconates. This behaviour is due to greater association between solute and solvent molecules through hydrogen bonding. It may also originate from the change in viscosity of these solutions particularly due to the molecular weight of the magnesium gluconate and from the structure-making effect of Mg (Arulmozhi & Srinivasa Rao, 1993).

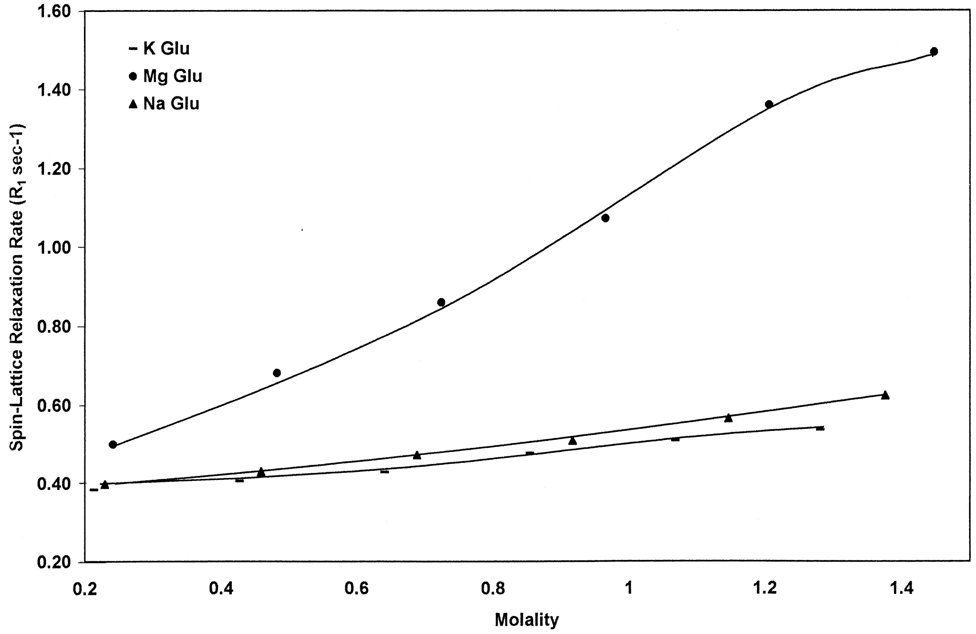

Fig. 4. The dependence of proton spin-lattice relaxation rate (R_1) as a function of increasing molality of pure Mg, K and Na gluconates.

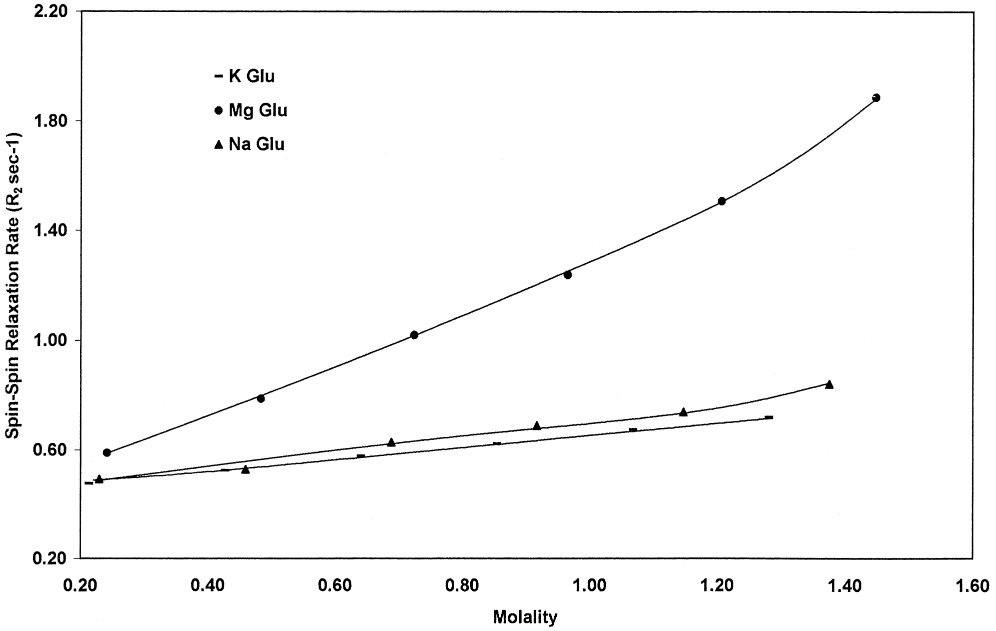

Fig. 5. The dependence of proton spin-spin relaxation rate (R_2) as a function of increasing molality concentration of pure Mg, K and Na gluconates.

