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Thermodynamic strength of the glassy state and the maximum enthalpy stored in the propylene glycol–D₂O system¹

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Abstract

The glassy state of several concentrations of propylene glycol in D₂O is presently characterized by enthalpy relaxation experiments. The existence of a lowest glass transition temperature T_g has defined an utmost excess enthalpy that can be stored by the glass during cooling. Similar to the thermal behavior of the shear viscosity for liquids, these T_g values are maximum for the binary system with compositions in the range 78–82% (w/w) propylene glycol in D₂O, suggesting that these concentrations correspond to the strongest glasses, and provide a higher thermodynamic strength for these glasses. These glasses correspond also to the maximum excess enthalpy that can be stored by the glassy state during cooling. These concentrations present, however, an apparent minimum threshold stress to induce fracture nucleation in the glasses with the definition of a maximum mechanical fragility. The present results underline a problem in the definition of the thermodynamic and mechanical strength of the glassy state as an extension of the fragility definition for liquids.

Keywords: D₂O; Fragile glasses; Glass transition; Kinetics; Propylene glycol; Strong glasses

1. Introduction

The definition of a new characteristic of the glassy state, the lowest glass transition temperature, T_g , that can be reached by glass-forming aqueous solutions [1–3], which is

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independent of cooling/warming rate, has led to the definition of an utmost excess enthalpy that can be stored by the glassy state during cooling [4]. These values are physically important as the relaxation of the glassy state can be followed by calorimetry from the glassy state after cooling towards the ideal glassy state reached after an infinite time of annealing, providing that the annealing temperature is sufficiently low below the Kauzmann temperature defined as the isentropic point between the liquid and the crystalline states [5]. The enthalpy relaxation between the glass transition and the Kauzmann temperature has also been described as the relaxation of the glassy state towards the extrapolated supercooled liquid [6, 7].

Recent developments on the glassy state have shown that a new point can be used for the characterization of the glassy state [1–3]. The variation of the glass transition temperature is limited to the lowest value than can be reached using an infinitely slow cooling rate [8–10]. The relaxation process is limited by the definition of an isenthalpic point between the supercooled liquid and the crystalline phase. The definition of such a point provides the maximum excess enthalpy than can be stored by the glassy state after cooling [4].

The relaxation process is also related to the ability of the glassy state to release the thermal stresses within it. The creation of fractures is similar to a thermally activated process such as bond breaking and the literature suggests that the activation energy for crack formation rates is decreased by a factor proportional to the thermal stresses applied to the glassy state [11]. Therefore the dissipation of the thermal stresses will be associated with the relaxation of the local energy through the elastic energies stored in the intermolecular bonds. Enthalpy relaxation times of the glassy state as a function of the temperature are, therefore, of great importance for the characterization of the glassy state.

Curran et al. have reviewed the dynamics of the nucleation and growth of fractures in materials within various theories, but all defining a threshold stress which is proportional to the ratio of temperature to bond-breaking strain [12]. The glass strength has been assumed to be related to the definition of a fragility factor provided by a similar ratio of the activation energy for the shear viscosity divided by the glass transition temperature. The activation energy similarly represents the energy of breaking bonds at the glass transition. One notes that this ratio is the inverse of that defining the threshold stress for the nucleation of fractures. A higher ratio leads to an (Arr)-like representation and a lower value to a Vogel–Fulcher–Tamman (VFT)-like representation [13] with a higher fragility for the VFT-like glasses.

Angell has shown a correlation between the variation of the specific heat at the glass transition and the strength of the liquid state. Therefore he characterizes the strength of the material with the variation of the specific heat at the glass transition [14]. Other authors, however, disagreed with this definition and the discussion is still open [15].

Extending the definition of fragile/strong liquids to the glassy state, which can be considered as the frozen state of the supercooled liquid, the strength, or the notion of strong/fragile glass, will reside in determining the strength of the bridging network between the molecules; the two last characterizations provide an ambiguous view of the strength of glasses compared to the definition of the thermal activation theory of the nucleation of fractures.

With the example of the binary system propylene glycol–D₂O, we intend to show that the definition of the strength of the glassy state is at least related to the ability of the glassy state to store a maximum energy, but leads to a minimum threshold stress as related to the ratio of apparent activation energy to temperature.

