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Isothermal Enthalpy Relaxation of Glycerol

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The isothermal enthalpy relaxation of glycerol has been measured at 13 different annealing times at temperatures of 170, 175, 180, and 185 K. The glasses were formed by linear cooling at 0.667 and 0.083 $K \cdot s^{-1}$ in a differential scanning calorimeter (DSC). The Williams–Watts relaxation function was fitted to data of enthalpy versus time. A strong temperature dependence was found for the relaxation time. The distribution parameter, β, showed an increase from 0.49 at 170 K to 0.65 at 185 K. We also found indications of an enthalpy dependence in β. Comparison with a theory of volume relaxation showed differences between rates of volume and enthalpy relaxation.

KEY WORDS: calorimetry; isothermal enthalpy relaxation; glycerol.

1. INTRODUCTION

In 1953 Davies and Jones [1] studied enthalpy relaxation phenomena in glycerol and glucose. Glasses were formed by linear cooling in a modified Nernst calorimeter. They studied the enthalpy relaxation under adiabatic conditions and found the relaxation to be controlled by the temperature but also by the enthalpy.

The advent of differential scanning calorimetry (DSC) one decade later facilitated the study of thermal properties. Many investigations of time-dependent heat capacity using DSC were published, mostly concerning long and/or complex macromolecular glass formers.

Theories of thermal relaxation in glasses have been proposed by Kovacs [2, 3] and Vol'kenshtein and Ptitsyn [4]. In the work by Wunderlich et al. [5] the experimental results on polystyrene were interpreted using the latter theory. Later Moynihan and co-workers reported on the heat capacity of some inorganic glasses [6, 7] and on polyvinyl acetate

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[8]. Hutchinson and Kovacs [9] compared dilatometric measurements on the relaxation of polystyrene with theory.

Enthalpy as a function of time at a constant temperature constitutes a central element in relaxation theories. Petrie [10] was the first to use DSC in a direct measurement of isothermal enthalpy relaxation. In 1982 the technique was improved by Lagasse [11], who emphasized the problem of thermal lag between the sample and the calorimeter vessel. His simple and accurate technique for measuring enthalpy relaxation is described in the following section, as well as the improvement that we have introduced in this investigation.

The purpose of the present work is to study isothermal enthalpy relaxation in a simple organic glass-former of well-defined molecular mass. We consider it important to start with a simple molecular substance, such as glycerol, since certain basic characteristics of the relaxation might be obscured by a distribution of molecular mass and by cross-linking.

2. EXPERIMENTAL

A differential scanning calorimeter, Perkin–Elmer DSC-2, was used with liquid nitrogen cooling in the temperature range 170–225 K. The analogue outputs of the instrument are connected to a digital voltmeter via a multiplexer, and all units are controlled by a program from a PDP-11/34 computer. The two calorimeter signals and the times of measurement are recorded. Many of the problems concerning low-temperature DSC in connection with liquid nitrogen cooling have already been discussed by us [12]. We found that the reproducibility is improved if neon rather than helium is used as the purge gas, if all scans are started at a standardized liquid nitrogen level, and if the dry box gas flow is stopped during scans. These procedures were applied throughout the present work.

The temperature signal was converted to temperature using measurements of incipient melting in 1-hexene (99.9%, Fluka, BRD), *n*-octane (99.8%, Fluka), cyclohexane (99.95%, BHD Chemicals, Great Britain), and indium (standard sample provided by Perkin–Elmer) with transition temperatures of 133.38, 216.4, 279.75, and 429.78 K, respectively. Power signal calibration was performed by measurements of the transition enthalpies of *n*-octane, cyclohexane, and indium.

