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# Determination of enthalpy relaxation times using traditional differential scanning calorimetry for glycerol and for propylene glycol[1]

Patrick M. Mehl[2]

*Holland Laboratory, American Red Cross, 15601 Crabbs Branch Way, Rockville, MD 20855, USA*

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## Abstract

The isothermal enthalpy relaxation of glycerol and propylene glycol is studied for different sub-glass transition annealing temperatures using our usual method. The kinetics of the glass transition is analyzed using the Kohlrausch–Williams–Watts model. The Vogel–Fulcher–Tamman model was previously used for the spectrometric specific heat analysis of glycerol and propylene glycol by Birge and co-workers at temperatures higher than the glass transition. We present the comparison of the enthalpy relaxation times as a continuation of their data for sub-glass transition temperatures. The results show an intermediate thermal domain between the liquid state and the glassy state. The relaxation times are experimentally determined within the model of the non-exponential relaxation theory. The effects of the cooling and warming rates are also investigated for their relevance in the determination of the relaxation times.

*Keywords:* DSC; Glycerol; Propylene glycol; Enthalpy; Relaxation

## 1. Introduction

Propylene glycol and glycerol are commonly used in the biological and pharmaceutical sciences. They are actually pharmaceutical additives and used as glass formers in aqueous solutions for applications such as freeze-drying techniques. They are common

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[1] Presented at the 23rd North American Thermal Analysis Society Conference, Toronto, Ont., Canada, 25–28 September, 1994.

[2] Present address: Transfusion Medicine Research Program, Naval Medical Research Institute, 8901 Wisconsin Avenue, Bldg. 29, Bethesda, MD 20889, USA.

*SSDI* 0040-6031 (95) 02455-7

cryoprotectants for the preservation of simple biological systems at low temperatures by preventing massive ice crystallization. They are also used as vitrification agents in the design of vitrification solutions for the cryopreservation of organized tissues and organs by vitrification. Therefore for their capability to vitrify and for a better understanding of the glassy state, the study of the enthalpy relaxation is presented for the pure compounds as an introduction to the investigation of their aqueous solutions. The method for the investigation of the calorimetric enthalpy relaxation has been developed to have access to the enthalpy relaxation times using isothermal experimental conditions [1,2]. The importance of the enthalpy relaxation processes is underlined by the uncertainty of the behavior of the materials below the glass transition. Macroscopic consequences are fracture creations or collapses of the freeze-dried products or phase separations. As a first step to understanding these processes, isothermal experiments at sub-glass transition temperatures for propylene glycol and glycerol provide a method for the calculation of enthalpy relaxation times. These results are then compared with published data of enthalpy relaxation times for experiments above the glass transition temperatures [3,4]. The introduction of the notion of the lowest glass transition temperature by Shi which is presented in a separate paper, allows the determination of a specific domain below the glass transition where the configuration of the material is similar to that of the ideal glass and completes the characterization of the glassy state [5,6].

## 2. Materials and methods

Propylene glycol (99%+ from Aldrich) and glycerol (ACS reagent from Sigma) were without any further purification. The calorimetry was carried out using a DSC-4 from Perkin-Elmer adapted for low temperatures. The temperature and energy calibration of the DSC-4 was done as usual with various melting peaks of pure compounds [1]. Samples were placed in the calorimeter at room temperature and cooled at 40°C min$^{-1}$ to below the glass transition at −150°C and −130°C, respectively, for propylene glycol and glycerol before annealing.

The analysis of the glass transition kinetics was done as usual [1,2]. The excess enthalpy released during annealing by the glassy state was calculated using the glassy state with annealing of 0 min as a reference. This excess enthalpy was analyzed using the Kohlrausch–Watts–Williams function or stretched relaxation function for non-linear relaxation [7]:

$$\frac{\delta H[t_a;T_a]}{\delta H[\infty;T_a]} = \exp\left[-\left(\frac{t_a}{\tau[T_a]}\right)^{\beta}\right] \tag{1}$$

where $t_a$ and $T_a$ are the annealing time at the temperature $T_a$. $\beta$ is an exponent reflecting the non-linearity of the relaxation process of the glassy state and $\tau(T_a)$ is the relaxation time at the temperature $T_a$. The determination of the different parameters was done as usual [1,2].

