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THERMAL PROPERTIES OF ISOMALT
A diastereomer mixture

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Abstract

Isomalt, a commercial sugar alcohol widely used as a sweetener, is approximately a 1:1 mixture of two diastereomers, α-*D*-glucopyranosyl-1-6-mannitol (GPM) and α-*D*-glucopyranosyl-1-6-sorbitol (GPS). A calorimetric investigation has been carried out on mixtures of isomalt with GPS, in the (molar) composition range $0.45<x_{\mathrm{GPS}}<1$, for both crystalline and amorphous states.

The GPS-rich portion of the solid-liquid GPM/GPS phase diagram was established and discussed in light of the existing literature. New evidence was given for the non-ideality of GPM/GPS mixtures, by indicating excess interactions in the melt and/or in the solid state. The commonly accepted hypothesis of a simple GPM/GPS eutectic forming isomalt was refuted in favour of more complicated mixture behaviour with possible formation of a complex.

Glass transition and physical ageing of isomalt and GPS were re-visited, with peculiar attention given to the measurement conditions. Standard thermal histories were adapted to each sample and the fictive temperature was used for the characterisation of the structural glass states. A linear increase of the fictive temperature was found upon passing from pure GPS to $x_{\mathrm{GPS}}=0.45$. GPS showed a slightly higher enthalpy relaxation rate than isomalt.

Keywords: diastereomers, differential scanning salorimetry, glass transition, GPM, GPS, isomalt, solid–liquid phase diagram

Introduction

Great attention has continuously been paid to characterisation and resolution methods of mixtures of optically active molecules. The key reason for this research effort, in particular in the pharmaceutical and related sciences [1–4], resides in the frequent toxic activity of one of the enantiomers, a fact which itself is at the basis of the asymmetry of living organisms. A mixture of configurational isomers is also a technological problem when the two isomers have contrasting properties in the final product. A clear distinction must be made, however, between a mixture of enantiomers (mirror-image molecules) and a mixture of diastereomers, in which only some of the chiral centers are in the opposite configuration. Enantiomers have identical properties

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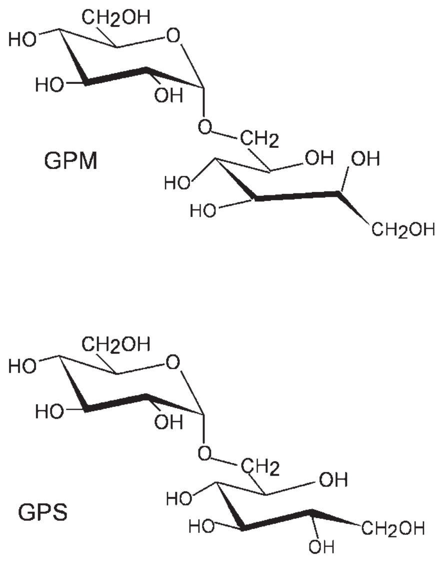
and behaviour, except for the interaction with asymmetric molecules or polarised light; two diastereomers must be considered in all aspects as different molecules. In particular, diastereomeric conglomerate (eutectic) differs substantially from the enantiomeric eutectic and the differences in melting temperatures and enthalpies give non-symmetric phase diagram [5–6].

From simple thermodynamic considerations, it is evident that the solubility of the conglomerate in a solvent is greater than that of the individual enantiomers (or diastereomers). The old rule of Meyerhoffer, which says that the racemate is twice as soluble as the enantiomers, can also be reached by the application of the Schroeder–Van Laar equation. Apparently, most experimental results are in agreement with the foregoing statements and the solubility is twice that of the single component [1]. In the case of two diastereomers, attention has to be paid to the fact that solubility-concentration relations are based on different thermodynamic values of enthalpic and entropic nature. With these premises out of the way, one should also recognise that most often physico-chemical interactions within diastereomers are basically similar and that in general one would expect only minor, but still significant, changes from the behaviour of an enantiomeric mixture.

