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Carbohydrate Research 341 (2006) 2516–2520
Carbohydrate RESEARCH

The glass transition temperatures of sugar mixtures

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Received 4 July 2006; received in revised form 9 August 2006; accepted 16 August 2006
Available online 7 September 2006

Abstract—We measured the glass transition temperatures of mono-, di-, and trisaccharide mixtures using differential scanning calorimeter (DSC) and analyzed these temperatures using the Gordon–Taylor equation. We found that the glass transition temperatures of monosaccharide–monosaccharide and disaccharide–disaccharide mixtures could be described by the conventional Gordon–Taylor equation. However, the glass transition temperatures of monosaccharide–disaccharide and monosaccharide–trisaccharide mixtures deviated from the conventional Gordon–Taylor equation and the amount of deviation in the monosaccharide–trisaccharide mixtures was larger than those in the monosaccharide–disaccharide mixtures. From these results, we conclude that the size and shape of the sugars play an important role in the glass transition temperature of the mixtures.

Keywords: Sugar mixture; Glass transition temperature; Gordon–Taylor equation; DSC; TG-DTA

1. Introduction

Glass forming sugars have a great significance in nature. Nature makes use of sugar glasses to protect biological tissues in the dehydrated state.[1–10] It has generally been accepted that sugar-containing cells usually form a glassy state of sugars under extreme conditions. The ability of sugars to preserve biological molecules has been recognized for many years in food science, biology, biochemistry, and pharmaceutical disciplines.[11–15] Recently, several groups have studied the microscopic origins of the cell protection processes of sugar glasses using a variety of experimental techniques[7,16–21] and have reported that the glass transition temperature of sugars and sugar-containing materials may be linked to cell protection abilities.[22] Therefore, the study of the glass transition temperatures of various sugar mixtures is an interesting and important topic for understanding the mechanism of these protection processes.[3,23–26] The glass transition temperatures of mixtures were studied by Gordon and Taylor,[27] Fox,[28] and Couchman and Karasz[29] about 50 years ago. In 1993, Roos found that the Gordon–Taylor equation was a good approximation of glass transition temperatures in sugar–water mixtures.[30]

In this paper, we studied the glass transition temperatures of various sugar mixtures. We found that glass transition temperatures of monosaccharide–monosaccharide (sorbitol–glucose) and disaccharide–disaccharide (sucrose–trehalose) mixtures could be described by the conventional Gordon–Taylor equation. However, the glass transition temperatures of monosaccharide–disaccharide (sorbitol–sucrose, glucose–sucrose) and monosaccharide–trisaccharide (glucose–maltotriose) mixtures showed a deviation from the Gordon–Taylor equation. We introduced the modified Gordon–Taylor equation to analyze the glass transition temperatures and were able to fit the glass transition temperatures of monosaccharide–disaccharide, monosaccharide–trisaccharide mixtures. Based on our observations, we conclude that the size and shape of the mixture components play an important role in the glass transition temperature.

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doi:10.1016/j.carres.2006.08.014

2. Experimental

The sugars used in this study were monosaccharides (sorbitol, glucose), disaccharides (sucrose, trehalose), and trisaccharides (maltotriose). The molecular weights of the monosaccharides, disaccharides, and trisaccharides are 180.2, 342.3, and 504.5 g/mol, respectively. Glucose, sorbitol, sucrose, and maltotriose were purchased from Sigma Chemical Co. and were used without further purification. Trehalose dihydrate was donated by the Cargill Corporation. All sugar samples were dried by using a moisture analyzer (Sartorius MA100, Germany)[31–33] before the experiments.

