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Calorimetric investigation of the glass transition and relaxation in 60:40 ethylene glycol:water. Part 1. Isothermal annealing experiments

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Abstract

Annealing experiments around the glass transition were performed for 60% w/w ethylene glycol in water. Specific calorimetric measurements allow the calculations of excess entropies and enthalpies as a function of annealing temperatures. Nucleation and crystallization are assumed not to occur. However, the analysis shows that the relaxation is not complete and that its kinetics is overlapping another phenomenon which is concluded to be a nucleation processus. This nucleation is observed during and after the relaxation processus. The kinetics parameters of the glass transition in isothermal conditions are, however, determined in the range of annealing time where the nucleation is still depressed.

INTRODUCTION

Glass-forming aqueous solutions are of interest for cryobiological purposes for their possible application in the solution to the problem of long-term organ preservation at very low temperatures [1]. So far the vitrification technique represents the only possibility of avoiding damages created by crystallization during cooling and warming back. Yet only recently have studies been made in the investigation of the physical properties of different solutes when diluted in water, such as their vitrification ability and the kinetics of crystallization in solutions [2–6]. However these glass-forming aqueous solutions give fragile glasses which fracture at temperatures below the glass transition [6–8] due to stress storage during the crossing of the glass transition on cooling. The stress release produces cracks with possible release of heat, chemicals, electrons

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and light at the tip of the cracks [9, 10] and these cracks induce nucleus formation during rewarming [6–8]. Therefore, storage presents a technical problem for vitrified organs which obviously have to remain intact. The effect of storage and, therefore, the effect of the relaxation has to be known for an optimization of the vitrification technique. Nucleation during storage and during relaxation of the glassy state is also a very important question. However in the present paper, as a first step, the nucleation is not investigated as a parameter but will be related to the present results in a subsequent paper.

Relaxation experiments are numerous in the literature, considering the different kinds of glass-forming materials with different models and interpretations [11–17]. At present, only isothermal approaches are used to investigate the glass transition via calorimetric measurements. DSC has been used for the analysis of the glass transition of glass-forming organic liquids [11, 12, 15, 16–20] and, recently, for 22 mol.% ethylene glycol in water [21]. The DSC technique has also been presented as a possible means of studying the glass transition and its relaxation processus for glass-forming aqueous solutions, even if it is, however, less sensitive than other thermal techniques such as dilatometry or mechanical relaxation [22]. Different authors have modelled the change in the specific heat during the glass transition for continuous warming or cooling or for annealing experiments at different temperatures. Isothermal and non-isothermal conditions are usually considered with models related to the interpretation of the Williams–Watts fractional or non-fractional exponential relaxation [11–18]. In the present study, only the consequences of isothermal experiments are considered through a superposition of thermal treatments. A new practical approach is used for the definition of the relative thermodynamics functions that are accessible directly by calorimetry.

The eutectic composition of ethylene glycol in water, 60% w/w [23], was chosen for its slow crystallization during cooling or warming. The stability of the glassy state for this solution, manifested as a resistance to crystallization, is important for the analysis of the behavior of the glassy state through the investigation of the glass transition. It is assumed that nucleation is avoided for temperatures in the range of the glass transition. However, new sets of experiments are necessary to demonstrate an association between nucleation and the overshoot in the glass transition during annealing experiments in glass-forming aqueous solutions. For the cooling and warming rates used here, no devitrification or melting peaks were observed during the last warming at 10°C min^{-1} back to temperatures above the melting point. However these direct observations do not indicate the absence of nuclei. Only other methods of thermal analysis will show such a behavior overlapping the relaxation processus.

MATERIALS AND METHODS

The ethylene glycol was purchased from Fisher. The samples were prepared with deionized water at a concentration of 60% w/w solute, close to the eutectic concentration of the ethylene glycol [23]. The calorimetric measurements were conducted in a DSC-4 from Perkin-Elmer adapted down to liquid nitrogen temperatures with a stability limit of −170°C. The samples weighed between 8 and 12 mg and were filtered through a 0.22 μm filter prior to the experiment to avoid excess heterogeneous nucleation induced during cooling or during the subsequent thermal treatment.

Sets of annealing experiments were performed using two techniques: indirect and direct isothermal experiments.

Indirect isothermal experiments

(a) The sample was cooled down at $10°\mathrm{C\,min^{-1}}$ to −160°C, well below the glass transition which is located between −145 and −115°C, and then warmed at $10°\mathrm{C\,min^{-1}}$ to a temperature T, different for each set of experiments, and maintained there for different periods of time t (min). The sample was then cooled back to −160°C and equilibrated, and finally warmed and recorded at the same rates above the glass transition.

(b) The sample was cooled to the temperature T at the same rate and maintained there for different periods of time t (min). The sample was then cooled to −160°C, equilibrated, warmed and recorded above the glass transition.

(c) A control experiment was carried out with the sample cooled directly to −160°C, equilibrated and then warmed, and recorded back at $10°\mathrm{C\,min^{-1}}$ above the melting point to check any crystallization.

Direct isothermal measurements

The samples were cooled at $10°\mathrm{C\,min^{-1}}$ to −160°C, warmed back to a desired temperature, chosen as −133°C, and then held there for 2 hours to allow the relaxation of the glassy state. The sample was then cooled back to −160°C. The direct isothermal thermograms were recorded using the isothermal software from Perkin-Elmer, by warming the sample directly to a chosen temperature above −130°C and maintaining it there isothermally until the release of the excess enthalpy becomes negligible with respect to the sensitivity of the DSC.

Control experiments took place by recording the thermogram during warming of the sample warmed and held for 0 min at −133°C or for 2 h at −133°C.

ANALYSIS AND METHODS

The analysis of the present data was based on the relative behavior before and after the annealing experiments.

Indirect isothermal method

Determination of the relative excess entropy and relative excess enthalpy stored in the sample during the annealing experiments was made by subtracting a reference thermogram from the experimental thermograms after annealing. Only set (a) described above was analyzed in a systematic manner. Set (b) was analyzed for comparison with set (a), without leading to a more complete analysis.

