

# Enthalpy relaxation of freeze concentrated sucrose–water glass <sup>☆</sup>

Chiharu Inoue <sup>a,\*</sup>, Toru Suzuki <sup>b</sup>

<sup>a</sup> *Unilever R&D Vlaardingen, Olivier van Noortlaan 120, 3130AC Vlaardingen, The Netherlands*

<sup>b</sup> *Department of Food Science and Technology, Tokyo University of Marine Science and Technology, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan*

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## Abstract

The enthalpy relaxation of freeze concentrated sucrose–water glass was investigated using 40% sucrose, differential scanning calorimetry (DSC) with isothermal ageing for 1–6 days at various temperatures (–70, –65, –60, and –55 °C). The enthalpy relaxation was observed as an endothermic peak superimposed on the endothermic step-wise change due to the glass transition around –47 °C. The enthalpy relaxation was found to increase with ageing time and temperature. An 80% sucrose glass was also investigated at ageing temperatures of –60 and –65 °C, and this material exhibited a similar glass transition and enthalpy relaxation to that observed with the frozen 40% sucrose solution. The calculated activation energy of the enthalpy relaxation of the sucrose–water glass was smaller than that reported for pure sucrose. These results suggest that the freeze concentrated sucrose–water glass could have a higher molecular mobility and less stability than pure sucrose glass.

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The glassy state has been widely studied in food in relation to the universal issues of food stability and safety [11]. Good stability of dried food can be achieved within the glassy state [5]. It is generally assumed that food is stable in the glassy state over a practical time scale [17] and that the glass transition temperature  $T_g$  is very sensitive to moisture [5]. From this point of view, many studies have been done to measure the  $T_g$  of food materials [17] and

real foods [7–9]. However, much less attention has been paid to the stability of the glassy state [13].

Recently, the enthalpy relaxation of the glassy state has been reported for food materials such as starch [13], sugars [12], and boiled/dried fish meat [6]. According to these studies the permeability of the glassy starch film to water vapour decreased with the level of enthalpy relaxation, the permeability coefficient being a function of the ageing time at temperatures below the  $T_g$  [13]. This suggests that changes in the quality of food can happen, even when it is stored at temperatures below  $T_g$ . Although enthalpy relaxation has been widely studied in the field of polymer science, particularly in relation to the stability of glassy state [15], there is

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\* Corresponding author. Fax: +31 10 460 6747.

E-mail address: [Chiharu.Inoue@unilever.com](mailto:Chiharu.Inoue@unilever.com) (C. Inoue).

much less data on enthalpy relaxation in glassy food materials.

The enthalpy relaxation of glassy pure sugars (glucose, sucrose, maltose, and trehalose) has been reported and analysed by the theories proposed in the field of polymer science [12,15]. The calculated activation energy was shown to be an useful index for comparing the stability of various glassy sugars, and these may be considered as models for food systems [12,15]. These studies showed that glucose glass has the smallest activation energy of enthalpy relaxation, and trehalose has the largest, with sucrose and maltose being intermediate. It was proposed that the stability of these glassy sugars could depend on molecular size and structure, which in turn could influence their ability as a stabilizers [12]. These studies suggest that the enthalpy relaxation of various glassy food systems are worth investigating to evaluate their relative instability.

In many frozen foods, the glass transition takes place in the maximally freeze concentrated solution ( $C'_g$ ) at a temperature  $T'_g$ , which can be considerably lower than the freezing point of water [14]. Thus, it has been generally assumed that it is possible to minimise the degradation of frozen food during storage by maintaining it below  $T'_g$  [2]. The enthalpy relaxation of freeze concentrated glasses has been observed by DSC for galactose–water [3] and trehalose–water [16]. However, there is not sufficient data to make it possible to calculate the activation energy of the relaxation and thereby consider the relative instability of the glassy state.

The objective of the present study was to investigate the enthalpy relaxation of a very common model food system, sucrose–water, by using DSC. According to the previous study, the Kohlrausch–Williams–Watts (KWW) equation and extended

Adam–Gibbs theory have been applied to calculate the relaxation time and the activation energy of the enthalpy relaxation [12].