Five different mixtures (sorbitol–glucose, sucrose–trehalose, sorbitol–sucrose, glucose–sucrose, and glucose–maltotriose) were used in this study. We prepared 2 g of a powder mixture and ground it in an agate bowl for 5 min. We then used 20 mg of mixed powder to measure the glass transition temperature. The glass phases of the mixtures were prepared by using the thermogravimetry-differential thermal analysis (TG-DTA: MAC science, DTA 2000S, Japan) and were confirmed by X-ray diffraction measurements.[34] The glass transition temperatures of mixtures were measured by using the differential scanning calorimeter (DSC; MAC science, DSC3100, Japan). The glass transition temperatures were measured during heating at a rate of 4 °C/min and were determined as the midpoint between the onset and the end point in the heat flow versus temperature plot. We observed only one glass transition temperature in the DSC measurements. All measurements were repeated more than four times and the sample was newly prepared for every measurement. The glass transition temperatures in different measurements were agreed well with each other, indicating that the weight ratio of components in mixtures was constant. A cylindrical shape aluminum cell was used and the size of the sample cell was 5.2 mm in diameter and 5.1 mm in height. Al_2O_3 was used as a reference material.

3. Results and discussion

The Gordon–Taylor equation has been used for many years to describe the glass transition temperatures of mixtures.

$$T_g = \frac{w_a T_a + k w_b T_b}{w_a + k w_b} \tag{1}$$

Here, T_g is the glass transition temperature of the mixture, w_a and w_b are weight fractions, T_a and T_b are glass transition temperatures of components a and b. The constant k represents the ratio of the thermal expansion coefficient difference between a glassy state and a liquid state between the components a and b.

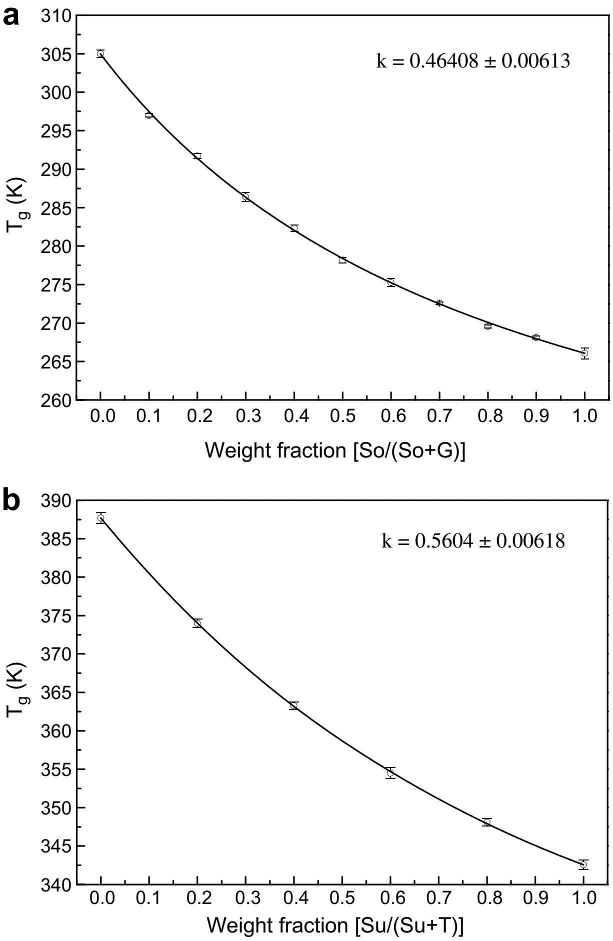

Figure 1. Glass transition temperatures of (a) monosaccharide–monosaccharide (sorbitol–glucose) and (b) disaccharide–disaccharide (sucrose–trehalose) mixtures as a function of weight fraction. The solid lines are fitted results using the Gordon–Taylor equation. In these figures, So, G, Su, and T represent sorbitol, glucose, sucrose, and trehalose, respectively.

Figure 1 shows the glass transition temperatures of monosaccharide–monosaccharide (sorbitol–glucose) and disaccharide–disaccharide (sucrose–trehalose) mixtures. The open circles are the experimental results and the solid lines are the fitted results using the Gordon–Taylor equation. As can be seen in Figure 1, the glass transition temperatures of monosaccharide–monosaccharide (sorbitol–glucose) and disaccharide–disaccharide (sucrose–trehalose) mixtures are well described by the Gordon–Taylor equation. In Figure 1, the k values of the sorbitol–glucose and sucrose–trehalose mixtures and 0.464 and 0.560, respectively, indicating that the thermal expansion coefficient difference between a glassy state and liquid state in glucose and trehalose is about two times larger than those in sorbitol and sucrose.

