

## GLASS TRANSITION OF THE AMORPHOUS PHASE IN FROZEN AQUEOUS SYSTEMS

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### ABSTRACT

Thermal analysis can be successfully used for studying the enthalpy of complex glass transitions. The comparison of the incremental change in heat capacity in the glass transition temperature range for glassy or freeze-concentrated systems had indicated a large discrepancy. Theoretical calculations of heat capacity change in solid–liquid transitions show that the complex events observed in freeze-concentrated materials might be considered as the appearance of the glass transition of their amorphous fraction.

### INTRODUCTION

When a liquid is subjected to a sudden decrease in temperature, its properties (volume, enthalpy, viscosity . . .) exhibit an instantaneous solid-like change. This second-order transition called the glass transition must always be accompanied by a decrease in heat capacity and expansion coefficient.

It has long been recognized that some polymers undergo important changes in properties when plasticized by a relatively small amount of a plastifying agent such as water. These changes are associated with a considerable decrease in the glass transition temperature  $T_g$ .

Some equations have been given to predict the value of  $T_g$  as a function of the mass fraction [1], and of the incremental change in heat capacity of each compound [2].

The plasticizing effect of water has been demonstrated largely with polymers completely miscible with water such as polyvinylpyrrolidone (PVP) [3–5]. The same effect has been described with sugar–water systems, e.g. glucose [6], sorbitol [7] and galactose [8].

When the dilution of the solute becomes high, the experimental cooling rates are too slow to avoid the formation of ice crystals. With the aqueous solutions of many organic compounds such as those mentioned above, usually no eutectic formation is observed and the ice crystals are surrounded by an undercooled freeze-concentrated solution which contains all the solute

in the unfrozen fraction of the water. This undercooled solution undergoes a rubber-glass transition.

At present, if the reality of this glass phase is undoubted, the description and temperature of the transition are still a matter of debate [8,9]. To help characterize the features which are involved in the glass transition, we measured the enthalpy of observed thermal transitions for two different compounds in aqueous solution: polyvinylpyrrolidone and galactose.

## EXPERIMENTAL

Galactose (analytical reagent grade) was obtained from Merck and used as supplied. PVP of average molecular weight 40 000 (characterized by the manufacturer Sigma) was extensively dialysed against distilled water and recovered by freeze-drying.

The solutions were prepared with distilled water at concentrations of 10–50%. For higher concentrations, the solutions were obtained by evaporation, the solutions being heated in the volatile sample pan, the pan sealed and the concentration then determined by weighing. The concentrated PVP samples were used at least 12 h after dehydration; the concentrated galactose samples were used more rapidly (after 1 h) in order to avoid the crystallization of the sugar.

Calorimetric measurements were carried out on a Perkin-Elmer DSC2 differential scanning calorimeter, equipped with an ice-water bath (0 °C) or with a liquid nitrogen accessory.

The glass-rubber transition was observed during the rewarming of the sample. The glass transition temperatures were defined as the midpoint of the specific heat increments.

It is well recognized that the glass transition studied in the calorimetric measurement is a kinetic phenomenon determined by the relation between the structural relaxation time of the liquid and the experimental time scale, and therefore it is reasonable to use the same cooling and heating rates. The scanning rate was 10 K min<sup>-1</sup> and it was found to be low enough compared with glass relaxation rates.

Temperature calibration was carried out at the same scan rate using cyclohexane and water transitions for lower temperatures and azobenzol and indium for higher temperatures. Calibration of the heat flow was carried out by reference to the melting enthalpy of indium.

The increase in heat capacity was calculated from the experimental change in heat flow, the scanning rate and the sample weight:

$$\Delta C_p \text{ (J g}^{-1} \text{ K}^{-1}\text{)} = \Delta Y \text{ (W)} / W_s \text{ (g)} \times \text{scan rate (K s}^{-1}\text{)}$$

where  $\Delta Y$  is the heat flow and  $W_s$  is the sample weight. The main source of variability was the difficulty in determining the moisture content of the dry material accurately.