Among all the organic chiral molecules, sugars have always been considered as a source of intriguing chiral primers. Unfortunately, the complexity of sugars – due to their structural, configurational and conformational diversities – has often hampered a careful characterisation of the physico-chemical properties of their mixed phases. According to the basic chemistry, sugars constitute a class of few homologous compounds, though differing in their stereochemistry. The following examples are quoted in order to focus on some sources of misunderstanding, which may arise from the complexity of these molecules. A strong difference is reported for the solubility in water of galactaric and glucaric acids, molecules that differ from each other only by the hydroxyl configuration at carbon C3. As a counterpart, their melting points are significantly different (respectively 225 and 125°C) [7]. The two isomers mannitol and sorbitol have radically different properties in solution and in the solid state although they differ only in the configuration of their C2 [8]. These differences are ascribable to the conformational thermodynamic stabilities of these sugars which eventually determine the crystalline forms.

The commercial sugar alcohol isomalt is an approximately equimolar mixture of α-*D*-glucopyranosyl-1-6-mannitol (GPM) and α-*D*-glucopyranosyl-1-6-sorbitol (GPS) that crystallises readily from an aqueous solution (Scheme 1). The industrial process yields an agglomerate of variable water content (typically 5%). GPM crystallises with two water molecules whereas GPS is anhydrous [9, 10]. Isomalt is considered as a eutectic mixture of GPM and GPS [11], however, clear evidence of this situation is still lacking. Furthermore, experimental results reported on its thermal behaviour [12–14], putative phase diagram [11], and solubility properties [10] show some inconsistencies. In addition, little information is available on the dependence of glassy state properties and glass transition temperature on the composition of diastereomer mixtures. All these data are relevant for the technological applications of these compounds.



Scheme 1

Thermal properties of isomalt were previously studied with a peculiar focus on hydration-dehydration effects and glassy state stability [12]. In order to provide a further characterisation of this diastereomeric mixture, the properties of the GPS-rich portion of the GPM/GPS state diagram have been investigated in the present study. Unfortunately, the other half of the diagram could not be explored, pure GPM being unavailable. However, the data here presented suffice for a thermodynamic analysis and a re-visitation of the behaviour of this mixed system in both crystalline and amorphous states.

Experimental

Materials

Isomalt (Palatinit produced by Sudzuecker AG-Mannheim/Ochsenfurt) was a commercial sample, kindly provided by Dr. R. Khan. The sample received as white crystalline grains (typically 2 mm in diameter), was powdered by gentle hand grinding in a mortar. This sample contained 45% of GPS [12]. GPS, labelled as isomaltitol, α-*D*-glucopyranosyl-1-6-glucitol (glucitol is a synonym of sorbitol) was obtained from Sigma and used as received (purity>98%).

Physical mixtures of isomalt and GPS of various compositions were done by mixing the powders directly in the DSC pans. The composition of these mixtures will be designed by means of the molar percentage of GPS, x_{GPS}. The x_{GPS} values were calculated on the basis of the dry product, i.e. subtracting the water present in the isomalt samples (checked by mass loss in oven at 120°C). Samples of composition ranging from x_{GPS}=0.45 (isomalt) to x_{GPS}=1 (pure GPS) were prepared by adding GPS to isomalt.

Calorimetric measurements

Calorimetric measurements were carried out by using a Perkin Elmer DSC6. Temperature and heat flow were periodically calibrated with indium and tin standards using a heating rate Q_h of 10 K min^{-1}. Samples of 2 to 6 mg were sealed in aluminium pans: a hole made with a syringe needle (ϕ=0.5 mm) in the pan cover allowed free water evaporation during measurements. Baselines were recorded for each set of measurements, and automatically subtracted from the total heat flow.

Crystalline diastereomer mixtures

Determination of the melting behaviour of a mixture by DSC allows the construction of a phase diagram. In case of mixtures exhibiting a conglomerate behaviour, the eutectic composition can be evaluated by DSC by calculating the areas of the eutectic and remaining phase melting [2].

First heating scans of isomalt/GPS physical mixtures sometimes showed traces of pure GPS in the DSC curves. For the establishment of the GPM/GPS solid-liquid phase diagram, a preliminary annealing treatment was therefore used in order to get a convenient homogenisation of isomalt and GPS. Samples were heated to 100°C, left in isotherm for one hour and cooled again to 20°C (Q_h=Q_c=10 K min^{-1}). Isomalt and GPS were similarly annealed even if their melting peaks were not significantly affected by this thermal treatment. In an alternative annealing treatment, samples were heated to 90°C, annealed for one minute, and cooled back to 20°C (Q_h=Q_c=10 K min^{-1}).