## Materials and methods

Sucrose (food ingredient grade) and distilled water were weighed and mixed to give 40 and 80 wt% sucrose. These mixtures were heated and completely dissolved, and any water that evaporated during preparation was added back.

Enthalpy relaxation was observed by DSC (Perkin Elmer DSC7). The temperature sequence of the DSC scan is shown in Fig. 1. First, the sample was initially kept at  $-35\text{ }^\circ\text{C}$  for 30 min to allow the maximum freeze concentration to develop. The temperature was then dropped to each of the following values  $-70$ ,  $-65$ ,  $-60$  or  $-55\text{ }^\circ\text{C}$ , and aged for between 24 and 144 h prior to the DSC scan.

The enthalpy relaxation time and the activation energy were calculated by KWW [18] and CRR (co-operative rearrangement region) [1] theories in accordance with previous work [1,12,18,19].

## Results and discussion

The DSC measurements were carried out using the temperature program shown in Fig. 1. The sample was initially annealed by holding it for 30 min at  $-35\text{ }^\circ\text{C}$  before ageing to allow the maximum amount of ice to develop [10]. This procedure was required to give good reproducibility to the DSC heating curves for 40% sucrose, and it was found that keeping the sample for any longer than at  $-35\text{ }^\circ\text{C}$  did not cause any difference (data not shown). This suggests that the procedure helped to complete the freeze concentration of 40% sucrose

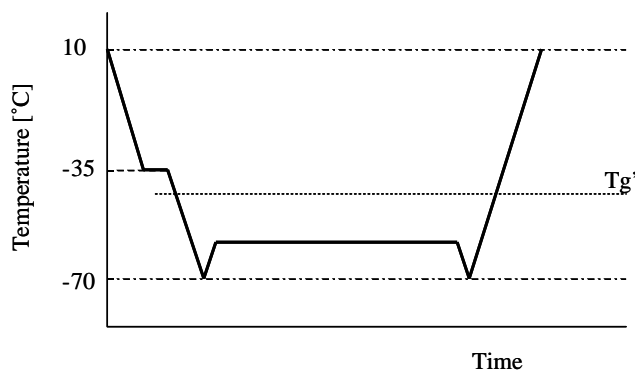


Fig. 1. Temperature program of DSC measurements.

and gave good reproducibility to the DSC heating curve.

Typical DSC heating curves for 40 and 80 wt% sucrose are shown in Fig. 2. The curve of 40% sucrose (non-annealed) showed three main features in the heat flow; an endothermic step-wise change identified as a glass-to-rubber transition on the freeze concentrated matrix, a small endothermic peak probably due to the onset of ice melting, and a large endothermic peak identified as the melting of the majority of the ice (Fig. 2). Those features are quite similar to previously reported results for sucrose [10]. The DSC curve of aged 40% sucrose showed an endothermic peak overlapping the glass transition. The curve of repeated scans without ageing (data not shown) did not show the peak and gave a similar trace to that of the non-aged glass. These results suggest that this peak appeared during the ageing process in the glassy state and may be the same enthalpy relaxation commonly observed with synthetic polymers.

The ageing procedure affected only the size of the initial peak that preceded the glass transition in the DSC curve and did not influence either the onset peak for ice melting or the main ice-melting peak.

These DSC features can be compared with those reported for 41% galactose [3] and 45% trehalose [16], where the ageing procedure was carried out at temperatures both below and above  $T_g$ . Our results showed trends that were very similar to those reported for the other types of sugar when the sample was aged below  $T_g$  [3,16].

