# Suplementary Information:

## Glass Transition Temperature of Saccharide Aqueous Solutions Estimated with the Free Volume / Percolation Model

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## 1. Calculation of the molar volume of pure trehalose at supercooled conditions

The molar volumes, $V_m$, of the aqueous trehalose solutions in the liquid and supercooled regions were calculated from the volumetric data for aqueous trehalose solutions reported by Miller et al. [1] in the trehalose mole fraction $0.0890 \leq x_2 \leq 0.0117$, and temperatures between 258 K and 293 K. As can be observed in Fig. S1, $V_m$ is linear with temperature all over the concentration range studied.

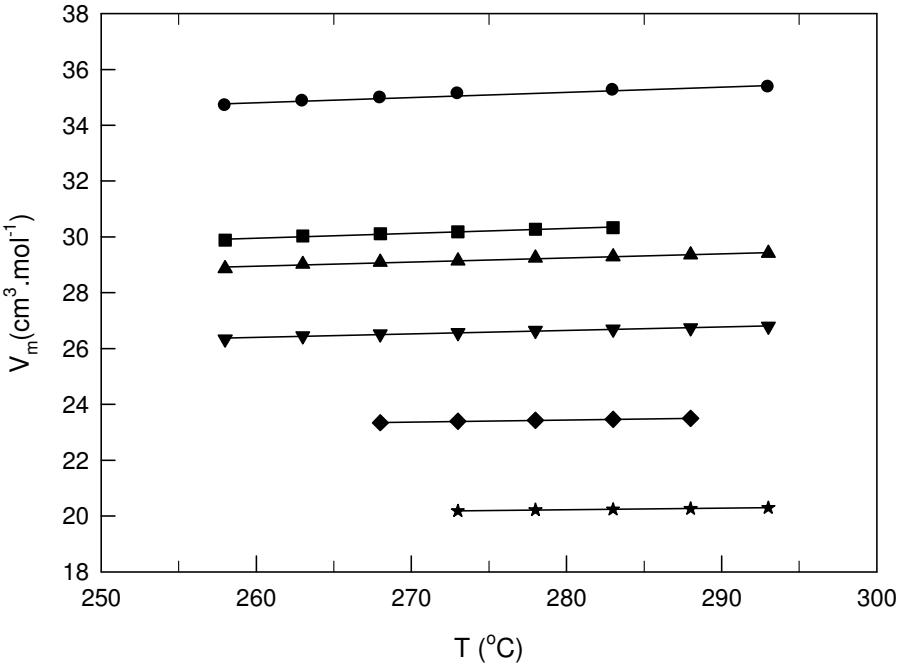


**Figure S1:** Molar volume of trehalose aqueous solutions as a function of temperature at different solute mole fraction ($x_2$): 0.0890 (●); 0.0640 (■); 0.0588 (▼); 0.0454 (▼); 0.0287 (♦); 0.0117 (★).

The molar volume of a hypothetical liquid trehalose, $V_2$, as a function of temperature between 258 K and 293K can be obtained by ploting $V_m$ *vs.* $x_2$, in the range $0.0890 \leq x_2 \leq 0.0117$ at

each temperature, as depicted in Fig. S2 for the data at 283 K. The concentration dependence of $V_m$ is linear, indicating that the excess volume is close to zero in this concentration range. The same behavior is observed at other temperatures in the studied interval. Therefore, $V_2$ can be obtained as a function of temperature by extrapolating $V_m$ to $x_2 = 1$.

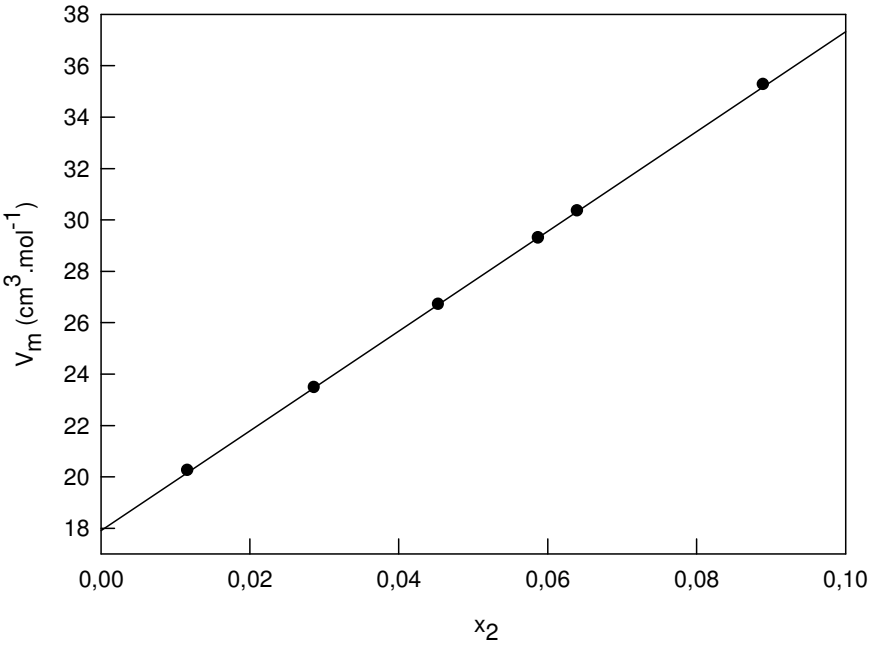


**Figure S2:** Partial molar volume of trehalose aqueous solutions as a function of trehalose mole fraction at 283 K.

Extrapolation from $x_2 \approx 0.08$ to pure trehalose leads to considerable errors, even when the uncertainties in the slopes of the plots $V_m$ *vs.* $x_2$ are small. This is reflected in the results shown in Fig. S3, where $V_2$ increases with increasing temperature but the behavior is far of being linear. For this reason we employed and alternative procedure to estimate $V_2$.

