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Mobility of water in various sugar–water systems as studied by oxygen-17 NMR

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Proton decoupled oxygen-17 NMR transverse relaxation rates (R_2, s^{-1}) were used to measure the mobility of water in three sugar solutions, lactose (L), sucrose (S) and fructose (F), and their solution combinations, L : S, L : F and S : F, as a function of concentration and combination ratio (1 : 9, 1 : 1 and 9 : 1). The behavior of R_2 as a function of concentration for the single sugar solutions was similar at low concentrations. However, at high sugar concentrations deviations for sucrose and fructose were observed. The R_2 of the sugar solution combinations (L : S, L : F and S : F) at low concentrations was not influenced by sugar type or combination ratio, but only by the total concentration of the sugars present. A mass balance approach was used to predict the R_2 of the sugar solution combinations; however only at low total sugar concentrations did the equation adequately predict the experimentally obtained R_2 values.

INTRODUCTION

Water is an important constituent of food systems, because it influences so many process variables, product characteristics, and stability attributes. It has been long recognized that the actual water content of a food is an imprecise indicator of stability (Van den Berg & Bruin, 1981; Franks, 1982); rather it is the 'availability' of water that determines its ability to participate in deteriorative reactions, such as non-enzymatic browning (Labuza & Saltmarch, 1981), lipid oxidation (Drapron, 1985) and microbial activity (Leistner & Rodel, 1976; Troller, 1980; Beuchat, 1981; Karel, 1989). Thus, controlling the 'availability' of the water in food systems is vital to extending the shelf-life of a food. One popular means of controlling water 'availability' in foods is the addition of sugars. For example, sucrose and glucose are used as humectants in intermediate moisture foods to help reduce the 'availability' of the water, while maintaining a soft palatable texture (Lindsay, 1985).

One of the most successful techniques to probe the 'availability' of water in food systems is nuclear magnetic resonance (NMR) spectroscopy (Richardson *et al.*, 1986; Mora-Gutierrez & Baianu, 1989; Kakalis *et al.*, 1990; Lai & Schmidt, 1990*a*; Schmidt & Lai, 1991). NMR spectroscopy provides a noninvasive means of determining the molecular mobility of water in complex systems. The molecular rotational mobility, as measured by the NMR longitudinal (R_1 or $1/T_1$, s^{-1}) and transverse (R_2 or $1/T_2$, s^{-1}) relaxation rates, is related to the 'availability' of the water in the system. That is, as R_1 or R_2 increases, the mobility or 'availability' of the water decreases.

The use of NMR spectroscopy to study the effect of individual sugars on the mobility of water has been investigated by several researchers (Tait *et al.*, 1972; Suggett *et al.*, 1976; Belton & Wright, 1986; Richardson *et al.*, 1987; Mora-Gutierrez & Baianu, 1989; Padua, 1989; Lai & Schmidt, 1990*b*, 1991; Hills, 1991; Belton *et al.*, 1991). Tait *et al.* (1972), studying the transverse relaxation time (T_2, s) of glucose solutions as a function of concentration (up to 35% solids), reported an increase in the ^{17}O NMR line widths with increasing concentration. They attributed this increase in the line widths to viscosity effects. Belton & Wright (1986) studied the ^{17}O NMR R_1 and R_2 of sucrose solutions over the range 0–70% w/w from 28 to 92°C. They also found that the ^{17}O NMR R_1 and R_2 values increased with increasing sucrose concentration and were depedent on viscosity and concentration effects. Padua (1989) investigated the mobility of water in concentrated sugar solutions (0·2–2 g sugar/g water) by low field proton (^{1}H) NMR R_1 measurements. Observed increases in water mobility with increasing sugar concentration were also hypothesized to be due to viscosity effects, in agreement with Tait *et al.* (1972). Lai & Schmidt (1990*b*) determined the water mobility and crystallization behavior of lactose–water systems using ^{17}O and carbon-13 (^{13}C) NMR spectroscopy. They reported that R_2 increased with increasing sugar concentration and

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hypothesized that the decrease in water mobility (i.e. increase in R_2) at high sugar concentrations was due to the development of hydrogen bonds between the water and the sugar and the sugar with itself. Belton *et al.* (1991) reported ^{17}O NMR relaxation data for a series of $\alpha(1\text{–}4)$ linked glucans. A two-site exchange model where the 'bound' water reorients anisotropically was used to quantitatively interpret their relaxation results.