2. Materials and methods

1,2-propanediol (99 + % from Aldrich) was mixed with deuterium oxide D₂O, 100 atom% D from Sigma) at various final concentrations. Both compounds were used without further purification. Samples of 10 to 20 mg were placed in a DSC-4 (from Perkin–Elmer) adjusted for low temperatures. Temperature and energy calibrations of the calorimeter were performed as usual [16]. Previous studies on aqueous solutions of polyalcohols have shown that the optimum variation of the glass transition temperature with the cooling and warming rates corresponds to an identical rate for the cooling and the subsequent warming [4, 8–10]. The determination of glass transition temperatures is always performed during warming because the calibration of the DSC-4 is not as precise during cooling as during warming, where the thermal control is more efficient. Under these conditions, the minimum temperature T_g is determined as the parameter which best fits the relationship [1–4]:

$$\ln(V_c) = S/(T_g - T_s) + \ln(C) \quad (1)$$

where V_c is the rate of the cooling which is identical to the warming rate, T_g is the glass transition during warming at V_c after being cooled at V_c down to 30°C below the recorded glass transition temperature, and C can be considered as a constant for the thermal range considered. A similar fragility coefficient F to that from the shear viscosity [13] is provided by:

$$F = -S/T_s \quad (2)$$

The determination of these values of T_g for different concentrations of propylene glycol in D₂O is used for the determination of the utmost excess enthalpies that can be stored by the glassy states during cooling to a common temperature below T_g . These excess enthalpies are calculated from a previous study on enthalpy relaxation with annealing experiments in the binary system propylene glycol in D₂O [17].

3. Results and discussion

A typical optimum representation of $\ln(V_c)$ versus $1000/(T_g - T_s)$ is reported in Fig. 1 for 90% w/w 1,2-propanediol in D₂O. The slope, as apparent activation energy, is determined for the best fit corresponding to the higher regression coefficient. The curves of the optimum values of T_g have been reported in Fig. 2 with the polynomial regression curve of the fourth order in propylene glycol concentration.

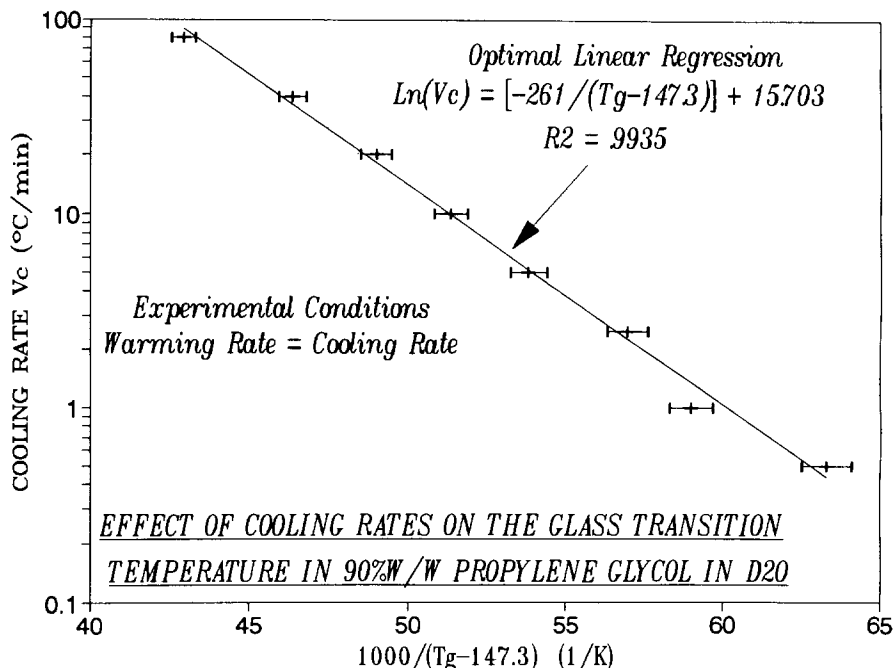


Fig. 1. Representation, using Eq. (1), of the effect of the cooling rate V_c on the glass transition temperature T_g . T_g is the optimum value providing the best fit to the linear regression for Eq. (1) The line is the regression line corresponding to the reported equation with the square of the regression coefficient, R^2 .

A similar fragility coefficient F can be defined as in Eq. (2). The values of the fragility coefficients are reported in Fig. 3 as a function of the propylene glycol concentration. The maximum of these values is observed for concentrations close to a 1 : 1 molar ratio. A previous study on the determination of the enthalpy of relaxation in the same binary system has shown that this concentration presents the lowest relaxation time at the same temperatures [10]. This concentration is similar to that of formation of the eutectic [10].