## RESULTS AND DISCUSSION

*Glass transition temperatures*

The glass-rubber transition of the amorphous galactose solutions could only be observed when the galactose concentration was greater than 55%. At lower concentrations the cooling rate was not fast enough to avoid ice crystallization. With the PVP + water system, the concentration limit was close to 50%.

Maximally freeze-concentrated solutions for the more dilute solutions were obtained by the following annealing procedure; after cooling a first heating was limited to 225 K, and followed immediately by cooling to 150 K and a complete rewarming. The comparison between thermograms of fully amorphous systems and freeze-concentrated solutions showed important differences (Fig. 1). So long as there was no ice in the analysed material the thermogram exhibited a typical change in heat capacity indicative of a glass transition (Fig. 1(a)). The glass transition temperature was markedly depressed with increasing water content for galactose [8] as for PVP [3-5].

When ice crystals were formed in the solutions the thermal transitions were more complex (Fig. 1(b)). The changes in the specific heat occurred in two steps, called here G1 and G2, at temperatures independent of the initial concentration. The middle transition temperatures were  $T_{g1} = 217$  K,  $T_{g2} = 230$  K for galactose solutions and  $T_{g1} = 240$  K,  $T_{g2} = 255$  K for PVP solutions. These transitions were immediately followed by ice melting endo-

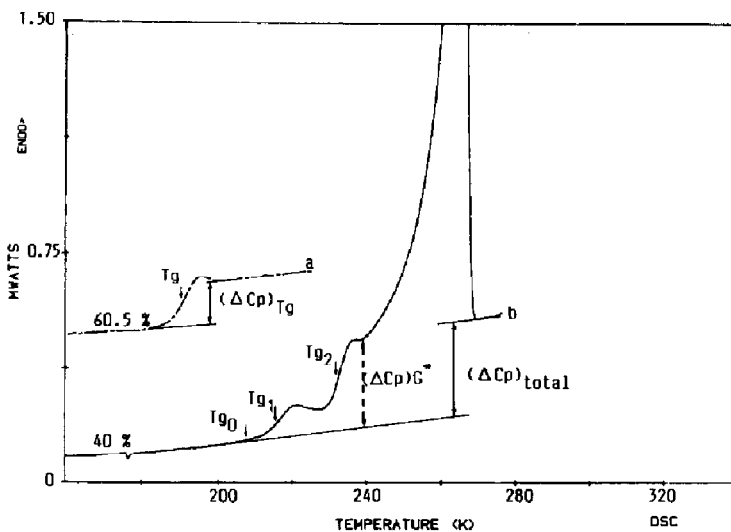


Fig. 1. Thermograms of galactose-water (mass fraction of galactose 0.40 and 0.605 respectively) to show the measurement of  $(\Delta C_p)_{T_g}$ ,  $(\Delta C_p)_{G^*}$  and  $(\Delta C_p)_{total}$ .

therms. The G1 event was often described as the glass transition of the amorphous phase, followed by two other events—ante melting and incipient melting [6].

Recently Levine and Slade [9] challenged the interpretation, considering the first event to be the transition due to an incompletely frozen amorphous phase followed by a devitrification. For these authors the unique important glass transition was the event G corresponding to our G2 event.

The two hypotheses we had proposed to explain these features in galactose solutions [8] were that they could be representative of either two distinct glass transitions taking place in two structured galactose phases or a single glass transition beginning at  $T_{g0}$  and involving an enthalpy relaxation process.

If the first hypothesis could be imagined for galactose solutions (hydrates having been described for different sugars [10]), there is no reason to expect a PVP hydrate to exist. The annealing experiments performed with galactose solutions to confirm the second hypothesis were not fully successful [8]. To explain these features a study of the enthalpy of the glass transitions could give some complementary information.

#### $\Delta C_p$ of thermal transitions

The difference in the heat capacities of glass and the undercooled melt ( $\Delta C_p$ ) is a useful variable when considering liquid state processes since it is the direct energy manifestation of changes in the material organization which occur once the glassy state has been lost by a sufficient increase in temperature. Liquids with a rapidly transforming structure will be characterized by large  $\Delta C_p$  values while those with temperature resisting organizations will show relatively small  $\Delta C_p$  values.