The NMR relaxation rates (R_1 and R_2) in aqueous 10 and 20% sucrose solutions containing Mg, Na and K gluconate with increasing molality are shown in Figs. 7–10. These figures show that the values of relaxation rates increase with the increase of solute concentration. It is appropriate to discuss the results obtained in pure sucrose solution first and then that of the sucrose–water system.

Figs. 8–12 show the increase of relaxation rates as the concentration of pure sucrose is increased. The increase in the value of relaxation rates generally indicates a greater association of molecules in these solutions (Srinivasa Rao et al., 1990a). This greater association may be due to the formation of hydrogen bonds between OH groups of sugars and oxygen of water molecules (Gutierrez & Baianu, 1989; Srinivasa Rao et al., 1990b). Furthermore, additional contributions to relaxation may arise from the chemical exchange of protons or cross-relaxation.

This behaviour can also be explained on the basis of a two-state fast exchange model proposed by Zimmerman

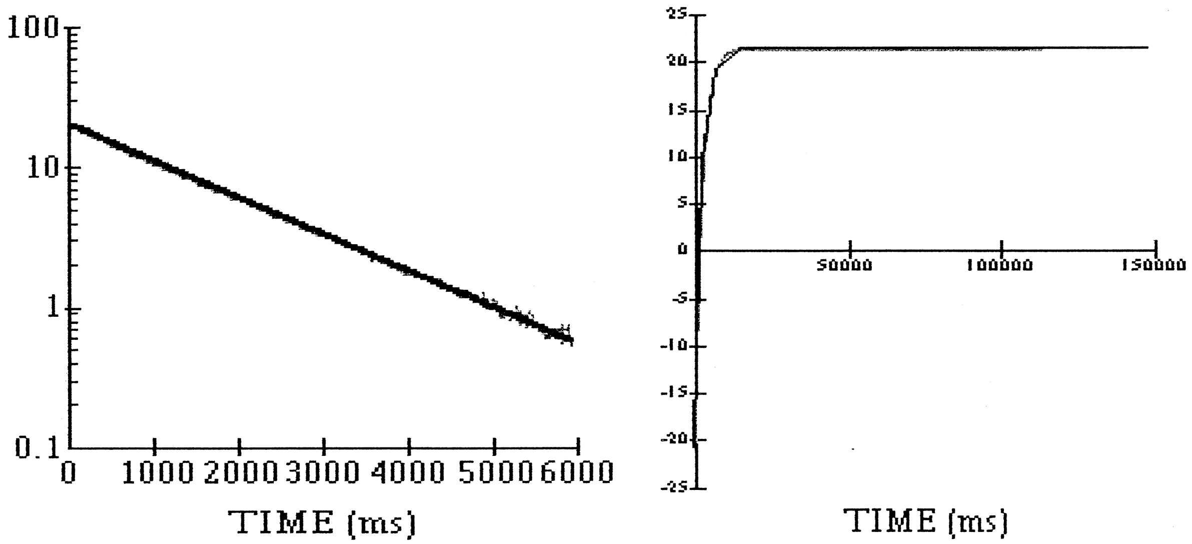

Fig. 6. The decay of magnetisation (showing mono-exponential).