Assuming that the activation energy is proportional to the mean bond breaking energy at the glass transition, the threshold stress that can be applied to the glass before the appearance of nucleating fractures is proportional to the inverse of F and to the molar number of bonds [12]. Therefore, as reported in Fig. 3, the maximum of F corresponds to a minimum in the threshold for the stress, assuming that the molar number of bonds is constant or at least decreases for propylene glycol molecules as D_2O molecules act as bridges between the solute molecules. The definition of F is, therefore similar to the maximum destabilization of the glassy state of propylene glycol by the addition of D_2O , as D_2O acts as a plasticizer for the glassy state of propylene glycol.

The analysis of the enthalpy relaxation in the binary system propylene glycol- D_2O is related to the determination of the maximum excess enthalpy stored during cooling

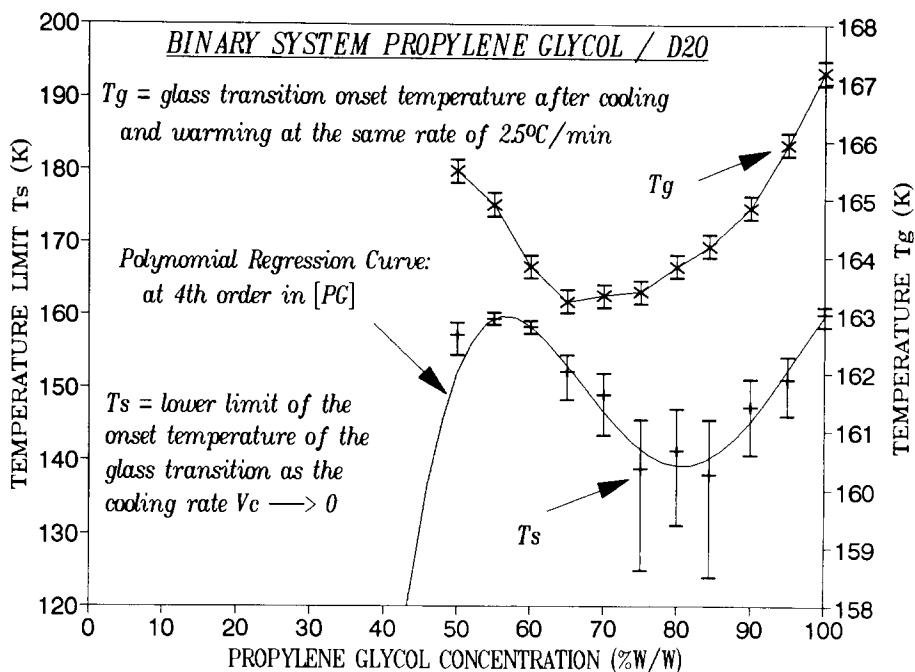


Fig. 2. Representation of the glass transition temperature T_g and of its lowest value T_s as functions of propylene glycol concentration [PG]. The lines are placed between results for T_g for greater clarity. The line for T_s is a polynomial regression line of the fourth order in [PG]. Below 60% w/w propylene glycol, ice nucleation during cooling is possible.

in the glassy state. This excess enthalpy is defined as the difference between the enthalpy of the glassy state after cooling and that of the extrapolated supercooled liquid [4,17]. The enthalpy relaxation times can be obtained by using the Kohlrausch–Watts–Williams function as the best fitted function for the relaxation function [4,17]. The maximum excess enthalpy as a function of temperature has been approximated to a linear function such as:

$$H(\text{glass}) - H(\text{supercooled liquid}) = CT + H_0 \quad (3)$$

where T is the temperature. The glassy state is obtained after cooling at $40^\circ\text{C min}^{-1}$ from room temperature for various concentrations [17]. This representation gives results only slightly different (less than 3%) from those given by the C/T representation used to convert the Adam–Gibbs equation into the Vogel–Fulcher–Tamman equation for the relaxation times [14]. The values of the constants C and H_0 are reported in Fig. 4 with the polynomial regression curves associated with the experimental values. The polynomial regression curves are second order in propylene glycol concentration [PG]. Eq. (3) is similar to the approximate representation of the difference of enthalpy