The step-wise change of the glass transition for 40% sucrose without ageing exhibited a broad peak on the DSC trace (Fig. 2). This is similar to results that were previously reported for solutions of sucrose [10] and other disaccharides [3,16]. This suggests that enthalpy relaxation could easily happen in freeze concentrated sugar–water glasses under the present experimental conditions, and that some amount of enthalpy relaxation happens during the cooling and heating processes below  $T_g$  without a special ageing procedure. Thus, there is likely to be some contribution of enthalpy relaxation to the  $T_g$  transition, giving rise to the shape of the broad peak. Previous work on glassy starch has shown that the temperature at which the enthalpy relaxation occurs is related to the ageing temperature and increases with increase in the ageing temperature [13]. When the ageing temperature was low

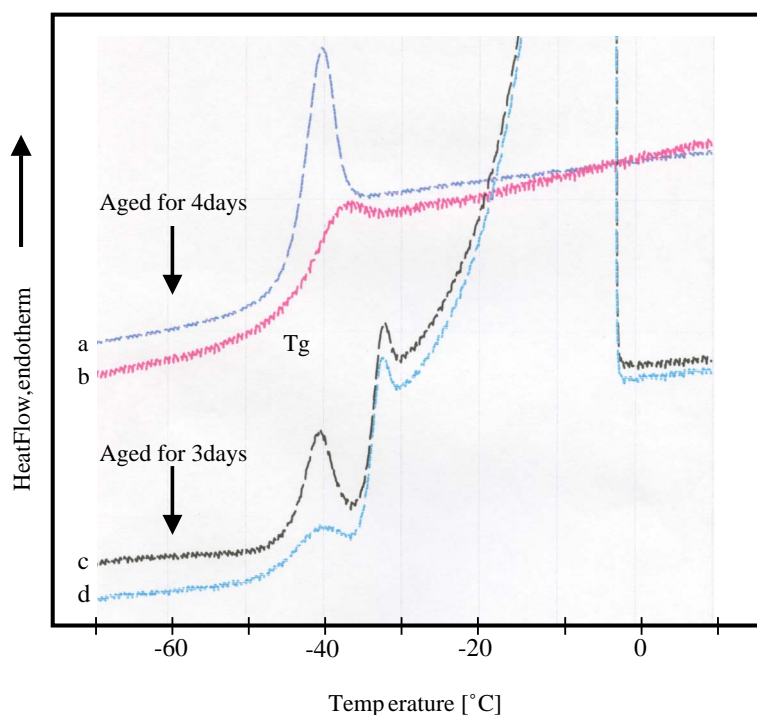


Fig. 2. DSC heating curves of sucrose solutions. Curve a, 80% aged at  $-60^{\circ}\text{C}$  for 4 days. Curve b, 80% not aged. Curve c, 40% aged at  $-60^{\circ}\text{C}$  for 3 days. Curve d, 40% not aged.

enough, the enthalpy relaxation peak appeared to be lower than, and independent of, the glass transition step. In contrast to this, when the ageing temperature was sufficiently high, the enthalpy relaxation peak overlapped the glass transition [13]. The latter seems to be the case in the present results.

The DSC curve of 80% sucrose (non-annealed) showed a single, step-wise change due to these glass transition, at a temperature that is in good agreement with the glass transition of 40% sucrose and did not show any evidence of freeze concentration, such as ice melting peaks (Fig. 2). Also the specific heat change of 40% sucrose at  $T_g$ , was 0.866 J/(g of 80% sucrose °C), which was in good agreement with that of 80%, 0.863 J/(g of 80% sucrose °C). These results suggest that the concentration of the freeze concentrated matrix of 40% sucrose corresponds to approximately to that of 80% sucrose, which is in agreement with previously reported maximally freeze concentrated concentrations ( $C'_g$ ) for sucrose of 79% [10] and 80.9% [14]. The DSC heating curve of aged 80% sucrose showed an endothermic peak overlapping the glass transition, similar to that seen with 40% sucrose, which is also considered to be due to enthalpy relaxation (Fig. 2).

According to the previous study [12], data for the enthalpy relaxation of the freeze concentrated sucrose–water glass were analysed in relation to molecular mobility. The peak area of the enthalpy relaxation was plotted against ageing time (Fig. 3).