A heating rate of 3 K min^{-1} was used for the determination of melting points T_{fus} and melting enthalpies, ΔH_{fus}. Because of the variation in shape of the melting peaks, transitions were identified by the peak temperature T_{fus} rather than with T_{onset}. The enthalpy changes for melting ΔH_{fus} were determined with a 4% uncertainty and expressed per mole of anhydrous product.

Amorphous and glassy states of diastereomer mixtures

The glass transitions of amorphous samples were studied immediately after cooling the melt. DSC scans were performed between 10 and 150°C using Q_c=Q_h=10 K min^{-1}. Fictive temperatures, T_{fict}, were determined by following the procedure given in literature [15]. Heat capacity increments at the glass transition, ΔC_p, were taken at the middle of the transition. The parameters T_{fict} and ΔC_p were calculated using the Pyris Software by Perkin Elmer. For T_{fict}, the uncertainty was typical of the order of (or less than) 0.4°C.

For the ageing experiments, the fictive temperature of the unaged glasses, T_{fict0} was taken as a reference parameter related to the structural state of the glass before ageing. After melting, samples were cooled to 10°C, heated to the chosen ageing temperature T_e and left in isotherm for ageing times t_e ranging between 20 min and 9 h. After a cooling scan to 10°C, the fictive temperatures of the aged samples were measured on DSC heating scans to 150°C. The same sample was submitted to all thermal cycles without being removed from the calorimeter.

Results and discussion

Isomalt/GPS mixtures: crystalline phases

Mixtures DSC curves and GPM/GPS phase diagram

In order to construct the GPM/GPS phase diagram, a series of mixtures were annealed for 1 h at 100°C and submitted to a DSC heating scan from 20 to 180°C. This procedure has been useful to improve the quality of the physical mixtures. DSC curves are presented in Fig. 1 for x_{GPS} ranging between 0.45 (isomalt) and 1 (GPS). GPS is a single component and consequently shows a sharp melting peak with a maximum at T_{fus}=170.6°C (width 7°C) and a fusion enthalpy change ΔH_{fus} of 56.1 kJ mol^{-1}. However, melting of some impurities appears at lower temperatures between 155 and 165°C. The diastereomer mixture isomalt melts within a larger temperature range extending from 130 to 154°C. The peak maximum temperature T_{fus} is 149.1°C and the fusion enthalpy change ΔH_{fus} amounts to 44.3 kJ mol^{-1}.

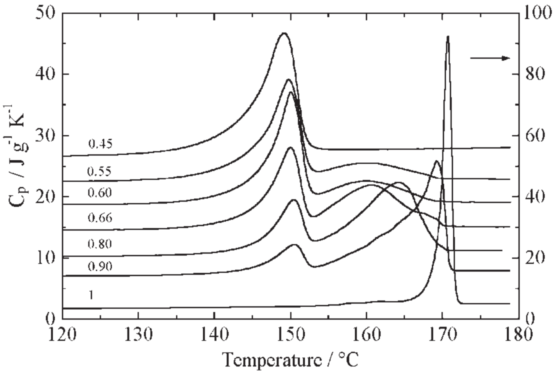


Fig. 1 DSC curves recorded for isomalt/GPS mixtures (0.45<x_{GPS}<1) after a previous annealing treatment of 1 h at 100°C. (Q_h=3 K min^{-1} – Curves have been shifted for sake of clarity, note the right scale for GPS curve. Composition x_{GPS} is indicated on each curve)

For isomalt/GPS mixtures, two distinct melting phenomena are observed in the DSC curves. The low-temperature melting peak, in the region of isomalt melting, decreases in intensity and moves slightly to higher temperatures upon enriching the mixture in GPS. This peak corresponds to the melting of the eutectic mixture and therefore its area depends on the composition: the proportion of solid eutectic decreases by increasing the GPS content. Although in principle melting of the eutectic is isothermal, our experiments illustrate a slightly different behaviour. Normalisation of these curves by the peak area shows that both the onset and the end temperatures are constant. This behaviour may indicate the convolution of two peaks of varying relative intensity and will be re-examined in the discussion.