A recent description of the nature of the glass transition showed a characteristic parameter of the glass transition with the lowest glass transition temperature $T_s$ which can be reached by the glassy state [5,6]. $T_s$ is rate independent, even if the glass transition itself is. These temperatures $T_s$ are determined with the best fit of the representation

$$\ln(V_c) = \frac{-S}{T_g - T_s} + \ln(C) \quad (2)$$

where $V_c$ is the rate of cooling or heating. These experimental conditions optimized the identification of the fictive temperature of the glassy state with the glass transition temperature $T_g$. The determination of $T_s$ allowed the estimates of the utmost excess enthalpy that can be stored by the glassy state. Therefore three thermal domains were considered for the present study. The first domain was the liquid domain above the glass transition, the second in the range between $T_g$ and $T_s$ where the maximum excess enthalpy is temperature dependent, which is similar to the rubbery state for polymers and the third below $T_s$ where the maximum has reached its utmost value. For the last two thermal domains, the enthalpy relaxation times were represented by an Arrhenius thermal variation as reported in other publications for ion conductance below the glass transition. For the thermal domain above the glass transition, a Vogel–Fulcher–Tamman was assumed as the best representation of the published data.

## 3. Results

The variations with the annealing time of the excess enthalpy for propylene glycol and for glycerol for chosen annealing temperatures are reported respectively in Figs. 1 and 2. The data are fitted with Eq. (1). A relaxation function $\theta$ can be defined as

$$\Phi[t_a; T_a] = \frac{\delta H[t_a; T_a]}{\delta H[\infty; T_a]} \quad (3)$$

This relaxation function is calculated and reported in Fig. 3 for glycerol as a function of the annealing time $t_a$. $t_a$ is reported in a logarithmic scale and the relaxation function is reported as $\ln(-\ln(\theta))$ as usual. The representation gives theoretically linear curves. The regression determines the relaxation times $\tau$ and the exponent $\beta$ by combining Eqs. (1) and (3).

Then the relaxation times $\tau$ can be analyzed as a function of the annealing temperatures. But the temperatures $T_s$ have still to be determined based on Eq. (2). The variation of $\ln(V_c)$ with $1000/(T_g - T_s)$ is reported in Figs. 4 and 5 with an excellent fit for the estimate of $T_s$ for both compounds, propylene glycol and glycerol. Indeed, for annealing temperatures below $T_s$, the maximum excess enthalpy recovery will then be relatively constant assuming that the thermal variation of the specific heat of the glass and the ideal glassy state is constant.

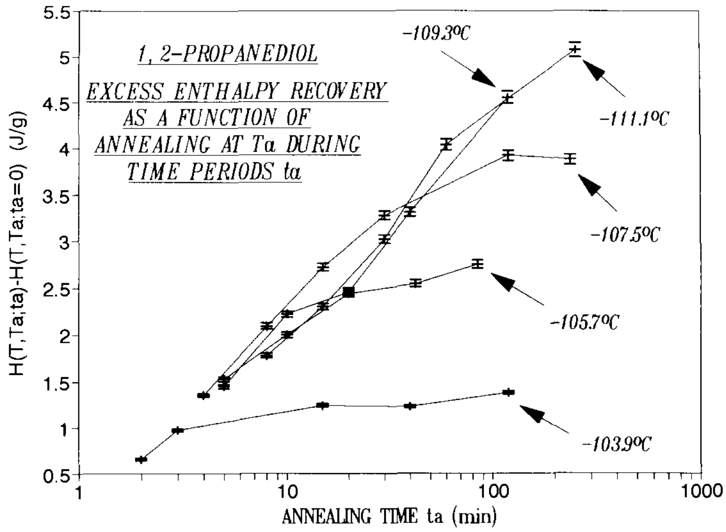

Fig. 1. Variations of the excess enthalpy released during annealing as a function of the annealing time $t_a$ for various annealing temperatures $T_a$ for propylene glycol. The line between the data is for clarity of the figure.

Having determined the different thermal ranges for the enthalpy relaxation times, these enthalpy relaxation times are reported for propylene glycol and for glycerol in Figs. 6 and 7, respectively. These relaxation times are compared with those determined by