The middle fraction of distilled glycerol (>99.0%, May and Baker LTD, Great Britain) was used for these experiments. Tests by an amperometric Karl Fischer method showed the water content to be less than 0.05% by volume. A sample (16.49 mg) of this glycerol was enclosed in a gas-tight Al capsule, the transfer being performed under a dried argon atmosphere to avoid contamination with water. We used two cooling rates, 0.667 and 0.083 $K \cdot s^{-1}$, and a calorimeter sensitivity of 0.84 W/V. Most of the data were taken after cooling at 0.667 $K \cdot s^{-1}$, where we used 13 different annealing times, approximately equally spaced in the logarithm of time from 30 s to 37 h. The four annealing temperatures were, 170, 175, 180, and 185 K. At the lower cooling rate, 0.083 $K \cdot s^{-1}$, we studied the relaxation at 180 K only. The procedure for the relaxation measurements conformed to the following standard.

We place the sample capsule in the left calorimeter vessel and an empty, similar capsule in the right vessel. All experiments begin at a fiducial temperature, T_h, ($T_h = 225$ K chosen in the case of glycerol) in the undercooled liquid state, where relaxation is virtually instantaneous. From this temperature the sample is cooled at a constant rate, $\dot{T}_c$, down to the annealing temperature, T_a. After an annealing time, t_a, we heat the sample at a standard rate (0.167 $K \cdot s^{-1}$ in these experiments) up to T_h. Measurements of the calorimeter signals continue until equilibrium conditions are attained at the temperature T_h. By repeating this cycle using various annealing times (Fig. 1), we obtain values of enthalpy versus time.

The calorimeter power signal is a sum of two terms,

$$U_H(t_a, t) = U_s(t_a, t) + U_b(t) \tag{1}$$

The first term arises from the heat capacity of the sample. The second term corresponds to the baseline and originates from differences in heat capacity

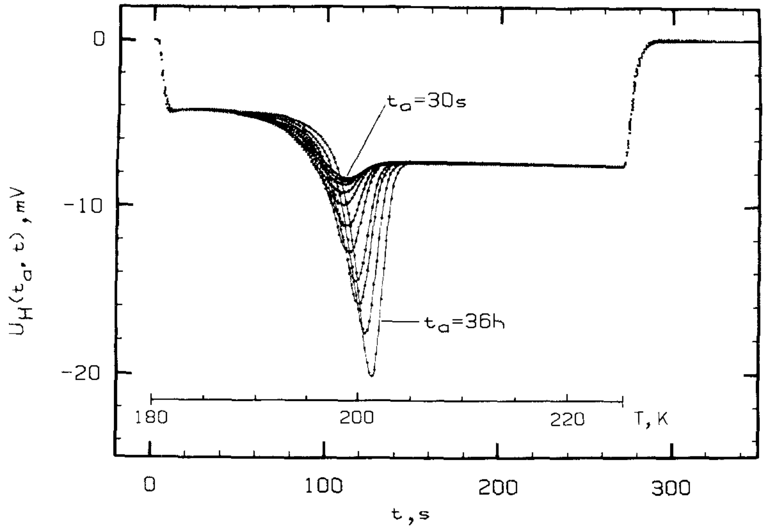

Fig. 1. DSC power signal, U_H, versus scanning time, t, for various annealing times. $\dot{T}_c = 0.667\ K \cdot s^{-1}$ and $T_a = 180$ K.

between the two calorimeter vessels, differences in heat losses by radiation and conduction, and also instrumental drift. We have found [12] that the baseline time drift is negligible, if the calorimeter vessels are left undisturbed. If sample capsules are exchanged, however, there may be an appreciable shift in baseline, $U_b(t)$, even if strict precautions are observed. For this reason we prefer to leave the sample in the calorimeter throughout the experiment, and here our procedure differs from that proposed by Lagasse [11].