Upon increasing GPS content, the high-temperature melting peak (GPS-rich phase) increases in intensity and moves towards higher temperatures, as do the onset and end temperatures of the melting. The behaviour of this peak is characteristic of the melting of a crystalline phase in the presence of a second component miscible in the liquid phase. The whole process corresponds to the formation of a liquid phase whose composition varies from the eutectic (as a result of the first melting peak, at ca 153°C) to the total mixture compositions. It expands therefore to a large temperature range, the amplitude of which depends on the composition.

Melting peak temperatures are reported in a tentative phase diagram in Fig. 2 for the compositions of Fig. 1. The results corresponding to the samples annealed for one minute at 90°C are also presented. Very similar results are obtained for both annealing treatments, indicating that a reduced thermal energy was sufficient to bring our samples towards thermodynamic equilibrium. The process of water removal may also play a role in the sample homogenisation, possibly accentuated in the low GPS composition part (water stemming from isomalt only).

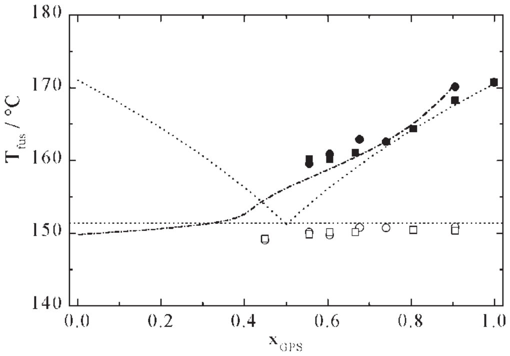


Fig. 2 Tentative solid-liquid GPM/GPS phase diagram: experimental and theoretical points. Fusion temperatures T_{fus} measured for eutectic (open symbols) and GPS-rich phase (full symbols) after 1 h at 100°C (■) and 1min at 90°C (●). Fusion temperatures calculated by means of the Schroeder–Van Laar equation (···). x_L composition calculated from the curve of the mixture x_{GPS}=0.9 as a function of temperature (·–·–)

In addition to the experimental melting points, Fig. 2 shows the dotted line calculated by means of the Schroeder–Van Laar equation, and using the T_{fus} and ΔH_{fus} measured for GPS and the T_{fus}=444.2 K and ΔH_{fus}=55.0 kJ mol^{-1} given in literature for GPM [14]. For high GPS contents, a very good agreement is observed between the theoretical curve (ideal behaviour) and the experimental melting point T_{fus}. For x_{GPS}<0.75, melting points clearly show a positive deviation from the ideal behaviour, being up to 5 K higher than the line values.

Fractional liquid transformation and eutectic fraction

The fractional liquid transformation f_L may be defined as the fraction of the mixture that has liquefied at a given temperature. It is therefore equal to the ratio of the heat flow $dh(t)/dt$ exchanged during the temperature interval between T_0 and T and the total heat absorbed during the whole fusion process, ΔH_{fus}:

$$f_L(T)=\frac{\int_{T_o}^{T}\frac{dh(t)}{dt}dT}{\Delta H_{\text{fus}}}$$

For all compositions presented in Fig. 1, f_L has been calculated as a function of temperature and represented in Fig. 3. All the intermediate mixtures show a two-step curve traducing the two melting events observed on their respective DSC curves.

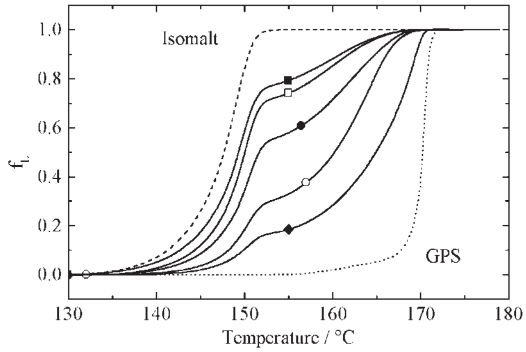


Fig. 3 Fractional liquid transformation f_L as a function of temperature for isomalt (- - -), x_{GPS}=0.55 (■), 0.6 (□), 0.67 (●), 0.8 (o), 0.9 (◆) and GPS (···)