Although NMR spectroscopy has been used to study the mobility of water in several individual sugar–water systems, the combination of various sugars and their resultant effects on water mobility has not received equal attention. Thus, the objectives of this research were: (1) to investigate the water mobility of three single sugar–water solutions (lactose, sucrose and fructose) and their combinations (lactose : sucrose, lactose : fructose and sucrose : fructose) by ^1H decoupled ^{17}O NMR transverse relaxation rate measurements as a function of concentration and sugar : sugar ratio, and (2) to compare the experimentally obtained mobility values for the sugar solution combinations to calculated mobility values. The calculated mobility values were based on the mobility of the water in the single sugar–water solutions, using a mass balance approach.

MATERIALS AND METHODS

Materials

Lactose (Sigma Chemical Co., St Louis, MO), which contained 98% α-lactose monohydrate and 2% β-lactose (manufacturing specifications), sucrose (J. T. Baker, Phillipsburg, NJ) and fructose (A. E. Staley Manufacturing Co., Decatur, IL) were used to prepare the sugar solutions. The moisture content of the sugars was determined by the vacuum oven method, using 60°C and 29·8 inches Hg vacuum for 24 h. The moisture content of lactose was 0·025 g water/100 g sample, while sucrose and fructose contained no removable moisture.

Sample preparation

Three different sugar solution combinations, lactose and sucrose (L : S), lactose and fructose (L : F), and sucrose and fructose (S : F), at three different ratios, 1 : 9, 1 : 1 and 9 : 1, were prepared with distilled water (pH = 5·6 ± 0·1). Concentration of the solutions ranged from 5·26 to 66·67 g sugar/100 g water for L : S and L : F, and 11·11 to 175 g sugar/100 g water for the S : F combination. Single sugar solutions, lactose, sucrose and fructose alone, were prepared at concentrations corresponding to the sugar solution combination concentrations.

For example, to prepare a 5·26 g sugar/100 g water solution at the ratio of L : S = 1 : 9, 0·526 g of lactose crystals (5·26 g sugar × 1/10) and 4·734 g of sucrose crystals (5·26 g sugar × 9/10) were added to the same screw capped test tube. Then 100 g distilled water were added to make the L : S sugar solution combination. At the same time, the same amounts of lactose (0·526 g lactose) and sucrose (4·734 g sucrose) were added separately to two test tubes, then 100 g of distilled water were added to each test tube to make the single sugar solutions. The sugar solutions were then kept in a 75°C water bath and inverted several times until the sugar crystals were completely dissolved. The sugar solutions were then cooled to room temperature (23 ± 1°C) and transferred to 10 mm NMR tubes.

^1H decoupled ^{17}O NMR R_2 measurements

A GN 300NB NMR spectrometer (General Electric Inc., Fremont, CA) operating at 40·68 MHz ^{17}O NMR resonance frequency was used for the ^{17}O NMR measurements. A multinuclear 10 mm probe was used. Single-pulse ^1H decoupled ^{17}O NMR experiments were done in duplicate at 20 ± 1°C. A 90° ^{17}O pulse width of 35 μs and a recycling time of 205·87 ms were used. The MLEV decoupling sequence with a proton frequency of 300·06 MHz and a 90° proton pulse of 71 μs was used. The decoupling field was 3521 Hz. The number of scans necessary to obtain an adequate signal to noise ratio ranged from 500 to 2000 depending on the concentration. The spectra were retained in an 8 K point array with an ADC of 12 bits.