(The peak area was calculated from the curve by subtracting the non-aged curve from the aged curve.) Enthalpy relaxation increased as the ageing time lengthened, and as the ageing temperature was raised. The results with 40 and 80% sucrose were in good agreement, within the scatter of the data (Fig. 3). The results show similar trends to those of reported for pure sugar glasses [12] and polymer glasses [4].

In KWW theory, the enthalpy relaxation is expressed by the equation [18],

$$\Delta H_{\text{relax}} = \Delta H_{\infty} \left\{ 1 - \exp \left[ - (t / \tau^{\text{KWW}})^{\beta} \right] \right\}, \quad (1)$$

where  $t$ ,  $\tau^{\text{KWW}}$ , and  $\beta$  are the ageing time, characteristic enthalpy relaxation time, and the non-exponential parameter, respectively.  $\Delta H_{\text{relax}}$  corresponds to the peak area due to the enthalpy relaxation.  $\Delta H_{\infty}$  is the maximum enthalpy recovery at the given temperature and is calculated from the following equation:

$$\Delta H_{\infty} = \Delta C_p (T_g - T), \quad (2)$$

where  $\Delta C_p$  is the specific heat change at  $T_g$  (determined from the DSC measurements.)  $T$  is the ageing temperature in Kelvin.

The calculated values of  $\beta$ s for 40 and 80% sucrose were in the ranges of 0.44–0.87 and 0.53–0.63, respectively, which is comparable to that reported for pure sucrose (0.53–0.62 [12]). Values that were calculated by using  $\beta$ ,  $\Delta H_{\infty}$ , and  $\tau^{\text{KWW}}$

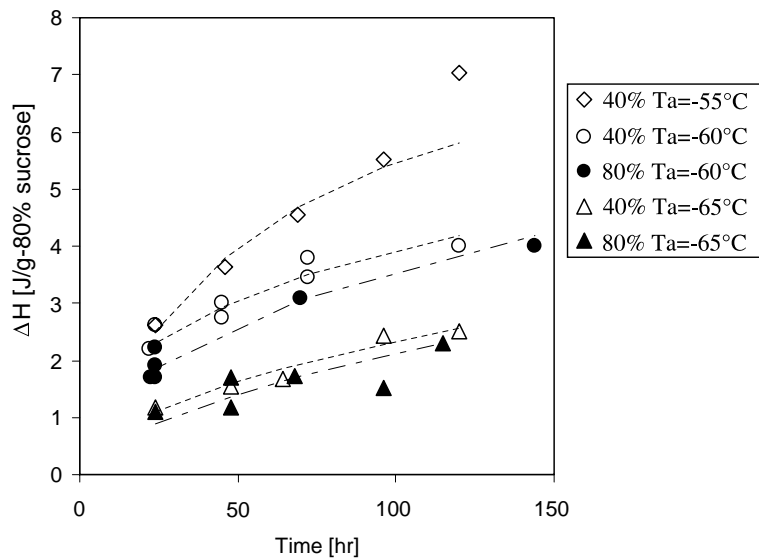


Fig. 3. Enthalpy relaxation of freeze concentrated glassy sucrose–water system versus ageing time.

are also plotted in Fig. 3 as lines, which gave good fits.

The Arrhenius plot of  $\tau^{\text{KWW}}$  for 40 and 80% sucrose is shown in Fig. 4, where the activation energy,  $\Delta E^{\text{KWW}}$ , is calculated to be 143.5 kJ/mol ( $R^2 = 0.8644$ ) and is smaller than that reported for pure sucrose (172.9 kJ/mol [12]). This suggests that the molecular structure of the sucrose–water glass may be different from that of pure sucrose glass and may be less stable than that of pure sucrose glass.