The Gordon–Taylor equation, shown in Eq. 1, was derived under the assumption that the size and shape of the two components in a mixture are the same so that the packing fraction of the mixture remains the same.[27]

Therefore, as we observed in Figure 1, the glass transition temperatures of sugar mixtures composed of the same sugar units, such as monosaccharide–monosaccharide and disaccharide–disaccharide mixtures, can be well described by the Gordon–Taylor equation. However, when the components of the mixture have different sizes and different shapes the packing fractions of the mixture and the components are different. Therefore, we can predict that the glass transition temperatures of sugar mixtures consisting of sugar units with different sizes and shapes will deviate from the Gordon–Taylor equation.

Figure 2a and b shows the glass transition temperatures of two monosaccharide–disaccharide ((a) sorbitol–sucrose and (b) glucose–sucrose) mixtures. We tried to fit the data with the Gordon–Taylor equation and showed the fitting results as dashed lines. It can clearly be observed that the measured data deviated from the fitting lines. Therefore, we modified the Gordon–Taylor equation to analyze the glass transition temperatures of sugar mixtures. It was not possible to have an analytical solution of the Gordon–Taylor equation with a nonlinear volume mixing effect, so we simply appended the exponent n to the weight fraction w in the Gordon–Taylor equation as shown below:

$$T_{\mathrm{g}} = \frac{w_{\mathrm{a}}^{n} T_{\mathrm{a}} + k' w_{\mathrm{b}}^{n} T_{\mathrm{b}}}{w_{\mathrm{a}}^{n} + k' w_{\mathrm{b}}^{n}} \tag{2}$$

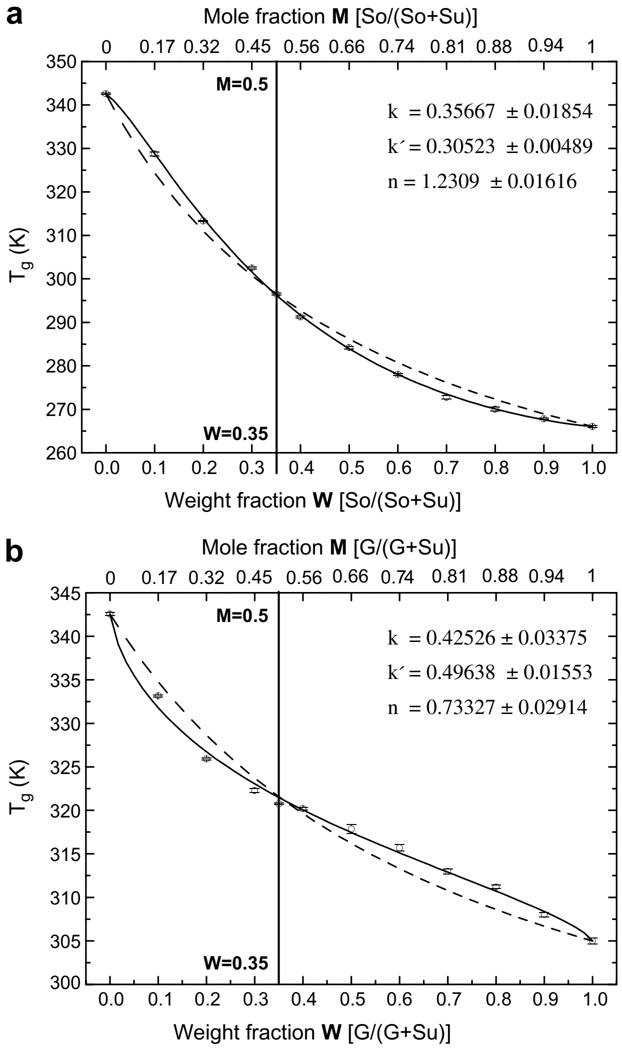

Figure 2. Glass transition temperatures of monosaccharide–disaccharide ((a) sorbitol–sucrose and (b) glucose–sucrose) mixtures as a function of weight fraction and mole fraction. The dashed lines are fitted results using the Gordon–Taylor equation and the solid lines are fitted results using the modified Gordon–Taylor equation. In these figures, So, S, and G represent sorbitol, sucrose, and glucose, respectively.