The mobility of water in each of the samples was monitored by measuring the ^1H decoupled ^{17}O NMR transverse relaxation rate (R_2, s^{-1}). The line width (ν_{obs}) at half-height of each spectrum was obtained by using the computer line fit routine available on the GN 300 NIC 1280 computer software (General Electric Inc., Fremont, CA). R_2 (s^{-1}) was then calculated from the line width by (Dwek, 1973):

$$R_2\,(s^{-1}) = \pi\nu_{obs}\,(s^{-1}) = 1/T_2\,(s) \qquad (1)$$

All R_2 measurements were done in duplicate. The experimental error associated with measuring R_2 was 0·8%.

Mass balance calculations of R_2

A mass balance approach was used to calculate a predicted value of R_2 for the sugar solution combinations. It was hypothesized that the R_2 of the sugar solution combination was equal to the sum of the net relaxation rates of the component single sugar solutions ($R_{2i} - R_{2(water)}$), at the concentration they were present at in the sugar solution combination, plus the relaxation rate of pure water at the same temperature ($R_{2(water)}$):

$$R_{2(cal)} = \sum_{n} (R_{2i} - R_{2(water)}) + R_{2(water)} \qquad (2)$$

where $R_{2(cal)}$ is the calculated R_2 for the sugar solution combination at the desired total sugar concentration and ratio; n (n = 2) is the number of different sugars in the sugar solution combination; R_{2i} is the R_2 of each single sugar solution at the concentration they were present at in the sugar solution combination; and $R_{2(\mathrm{water})}$ is the R_2 for pure water.

For example, to calculate $R_{2(\mathrm{cal})}$ for a 5·26 g sugar/100 g water lactose : sucrose solution combination at the 1 : 9 ratio, R_{2i} values for lactose at 1/10 of the concentration of the solution combination (162·55 s^{-1}), sucrose at the 9/10 of the concentration of the sugar combination (182·33 s^{-1}) and pure water (162·09 s^{-1}) must be measured. $R_{2(\mathrm{cal})}$ can then be calculated using eqn (2) as:

$$R_{2(\mathrm{cal})} = (162{\cdot}55 - 162{\cdot}09\ (\mathrm{s}^{-1})) + (182{\cdot}33 - 162{\cdot}09\ (\mathrm{s}^{-1})) + 162{\cdot}09\ \mathrm{s}^{-1} = 182{\cdot}79\ \mathrm{s}^{-1}$$

The calculated R_2 values were then compared to the experimentally obtained R_2 values, in order to assess possible interactions in the various sugar combinations studied.

Viscosity data

Kinematic viscosity values (η/ρ, cS) at 20°C for the single sugar–water systems were obtained from the *CRC Handbook of Chemistry and Physics* (CRC Handbook, 1986).

RESULTS AND DISCUSSION

Single sugar solutions

The ^1H decoupled ^{17}O NMR transverse relaxation rate (R_2, s^{-1}) measurements for lactose, sucrose and fructose solutions as a function of concentration are shown in Fig. 1. The insert in Fig. 1 shows details of the lower concentration range, 0–80 g sugar/100 g water. The concentration of these sugar solutions ranged from 0·526 to 75 g lactose/100 g water for the lactose solutions and 0·526 to 157 g sucrose or fructose/100 g water for the sucrose and fructose solutions. The upper concentration limit of these solutions was based on the saturation solubility value of each sugar. At 20°C sucrose and fructose have saturation solubility values of 199·4 g sucrose/100 g water (Charles, 1960) and 374·8 g fructose/100 g water (Bates & Associates, 1942), respectively, while lactose has a much lower saturation solubility of 19·25 g lactose/100 g water (Whittier, 1944). All three of the single sugar solutions exhibited an increase in R_2 (i.e. a decrease in water mobility) with increasing sugar concentration. This behavior has also been observed by other researchers for solutions of glucose, sucrose, ribose, maltose, fructose and lactose (Tait *et al.*, 1972; Suggett *et al.*, 1976; Belton & Wright, 1986; Richardson *et al.*, 1987; Mora-Gutierrez & Baianu, 1989; Padua, 1989; Lai & Schmidt, 1990*b*, 1991; Belton *et al.*, 1991; Hills, 1991).