From Eq. (1) we obtain the following expression for the enthalpy increment of the sample during a scan from T_a to T_h (see Fig. 2):

$$H_h - H_a(t_a) = k \int U_H(t_a, t)\, dt - k \int U_b(t)\, dt \tag{2}$$

Here the integrals are taken over the scanning time from temperatures T_a to T_h and include the start and stop transients. The coefficient k is a

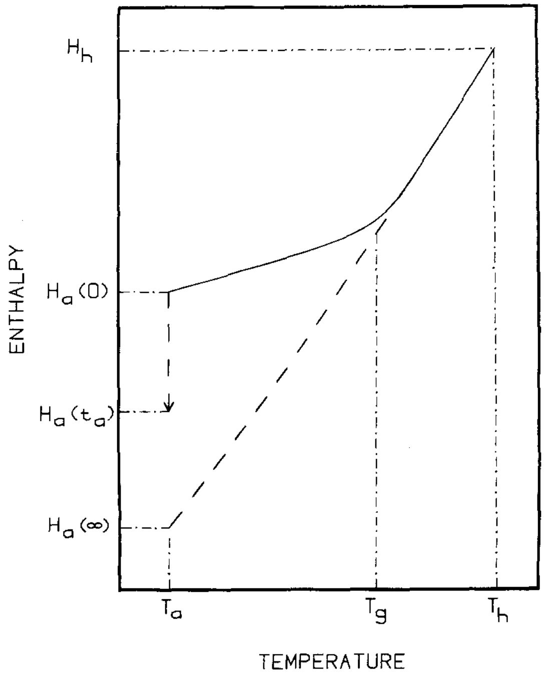

Fig. 2. Enthalpy, H, as a function of temperature, T. Solid curve, cooling path during glass formation. Dashed vertical arrow, enthalpy decay during isothermal relaxation. Dashed curve, equilibrium enthalpy of the glass.

calibration constant which converts from signal voltage to power. The equilibrium enthalpy, H_h, is a constant for a given sample, and so is the last integral, if we leave the calorimeter vessels undisturbed. A relaxation study concerns changes in $H_a(t_a)$ for different values of t_a, and hence we may use the simple formula

$$H_a(t_a) = \text{constant} - k \int U_H(t_a, t)\,dt \tag{3}$$

for analyzing the scans.

It is customary to define a normalized isothermal relaxation function

$$\varphi(t_a) = [H_a(t_a) - H_a(\infty)]/[H_a(0) - H_a(\infty)] \tag{4}$$

This function is initially unity and approaches zero asymptotically at large times. Substituting the expression (3) for $H_a(t_a)$ into Eq. (4), we obtain a more practical representation:

$$\varphi(t_a) = \left[\int U_H(t_a, t)\,dt - \int U_H(\infty, t)\,dt\right] \Big/ \left[\int U_H(0, t)\,dt - \int U_H(\infty, t)\,dt\right]$$
$$= (S_a - S_\infty)/(S_0 - S_\infty).$$

Rearranging the expression using the latter notation for the integral values, we finally have

$$S_a(t_a) = (S_0 - S_\infty)\,\varphi(t_a) + S_\infty \tag{5}$$

The following empirical function due to Williams and Watts [13] has been successfully used in describing relaxation phenomena in many materials:

$$\varphi(t_a) = \exp[-(t_a/\tau_0)^\beta] \tag{6}$$

Here τ_0 is an effective relaxation time, and β is a distribution parameter. Substituting this expression for φ into Eq. (5), we obtained the parameters S_0, S_∞, τ_0, and β by fitting, using the Simplex algorithm [14].

3. RESULTS AND DISCUSSION

In Figs. 3–6 we show the variation of the integral value, S_a, with annealing time for the five cooling paths investigated. Three recordings with $\dot{T}_c = 0.083\ \text{K} \cdot \text{s}^{-1}$, $T_a = 180$ K, and $t_a = 150$ s gave a maximum difference in S_a of 0.012 V · s or 0.62 J · g^{-1}. A smaller maximum difference of 0.34 J · g^{-1} was obtained at $t_a = 1000$ s, where five measurements were