For samples without ice the heat capacity increment could be measured directly on the thermograms (Fig. 1, curve (a)). For galactose solutions with a concentration greater than 55%, the variation of  $(\Delta C_p)_{T_g}$  as a function of concentration (Fig. 2, curve (b)) is described by the regression equation

$$(\Delta C_p)_{T_g} = -0.17X_s + 0.93 \quad (1)$$

where  $X_s$  is the mass fraction of solute. Corresponding measurements with PVP solutions (Fig. 3, curve (b)) give the relation

$$(\Delta C_p)_{T_g} = -0.99X_s + 1.39 \quad (2)$$

The experimental values (eqn. (1)) are consistent with a linear variation between the  $(\Delta C_p)_{T_g}$  values measured for dry galactose and amorphous water.

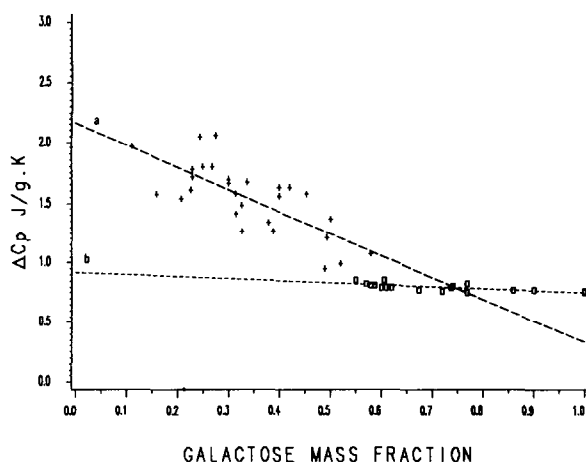


Fig. 2. Change in heat capacity as a function of galactose mass fraction between the glass and the supercooled melt  $\Delta C_{pT_g} = \square$  for samples without ice (correlation coefficient = 0.70, high significant value as the critical value at  $P = 0.01$  is equal to 0.57) (plot a) and between the solid state and the solution  $\Delta C_{p(\text{total})} = +$  for sample with ice (correlation coefficient = 0.74, very highly significant value,  $P = 0.001$  to  $cv = 0.59$ ) (plot b). (Straight lines are drawn by the least squares regression method).

The experimental value of  $\Delta C_p$  found in the present study for dry galactose ( $0.75 \text{ J g}^{-1} \text{ K}^{-1}$ ) is similar to the figures published by Weitz and Wunderlich [11] for sucrose ( $0.75 \text{ J g}^{-1} \text{ K}^{-1}$ ) and more recently by Orford et al. [12] for some oligosaccharides ( $0.88$  and  $0.79 \text{ J g}^{-1} \text{ K}^{-1}$  for glucose and maltose respectively). However, Finegold et al. [13] gave significantly different values for glucose and sucrose ( $0.55$  and  $0.31 \text{ J g}^{-1} \text{ K}^{-1}$  respectively).

The heat capacity change which was considered as the glass transition for dry galactose was the one occurring at a lower temperature (302 K). Although the thermal event taking place at a higher temperature was claimed to represent the glass transition by Slade and Levine [14], it is probably not so [13].

Equation (1) gives an extrapolated value for pure water of  $(\Delta C_p)_{T_g} = 0.93 \text{ J g}^{-1} \text{ K}^{-1}$  and eqn. (2) gives  $(\Delta C_p)_{T_g} = 1.39 \text{ J g}^{-1} \text{ K}^{-1}$ ; these values are consistent with the ones determined by Angell and Tucker [15] by extrapolation of the figures obtained with several electrolyte aqueous solutions over a range of concentrations,  $(\Delta C_p)_{T_g} = 19\text{--}25 \text{ J mol}^{-1} \text{ K}^{-1}$ .

These values can be discussed because different values have been reported by other authors. Sugisaki et al. [16] using a sample of vapour-deposited water determined  $(\Delta C_p)_{T_g} = 1.94 \text{ J g}^{-1} \text{ K}^{-1}$  (with 134 K for the glass transition temperature).