(1) The reference thermogram is the thermogram corresponding to the same annealing temperature with an annealing time $t = 0$ min in experimental conditions (a) above. Thermal equilibrium is assumed to be achieved in 10 s. The experimental thermogram after annealing was recorded, subtracted from the reference and analyzed manually by determination of the variation of the specific heat δC_p versus the temperature. The integration of δC_p and $\delta C_p/T$ over the glass transition defines respectively the excess enthalpy and excess entropy between the glassy state warmed to T and the glassy state relaxed after a time t at the same T. Because the liquid or rubbery state above the glass transition must be at equilibrium and have the same specific heat with or without annealing, the subtraction of the thermograms will give a zero baseline for δC_p above the glass transition. This yields an approximatly zero baseline below the glass transition because, through the relaxation, the change in the specific heats for the relaxed glassy state and for the reference glassy state is not large enough for the sensitivity of the calorimeter. The variation in the specific heat below the glass transition will depend on the experimental conditions especially with different cooling and warming rates. This set of experiments is still under investigation.

(2) To observe the effect of the transient warming and cooling in the sample for the annealing experiments, the above reference thermograms were compared to the thermogram obtained from a direct warming at 10°C min^{-1} from −160°C to −30°C after cooling the sample to −160°C at 10°C min^{-1}.

(3) Calculations were initiated from the general measure of the variation of the specific heat defined as

$$\delta C_p = C_p(T; T', t) - C_p(T; T', t = 0\ \text{min}) \qquad (1)$$

where the annealing experiment was carried out at the temperature T' for a period of t min, with T being the temperature of the material. This difference δC_p was calculated through the TADS program of the Perkin-

Elmer DSC-4, as the difference betwen thermograms of corresponding annealing temperatures T at annealing time t min and $t = 0$ min under conditions (1) or (2) above.

From this definition of the variation of the specific heat associated with the annealing experiments, the excess of configurational entropy δS and the excess of enthalpy δH can be defined respectively as

$$\delta S(T', t) = \int_{T_1}^{T_2} \frac{[C_p(T; T', t) - C_p(T; T', 0)]}{T} \mathrm{d}T \tag{2}$$

$$\delta H(T', t) = \int_{T_1}^{T_2} [C_p(T; T', t) - C_p(T; T', 0)] \, \mathrm{d}T \tag{3}$$

where T_1 and T_2 are respectively sufficiently lower and higher than the glass transition. T_2 might also be taken as the variable T of the temperature during the warming to calculate the evolution of the enthalpy δH and of the entropy δS of the glassy state during the glass transition.

The assumption of a similar enthalpy of the liquid above the glass transition allows the determination of the enthalpy of the glass compared to the enthalpy of the liquid with the conditions T_1 and T_2, respectively well below and well above the observed glass transition. The enthalpy variation for the reference thermogram without any annealing was determined between two temperatures well below and well above the glass transition. Then, the enthalpy after annealing was calculated from the measure of the variation δH. δS and δH have similar behavior considering the thermal range over which the glass transition occurs.

The relative stored enthalpy during annealing is given by the integral (3) above, and represents the difference in enthalpy between the glassy state before and after annealing. This definition can be used to reconstruct the enthalpy variation during warming, assuming the same enthalpy for the liquid above the glass transition as a limit condition of the enthalpy curves during warming. However, this only gives the relative variation of the enthalpy versus the temperature during warming and not the absolute variation. The reference was taken as the unannealed glassy state warmed directly at 10°C min^{-1} above the glass transition to the liquid state. The enthalpy variation of the liquid state was also assumed to be linear in the thermal range of the glass transition.

The kinetics approach of the effect of the annealing, as already determined by Hofer et al. [21] on the glassy state of the vitrified aqueous solution of ethylene glycol, is not presented here but will be correlated to the present data in a later paper. The response function $\phi(T, t)$ is the enthalpic form of the common function used to describe the relaxation behavior in the glassy states:

$$\phi(T, t) = [H(T, t) - H(T, \text{infinite})]/[H(T, t = 0) - H(T, \text{infinite})] \tag{4}$$

and is chosen to obey the Kohlrausch–Williams–Watts form:

$$\phi(T, t) = \phi_0 \exp[-(t/\tau)^{\beta}] \tag{5}$$

with ϕ_0 being a pre-exponential constant, the stretched exponent β being a constant and the relaxation time τ being temperature dependent:

$$\tau = t_0 \exp(-C/TS_{\text{conf}}) \tag{6}$$

This expression gives a Vogel–Fulcher–Tamman behavior for this relaxation time τ [11, 12, 24] with the configuration entropy S_{conf} being defined by the integral from Adams–Gibbs:

$$S_{\text{conf}} = \int_{T_0}^{T} [C_p(\text{liquid}) - C_p(\text{crystal})] \, \mathrm{d} \ln(T) \tag{7}$$

leading to

$$\tau = \tau_0 \exp[-A/(T - T_0)] \tag{8}$$

The temperature dependence of τ is therefore assumed to follow eqn. (8). The determination of the different parameters was made by:

1. Plotting $\ln(-\ln(\phi(T, t)))$ versus $\ln(t)$ giving a slope equal to β, and the value at 0 giving the relation $t = \tau$.
2. Plotting $\ln(\tau)$ versus $1/(T - T_0)$ with optimization of the data versus T_0. This gives an activation energy A in kelvin units.

Direct isothermal method

The indirect isothermal method described above allows the determination of the excess enthalpy stored as a function of the temperature during the warming of an annealed sample. For the determination of the parameters of the kinetics of the glass–liquid transformation, the samples were cooled to −160°C and then annealed at −133°C for 120 min to allow a partial relaxation of the glassy state and to keep the nucleation suppressed. The sample was then cooled to −160°C to proceed afterwards to the isothermal recording at −128°C. The release of energy during the isothermal exposure is assumed to be the release of the enthalpy stored in the annealed glassy state. Therefore, by the definition that the response function remains the same, $\phi(t)$ can be determined as the ratio of the energy release from the time t over the estimated excess stored enthalpy in the annealed glass at −128°C compared to the enthalpy of the ideal liquid at the same temperature, assuming constant specific heat of the liquid in the thermal range of the glass transition. The parameters for eqn. (8) were determined by plotting $\ln(\ln(-\phi(t)))$ versus $\ln(t)$, giving a linear variation whose slope is β, and with the value at 0 giving $\tau(T)$.