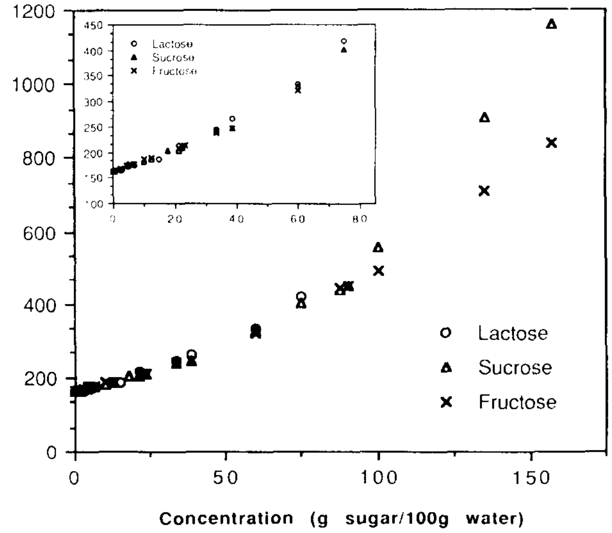

Fig. 1. Variation of ^1H decoupled ^{17}O NMR transverse relaxation rates (R_2, s^{-1}) with increasing single sugar solution concentration. Insert shows details of the low concentration range, 0–80 g sugar/100 g water.

From 0·526 to 75 g sugar/100 g water, all three single sugar solutions yielded very similar R_2 values. This similarity in R_2 values is attributed to the similarity in viscosities of these sugars in this concentration range (discussed in detail below). Above approximately 90 g sugar/100 g water, however, the fructose solutions showed consistently lower R_2 values than the sucrose solution at the same concentration. This indicates that at the same concentration of fructose and sucrose the water in the fructose solution is more mobile than the water in the sucrose solution. This difference in R_2 values between the two sugars corresponds to an emerging difference in their kinematic viscosity values at higher concentrations (Fig. 2). At low sugar concentrations, the differences in the kinematic viscosity values at the same sugar concentration are negligible, whereas at higher concentrations (greater than approximately 90 g sugar/100 g water) the differences become more sizable. For example, at 25 g sugar/100 g water the kinematic viscosity values for fructose and sucrose are 1·7 and 1·8 cS, respectively, whereas at 150 g sugar/100 g water, the values are 25·3 and 45·5 cS, respectively (CRC Handbook, 1986). Padua (1989) also reported higher R_1 values in sucrose solutions than in fructose solutions at the same concentration using low-field ^1H NMR spectroscopy.

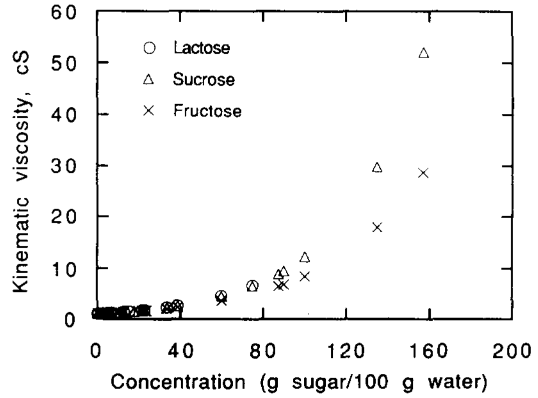

Fig. 2. Kinematic viscosity values (η/ρ, cS) for lactose, sucrose and fructose as a function of concentration (g sugar/100 g water).