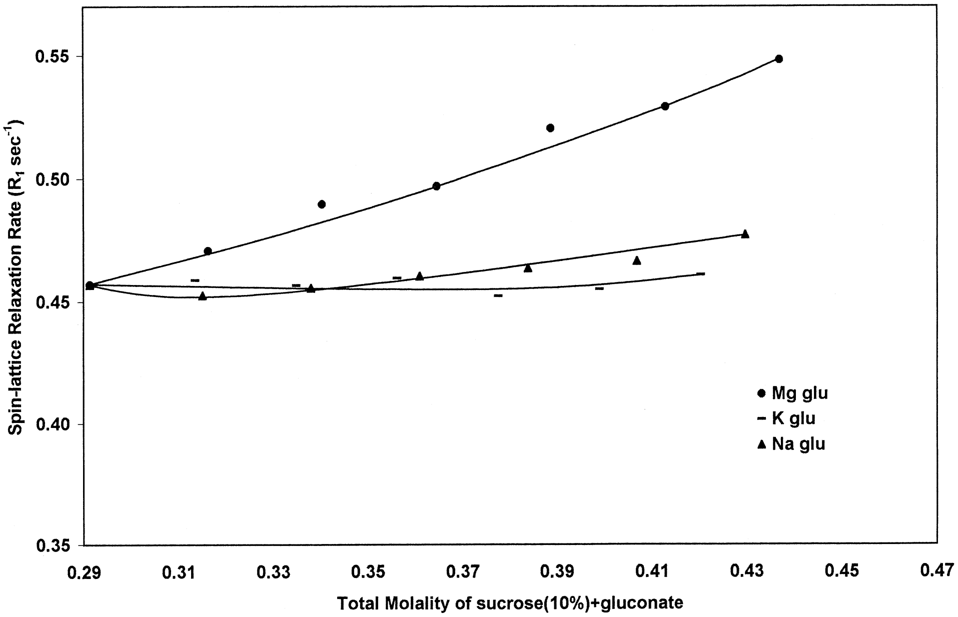

Fig. 7. The dependence of proton spin-lattice relaxation rate (R_1) as a function of fixed (10% sucrose) with increasing concentration of Mg, K and Na gluconate. The measurements were carried out using Oxford QP20+ NMR Process analyser as described in the experimental set-up.

and Brittin (1957). This assumes that when substances of large molecular weights are dissolved in water, a small fraction of water is attached to the macromolecules and this is highly immobilized. The rest of the water is like ordinary water (called bulk water) and rapid exchange between these two fractions would yield average spin-lattice relaxation rate (R_{1s}) weighted heavily by the small immobile fraction. If "f" is the fraction of water attached to the molecules, then spin-lattice relaxation R_{1s} of the solution can be written as

$$R_{1s} = f.R_{1A} + (1 - f).R_{1w}$$

where R_{1w} is the relaxation rate of the free water (bulk water) and R_{1A} is the relaxation rate of the small fraction

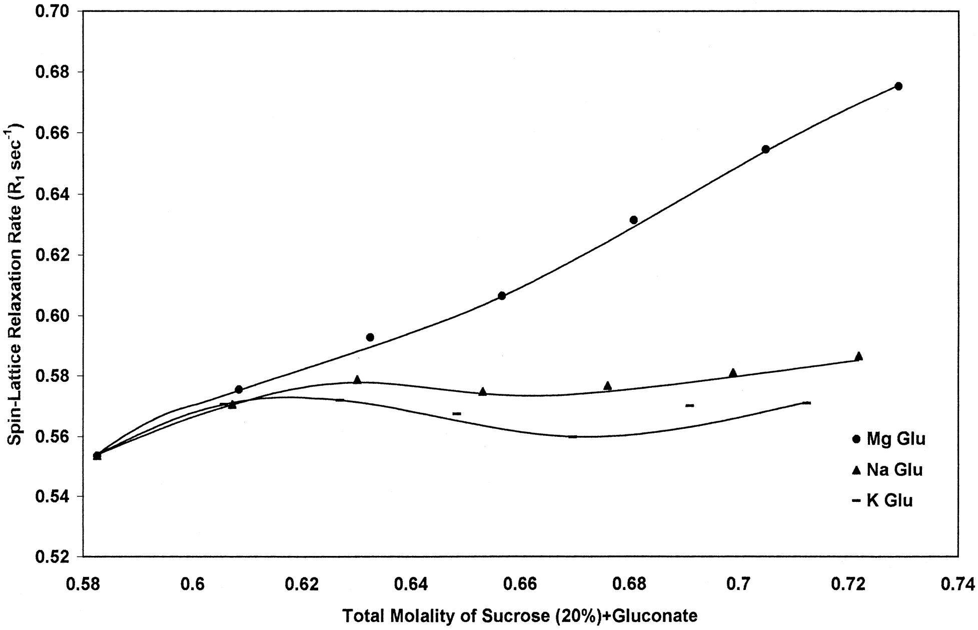

Fig. 8. The dependence of proton spin-lattice relaxation rate (R_1) as a function of fixed (20% sucrose) with increasing concentration of Mg, K and Na gluconate.