We adopted $T_0$ = 283.15 K as a reference temperature and extrapolated the data reported in Fig. S2 to $x_2$=1 obtaining $V_2$ (283.15 K) = (212.1 ± 0.8) $cm^3.mol^{-1}$. Then, we calculated $V_2$ at all the temperatures by resorting to the expression derived from Eqn. (11) by assuming that the average thermal expansion coefficient does not change with temperature:

$$V_2(T) = V_2(T_0)\left[1 - \frac{0.19}{T_{g2}}(T - T_0)\right]^{-1} \qquad \text{(S1)}$$

Thus, we obtained the results indicated in Figure S3.

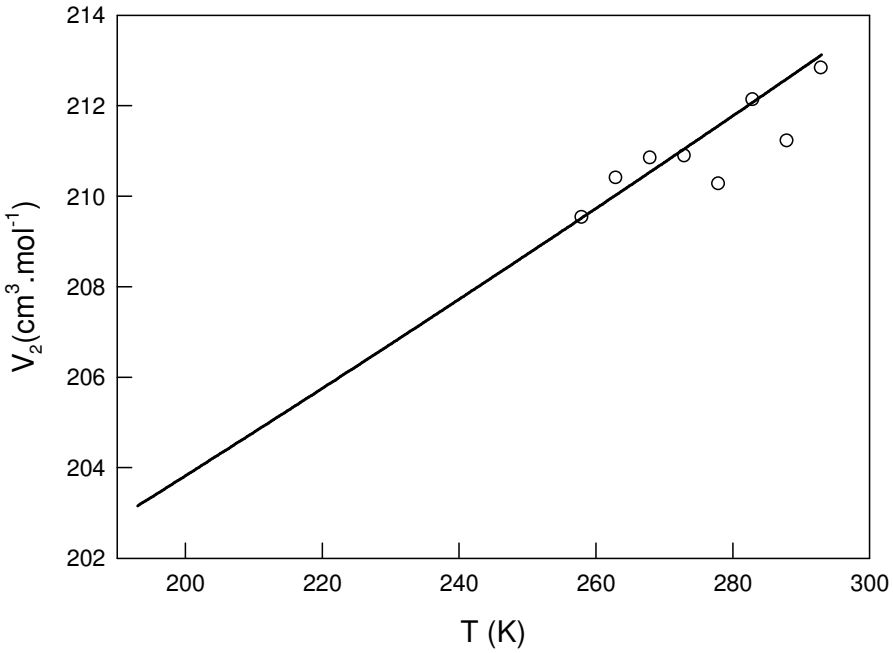


**Figure S3:** Molar volume of hypothetical liquid trehalose as a function of temperature. Closed circles correspond to the extrapolatation of $V_m$ to $x_2$ =1, and the solid line corresponds to the calculation based on the $V_2$ value at 283.15 K and Eqn. S1.

It is observed that, except for the data at 5 $^{o}$C and 15 $^{o}$C, the molar volume of liquid trehalose obtained with this procedure agree within the experimental error with the direct procedure. The molar volume of crystalline anhydrous trehalose (216.6 cm$^3$.mol$^{-1}$) at room temperature [2] is close to $V_2$ (293.15 K) obtained here, which validates the assumption that the excess volume in the water-trehalose mixture is zero all over the concentration range and

temperatures considered. The maximum deviation to the ideal behavior is 0.20 $cm^3.mol^{-1}$ at 20 $^oC$ and 0.36 $cm^3.mol^{-1}$ at -15 $^oC$.

## 2. Calculation of the molar volume of other pure saccharides at supercooled conditions

The procedure described for trehalose was also used to obtain the molar volume of the polyols studied in this work by resorting to the volumetric data reported for sucrose [3-6], glucose [4-6], and fructose [5,6]. Table S1 summarizes the parameters used to calculate $V_2(T)$ of the different solutes. The values of the onset and midpoint glass transition temperatures used in the calculations were obtained from reported data for the pure saccharides [7-11].

Table S1: Parameters for the estimation of molar volume of polyols using Eqn. (S1)

| **Solute** | $T_{g,onset}$ **(K)** | $T_{g,mid}$ **(K)** | $T_0$ **(K)** | $V_2(T_0)$ **($cm^3.mol^{-1}$)** |
|---|---|---|---|---|
| Trehalose | 389 | 389 | 283.15 | 212.1 ± 0.8 |
| Sucrose | 341 | 346 | 273.15 | 214.1 ± 0.8 |
| Glucose | 304 | 310 | 293.15 | 114.0 ± 0.8 |
| Fructose | 278 | 283 | 293.15 | 112.3 ± 0.6 |

## 3. Comparison of the different glass transition models

We used the R-squared statistical parameters to compare the fit of the different models (FVPM, CKM, and GTM) to the experimental data for the saccharides studied in this work. The results are summarized in Table S2.

Table S2: R-squared parameter for the fit of experimental data for sucrose, glucose and fructose aqueous mixtures using the GTM, CKM and FVPM.

| Saccharide | GTM | CKM | Modified CKM | FVPM |
|---|---|---|---|---|
| Sucrose | 0,9578 | 0,9708 | ----- | 0,9779 |
| Glucose | 0,9682 | 0,9486 | 0,7631 | 0,9867 |
| Fructose | 0,8442 | 0,9730 | 0,9603 | 0,8992 |

The R-squared confirm that FVPM is the model that better represents the experimental data sets for sucrose and glucose, whereas for fructose CKM and modified CKM perform better (see main article for further discussion).

**References**


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