CALIBRATION

The temperature calibration of the DSC-4 was measured with deionized water, with an aqueous solution of $CaCl_2$ at 32% w/w, with pure methylcyclohexane, and with pure methylcyclopentane (both from Aldrich) for their respective melting temperatures (0, −49.7, −126.6 and −142.5°C), and by analyzing the heat of fusion as a function of the warming rate and as a function of the initial temperatures of the thermograms. In order to avoid supercooling and incomplete crystallization, several cycles between a temperature below the glass transition, or at least 40°C below the melting tempratures, and 5–10°C below the melting temperature were carried out for seeding and allowing crystal growth. The variations in the onset temperature of the melting peak versus the warming rates are reported in Fig. 1(A). As already reported by Sandu and Singh [25], the extrapolation to zero warming rate gives the equilibrium and the real temperatures (Fig. 1(B)). The slope of the linear regression lines for the four different solutions are similar, with a mean value of 0.044 ± 0.002. The temperature gradient, present in the pan for the warming rates used, is therefore created before the steady state of warming is established during the transient warming up. For a better proof, with deionized water, the effect of increasing the initial temperature from −160°C to −40°C on the variation $T_{\mathrm{measured}} - T_{\mathrm{real}}$ does not show an increase higher than 0.5°C for high warming rates. Therefore, the observed temperature gradient is not dependent on the initial temperature, provided that this temperature, relative to the warming rate used, is not too far from the considered calibration temperature.

For our purposes, the recorded temperatures were corrected on the basis of this calibration by considering the variations with the warming rates for continuous heating conditions and by extrapolation of the correction to a zero warming rate, as reported in Fig. 1(B) for the isothermal conditions. Moreover, the determination of the heat of fusion for the different pure compounds shows discrepancies that are less than 0.7% for the highest temperatures and up to 1.5% for the lowest temperature (−142.5°C for the melting of methylcyclopentane) with warming rates less than 10°C min^{-1} for sample weights less than 12 mg. Therefore the calibration for the energetic values measured in the present calibration conditions gives a systematic error of around 1% for the temperature range presently considered.

Another uncertainty is the determination of the basal line for the thermograms needed for the analysis of the glass transition. The effect of choosing the basal line is not presented here. However, only a weak variation in the temperature range of the glass transition is assumed. The technique of considering the subtraction of two thermograms lowers the effect of this choice with a linear extrapolation of the specific heat of the glassy state to temperatures higher than the glass transition.

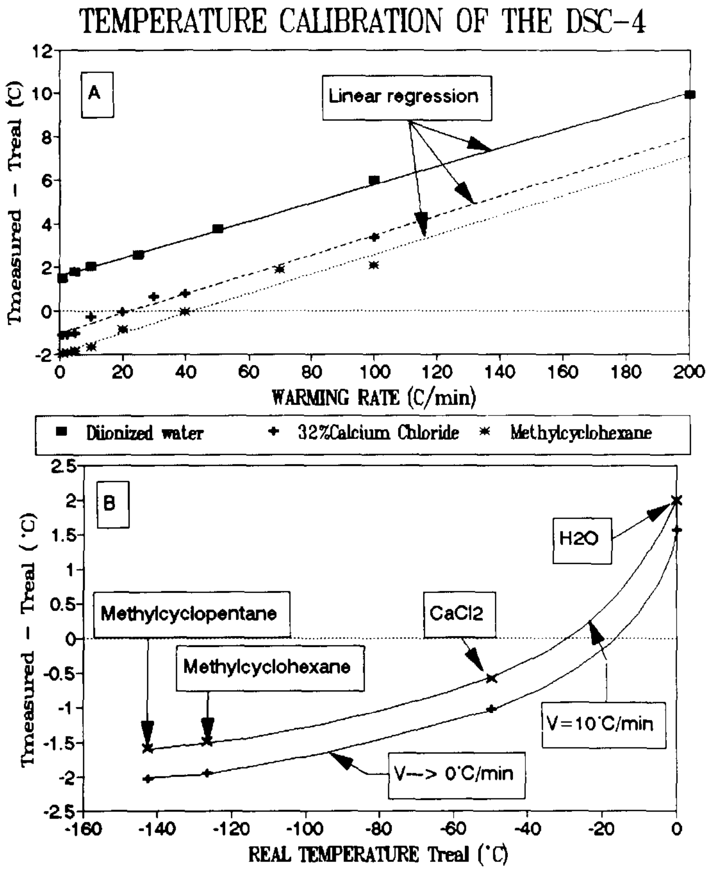

Fig. 1. Temperature calibration with different solutions of known melting temperatures for the DSC-4: (A) variation of the difference $T_{measured} - T_{real}$ as a function of the warming rate (°C min^{-1}); the lines are the least-squared linear regression for each solution with a slope of 0.042, 0.045 and 0.045 for respectively deionized water, 32% w/w $CaCl_2$ in water, and methylcyclohexane; (B) variation of the difference $T_{measured} - T_{real}$ as a function of the real temperature T_{real} of the melting peaks of pure ice (H_2O), of the eutectic at 32% w/w calcium chloride ($CaCl_2$), of pure methylcyclohexane and of pure methylcyclopentane. The variations are reported for a warming rate of 10°C min^{-1} and for the extrapolation of the values as the warming rate V tends to 0°C min^{-1}.