Owing to this representation, it is easy to evaluate f_E, the proportion of eutectic in the initial mixture [16]. For each composition, f_E is taken as the value of f_L corresponding to the completion of the first step. f_E values are presented as a function of composition in Fig. 4. The values obtained for f_E may be fitted by a straight line passing through (1.0). This line passes through f_E=1 for a eutectic composition of x_{GPS}=0.42. In the hypothesis of a phase diagram presenting a simple eutectic, the

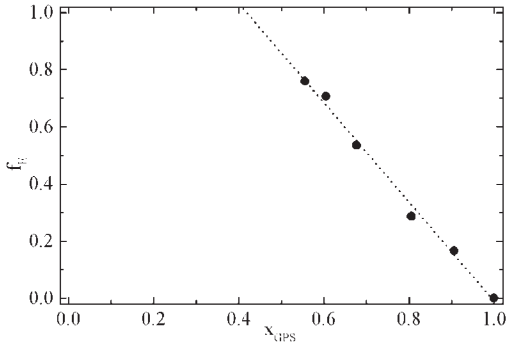


Fig. 4 Eutectic fraction f_E as a function of composition

knowledge of the liquid fraction f_L allows also the evaluation of the liquid fraction composition, x_L. Applied to our half diagram, the lever rule [5] indicates:

$$f_L(x_0 - x_L) = (1 - f_L)(1 - x_0)$$

For a given mixture composition x_0, let f_L be a function of temperature, the x_L corresponding can be calculated. Since the composition of the liquid fraction varies between x_E and x_0, the corresponding part of the phase diagram can be re-constituted. This calculus can be made without any hypothesis in the high GPS content zone where experiments revealed quasi-ideal mixture behaviour. The curve corresponding to $x_{GPS}=0.9$ is presented in the general phase diagram (Fig. 2). A rather good agreement is obtained between this curve and our experimental points over the whole composition range. In the hypothetical eutectic zone, the x_L values drawn for $x_{GPS}=0.9$ indicate melting temperatures significantly higher than those of the theoretical diagram and a eutectic composition significantly lower than 0.5. This observation confirms the non-applicability of the Schroeder–Van Laar equation for the GPM/GPS phase diagram for low GPS contents.

Isomalt – GPS mixtures in the amorphous and glassy states

Glass transitions

After complete melting and cooling, all samples prepared for the GPM/GPS phase diagram became glassy. The glass transitions have been studied by means of DSC heating scans performed immediately after a controlled cooling ($Q_c=Q_h=10$ K min^{-1}). Some DSC curves are presented in Fig. 5 for x_{GPS} ranging between 0.45 and 1. Apart from the changes in the glass transition temperatures and enthalpy recovery effects, all curves show a C_p step with a linear variation of C_p before (glassy state) and after (amorphous) the glass transition. Increasing isomalt content, increases ΔC_p from 234±19 J mol^{-1} K^{-1} (GPS) to 273±22 J mol^{-1} K^{-1} (isomalt). The glass transition and fictive temperatures increase progressively when passing from GPS ($T_{fict}=54.8$°C) to isomalt ($T_{fict}=59.6$°C).

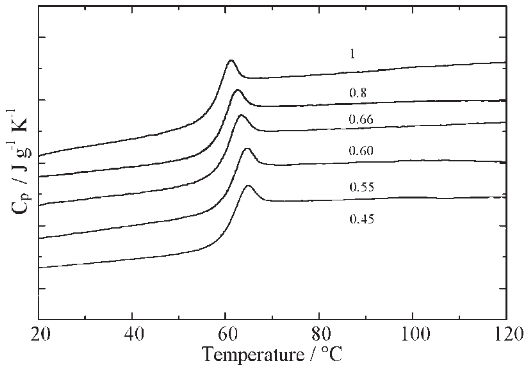


Fig. 5 DSC curves recorded for isomalt/GPS mixtures ($0.45<x_{GPS}<1$) after complete melting followed by a cooling at 10 K min^{-1}. ($Q_h=10$ K min^{-1} – Curves have been shifted for sake of clarity. Composition x_{GPS} is indicated on each curve)