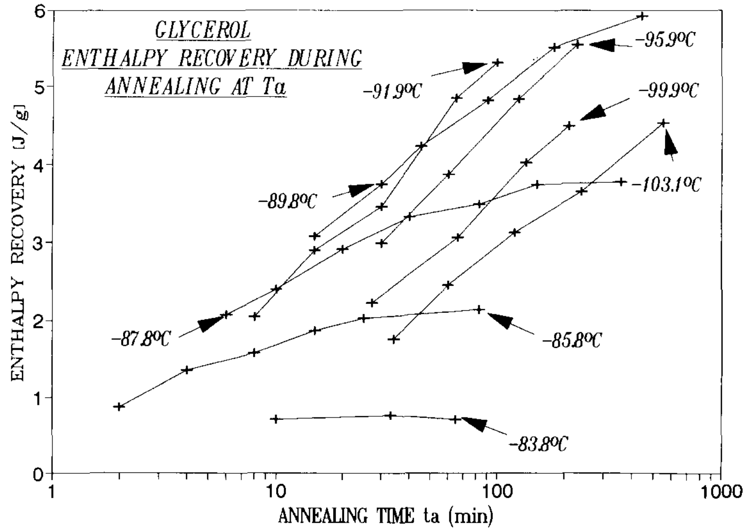

Fig. 2. Variations of the excess enthalpy released during annealing as a function of the annealing time $t_a$ for various annealing temperatures $T_a$ for glycerol. The line between the data is for clarity of the figure.

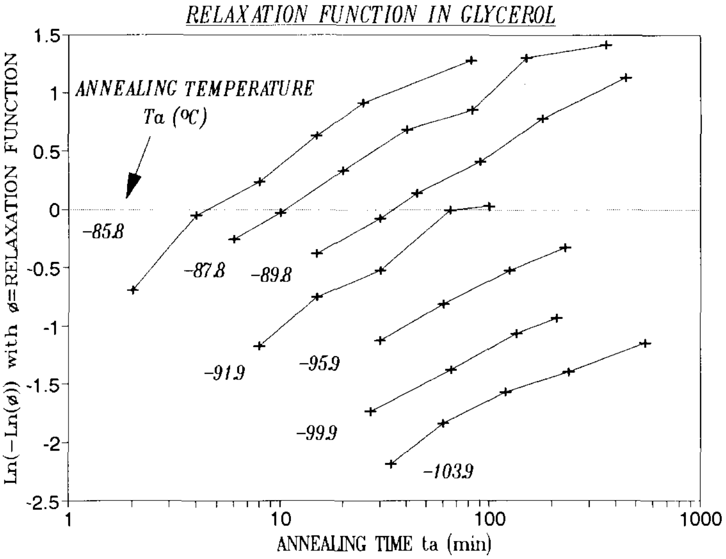

Fig. 3. Variations of the enthalpy relaxation function reported as $\ln(-\ln(\theta))$ as a function of the logarithm of the annealing time period $t_a$ for glycerol.

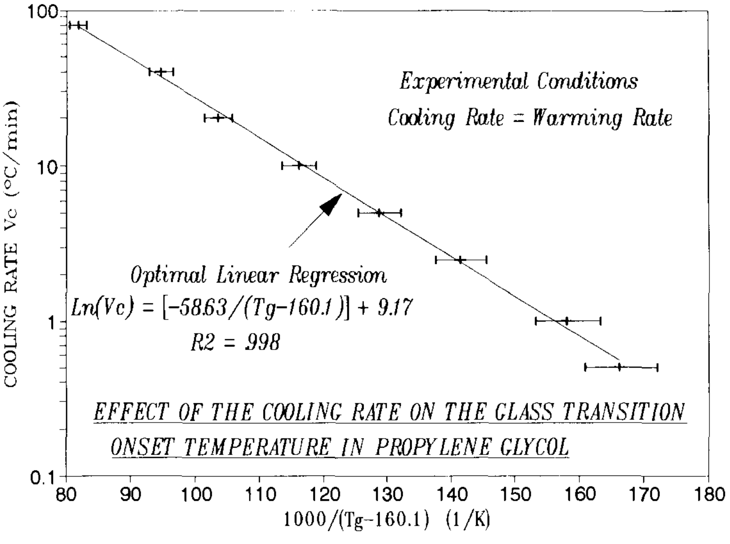

Fig. 4. Variations of the cooling rate $V_c$ represented in a logarithmic scale as a function of the ratio $1000/(T_g - T_s)$ for propylene glycol. $T_g$ is the recorded glass transition at the rate $V_c$ and $T_s$ is the optimal value for the best fit of the linear regression. The equation of the line is reported below the line with regression coefficient $R^2$.