We expected that the exponent n would compensate for the nonlinear volume mixing effect due to the different sizes and the different shapes of the sugar component. A possible physical meaning of the exponent n might be the degree of nonlinearity in the volume mixing, that is, a larger value of $|\Delta n| \equiv (n-1)$ represents a strong nonlinear effect in the volume mixing. The new parameter k' in Eq. 2 is still related to a thermal expansion coefficient difference between glassy and liquid. However, it is not the same as the parameter k in Eq. 1 because we simply introduced power n to compensate the nonlinear volume effect. We fitted the glass transition temperature of mixtures to Eq. 2 and the results are shown as the solid lines. As can be seen in Figure 2a and b, the modified Gordon–Taylor equation described the measured data well.

A careful inspection of Figure 2a and b revealed that the dashed lines crossed with the solid lines at the point where the weight fraction $W = 0.35$. In the case of monosaccharide and disaccharide mixtures, these crossing points correspond to the case when a mole fraction of the mixture is 0.5. Also, we observed that the trend of curvature of the glass transition temperatures changed at the crossing point. In the case of the sorbitol–sucrose mixture, the data showed downward and upward curvatures when $M < 0.5$ and $M > 0.5$, respectively. On the other hand, in the case of the glucose–sucrose mixture, the trend was the opposite: that is, when $M < 0.5$ the data showed an upward curvature and when $M > 0.5$, the data showed a downward curvature. The fitting parameters also showed opposite trends. In the case of the sorbitol–sucrose mixture, $k' \simeq 0.305$, which is smaller than $k \simeq 0.357$ and $n \simeq 1.231$, which is larger than 1. On the other hand, in the case of glucose–sucrose mixtures, $k' \simeq 0.496$, which is larger than $k \simeq 0.425$ and $n \simeq 0.733$, which is smaller than 1.

In these two mixtures, sucrose was a common component; therefore, the difference must have originated from the difference between glucose and sorbitol. The molecular weights of glucose and sorbitol are 180.16 and

182.2 g/mol, respectively. The weight difference between glucose and sorbitol is less than 1%. On the other hand, the molecular shapes are very different. Glucose is a ring (cyclic) shape and sorbitol is an open-chain (acyclic) shape. Therefore, we believe that the shape of the molecule also plays a critical role in the glass transition temperature of the mixture.

We propose that the deviations of glass transition temperatures from the conventional Gordon–Taylor equation could be caused from the size and shape difference of sugar molecules of mixtures. Therefore, we predicted that the deviation of the glass transition temperature from the conventional Gordon–Taylor equation in monosaccharide–trisaccharide mixtures must be larger than the deviation in monosaccharide–disaccharide mixtures. Figure 3 shows the glass transition temperatures of the monosaccharide–trisaccharide (glucose–maltotriose) mixtures. The solid line is the fitted result using the modified Gordon–Taylor equation and the dashed line is the fitted result using the conventional Gordon–Taylor equation. As expected, the glass transition temperatures showed a clear deviation from the Gordon–Taylor equation and the amount of deviation is larger than that in the monosaccharide–disaccharide mixtures. In the case of the monosaccharide–trisaccharide mixture, the dashed lines also crossed with the solid lines at the point where the weight fraction $W = 0.26$, and this crossing point also corresponds to the case when $M = 0.5$. This is a similar behavior with sorbitol–sucrose mixtures. The k, k', and n values are 0.249, 0.132, and 1.560, respectively. The k and k' of monosaccharide–trisaccharide mixture were the smallest values among the mixtures. We also analyzed $|\Delta n| \equiv (n-1)$ for a quantitative comparison of the degree of deviation from the conventional Gordon–Taylor equation. In the sorbitol–sucrose, glucose–sucrose, and glucose–maltotriose mixtures, $|\Delta n|$ are 0.231, 0.267, and 0.560, respectively, indicating that $|\Delta n|$ increased as the size and the shape differences of components in the sugar mixture increased.