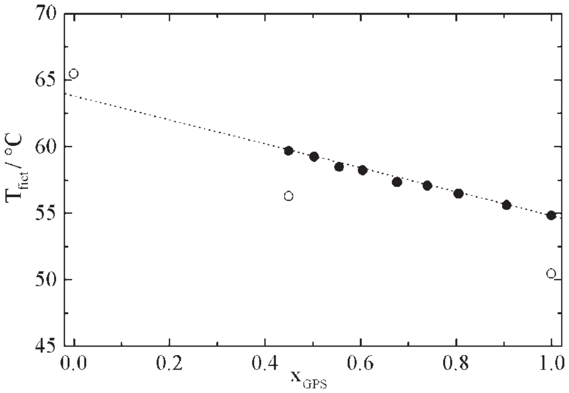


Fig. 6 Fictive temperatures T_{fict} (●) measured on DSC curves of Fig. 5 and linear fitting (····) curve. Fictive temperatures (o) given in [13] for GPM, isomalt and GPS

The fictive temperatures measured on the DSC curves of Fig. 5 are reported in Fig. 6 as a function of composition. For both temperatures, a linear decrease is observed from isomalt to GPS, and is well described by the following equation:

$$T_{fict}(x_{GPS})=63.8-9x_{GPS}$$

Data from literature [13] obtained for isomalt and its pure components are also reported in Fig. 6. The differences between these data and our results may be explained by the differences in the thermal histories preceding the measurements, as commented in the discussion of the experimental results.

Physical ageing: enthalpy relaxation

To properly characterise the effect of composition on the physical ageing of GPM/GPS mixtures, a standard ageing experiment was chosen and applied either to GPS or isomalt. The process of enthalpy relaxation depends extensively on the ageing temperature, as in-

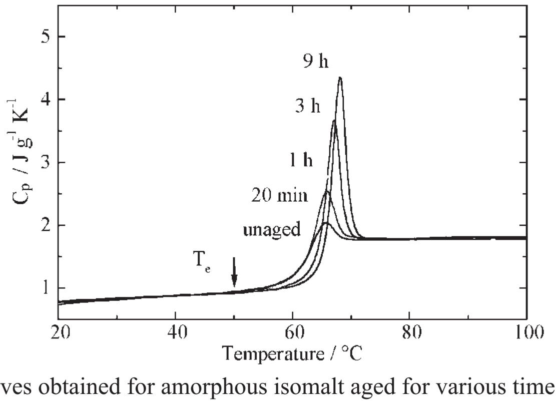


Fig. 7 DSC curves obtained for amorphous isomalt aged for various times at 50°C corresponding to T_{fict0}= –9.7°C

fluenced by the molecular mobility in the glass [17]. Using T_e=45°C for GPS (T_{fict0}=54.8°C) and T_e=50°C for isomalt (T_{fict0}=59.6°C), both materials were aged in similar conditions i.e. with T_e≈T_{fict0} = –9.7°C. These high ageing temperatures were similarly used to produce marked relaxation effects on a reasonably small time scale. The DSC curves corresponding to these ageing experiments for ageing times extending from 20 min to 9 h are presented in Figs 7 and 8 for isomalt and GPS respectively. When increasing ageing time are considered, the enthalpy recovery peak at the glass transition increases in area and amplitude and shifts towards higher temperatures.

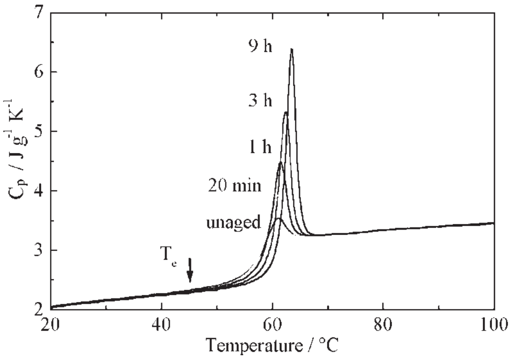


Fig. 8 DSC curves obtained for amorphous GPS aged for various times at 45°C corresponding to T_{fict0} = –9.7°C