RESULTS

As reported in Fig. 2, the thermograms for the conditions (a) and (b) at $T = -131$°C during an annealing time period of 1 hour, which exceeds the close completion time for the relaxation at this temperaure, are reported for comparison; the subtraction between the two thermograms is also reported. It can be seen that the difference does not show any variations at the sensitivity of the calorimeter. However, for lower temperatures, there is a hysteresis effect on the relaxation of the material. The quasi-relaxed state is not obviously reached at the same rates during

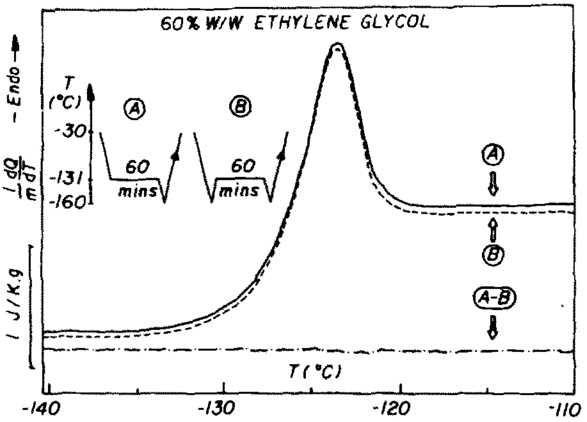

Fig. 2. Comparison of the thermograms during warming at 10°C min^{-1} of the glass transition for 60% w/w ethylene glycol in water after: (A) cooling at 10°C min^{-1} to $T = -133$°C for 1 h exposure before cooling the sample to −160°C at the same rate; (B) cooling at 10°C min^{-1} to −160°C, warming to $T = -133$°C for annealing during the same time before cooling the sample back to −160°C; (C) subtraction of curve (A) from curve (B). Records are effected during the last warming.

annealing initiated from the liquid state on cooling and that initiated from the glassy state on warming. It seems to take longer from the liquid side than from the glassy-state side. For −133°C, four hours are not sufficient to achieve similar stable states as defined by the maximum enthalpy release during the annealing after cooling. The discrepancy between annealing during cooling and during rewarming increases as the annealing temperature decreases. The calibration in temperature during cooling is

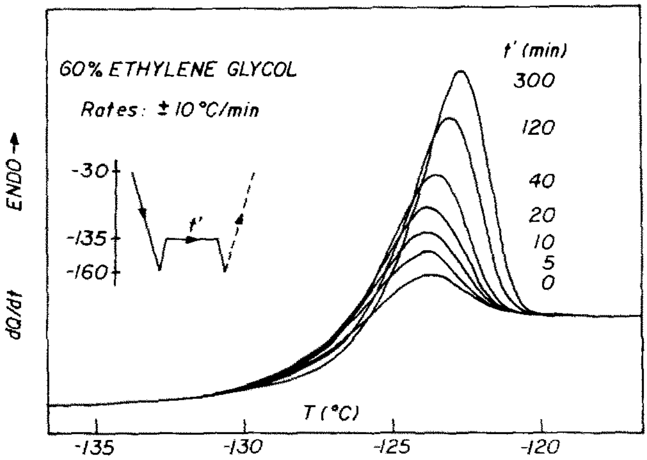

Fig. 3. Thermograms during warming for 60% w/w ethylene glycol in water showing the glass transition after annealing the sample for different periods between 0 and 300 min at $T = -135$°C.

different from that during warming. A slower control in temperature during cooling must be assumed because the cooling driving force is more limited than the heating driving force. This could explain the discrepancies between the relaxed state limits after cooling and after rewarming.

Figure 3 shows the thermograms during warming at 10°C min^{-1} after annealing the sample at −135°C for different periods of exposure, *t* min. As expected, the overshoot at the glass transition increases with the

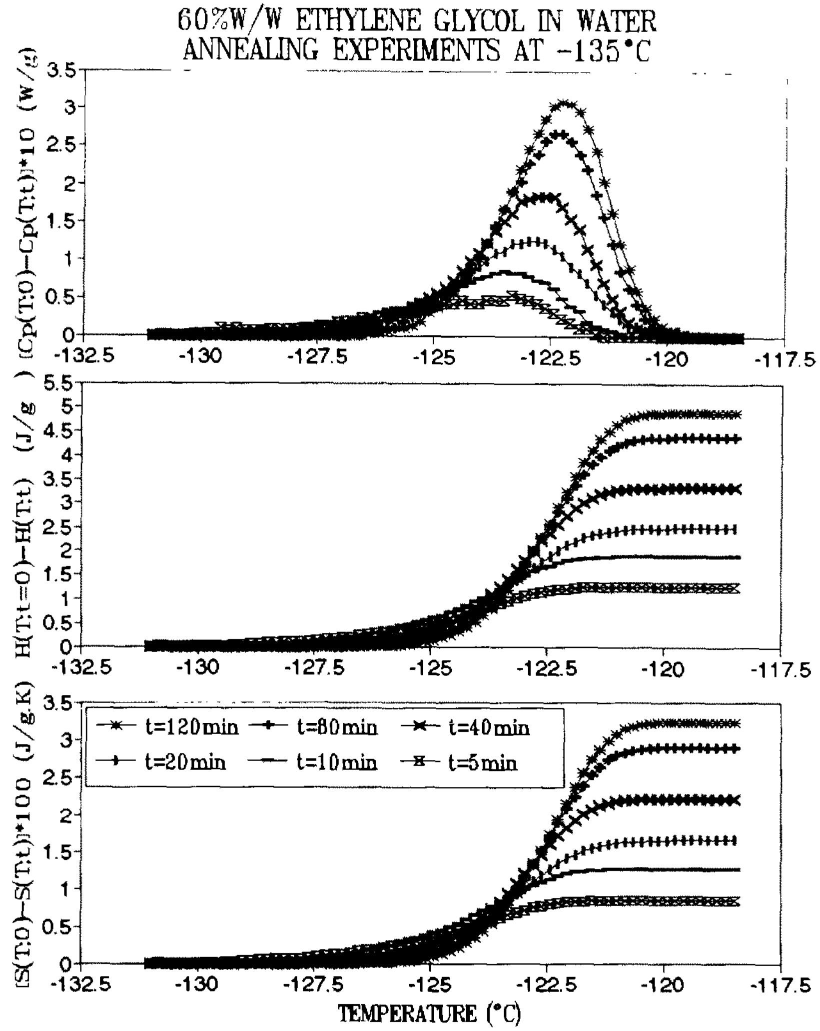

Fig. 4. Effect of the annealing time *t* on the glass transition of 60% w/w ethylene glycol in water: (top) comparison of the difference in specific heat during warming between the glassy state after an annealing time *t* and the glassy state after *t* = 0; (middle) comparison of the difference in enthalpy during warming calculated from (A); (bottom) comparison of the difference in entropy during warming calculated from (A).