Sugar solution combinations

The variation in R_2 for the various sugar solution combinations, S : F, L : S and L : F, at the three ratios (1 : 9, 1 : 1 and 9 : 1) as a function of concentration is shown in Figs 3–5, respectively. The R_2 values for the appropriate single sugar solutions as a function of concentration are also plotted in each figure for comparison purposes.

For the S : F sugar solution combination (Fig. 3), at sugar concentrations below 100 g sugar/100 g water, the increase in R_2 with increasing sugar concentration followed the same curve for both the sugar solution combinations and the single sugar solutions. This indicates that the mobility of water in each of the sugar solutions was dependent on the total sugar concentration, rather than the sugar type or ratio below 100 g sugar/100 g water.

At sugar concentrations above 100 g sugar/100 g water, the S : F (9 : 1) solutions had much larger R_2 values than the S : F (1 : 1) and S : F (1 : 9) solutions. At this concentration and above, the R_2 values of the sugar solution combinations were closest to the single sugar R_2 values of the dominant sugar component.

For the L : S and L : F sugar solution combinations (Figs 4 and 5), the increase in R_2 with increasing sugar concentration (from 5·26 to 75 g sugar/100 g water) followed the same curve for both the sugar solution combinations and the single sugar solutions, as observed in the S : F sugar solution combination up to 100 g sugar/100 g water. Neither the sugar type nor the sugar combination ratio appeared to greatly affect the water mobility in the L : S and L : F solutions at concentrations ranging from 0·526 to 75 g sugar/100 g water.

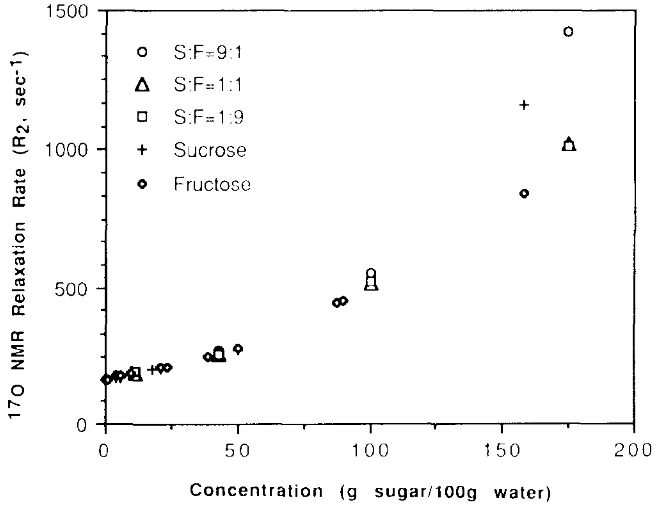

Fig. 3. Variation of ^{1}H decoupled ^{17}O NMR transverse relaxation rates (R_2, s^{-1}) with increasing concentration of the sucrose : fructose (S : F) sugar solution combination at three combination ratios, 1 : 9, 1 : 1 and 9 : 1. The R_2 values for sucrose and fructose solutions (alone) are also shown for comparison purposes.

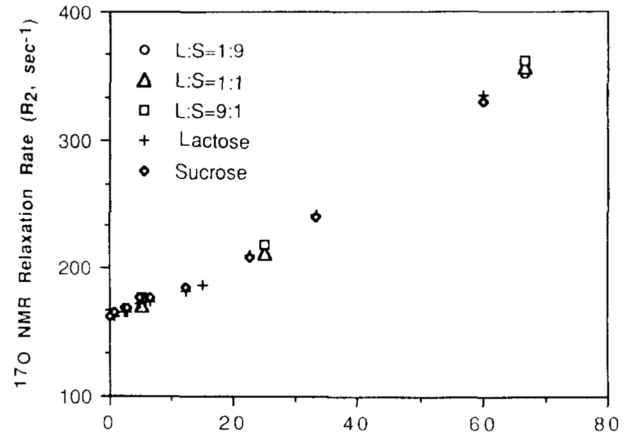

Fig. 4. Variation of ^{1}H decoupled ^{17}O NMR transverse relaxation rates (R_2, s^{-1}) with increasing concentration of the lactose : sucrose (L : S) sugar solution combination at three combination ratios, 1 : 9, 1 : 1 and 9 : 1. The R_2 values for lactose and sucrose solutions (alone) are also shown for comparison purposes.