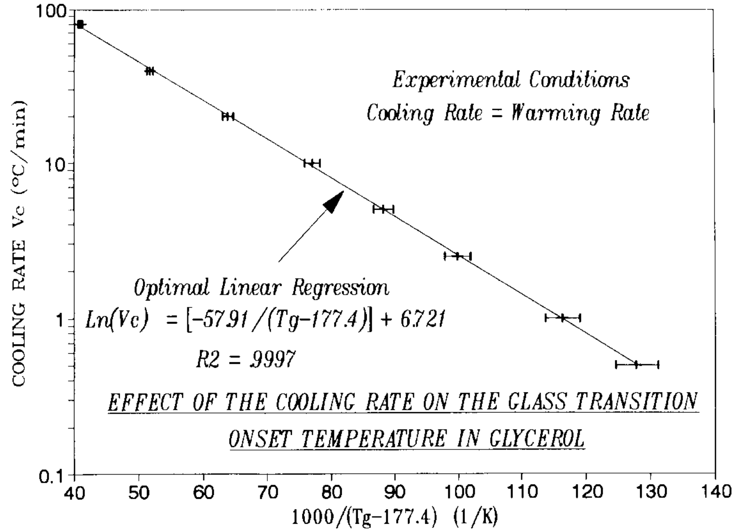

Fig. 5. Variations of the cooling rate $V_c$ represented in a logarithmic scale as a function of the ratio $1000/(T_g - T_s)$ for glycerol. $T_g$ is the recorded glass transition at the rate $V_c$ and $T_s$ is the optimal value for the best fit of the linear regression. The equation of the line is reported below the line with regression coefficient $R^2$.

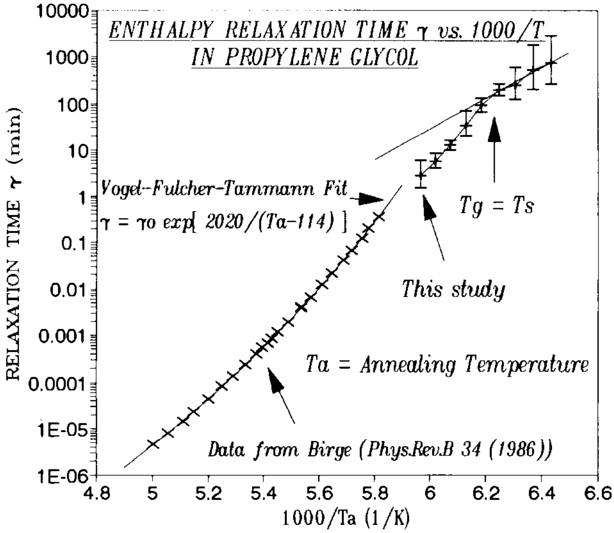

Fig. 6. Comparison of the enthalpy relaxation times determined by isothermal relaxation experiments at a sub-glass transition temperature in propylene glycol and enthalpy relaxation times calculated from spectroscopic specific heat analysis from Birge and Nagel [3,4] for temperatures above the glass transition.

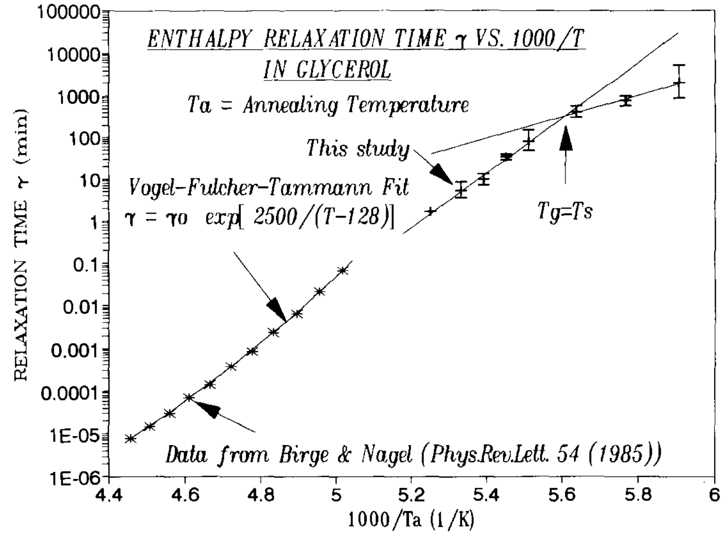

Fig. 7. Comparison of the enthalpy relaxation times determined by isothermal relaxation experiments at a sub-glass transition temperature in glycerol and enthalpy relaxation times calculated from spectroscopic specific heat analysis from Birge and Nagel [3,4] for temperatures above the glass transition.

Birge et al. on propylene glycol and glycerol using a spectroscopic calorimeter [3,4]. The exponents $\beta$ have been reported for glycerol and propylene glycol in Figs. 8 and 9 using an Arrhenius representation.