To quantify the consequences of ageing on isomalt and GPS, the fictive temperatures T_{fict} of the aged glasses are presented in Fig. 9 as a function of ageing time. In agreement with the standard behaviour of glassy materials [17], the fictive temperature of isomalt and GPS glasses decreases linearly as a function of the logarithm of the ageing time. The slope of this line is lower for GPS (–1.74) than for isomalt (–1.48), indicating that GPS possesses the highest relaxation rate. The time values evaluated for a complete equilibration of the glasses (T_{fict}=T_e) differ by one order of

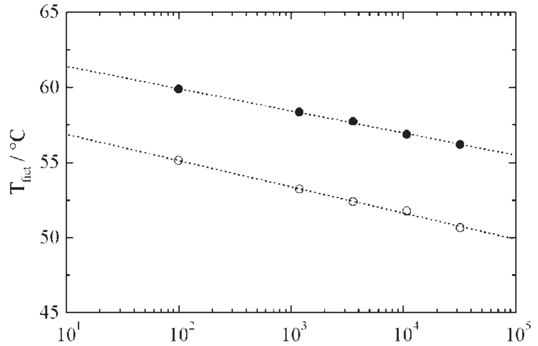


Fig. 9 Evolution of the fictive temperature T_{fict} as a function of ageing time for isomalt (●) and GPS (o)

magnitude in the two systems: the fictive temperature of isomalt would reach the ageing temperature after t_e=exp(8.7), whereas GPS would be equilibrated after t_e=exp(7.8). However, this evaluation remains purely qualitative given the complexity of structural relaxation.

Discussion

The portion of the GPM/GPS solid-liquid phase-diagram, obtained by the present calorimetric investigation, provides new elements for a better understanding of the interactions within the diastereomer mixture, isomalt. Apparently, the half phase diagram obtained from DSC experiments is typical of a binary mixture with the formation of a eutectic, as reported in the current literature. However, the new results presented as well as some other data from literature need to be carefully rediscussed, regarding, in particular, the mixture non-ideality, as developed below.

1. The theoretical diagram drawn from the simplified Schroeder–Van Laar equation cannot describe the GPM/GPS mixture behaviour since it overestimates the melting point depression of the mixtures approaching the eutectic composition. This observation indicates the non-ideality of GPM/GPS mixtures.

2. Considering the melting enthalpy changes for GPM, isomalt and GPS (respectively ΔH_{fus}=55.0, 44.3 and 56.1 kJ mol^{-1}), isomalt presents a significant anomaly. If the eutectic mixture formed by GPM and GPS involved no enthalpy of mixing or any other type of excess interactions, the heat of fusion of isomalt would have been given by the mixture law:

$$\Delta H_{\text{fus}} = x_{\text{GPS}} + x_{\text{GPM}} \Delta H_{\text{fus GPM}} = 55.5 \text{ kJ mol}^{-1}$$

The enthalpy difference between calculated and experimental value amounts to –11.2 kJ mol^{-1}. This negative value suggests the presence of interactions between the molecules in the binary melt and/or formations of complexes in the solid phase.

3. The eutectic point is one of the most relevant information in a phase diagram. Here it constitutes an intriguing point to be discussed in the light of the present data, having in mind that the two components are represented by distinct molecules (although diastereomers). Both the eutectic fractions obtained from the various mixtures (Fig. 4) and the composition of the liquid fraction calculated for x_{GPS}=0.9 (Fig. 2) indicate a eutectic point at $x_{GPS}\approx0.4$. Our isomalt sample has a composition $x_{GPS}\approx0.45$, which is consistent with our results, as isomalt should correspond to a eutectic mixture of hydrated-GPM/GPS, i.e. the saturation line in the ternary water/GPM/GPS system. The presence of water in the original isomalt mixture should not be discussed here inasmuch as the present study concerns the dried mixture. However, the original isomalt composition is necessarily related to the composition of the saturated aqueous solution.

4. Another point is the slight increase of the eutectic melting peak temperature reported when the GPS content is increased in the mixtures, although the broadness of the peak remains constant. This variation is thermodynamically unsound for a eutectic, unless associated with the presence of a complex mixture. The possibility

that the apparent peak temperature is actually due to the convolution of two slightly different peaks is a suggestive hypothesis, which needs to be verified.