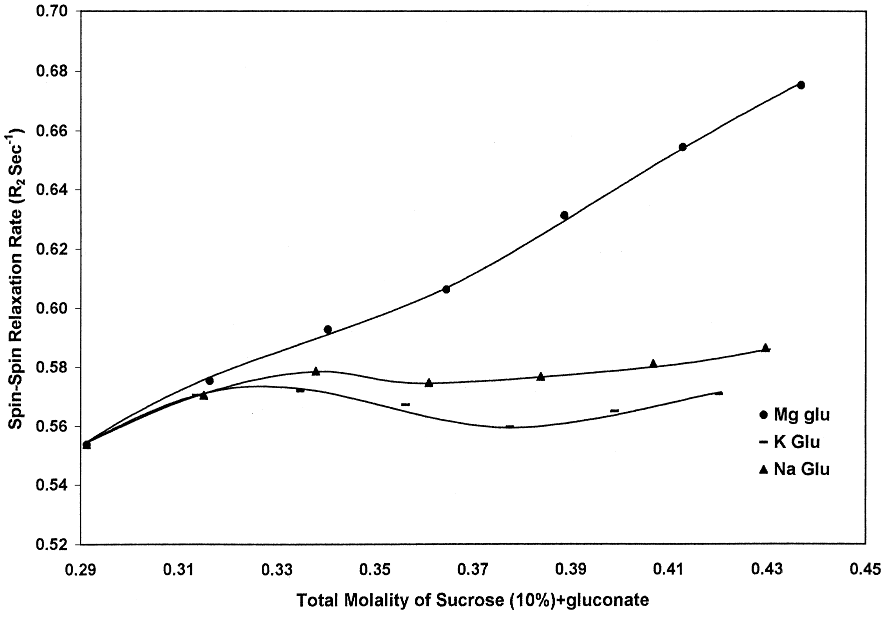

Fig. 9. Proton spin–spin relaxation rate (R_2) as a function of fixed (10% sucrose) with increasing concentration of Mg, K and Na gluconate.

attached to the molecules, R_{1A} being much faster than R_{1W}. From the above equation, it can be seen that an increase in the value of "*f*" results in an increase in the R_{1S}. The increase in the value of spin-lattice relaxation rate (R_1) in (pure) aqueous solutions of sugars with increase of solute concentration can be explained by the increase in the fraction "*f*" of the water attached to the sugar molecules (Arulmozhi & Srinivasa Rao, 1993). This fraction "*f*" is likely to decrease as the sugar concentration is increased which results in a further increase of spin-lattice relaxation rate (R_1).

The evolution of (R_1) and (R_2) of 10 and 20% sucrose solutions with increasing concentrations of magnesium, sodium and potassium gluconates show that the relaxation rates increase as the concentration of gluconate is increased. The increase is much more rapid in the case of Mg gluconate than with K and Na gluconates simply because of the higher molecular weight of the magnesium salt. Magnesium is also known as a water 'structure-maker', which restricts the overall motional freedom of water molecules. This restriction results in a decrease of 'bulk' water fraction, whereas the relative amount of 'bound' water increases. This leads to an increase in the values of relaxation rates (R_1) and (R_2). These results are in agreement with our earlier NMR relaxation studies in aqueous solutions of alkali halides and sugars (Arulmozhi & Srinivasa Rao, 1993; Sattiacoumar & Arulmozhi, 1993).

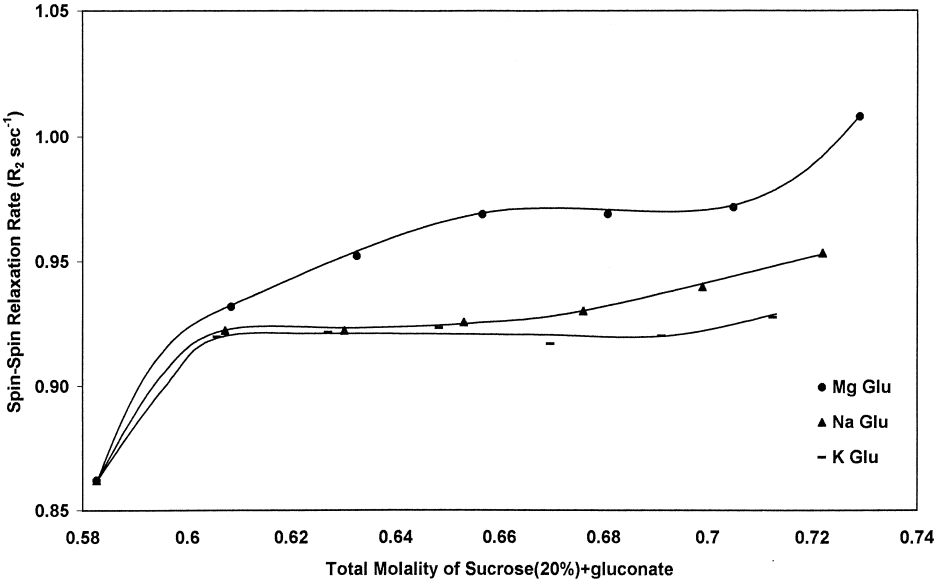

Fig. 10. Proton spin–spin relaxation rate (R_2) as a function of fixed (20% sucrose) with increasing concentration of Mg, K and Na gluconate.