In the extended Adam and Gibbs equation, the enthalpy relaxation is described as follows [1]:

$$\frac{d[\Delta H_{\infty} - \Delta H_{\text{relax}}]}{dt} = -\frac{1}{\tau^{\text{eff}}(t)} [\Delta H_{\infty} - \Delta H_{\text{relax}}], \quad (3)$$

where  $(\Delta H_{\infty} - \Delta H_{\text{relax}})$  is the enthalpy deviation from the equilibrium and  $\tau^{\text{eff}}(t)$  is the effective enthalpy relaxation time. The plot of  $d(\Delta H_{\infty} - \Delta H_{\text{relax}})/dt$  versus  $(\Delta H_{\infty} - \Delta H_{\text{relax}})$  shows the exponential relation, thus the  $\tau^{\text{eff}}(t)$  is calculated as follows:

$$\ln \tau^{\text{eff}}(t) = \ln \tau_{\infty}^{\text{eff}} + B(\Delta H_{\infty} - \Delta H_{\text{relax}}), \quad (4)$$

where  $B$  and  $\tau_{\infty}^{\text{eff}}$  correspond to the slope and intercept of the plot of  $\ln \tau^{\text{eff}}(t)$  versus  $(\Delta H_{\infty} - \Delta H_{\text{relax}})$ , respectively (Fig. 5). The  $\tau_{\infty}^{\text{eff}}$  means  $\tau^{\text{eff}}(t)$  at which the enthalpy relaxed up to the equilibrium state ( $\Delta H_{\infty} = \Delta H_{\text{relax}}$  in the equation). The plots of Fig. 5 show the linear relationships at all ageing temperatures tested and suggest that the  $\tau^{\text{eff}}(t)$

depends on the level of relaxation.  $\tau^{\text{eff}}(t)$  also increases with increase in the amount of relaxation, which has been interpreted in accordance with the co-operative rearrangement region (CRR) of the enthalpy relaxation [1,12]. The slope of the plot of Fig. 5 means the rate of change of  $\tau^{\text{eff}}(t)$  with enthalpy relaxation and was calculated to be 0.86, 1.01, and 1.11 at ageing temperatures for  $-55$ ,  $-60$ , and  $-65$  °C, respectively; it seems to depend on the ageing temperature. However, there are insufficient data to permit further discussion.

The Arrhenius plot of  $\tau_0^{\text{eff}}$  and  $\tau_{\infty}^{\text{eff}}$  are also shown in Fig. 4, where  $\tau_0^{\text{eff}}$  is the relaxation time in the initial (unrelaxed) state. The activation energies,  $\Delta E_0^{\text{eff}}$  and  $\Delta E_{\infty}^{\text{eff}}$ , for 40% sucrose were calculated to be 1.95 ( $R^2 = 0.7110$ ) and 426.3 kJ/mol ( $R^2 = 0.9449$ ), respectively, and correspond to those at the minimum and maximum CRR, respectively. Although there is not enough data to calculate the activation energy of 80% sucrose, the values of the relaxation time for 80% sucrose were comparable with those for 40% sucrose (Fig. 4). As shown in Fig. 4, the activation energies of 40% sucrose obtained from the two different equations were larger in the order of  $\Delta E_{\infty}^{\text{eff}}$ ,  $\Delta E^{\text{KWW}}$ , and  $\Delta E_0^{\text{eff}}$  (Fig. 4), which is in the same trend as those reported for pure sugars [12].

According to data calculated by Adam–Gibbs theory, the activation energy of the enthalpy relaxation can change greatly and increase with the increase in the level of the relaxation, that is, from 1.95 for  $\Delta E_0^{\text{eff}}$  to 426.3 kJ/mol for  $\Delta E_{\infty}^{\text{eff}}$  corresponding to