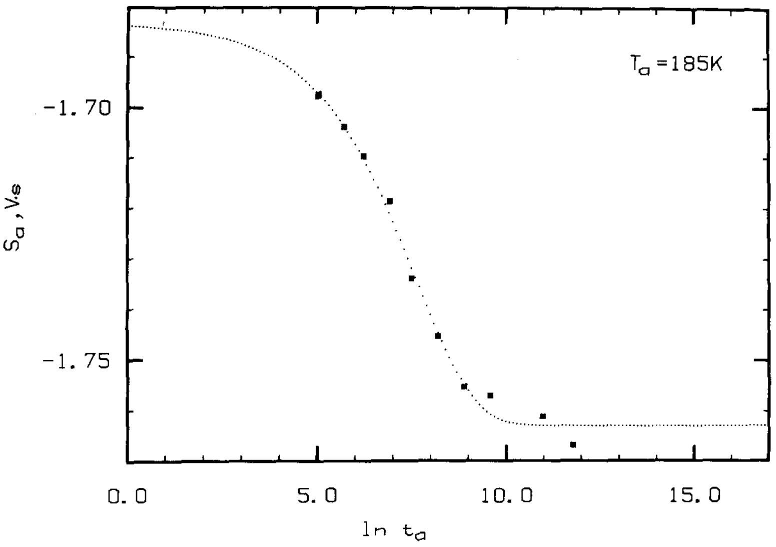

Fig. 3. Relative enthalpy difference, S_a, versus annealing time, t_a, at 185 K; t_a is in seconds. (■) Measured data after cooling at $\dot{T}_c = 0.667\ \mathrm{K \cdot s^{-1}}$. Dotted curve, Eqs. (5) and (6) with parameters according to Table I.

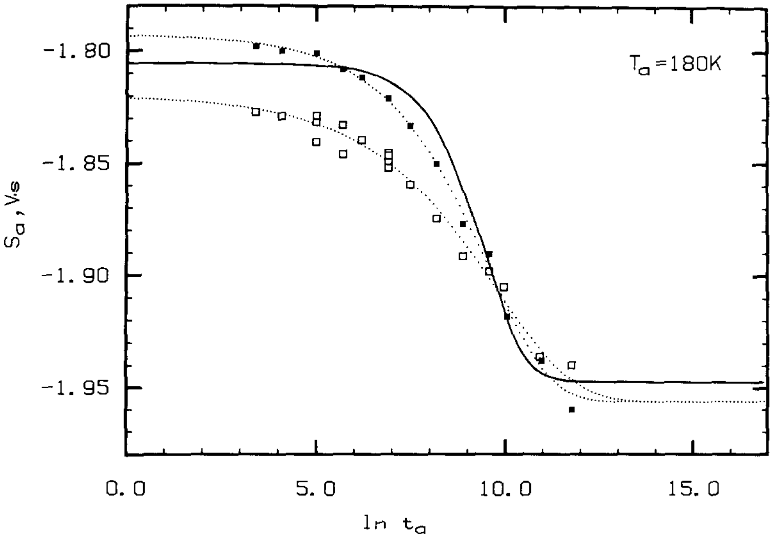

Fig. 4. Isothermal relaxation at 180 K; t_a is in seconds. (■) Measured data after cooling at $\dot{T}_c = 0.667\ \mathrm{K \cdot s^{-1}}$. (□) Measured data after cooling at $\dot{T}_c = 0.083\ \mathrm{K \cdot s^{-1}}$. Dotted curves, Eqs. (5) and (6) with parameters according to Table I. Solid curve, fitted relaxation expression according to Kovacs.