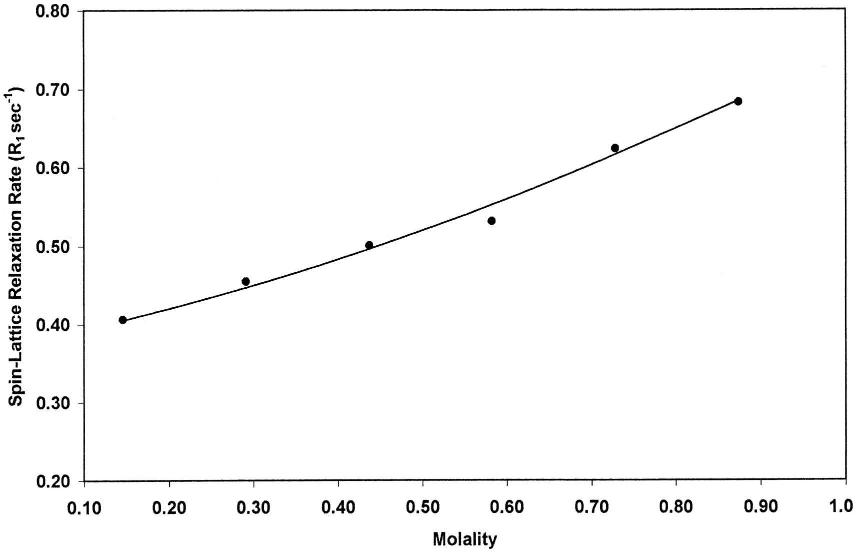

Fig. 11. Spin-lattice relaxation rate (R_1) versus molality of sucrose.

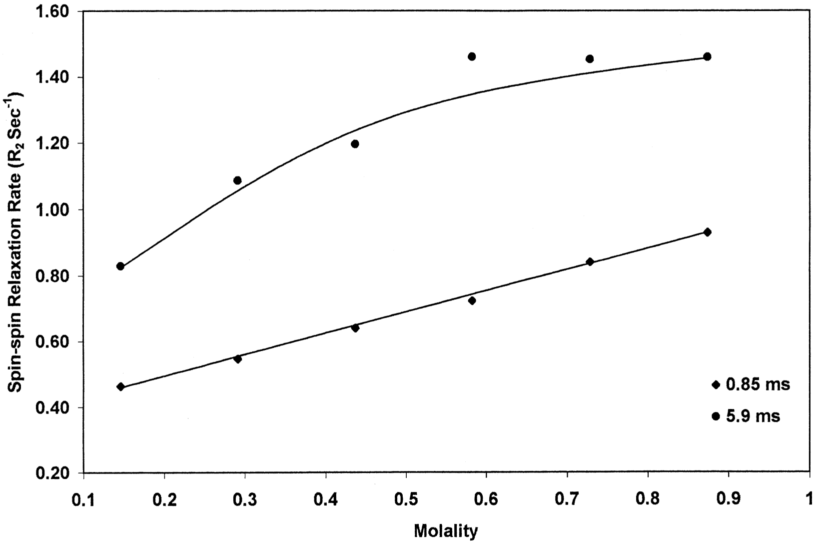

Fig. 12. Spin–spin relaxation rate (R_2) versus molality of sucrose with two interpulse delays.

The apparent specific volumes of all three gluconates examined in this work were similar and near the sour–sweet borderline (Shamil et al., 1987) though mainly in the sour range. They possess no free protons and therefore taste bland which makes them ideal candidates for possible taste modulation purposes. The solution properties reported here might be useful indices of their taste behaviour in mixtures.

4. Conclusion

Experimental data for density, sound velocity and ^{1}H NMR relaxation rates of pure Mg, K, Na gluconates and gluconate sucrose mixtures in aqueous solutions are reported. The values of AMV, ASV, hydration number and isentropic apparent molar compressibility are calculated from the measured data. The results of ASV indicate that the molecules of Na, K and Mg gluconates lie near the borderline of sour and sweet molecules. The results of IAMC show that Na and K gluconate fits into water structure best while the hydration layer is least disturbed as compared to bulk water, whereas the addition of Mg gluconate leads to a strong disturbance of the structure of water.

The results for IAMC of 10 and 20% sucrose solutions in the presence of Na, K and Mg gluconates show that, in the presence of Mg gluconate the hydration layer of the sucrose is more disturbed than is bulk water. We believe that all sapid molecules mediate their taste effects through water. Their effective size depends on their state of hydration. The variation of water compatibility affects molecular hydration, which in turn affects accession to site and interaction with receptor. Therefore molecules having better packing characteristics in the water structure can be anticipated to exchange hydration water for receptors the quickest. We are currently engaged in further research to examine the sweet–bitter interaction with reference to the bitterness masking effect of gluconates.

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