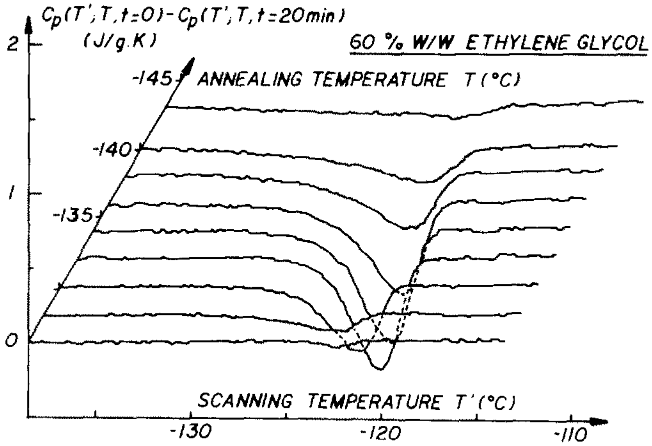

Fig. 5. Comparison for 60% w/w ethylene glycol in water of the difference in specific heat during warming between the glassy state after an annealing time $t = 20$ min and the glassy state after $t = 0$ for different temperatures of annealing T.

annealing time. After analysis, as respectively defined above, δC_p, δS and δH are reported in Fig. 4 versus the temprature during warming.

The effect of the temperature of annealing T is shown on Fig. 5 where the difference in the specific heat δC_p for an annealing time of $t = 20$ min is reported for different annealing temperatures. This difference passes

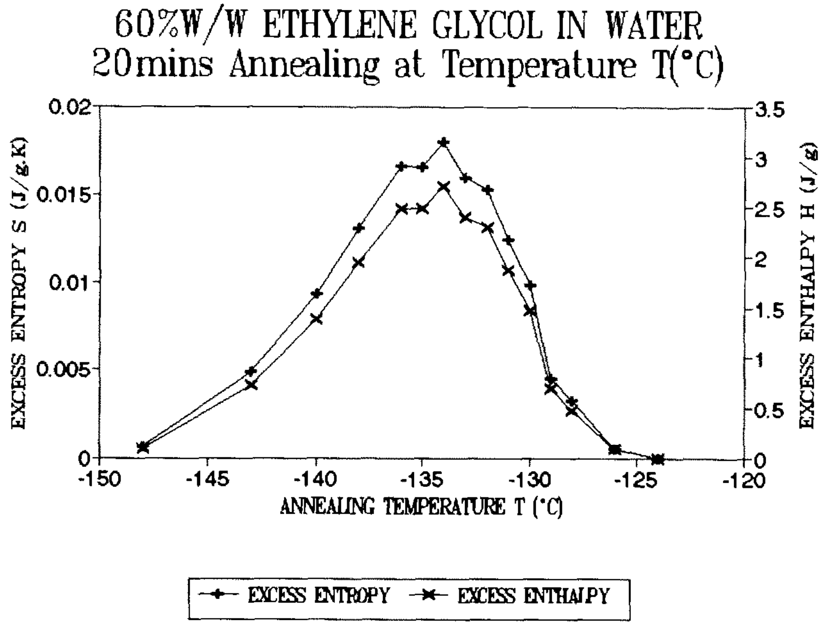

Fig. 6. Comparison for 60% w/w ethylene glycol in water of the variations of the excess enthalpy and excess entropy calculated from the variation of the specific heat reported in Fig. 5 after 20 min of annealing at different temperatures T.

through a maximum at around −133°C as T decreases from −126°C to −145°C. The calculated values of δS and δH for these experiments are reported in Fig. 6.

The dissociation between the effect of the exposure to the annealing temperature T and the effect of the warming from the initial temperature fixed constant at −160°C to the considered T, as a control process, is analyzed with the experimental set of conditions (2) from above. The variations of the excess enthalpy and excess entropy for the transient relaxation compared to no relaxation are reported in Fig. 7. By considering the enthalpic and the entropic variations, which are similar, the representation of only one of these variations are represented, even if both of them have been determined.

The effect of annealing time t at different temperatures T is shown in Fig. 8 for T varying from −129°C to −143°C for annealing time t varying from 1 to 1000 min. The variation in the excess entropy (and also the excess enthalpy) was then analyzed in order to reconstruct the variation of the relative enthalpy or entropy during warming for the annealed glassy state compared to the unannealed glassy state.

An example is reported in Fig. 9 for the annealing temperature $T = -133$°C with different times of exposure t. The variation in the

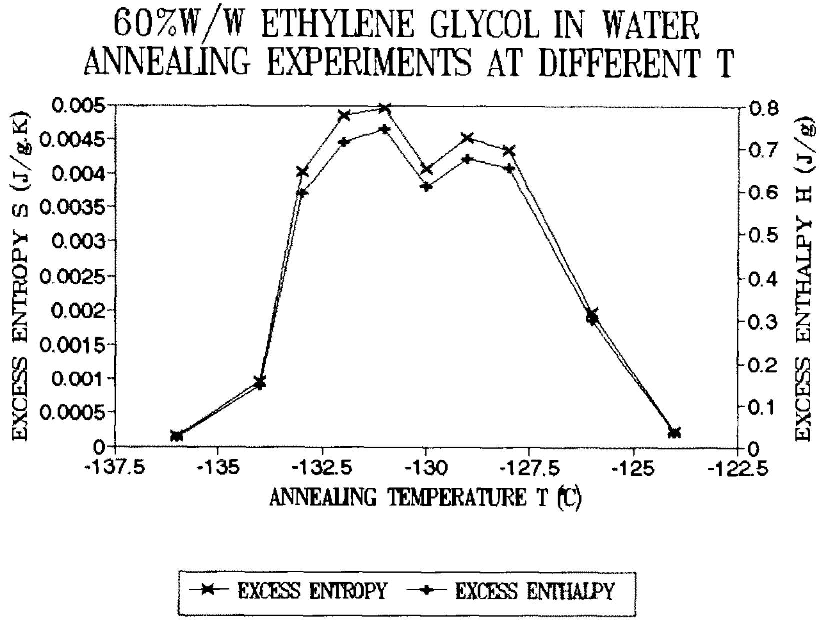

Fig. 7. Comparison for 60% w/w ethylene glycol in water of the variations of the excess enthalpy and excess entropy determined from the variations of the specific heat between the glassy state after annealing at different temperatures T reported in the abscissae during $t = 0$ min and the unannealed glassy state warmed directly from −160°C.

enthalpy during cooling is also reported, even with the uncertain calibration of the temperature during cooling. In Fig. 9, the assumed linear extrapolation of the enthalpy of the liquid above the glass transition towards the temperature of annealing defines the difference $H(T, t = 0\,\text{min}) - H(T, t = \text{infinite})$ needed for the analysis of the annealing processus through the function $\phi(T, t)$ previously defined. This value can be determined either above or below the intersection temperature of the sample enthalpy and of the ideal liquid enthalpy reported as the linear extrapolated line from the liquid side.