Comparison of experimental and calculated R_2 values for the sugar solution combinations

The experimental and calculated R_2 values for the S : F solution combination at the three combination ratios (1 : 9, 1 : 1 and 9 : 1) are shown in Figs 6(a), 6(b) and 6(c), respectively. At low total sugar concentrations (below 50 g sugar/100 g water) the differences between the experimental and calculated R_2 values were very small. This indicates that the R_2 of single sugar solutions was additive, and the R_2 of the sugar solution combinations can be predicted from eqn (2). However, at high total sugar concentrations the difference between the experimental and calculated R_2 values increased with increasing sugar concentration. Thus,

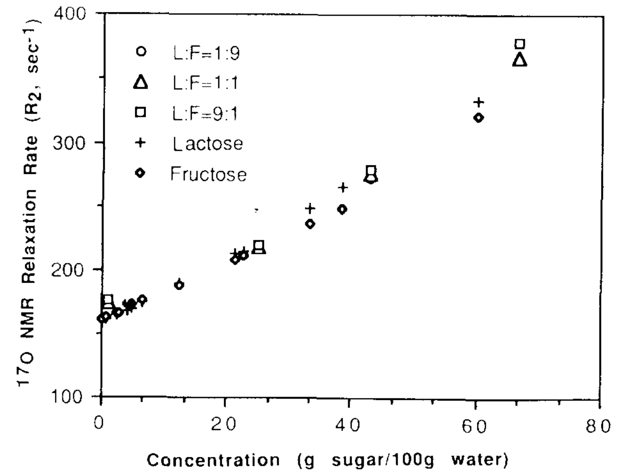

Fig. 5. Variation of ^{1}H decoupled ^{17}O NMR transverse relaxation rates (R_2, s^{-1}) with increasing concentration of the lactose : fructose (L : F) sugar solution combination at three combination ratios, 1 : 9, 1 : 1 and 9 : 1. The R_2 values for lactose and fructose solution (alone) are also shown for comparison purposes.