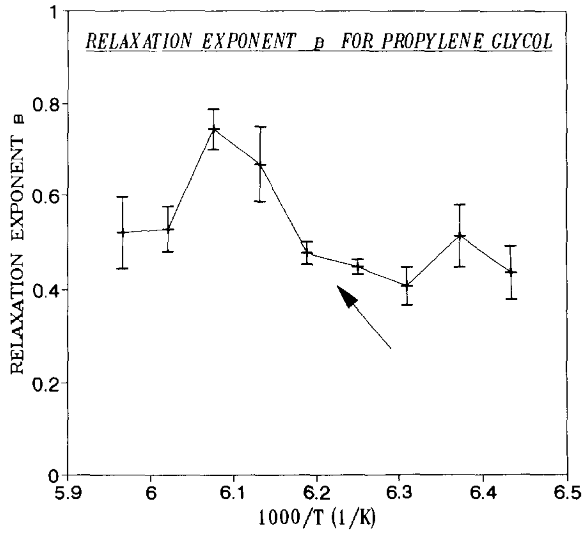

Fig. 8. Exponent $\beta$ as a function of $1000/T$ for propylene glycol.

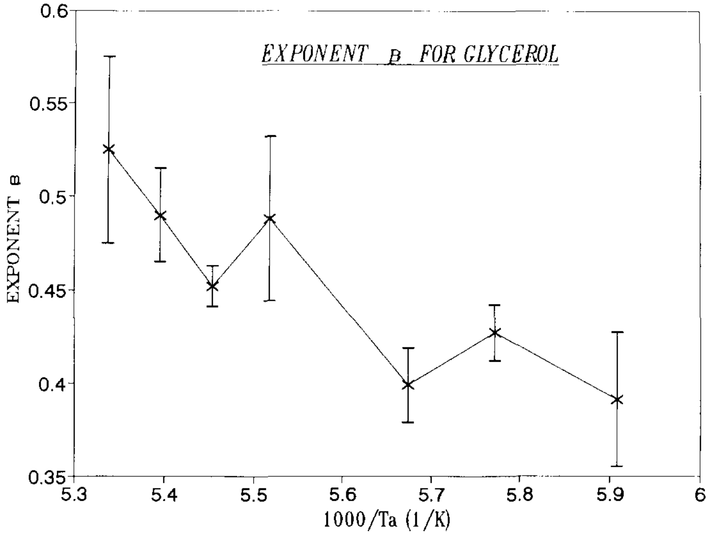

Fig. 9. Exponent $\beta$ as a function of 1000/$T$ for glycerol.

## 4. Discussion and conclusion

The Kohlrausch–Williams–Watts function or stretched function is introduced to report the effect of a wide distribution of relaxation times in the glassy state. This wide distribution has been used for the determination of the Vogel–Fulcher–Tamman law describing supercooled liquids in particular at very low temperatures. The exponent $\beta$ reflects the non-exponential nature of the relaxation processes and is a measure of the width of the relaxation time distribution. For molecular liquid such as propylene glycol or glycerol, it is thought that their relaxation time distribution is localized and well defined. The present study is supporting the existence of a widening of the relaxation distribution as the glass transition is approached. The present values of the exponent $\beta$ which is decreasing from 0.6 to 0.35 for both liquids is a characteristic behavior for the glassy state even for the present molecular glassy state.

The final comparison of the relaxation times as a function of the temperature in Figs. 7 and 8 with the published data shows good accord between the two techniques. One can also notice that the definition of the lowest temperature $T_s$ is in agreement with the theory developed by Shi specifying that the value of $T_s$ must be between the homogeneous nucleation temperature and the isentropic temperature of Kauzmann [5,6].

The combination of the two methods for the determination or the enthalpy relaxation times and for the determination of the lowest temperature of the glass transition $T_s$ is a good technique for the determination of the thermal properties of compounds such as propylene glycol and glycerol. The relaxation times, dependent on the temperature, are characteristics of the self and mutual diffusion coefficients for the two compounds below the glass transition. Expanding this combination to glass-forming aqueous solutions will characterize their glassy states in term of thermodynamic stability.

## Note

A recent publication was found after the presentation of the present paper supporting the use of the stretched relaxation function for the description of the relaxation of the glassy state of propylene glycol and glycerol. Indeed, Fujimori and Oguni [8] have used adiabatic calorimetry for the description of the relaxation process for the glassy state of the same compounds and using also the stretched relaxation function. They also found values of $\beta$ similar to those presently found and reported in Figs. 8 and 9.

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