5. As mentioned in the introduction, an ideal solution behaviour of the diastereomers GPM and GPS should imply -in the mixture- additivity of their water solubilities. On the contrary, the solubility of isomalt was found to be somewhat intermediate between the solubility values of GPM and GPS on a large temperature range [10], thus indicating a kind of perturbation of the system and competition between the two species for their dissolution in water.

Whatever the exact origin of the foregoing observations, the non-ideality of the GPM/GPS system is now no longer questionable. Additional experiments on the full compositional range are clearly necessary for a better understanding of the mixture behaviour, especially in the equimolar composition zone.

After a complete melting of the crystalline isomalt/GPS mixtures, cooling yields an amorphous homogeneous material. In this study, a linear variation of the fictive temperatures was found for glasses of composition varying from x_{GPS}=0.45 to 1. Different results are given in [13] for the fictive temperatures of isomalt, GPM and GPS, with a non-linear variation and significantly lower values (respectively, 56.2, 65.4 and 50.4°C). In a subsequent work, Zielasko reports a linear variation of $T_{g_{midpoint}}$ of a series of mixture glasses ranging from pure GPM to pure GPS [11], results that seem to be more consistent with our findings.

Description of the dependence of the glass transition temperature as a function of composition can be made by means of several empirical and thermodynamic models. Among those, the Couchmann-Karasz [18] seems to be appropriate here since it uses the values of temperatures and specific heat capacity increments, without any adjustable parameter. The non-linearity of the literature data [13] would imply a large difference in ΔC_p values of pure components (GPM and GPS) in the amorphous and glassy state, a fact that is not supported by experimental results. The values we found for isomalt and GPS are respectively 234 and 273 J mol^{-1} K^{-1}. The ΔC_p of maltitol (α-*D*-glucopyranosyl-1-4-sorbitol), given as 244 J mol^{-1} K^{-1} [19], is very comparable to the GPS value. The heat capacity increments seem to be poorly influenced by the molecule conformation. The values given for the ΔC_p of hexitols such as dulcitol, sorbitol, iditol and mannitol are for instance comprised between 223.7 J mol^{-1} K^{-1} (mannitol) and 227.9 J mol^{-1} K^{-1} (iditol) [20].

The best way to characterise the structural state of a glass by means of a DSC experience is undoubtedly the fictive temperature: its calculation involves the whole DSC curve, including enthalpy recovery effects. T_{fict} is more sensitive to the thermal history than any other parameter (e.g. $T_{g_{midpoint}}$) and precise results can be obtained only through carefully chosen analysis conditions. In the study of ref [13], glass transitions were measured after a long stabilisation treatment at –18 and 20°C before measurements. Using the same 'stabilisation' temperature T_e for glasses having different glass transition temperatures produces ageing effects of variable amplitude (typically proportional to the difference T_e–T_{fict}). As a consequence of the preliminary ageing of glasses, their fictive temperatures are lower than ours, and their variation as a function of composition is not representative of the glass transition, including also variable ageing effects.

All these observations make clear the necessity of a careful control of thermal history of glasses when characterising their glass transition and tendency for enthalpy relaxation. Considering GPM and GPS, precise measurements on the ΔC_p of GPM are still lacking. The behaviour of GPM during physical ageing may also be revisited as a complement of the present study on GPS and isomalt.

Conclusions

The calorimetric investigation of the GPS-rich portion of the GPM/GPS solid-liquid phase diagram has revealed a clearly non-ideal behaviour of the mixture. These results may be of critical importance for isomalt, an industrial product usually presented as a eutectic mixture of GPM and GPS. The possible formation of a compound suggested by our results in the eutectic zone constitutes a new element which requires additional experiments. Since GPM and GPS are diastereomers, a complete phase diagram is required for system characterisation. A deeper knowledge of the GPM/GPS phase diagram could also provide precious hints for a better and cheaper isomeric separation.

Future experiments with pure GPM and GPS may bring concerns because of the presence of water in the GPM crystal (di-hydrate), the crystalline anhydrous form of which seems more difficult to obtain. In this study, the water present in isomalt was found to help the mixture homogenisation, a fact that could not be easily reproduced in GPM-rich mixtures. Our knowledge of other systems in which water removal can be tuned to produce either amorphous or crystalline phases [21] should be helpful in such an investigation.

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