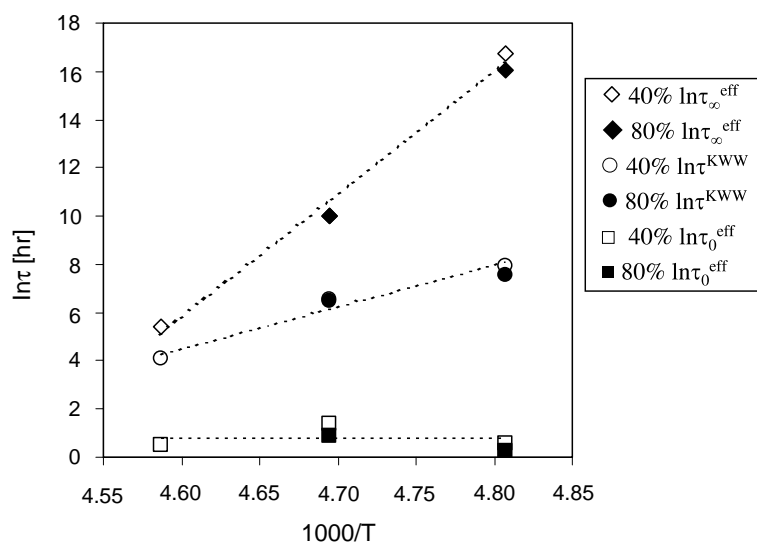


Fig. 4. Arrhenius plot of the calculated molecular relaxation time obtained by the enthalpy relaxation.

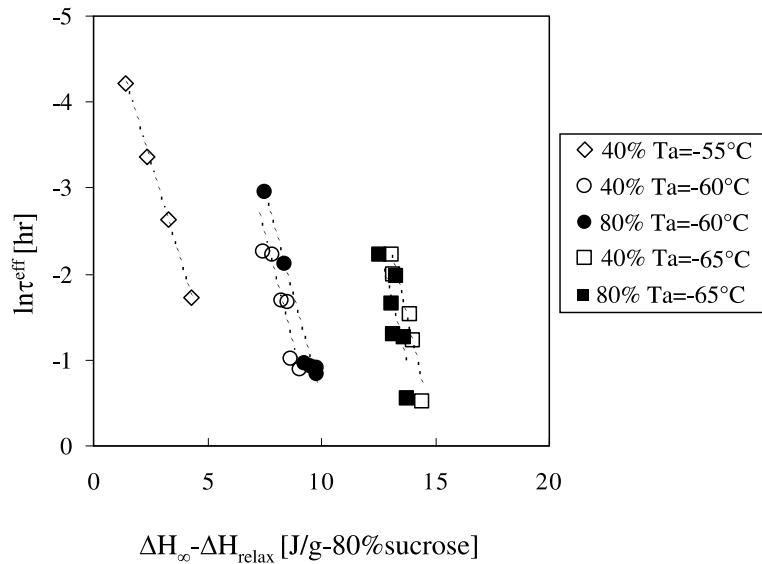


Fig. 5. Calculated molecular relaxation time versus the level of enthalpy relaxation.

the CRR. On the other hand, the  $\Delta E^{\text{KWW}}$  was evaluated to be between  $\Delta E_{\infty}^{\text{eff}}$  and  $\Delta E_0^{\text{eff}}$  (Fig. 4). The activation energies reported for pure sucrose are 172.9 and 320.0 kJ/mol of  $\Delta E_0^{\text{eff}}$  and  $\Delta E_{\infty}^{\text{eff}}$  [12], respectively. The present values for the 40 and 80% sucrose solutions are significantly smaller for  $\Delta E_0^{\text{eff}}$  and significantly larger for  $\Delta E_{\infty}^{\text{eff}}$ , with respect to those reported for pure sucrose. This suggests that the molecular arrangement in the sucrose–water glass might be different from that in the pure sucrose glass; it may have more molecular motion and less relative instability than pure sucrose in the non-aged state, and in turn, less molecular motion and more relative instability than pure sucrose in fully aged state.

## Conclusion

The enthalpy relaxation of freeze concentrated sucrose–water glass was investigated. The freeze-concentrated glassy matrix of 40% sucrose shows very similar behaviour to that of 80% sucrose, which is the maximal freeze concentration level for the frozen solution ( $C'_g$ ). The data have been successfully analysed by KWW and extended Adam–Gibbs theories. The freeze concentrated glass has a smaller activation energy than the pure sucrose glass, which suggests that it is relatively less unstable than the pure sucrose glass. These findings enable glasses to be determined from their enthalpy relaxation behaviour.

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