A much lower value  $(\Delta C_p)_{T_g} = 0.1 \text{ J g}^{-1} \text{ K}^{-1}$  was recently reported by Hallbrucker et al. [17]; it may be possible that in the latter case  $\Delta C_p$  was underestimated because the glass transition was immediately followed by the exothermic crystallization of the ice. Perhaps, as suggested by the authors,

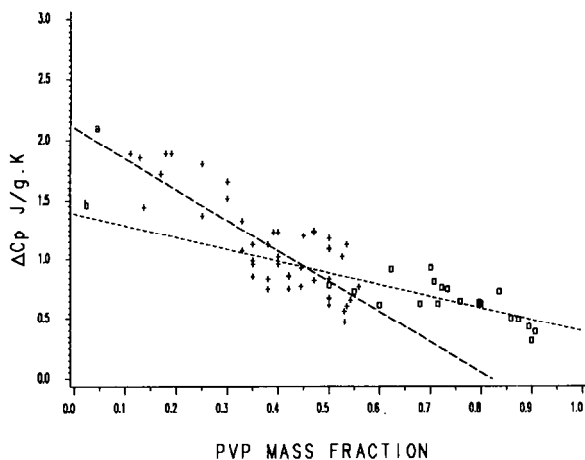


Fig. 3. Change in heat capacity as a function of PVP mass fraction between the glass and the supercooled melt  $(\Delta C_p)_{T_g} = \square$  for samples without ice (correlation coefficient = 0.71, very highly significant value,  $P = 0.001$  to  $cv = 0.69$ ) (plot a) and between the solid state and the solution  $(\Delta C_p)_{total} = +$  for samples with ice (correlation coefficient = 0.82, very highly significant value,  $P = 0.001$  to  $cv = 0.47$ ) (plot b).

this discrepancy could be an indication that the behaviour of aqueous amorphous solutions cannot be extrapolated to that of pure water.

With eqn. (2) the calculation gives a value of  $(\Delta C_p)_{T_g} = 0.4 \text{ J g}^{-1} \text{ K}^{-1}$  for dry PVP ( $T_g = 435 \text{ K}$ ), which is close to those found with polymeric systems [11]. Experimental dry PVP data have not been used (Fig. 3, curve (b)). The total dehydration was difficult because of thermal decomposition of the material and the measured  $\Delta C_p$  values were not reliable.

For samples containing ice the specific heat increment  $(\Delta C_p)_{G^*}$  corresponding to both steps G1 and G2 (Fig. 1, curve (b)) was measured. The results were very different from the observed glass transition values in fully amorphous materials. Figure 4 shows the results for galactose solutions. Considering the invariance of temperatures  $T_{g1}$  and  $T_{g2}$  it was assumed that the freeze-concentrated glass had a constant water content (unfreezable water content ( $W_{uf}$ )). The  $(\Delta C_p)_{G^*}$  is calculated per gram of glass phase, with  $W_{uf} = 0.42 \text{ g water (g galactose)}^{-1}$  for galactose solutions [8]. Similar behaviour was observed with PVP solutions.

Two hypotheses can be proposed to explain this discrepancy.

(i) the increase of the glass transition enthalpy increment could be due to a densification of the glass by the growth of ice crystals. Weitz and Wunderlich [11] indicated that the glass transition enthalpy increased almost linearly with increasing pressure for some glasses and particularly for sucrose glass,

(ii) The glass transition in the freeze-concentrated phase would be superimposed upon the incipient melting of ice (this second hypothesis seems more realistic).

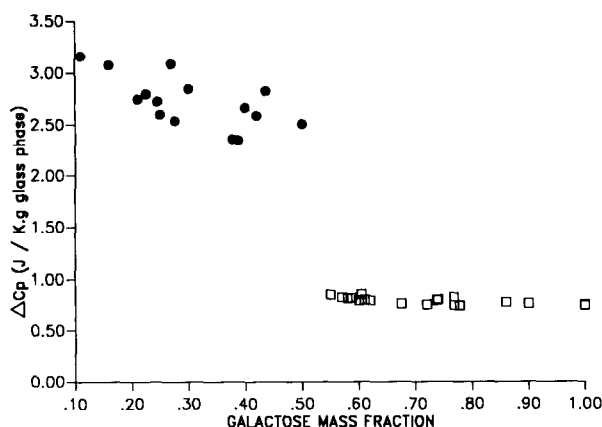


Fig. 4. Heat capacity increment of the amorphous phase transitions in galactose solutions: ●, G\* for samples containing ice; □, G for samples without ice.

