



## Determination of the glass transition temperatures $T_g$ of Maltose and its dependence on relative humidity by infinite dilution inverse gas chromatography (iGC-SEA)

Surface Measurement Systems Ltd.

**The glass transition temperature  $T_g$  is an important property for the characterisation of polymeric, food, pharmaceutical and many natural products. iGC SEA can provide a fast and accurate determination of this property as well as its dependence on relative humidity. This paper describes the characterisation of maltose with decane at infinite dilution.**

### Introduction

The glass transition temperature ( $T_g$ ) is a second order phase transition where an amorphous or partly crystalline material changes from being a glassy elastic solid to being a rubbery/leathery solid. This temperature signifies the onset of long range co-ordinated molecular chain motion in the material and many material properties change significantly at this transition temperature. Above the  $T_g$  the material exhibits macroscopic behaviour which is viscoelastic in nature.

$T_g$  depends strongly on environmental conditions and material properties such as humidity and morphology. Water is well known to act as a plasticising agent for many organic materials. In contrast to classical techniques for the characterisation of  $T_g$ , like differential scanning calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA), inverse gas chromatography (IGC SEA) can provide an easy and fast way for an investigation of  $T_g$  under different relative humidity conditions.

Polymers for example, either synthetic or natural macromolecules, exhibit  $T_g$ 's and many such transitions have been studied using iGC SEA during the last 30 years [1,2,3]. However, the use of iGC SEA to determine the effects of moisture on  $T_g$  has not been reported previously.

A suitable model substance used in the current study is maltose. Maltose is a disaccharide of two glucose units (Figure 1) and is used as sweetener or nutrient [4].

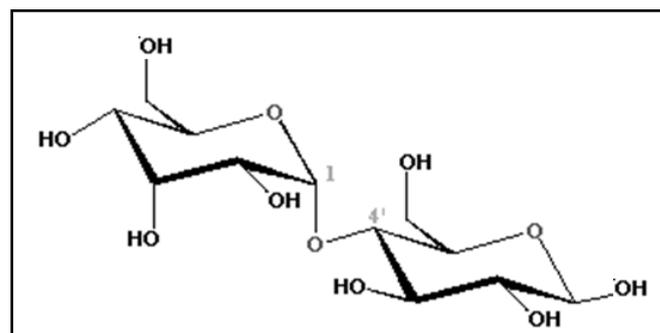


Figure 1. Structure of  $\alpha$ -D-Maltose.

### Theory

Phase transition effects can be studied by pulse inverse gas chromatography at infinite dilution. In this experiment a small amount of an organic vapour is injected into a carrier gas stream. At infinite dilution the adsorption is independent of the surface coverage of the adsorbed molecules. The result is a linear adsorption isotherm, which can be described by Henry's Law. In this case the experimental obtained peaks are symmetrical (Gaussian) and the retention time in the peak



maximum can be used to calculate the retention volume. The net retention volumes  $V_R^0$  are computed using Equation 1.

$$V_R^0 = j / m \cdot F \cdot (t_R - t_0) \cdot \frac{T}{273.15} \quad (1),$$

where  $T$  is the column temperature,  $F$  is the exit flow rate at 1 atm and 273.15K,  $t_R$  is the retention time for the adsorbing probe and  $t_0$  is the mobile phase hold-up time (dead time).  $j$  is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed.

$$j = \frac{3}{2} \left[ \frac{\left( \frac{P_i}{P_0} \right)^2 - 1}{\left( \frac{P_i}{P_0} \right)^3 - 1} \right] \quad (2)$$

In the Henry's Law region the net retention volume is related to the differential heat of sorption by Equation 3.

$$\ln V_N = -\Delta H_A / RT + C \quad (3)$$

where it is assumed that the adsorption enthalpy is constant over a wide temperature range. Under these conditions the heat of sorption is obtained from a plot of  $\ln V_N/T$  versus  $1/T$  [5].

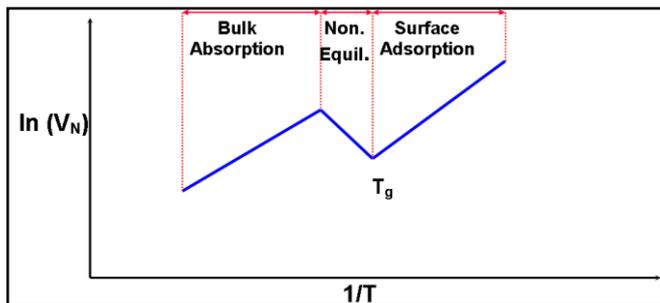


Figure 2. Schematic Diagram of iGC SEA retention around the  $T_g$  (from [1]).

In the case of a phase transition the dependency of enthalpy on temperature becomes non-linear.

This deviation from linearity of the curve depends very strongly on the nature of the adsorbent/adsorbate interactions, but it is dominated by the change in retention mechanism from surface adsorption below the  $T_g$  to bulk sorption around  $T_g$ . For many materials such as polymers and foods a retention curve with a minimum is observed [1,6] due to the complex

combination of both equilibrium and non-equilibrium sorption behaviour which occurs.

## Method

Four different columns were packed with  $\alpha$ -D-maltose monohydrate supplied by Sigma-Aldrich (>98% purity). All the sorption experiments were carried out on an SMS-iGC SEA 2000. Measurements were done with decane vapour (HPLC grade Sigma-Aldrich) as the molecular probe. Columns were studied at 0%, 5%, 10% and 15% RH (relative humidity). The 0% RH experiment was carried out between 65 and 101°C, experiments at 5%, 10% and 15% between 37 and 82°C, 30 and 75°C and 40 and 67°C. A simple drying pre-treatment was undertaken in each experiment for 3 hours at the starting temperature and the experimental RH.