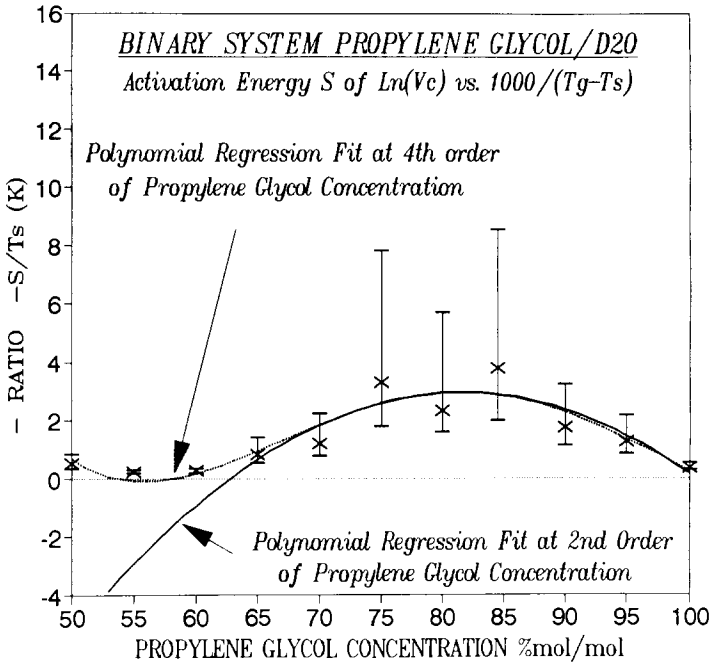


Fig. 3. Representation of the fragility factor (the ratio $-S/T_s$) as a function of the propylene glycol concentration. The best fit provided by polynomial regression of second and fourth orders is given for comparison. One must remember the possibility of ice nucleation during cooling at concentrations below 60% w/w.

between the glassy state after cooling at V_c and the supercooled liquid state as:

$$H(\text{glass}) - H(\text{supercooled liquid}) = g(\delta C_p^{T_g})(T_g - T_s) \tag{4}$$

where g is a factor taking into account the presence of the overshoot at the glass transition [4] and $\delta C_p^{T_g}$ is the variation of the specific heat at the glass transition temperature T_g , assuming that this variation is constant over the thermal range considered between T_g and T_s .

The polynomial regression curves from Figs. 2 and 4 have been used for the determination of the utmost excess enthalpy stored by the glassy state after cooling at $40^\circ\text{C min}^{-1}$ down to -150°C . The corresponding values are reported in Fig. 5 as a function of the propylene glycol concentration. A maximum value is noticed at the concentration which corresponds to the minimum value of T_s . The strongest interaction between the molecules of propylene glycol and D_2O at the molar ratio 1:1 corresponds, therefore, to the maximum excess enthalpy stored within the glassy state. As the thermal stresses are related to the energy stored and to the thermal gradient seen by the glassy state, the concentrations corresponding to these utmost values are those which will be submitted to the highest thermal stresses. These thermal stresses could be dissipated for rapid enthalpy relaxation times. As reported previously [17], these

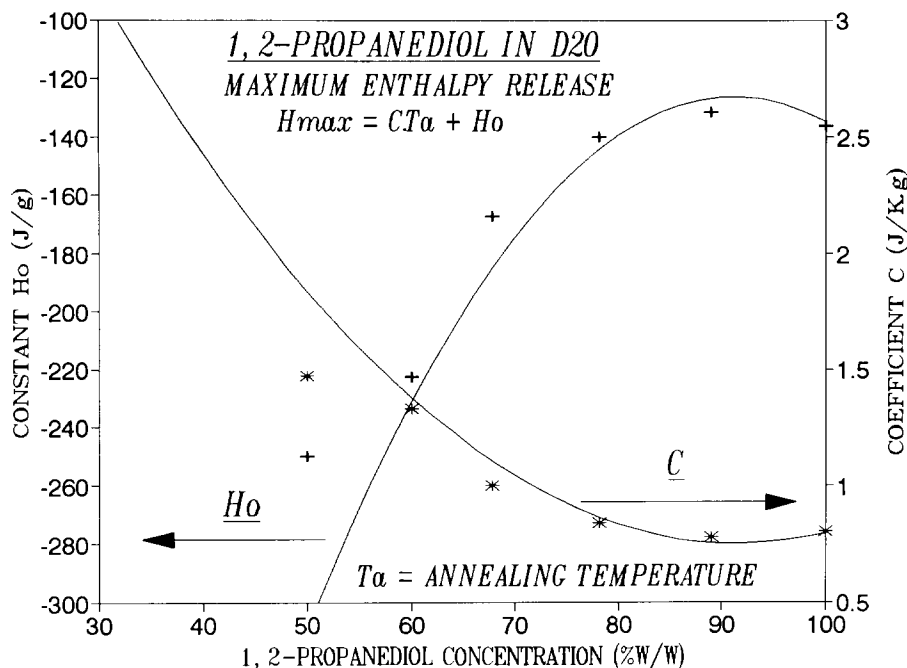


Fig. 4. Representation of the coefficients C and H_0 defining the thermal variations of the maximum excess enthalpy stored during cooling. The curves are second order polynomial regression curves as functions of the propylene glycol concentration.

concentrations around 80% w/w correspond to a minimum of enthalpy relaxation times for a fixed temperature and, therefore, to higher stress release rates.