Therefore, the total change in heat capacity between the solid state (glass + ice) and the solution was measured  $(\Delta C_p)_{total}$  (Fig. 1, curve (b)). The results for galactose solutions are reported in Fig. 2(a) and can be described by

$$(\Delta C_p)_{total} = -1.83X_s + 2.16 \quad (3)$$

The equation describing the regression line (Fig. 3, curve (a)) for the changes in heat capacity in the solid-liquid transition for freeze-concentrated PVP solutions is

$$(\Delta C_p)_{total} = -2.56X_s + 2.11 \quad (4)$$

The calculated intercept value is equal to 2.16 (confidence level at  $P = 0.95$ , 1.92–2.40) with eqn. (3) and 2.11 (confidence level at  $P = 0.95$ , 1.89–2.33) with eqn. (4). These values are very close to the ice-liquid heat capacity change at 273 K.

Eqns. (3) and (4) agree closely with the theoretical relation eqn. (5) considering that  $(\Delta C_p)_{total}$  is the sum of  $(\Delta C_p)_{T_g}$  for the freeze-concentrated glass and  $(\Delta C_p)_{ice-liquid}$  for the ice fraction.

For 1 g of sample

$$(\Delta C_p)_{total} = X_g(\Delta C_p)_{T_g} + X_i(\Delta C_p)_{i-1} \quad (5)$$

$X_g$  and  $X_i$  are the mass fractions of glass and ice respectively,  $X_g = X_s(1 + W_{ur})$ . Using  $(\Delta C_p)_{i-1} = 2.09 \text{ J g}^{-1} \text{ K}^{-1}$  for water and glass samples composed of 0.704 galactose and 0.633 PVP mass fraction respectively,  $(\Delta C_p)_{T_g} = 0.80$  (eqn. (1)) and  $(\Delta C_p)_{T_g} = 0.76$  (eqn. (2)) eqn. (5) gives

$$(\Delta C_p)_{total} = -1.90X_s + 2.09 \quad (3')$$

$$(\Delta C_p)_{total} = -2.10X_s + 2.09 \quad (4')$$

In writing eqn. (5) the value of  $(\Delta C_p)_{i-1}$  was assumed to be constant; this is not entirely correct, since the melting point of ice is a function of the concentration of the system. However, the variation of  $(\Delta C_p)_{i-1}$  in the interesting temperature range was found to have a negligible effect.

The change in  $\Delta C_p$  of the solution, caused by the dilution of the glass, was also neglected in eqn. (5) since data available on PVP solutions [18] showed this approximation was justified. These results demonstrate that both G1 and G2 events are truly associated with the glass transition of the amorphous freeze-concentrated phase.

For samples containing ice, the direct measurement of  $(\Delta C_p)_{T_g}$  is not reliable because of the overlap of the glass transition with the melting endotherm. The relaxation phenomena observed with the glass transition might be due to the incipient ice melting but techniques other than DSC have to be used to confirm this fact.

Moreover the experimental dependence of solid-liquid transition enthalpy on composition can be modelled by a simple empirical equation based on the rule of mixtures the same additivity is observed when different thermal events such as the glass transition and melting are associated.

## CONCLUSION

This study of glass transition enthalpy clearly shows the complexity of the glass transition of the amorphous fraction in a freeze-concentrated aqueous system. We have demonstrated that the heat capacity increment of the solid-liquid transition is the sum of the glass transition enthalpy of the glass fraction and the heat capacity change of the ice melting transition. However, if they permit determination of the beginning of the glass transition, the  $\Delta C_p$  data are no help in explaining the two events which are the thermal expression of this glass transition.

An additional feature of the thermal behaviour of these solutions is that the heat capacity of each mixture is a simple weighted average of the specific heats of pure materials. This indicates the mixture compatibility and suggests that the compounds interact weakly.

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