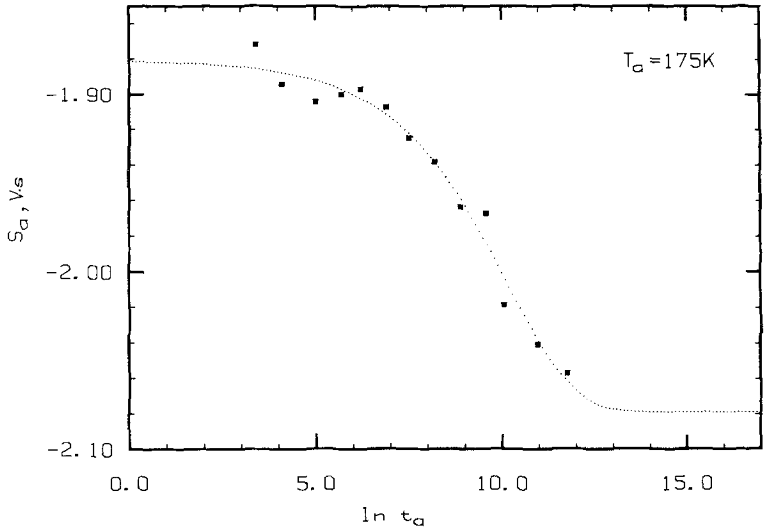

Fig. 5. Isothermal relaxation at 175 K; t_a is in seconds. (■) Measured data after cooling at $\dot{T}_c = 0.667\ \mathrm{K \cdot s^{-1}}$. Dotted curve, Eqs. (5) and (6) with parameters according to Table I.

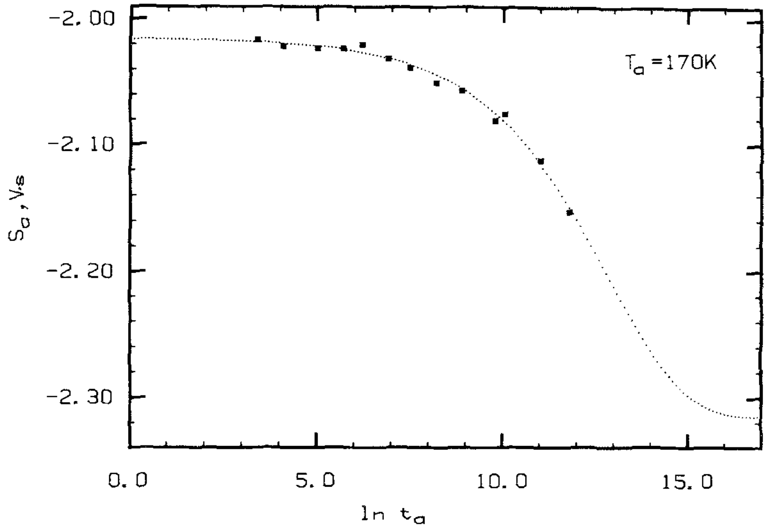

Fig. 6. Isothermal relaxation at 170 K; t_a is in seconds. (■) Measured data after cooling at $\dot{T}_c = 0.667\ \mathrm{K \cdot s^{-1}}$. Dotted curve, Eqs. (5) and (6) with parameters according to Table I.

taken. We are not aware of any previous measurements of this kind in the liquid nitrogen range. Lagasse [11] probably used water cooling, since his operating range was entirely above room temperature. Water cooling is expected to yield better baseline stability, and in fact Lagasse reports a difference of only 0.07 $\mathrm{J \cdot g^{-1}}$ between two experiments on polystyrene.

At the highest annealing temperature, 185 K (Fig. 3), the relaxation was initially very fast, and S_a virtually attained its equilibrium value after 36 h. At 170 K, however, the corresponding relaxation process would have taken about 4 months, according to our estimates.

The parameters extracted by nonlinear fitting to Eqs. (5) and (6) are given in Table I. At 180 K, we studied the relaxation after cooling at two different rates (Fig. 4). Here Eq. (5) was fitted to the two sets of data using a common value of S_∞. The relaxation time parameter τ_0 varies strongly with temperature, as is evident from Table I. Nonlinear fitting of the Vogel–Fulcher equation

$$\tau_0 = A \exp[\mathrm{B}/(T - C)] \tag{7}$$

yields $A = 1.64$ s, $B = 275.6$ K, and $C = 147.6$ K. Dielectric measurements [15] on glycerol in the temperature range 198–233 K resulted in $B = 957$ K and $C = 132$ K. Demoulin et al. [16] assumed an Arrhenius dependence ($C = 0$) but obtained a poor fit to their data (Fig. 2 in their paper). The distribution parameter, β, in this work increases by 30% over the temperature range (15 K) investigated. We have estimated the standard deviation in β by adding Gaussian scatter to our measured S_a values. The standard deviation of the imposed scatter, 0.002 V · s, was taken to be one-sixth of the observed maximum difference in S_a. The resulting standard deviation in β was found to be 3%, which is small compared to the observed increase. Values of β approaching unity are indeed expected at higher temperatures [17] as a result of weaker correlation between motions of molecules. Bucaro et al. [18] also reported increasing $\beta(T)$ for B_2O_3 glass.