Following the relaxation of the glassy state and knowing the previous

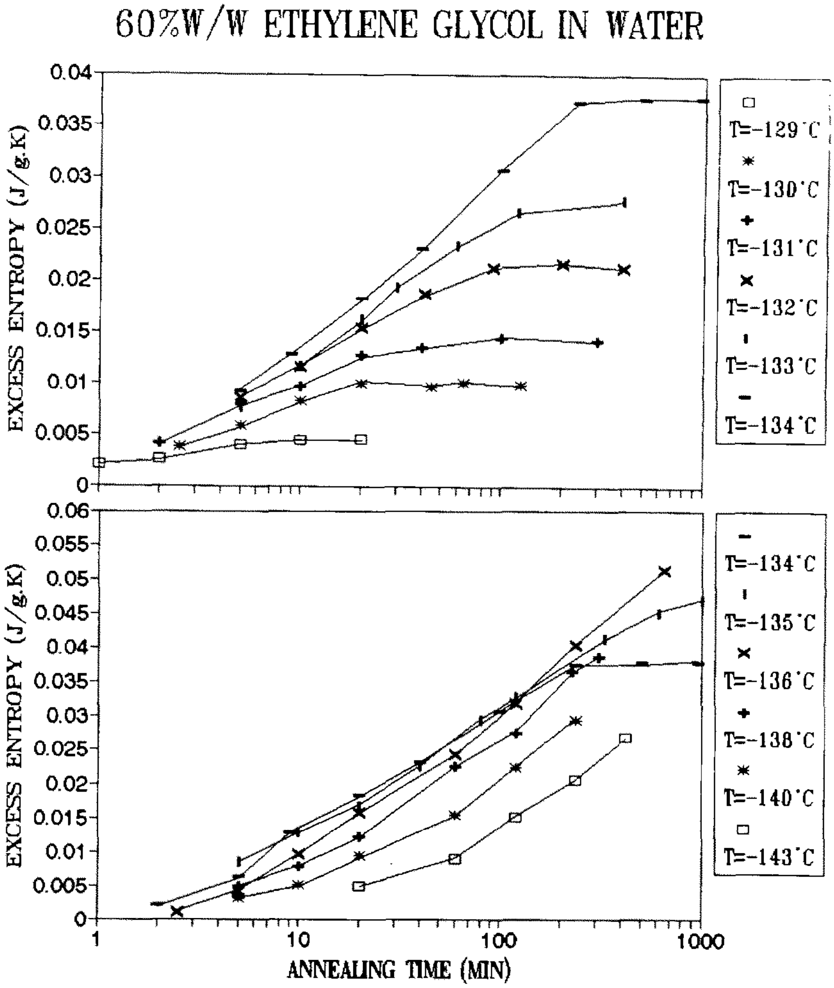

Fig. 8. Comparison for 60% w/w ethylene glycol in water of the variation in the excess entropy between the glassy state after annealing at different temperatures T for an annealing time t reported in the abscissae and the glassy state annealed at the same temperature for a period of 0 min.

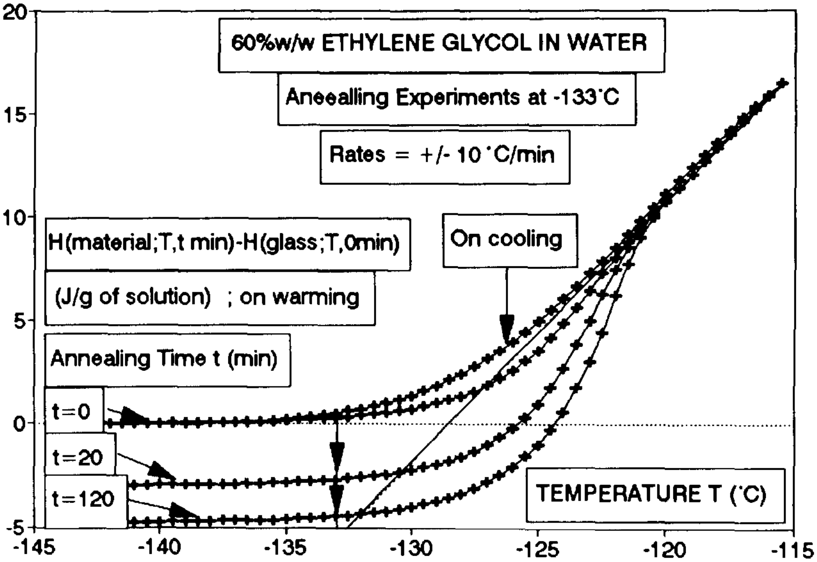

Fig. 9. Evolution for 60% w/w ethylene glycol in water of the difference in the enthalpy between the sample vitrified and annealed at −133°C for different times t and the glassy state annealed for $t = 0$ min chosen as reference for the difference in enthalpy. the evolution of this difference is also reported during cooling.