## Results

Figure 3 shows a typical experimental curve. On the right-hand side the curve shows clear linear behaviour typically associated with surface adsorption. At higher temperatures the curve starts to exhibit significant deviations from linearity and goes through a minimum before increasing on the high temperature branch of the curve. This part of the curve is assumed to represent non-equilibrium probe absorption.

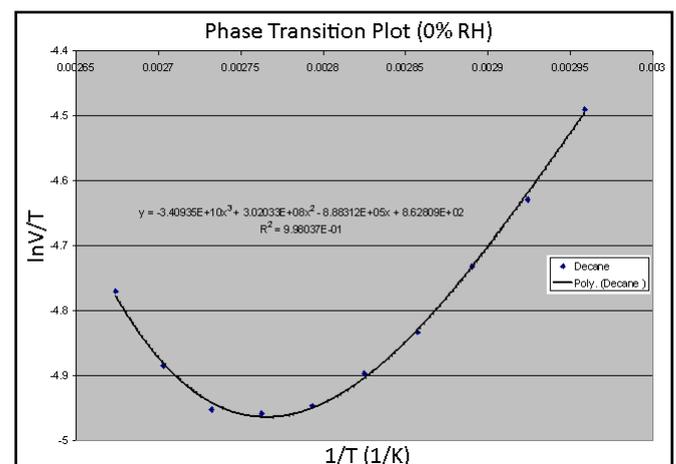


Figure 3. Experimental obtained curve from a measurement with decane between 65°C and 101°C at 0% RH and a three-parameter polynomial fit.

The temperature at the minimum represents the actual glass transition temperature and can be derived from the first derivation of the polynomial

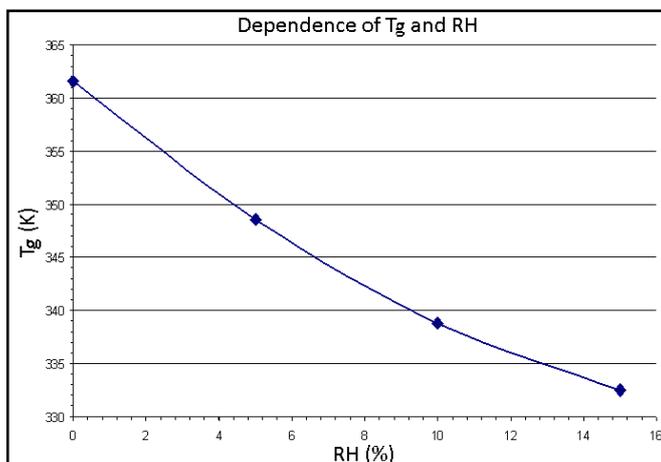


equation. The results for different relative humidity are listed in Table 1.

*Table 1. Dependence of glass transition temperatures and relative humidity.*

RH(%)	1/T (1/K)	T <sub>g</sub> (K)
0	0.0027657	361.6
5	0.0028688	348.6
10	0.0029515	338.8
15	0.0030078	332.5

The glass transition temperature shifts to smaller values with increasing relative humidity. The behaviour was also observed by Roos and Karel [7]. Figure 4 shows a plot of the glass transition temperature versus the relative humidity.



*Figure 4. Experimentally obtained glass transition temperatures in dependence of relative humidity (with decane).*

This data is in excellent agreement with published values for the T<sub>g</sub> of maltose at 0% RH of 360-365K [8]. Note that iGC-SEA T<sub>g</sub> experiments measure a surface glass transition, unlike thermal analysis methods. Therefore, T<sub>g</sub> measures by iGC-SEA can sometimes be more sensitive to weak glass transitions on the surface.



## Conclusion

Infinite dilution iGC SEA can provide a fast and easy way to determine second order phase transition effects of an organic material at different relative humidities. In the particular case of maltose the method was shown to allow an accurate determination of the glass transition temperature.

## Acknowledgement:

Surface Measurement Systems thank Daryl Williams and Frank Thielmann for their contributions to the application note.

## References

- 
- [1 ] Smidsrod, O. and Guillet, J.E., *Macromolecules*, 2 (1969), 272.
  - [2 ] Bogiollo, V.I. and Voelkel, A., *Journal of Chromatography* 715 (1995), 127.
  - [3 ] Hamieh, T. and Rezzaki, M., J., *Chim. Phys., Phys.-Chim. Biol.* 95 (1998), 1964.
  - [4 ] Johnson, A., *Specialized Sugars for the Food Industry*, Park Ridge, Noyes 1976.
  - [5 ] Thielmann, F. and Butler, D., *IGC Application Note 203*, Surface Measurement Systems, London, 2000.
  - [6 ] Surana, R., Randall, L., Vemuri, N. M. and Suryanarayanan, R., *Pharm. Res.* 20 (2003), 1647.
  - [7 ] Roos, Y.H. and Karel, M., *Journal of Food Science*, 56 (1991), 1676.
  - [8] Roos, Y.H., *Phase Transitions in Food*, Academic Press, (1995), 115.

*This paper was published in Deutsche Lebensmittel-Rundschau 96 (2000), 255.*

Head Office:  
Surface Measurement Systems, Ltd  
5 Wharfside, Rosemont Road  
London HA0 4PE, UK  
Tel: +44 (0)20 8795 9400  
Fax: +44 (0)20 8795 9401  
Email: [science@surfacemeasurementsystems.com](mailto:science@surfacemeasurementsystems.com)

United States Office:  
Surface Measurement Systems, Ltd, NA  
2125 28<sup>th</sup> Street SW, Suite I  
Allentown PA, 18103, USA  
Tel: +1 610 798 8299  
Fax: +1 610 798 0334