Table I. Parameters from Fit Using Eqs. (5) and (6)

T_a (K)	$\dot{T}_c$ ($\mathrm{K \cdot s^{-1}}$)	S_0 (V · s)	S_∞ (V · s)	τ_0 (s)	β
170	0.667	−2.0154	−2.3155	392124	0.49
175	0.667	−1.8806	−2.0788	25061	0.55
180	0.667	−1.7929	−1.9561	14347	0.61
185	0.667	−1.6832	−1.7629	1996	0.64
180	0.083	−1.8199	−1.9561	17890	0.49

They investigated the strain relaxation by photon correlation of scattered light as well as volume changes after an applied pressure jump.

Demoulin et al. [16] measured the structural relaxation of glycerol in the temperature interval 193–225 K. They used the Davidson–Cole distribution function [15] and obtained a temperature-independent distribution parameter, $\beta_{\mathrm{DC}} = 0.40$. The dielectric properties of supercooled glycerol were measured by Davidson and Cole [15]. Their experiments showed an increase in β_{DC} from 0.55 at 198 K to 0.61 at 233 K. The differences in the β_{DC} values obtained by the two groups might reflect the different nature of the two relaxation processes. It is plausible that a selective method, such as dielectric measurements, shows a more narrow relaxation distribution than the global methods of enthalpy and structural relaxation. A new method of measuring the frequency-dependent specific heat capacity was used in relaxation studies of supercooled glycerol by Birge and Nagel [19]. The best fits of the Williams–Watts relaxation function at temperatures from 204 to 219 K were reported for a constant β of 0.65. This is close to the value 0.64 we obtained at 185 K in the glassy regime.

In a recent theoretical treatment of enthalpy relaxation, Brawer [20] found an enthalpy decay of the form $\exp(-t^{1/4})$, independent of the initial excess enthalpy. The exponent 1/4 is smaller than reported values, but as Brawer noted, it may be a consequence of the set of parameters used.

Goldbach and Rehage [21] studied volume changes after both pressure and temperature jumps in polystyrene. The pressure experiments showed that the shape of the normalized relaxation curve did not change with the magnitude of the pressure step applied. Large deviations from a unique relaxation curve were, however, obtained in the temperature jump experiment. This is in accordance with our experiments at 180 K, where we obtained a 20% decrease in the shape (distribution) parameter β at the lower cooling rate.

In Fig. 7 the S_0 values are connected by a dotted curve, which represents the lower part of the cooling path for $\dot{T}_{\mathrm{c}} = 0.667\ \mathrm{K \cdot s^{-1}}$. The range of decay, S_0 to S_∞, during annealing is indicated by vertical bars. Integration of the DSC power signal, U_{H}, in the undercooled liquid regime yields the square points along the equilibrium curve. By fitting a Maxwell–Boltzmann function

$$S_\infty = A_1 \exp(-A_2/T) + A_3 \tag{8}$$

where A_3 allows for instrumental zero offset, to these equilibrium values, we obtain the parameter values

$$A_1 = 45.23\ \mathrm{V \cdot s}, \qquad A_2 = 523.95\ \mathrm{K}, \qquad A_3 = -4.4063\ \mathrm{V \cdot s}$$