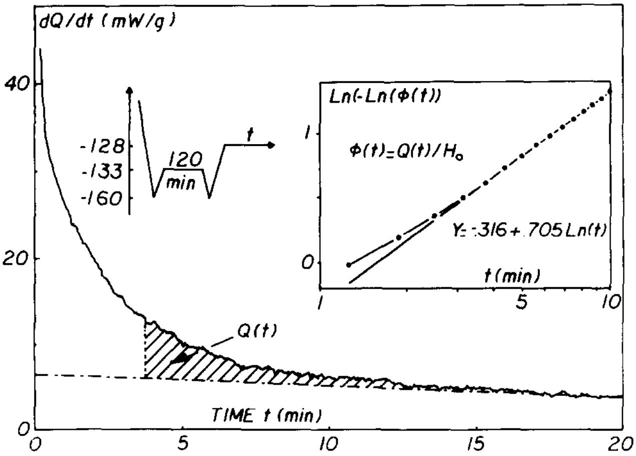

Fig. 10. Isothermal thermogram at −128°C for a 60% w/w ethylene glycol in water sample cooled initially to −160°C, then annealed at −133°C for 120 min, as reported above the thermogram. In the insert, the variation of $\ln(-\ln(\phi(t)))$ versus the time t of the isothermal exposure at −128°C is reported in a logarithmic scale. The response function $\phi(t)$ is defined as the ratio of the energy release from the time t to the end of the thermogram over the excess enthalpy H_0 of the sample annealed at −133°C for 2 h and warmed at −128°C, compared to the ideal liquid at the same temperature.

$H(T, t = 0) - H(T, t = \text{infinite})$ denoted H_0 in Fig. 10, the direct isothermal method can be analyzed for the determination of β and τ, as reported in Fig. 10. On this Fig. 10, the isothermal thermogram is reported with the insert of $\ln(\ln(-\phi(t)))$ versus $\log(t)$, allowing a least-squares regression to calculate $\beta(T)$ and $\tau(T)$.

Using the indirect isothermal method, $\ln(-\ln(\phi(T, t)))$ is drawn in Fig. 11 as a function of the annealing time t reported in a logarithmic scale for the annealing temperature $T = -135°\text{C}$. The analysis was made on the linear part of the curve observed for the lower values of t. A least-squares linear regression was used for the determination of $\beta(T)$ and $\tau(T)$. The same analysis was done for all the other annealing temperatures.

Figure 12 reports all the values of $\beta(T)$ and $\tau(T)$ determined by direct and indirect isothermal methods. The values for $\beta(T)$ are reported versus T. This stretched exponent does not depend on the annealing temperature as expected [24, 26] for the thermal range of the glass transition. The mean value of β is 0.58 ± 0.03 for the indirect isothermal method, but β increases with the temperature T for the direct isothermal method because the temperature is higher than the glass transition temperature. The value of $\beta(T)$ for the direct isothermal method increases as the temperature T increases. In the same figure, $\ln(\tau)$ is drawn as a function of $1/(T - 77)$ after optimization of the linear regression for the best linear fit for the lower

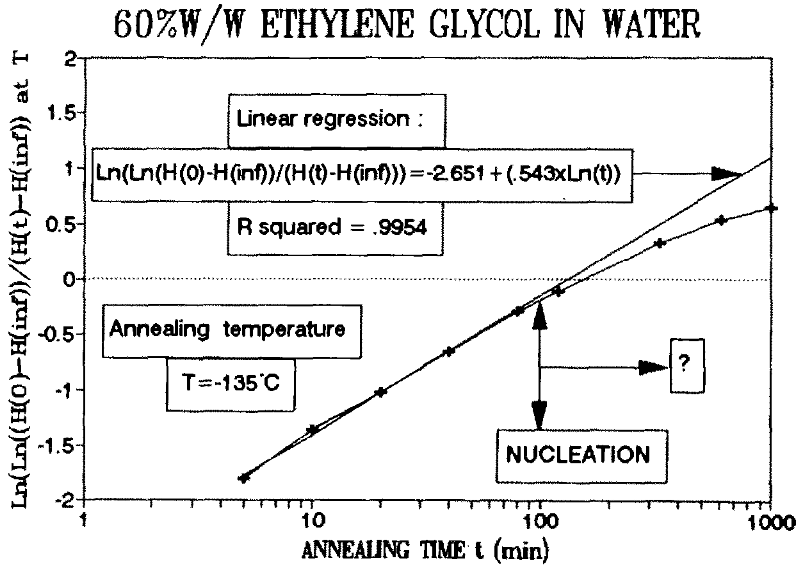

Fig. 11. Comparison for 60% w/w ethylene glycol in water of $\ln(-\ln(\phi(T, t)))$ as a function of the annealing time t reported in a decimal logarithmic scale for the annealing temperature $T = -135°\text{C}$, where $\phi(T, t)$ is the enthalpic response function. The least-squares linear regression calculated for the linear portion of the curve for small annealing times t is also reported.