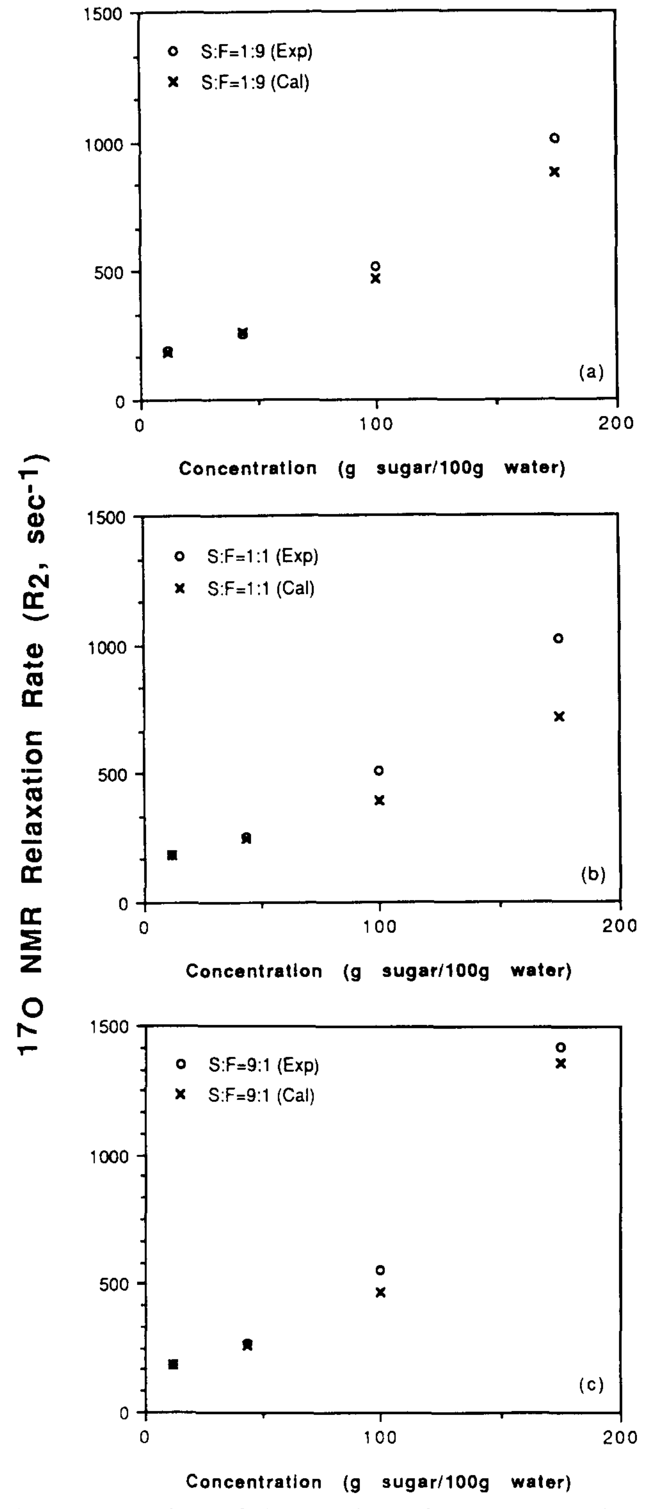

Fig. 6. Comparison of the experimental, $R_{2(exp)}$, and calculated $R_{2(cal)}$, relaxation values for the sucrose : fructose (S : F) sugar solution combination at the three combination ratios: (a) 1 : 9, (b) 1 : 1 and (c) 9 : 1.

eqn (2) was no longer able to predict the R_2 of the sugar solution combinations when the total sugar concentration was greater than 50 g sugar/100 g water.

As discussed above for the S : F sugar combination, the experimentally obtained R_2 of the sugar solution combination was closest to the single sugar solution R_2 value of the dominant sugar component at the same total sugar concentration. This behavior was also found to be the case for the $R_{2(cal)}$ values predicted by eqn (2) for the different sugar solution combination ratios. The difference between the experimental and calculated R_2 of the sugar solution combinations was largest at the 1 : 1 ratio than at the 1 : 9 and 9 : 1 ratios.

Similar results were found for the L : S and L : F sugar solution combinations (figures not shown). The differences between the experimental and calculated R_2 were largest for the 1 : 1 ratio than at the 1 : 9 and 9 : 1 ratios. Thus, eqn (2) fails to adequately predict the R_2 observed at high total sugar concentrations since it does not take into account the effect of viscosity on R_2.

CONCLUSIONS

The behavior of R_2 for lactose, sucrose and fructose solutions, as a function of concentration, was similar at low sugar concentrations, but differed at high sugar concentrations. At high sugar concentrations the water in the fructose solutions was found to be more mobile than the water in the sucrose solutions at the same concentration. This was attributed to the difference in the kinematic viscosity values between the two sugar solutions at higher concentrations. At low total sugar concentrations, the R_2 values of the sugar solution combinations were not affected by either sugar type or the sugar combination ratio. However, at high total sugar concentration the R_2 values of the sugar solution combinations were closest to the single sugar solution R_2 values of the dominant sugar component. At low sugar concentration, a mass balance approach can be used to predict the R_2 of the sugar solution combinations. However, at higher concentrations the mass balance approach no longer adequately predicted R_2, since the approach does not take into account the effect of viscosity on R_2.

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