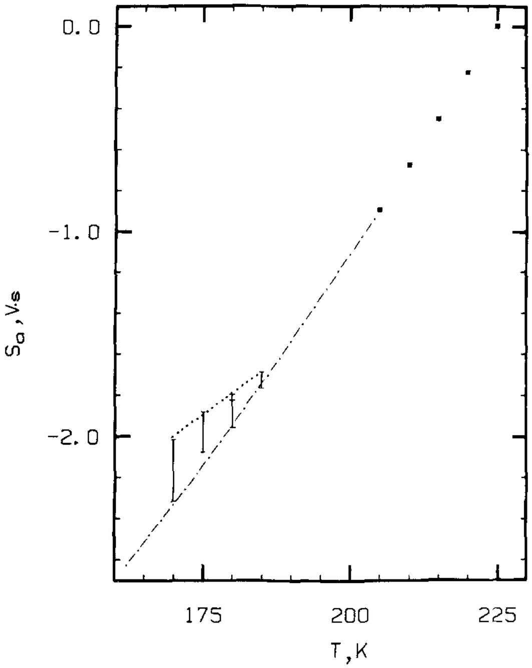

Fig. 7. Relative enthalpy difference, S_a, versus temperature. The vertical bars indicate the relaxation ranges, S_0 to S_∞. The dotted curve connects S_0 values at $\dot{T}_c = 0.667\ \mathrm{K \cdot s^{-1}}$. (■) Data from integration of the DSC power signal at temperatures above T_g. (-·-) Equilibrium curve according to Eq. (8).

Equation (8) is represented by a dot–dashed curve outside the fitting range. It is evident that our values of S_∞ agree well with the extrapolation of Eq. (8).

Substituting φ in Eq. (6) into Eq. (5) and differentiating with respect to time yields

$$dS/dt = -(S - S_\infty)/\tau_e \tag{9}$$

where the subscript **a** has been omitted and the effective relaxation time, τ_e, is

$$\tau_e = (\tau_0/\beta)(t/\tau_0)^{1-\beta} \tag{10}$$

A structurally independent relaxation time is obtained if β equals unity, since τ_0 depends mainly on temperature (see Table I). This simple form of the kinetic equation is known to apply to noncooperative processes, such as radioactive decay and relaxation of extremely diluted spin systems. Other τ_e expressions have been used to describe other relaxation processes [22, 23].

Kovacs [2] developed a free volume theory of the isothermal volume relaxation. Here the effective relaxation time, τ_e, is given by one temperature-dependent part, τ_T, and one volume-dependent part. His volume relaxation experiments on glucose showed good consistency with the theory. In an attempt to decide if volume and enthalpy relaxations obey the same kinetic equation, we replace the volume in Kovac's expression by S and obtain

$$\tau_e = \tau_T \exp\{[-bS_\infty/(S_\infty - S_0)][(S - S_\infty)/(S - S_0)]\} \qquad (11)$$

We introduced this expression for τ_e in Eq. (9), which was then solved using the Runge–Kutta method. A numerical fitting routine was used to match the solution to the measured data of $\dot{T}_c = 0.667\ \mathrm{K \cdot s^{-1}}$ at $T_a = 180$ K. The best fit was obtained for the parameters, $\tau_T = 14530$ s, $b = 5.07 \times 10^{-6}$, $S_0 = -1.8053\ \mathrm{V \cdot s}$, and $S_\infty = -1.9470\ \mathrm{V \cdot s}$. It is obvious from Fig. 4 that Kovac's expression is not applicable for the description of the isothermal enthalpy relaxation, since it results in too slow relaxation. A similar discrepancy between enthalpy and volume relaxation is reported by DeBolt et al. [6] in a B_2O_3 sample, where the enthalpy was found to relax considerably faster than the volume. Such dissimilarities in the relaxation rate have also been discussed in terms of free volume by Cohen and Grest [24].

Summarizing the results we conclude that the Williams–Watts relaxation function can describe isothermal enthalpy relaxation in glassy glycerol. The relaxation time parameter shows a Vogel–Fulcher temperature dependence and the distribution parameter increases with temperature. Furthermore, available data indicate that different properties of the same material relax differently.

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