4. Conclusion

The combination of the enthalpy relaxation study using annealing experiments and the determination of the lowest glass transition temperature, T_g , with the apparent activation energy provides a calorimetric method for the determination of the “strongest” glassy state in the binary system propylene glycol–D₂O. This strongest glassy state corresponds to the maximum excess enthalpy stored within the glass. This indicates that the strongest glassy state, as defined by C.A. Angell and coworkers [13, 14], for the liquids corresponds to the glassy state which is potentially able to store the highest enthalpy. This corresponds to the maximum thermodynamic stability of the glassy state as at this concentration it has the possibility of relaxing more rapidly at sub-glass-transition temperatures than at other concentrations.

This glass is not, however, directly associated to the maximum mechanical strength of the glassy state as defined by the threshold stress for the nucleation of fracture. This

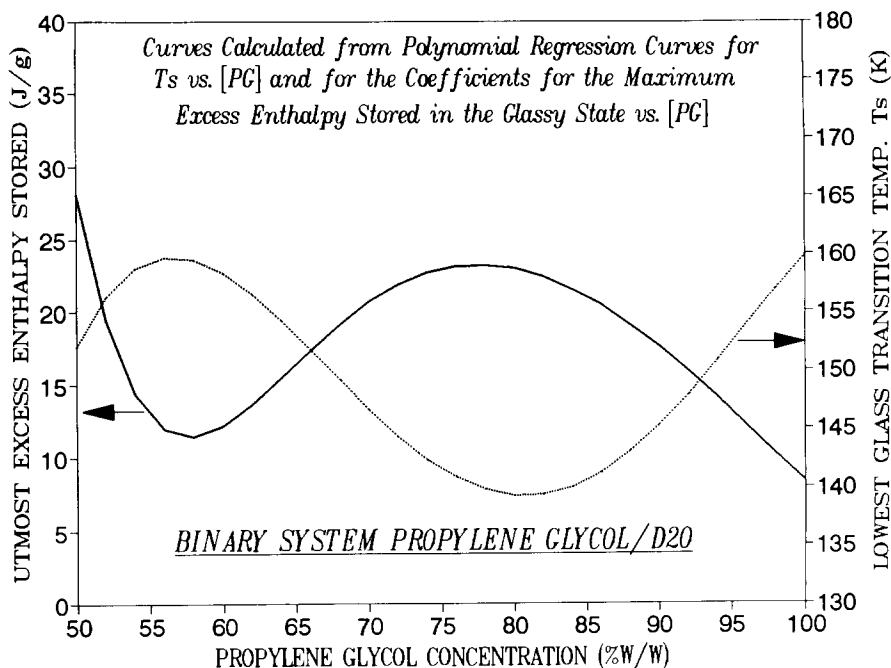


Fig. 5. Comparison of the utmost values of the excess enthalpy that can be stored by the glassy state after being cooled at $40^{\circ}\text{C min}^{-1}$ and of the lowest glass transition temperatures as functions of the propylene glycol concentration. The curves are calculated from the polynomial regression curves given in Figs. 2 and 4.

introduces confusion into the terminology of the strength of the glassy state, as the definition of the fragility factor, F , leads to opposite conclusions. An increase in the average number of bonds per unit of volume could be responsible for the apparent disagreement in the definition of the strength of the glassy states. A test with direct observations of fracture creation is therefore needed in order to reach a conclusion on the mechanical properties of these glassy states. The nature of the glassy state is more complex to define than to classify it as strong or fragile in terms of its thermodynamic or mechanical properties. Indeed, the capability of the glassy state to store energy, and the stress release rates characteristic of the glassy state, are two related processes which can be tested. These tests will then have also to master the geometric conditions inducing the thermal gradient through the thermal conductance of the sample if calorimetric results are to be compared with estimates of the stress threshold for the nucleation of fractures, in the glassy state by use of thermal mechanical tests.

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