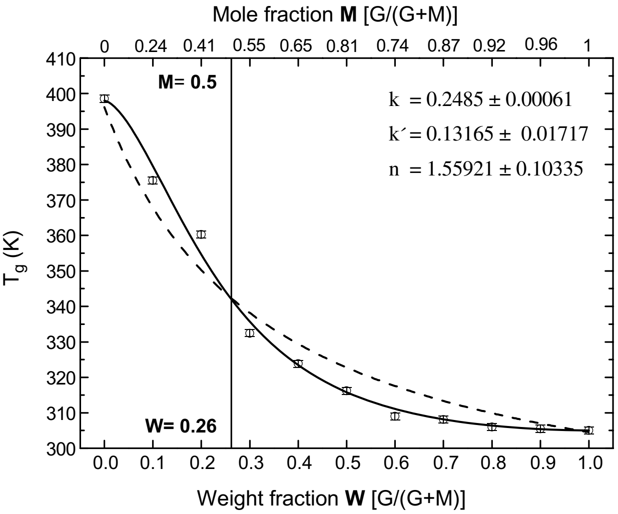

Figure 3. Glass transition temperatures of monosaccharide–trisaccharide (glucose–maltotriose) mixtures as a function of weight fraction and mole fraction. The dashed lines are fitted results using the Gordon–Taylor equation and the solid lines are fitted results using the modified Gordon–Taylor equation. In this figure, G represents glucose and M represents maltotriose.

The glass transition temperature usually depends on various factors such as structure, molecular weight, water quality, and hydrogen bonding between molecules. In this study, we found that the T_g of sugar mixtures deviate from the conventional Gordon–Taylor equation prediction when the components of sugar mixtures have different sizes or different shapes. Also, the deviation patterns depend on the size and shape differences as can be seen in Figures 2 and 3. At this point, we cannot find any systematic deviation pattern with a certain shape or size difference. For example, we were not able to explain why the glucose–sucrose mixture showed downward and upward curvatures when $M < 0.5$ and $M > 0.5$, respectively, and why the sorbitol–sucrose mixture showed the opposite trend. Therefore, it is important in future studies to conduct a microscopic study about the glass transition temperature in the mixture. Currently in progress are molecular dynamic simulations to address the effect of various factors, including size and shape differences and hydrogen bonding on the glass transition temperature.

4. Conclusions

We measured the glass transition temperatures of monosaccharide–monosaccharide (sorbitol–glucose), disaccharide–disaccharide (sucrose–trehalose), monosaccharide–disaccharide (sorbitol–sucrose and glucose–sucrose), and monosaccharide–trisaccharide (glucose–maltotriose) mixtures using differential scanning calorimetry. The glass transition temperatures of sugar mixtures were analyzed using the Gordon–Taylor equation and the modified Gordon–Taylor equation. The glass transition temperature of the monosaccharide–monosaccharide and the disaccharide–disaccharide mixtures were well described by the Gordon–Taylor equation. However, in the monosaccharide–disaccharide and monosaccharide–trisaccharide mixtures, the glass transition temperatures showed a deviation from the Gordon–Taylor equation and the deviation was larger in the glucose–maltotriose mixture. We introduced a modified Gordon–Taylor equation and were able to fit the experimental data. Based on our findings, we conclude that the glass transition temperatures of sugar mixtures are strongly affected by the size and the shape of sugar molecules.

Acknowledgements

We thank H. Z. Cummins for suggesting sugars for a glass transition study. This work was supported by Korea Research Foundation Grant (KRF-2004-005-C00065) and partially supported by BK 21 project.

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