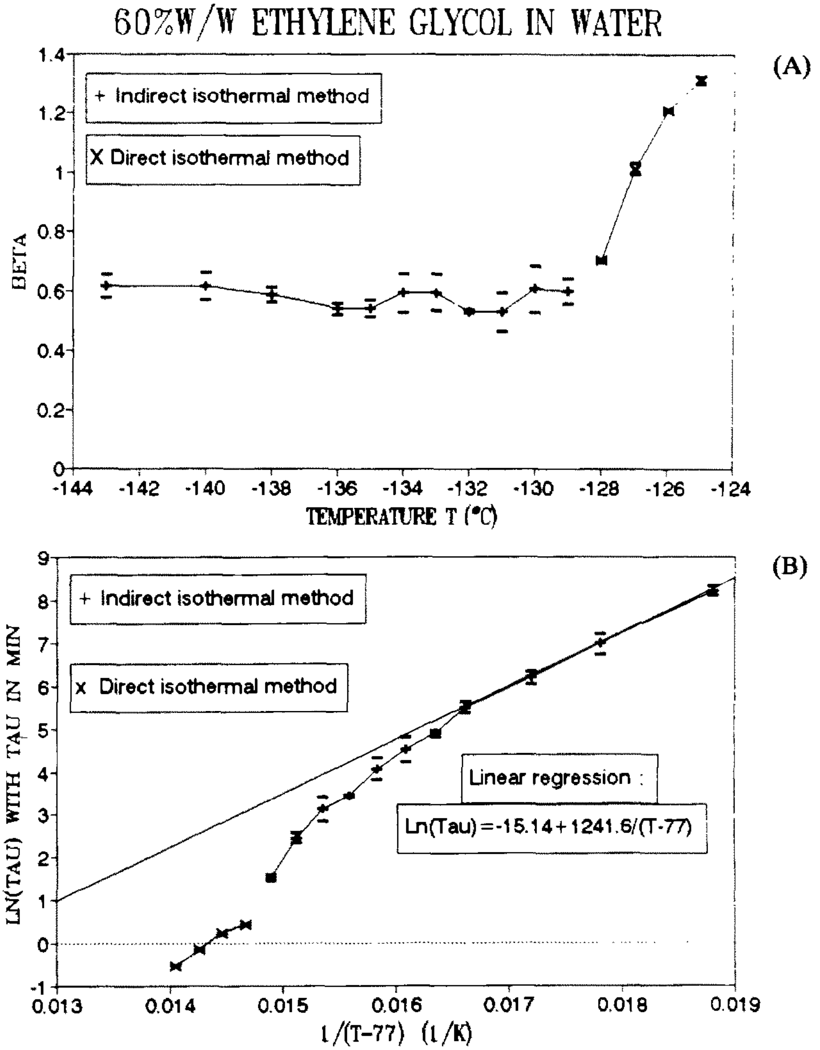

Fig. 12. Variations of the parameters for the stretched kinetic behavior of the annealed glassy state: (A) exponent β reported as a function of the temperature of annealing T; (B) natural logarithm of the relaxation time τ (min) versus the optimized scaled $1/(T\text{-}77)$ with the annealing temperature T. The calculated linear regression of the curve with its expression is also reported.

temperatures which are below the observed glass transition. Calculations give $\tau_0 = 2.66 \times 10^{-7}$ min or 1.6×10^{-5} s and an activation energy $A =$ 1242 K.

DISCUSSION

In accord with Sandu and Singh [25], the use of a multipoint calibration with extrapolation to 0°C min^{-1} warming rate gives an accurate determination of the temperature for the isothermal experiments at the low temperatures which are presently considered. The non-isothermal conditions are also calibrated in the limit imposed by the size and rates considered, either for the temperature or the energy exchange during transitions. The subtraction of two thermograms for the determination of relative behavior has already been used for the determination of the kinetics of crystallization in isothermal and non-isothermal conditions [6, 7] and allows the error to be minimized by defining the basal line for the different thermograms. A similar method is used here for the determination of the glass transition behavior and is assumed to be more correct than trying to define directly a baseline for each thermogram. The sensitivity of the method allows the determination of the relative variations of the glass specific heat C_p and its evolution during warming, with the thermodynamics functions associated with the variations in C_p. The uncertainty in the choice of the baseline for the analysis of the thermograms during warming is still present with the assumption of a linear behavior of the specific heat of the glassy state for temperatures in the glass transition thermal range in the determination of the evolution of the enthalpy of the vitrified medium. However the choice of its initial point can be intuited due to the transient relaxation recorded and reported in Fig. 7 as an internal verification that during the time spent by the sample in the corresponding thermal range during warming, no relaxation occurs. However, for the entire present study, the analysis assumes implicitly that the transient relaxation is not affecting the relaxation at the annealing temperature T.

The relative evolution during warming of the specific heat of the annealed glassy state compared to that annealed transiently, was not determined. The inter-relationship between temperature and time during warming is complex and is not treated in the present study. Only the total excess enthalpy and total excess entropy between the annealed glass and the unannealed glass have been considered, as defined previously over the thermal range of the glass transition as the integral of δC_p and of $\delta C_p/T$. These non-isothermal values have been used to analyze the isothermal relaxation of the glassy state of 60% ethylene glycol. Indeed, the evolution of the specific heat leading to the same final liquid state above the glass transition allows the back-determination of the initial stored enthalpy and stored entropy after annealing at the considered temperature for the considered annealing time. The stored enthalpy and the stored entropy are defined from the energy exchange during the glass transition. The analysis of the data from the recorded thermograms is straightforward.

The relaxation processus through the presented annealing experiments is accessible through calorimetric measurements for glass-forming aqueous solutions. The results are in a good accord with the model of the fractional exponential relaxation of Williams and Watts (see Angell [11, 12]) for small annealing times, as has already been used and generalized by other authors [11–21] for the description of the enthalpy relaxation.

The exponent β has generally been observed to fall between 0.3 and 0.7, depending on the nature of the glass-forming medium [15]. An analysis of the differential behaviors of the relaxation has been reported by Rajagopal et al. [27] by coupling model schemes for slow relaxation mechanisms. For 60% w/w ethylene glycol, this exponent is at present reported empirically as temperature independent, with a mean value of $\beta = 0.58$ in the peculiar case of the indirect isothermal methods. This value is close to 0.62 which has been published by Hofer et al. for 22 mol.% ethylene glycol in water [21]. Some authors have underlined the possibility of a temperature dependency of β assuming the existence of a second universality characteristic of the glassy state [26]. In the present data, the variation of the exponent β is not obvious for the temperatures considered in the indirect isothermal method within the sensitivity of the DSC. It must be noted that, according to Rajagopal et al. [27], this temperature dependence of β is one of the characteristics predicted for glass-forming viscous liquids with inter-molecular interactions, such as between solute/solute and solute/solvent, with a typical value of β being around 0.5 at the limit of the glass transition temperature.

According to Rajagopal et al. [27], the analysis of the characteristic relaxation time τ must follow a Vogel–Fulcher–Tamman equation. The determination of the characteristic relaxation time τ for the different annealing temperatures T shows its dependence on the temperature T as reported in Fig. 12. However no best fit has been able to make the least-squares line pass inside the error bars of the values $\tau(T)$. Therefore, the only data kept are those corresponding to temperatures lower than the recorded glass transition. At these temperatures, the assumption of suppressed nucleation is also the most reasonable. The value of T_0 is found to be 77 K for the best fit. T_0 is around 50 K below the thermal range of the glass transition presently observed for a cooling and warming rate of 10°C min^{-1}.

The uncertainty on T_0 is not known due to the uncertainty of the determination of $\tau(T)$, because an Arrhenius variation of $\tau(T)$ also gives a regression line inside the error bars of $\tau(T)$. One solution would be to extend the relaxation experiments to a wider thermal range which is limited by the time available for the experiments and by the possibility of fracturing the glass. Another approach is to extrapolate the viscosity data available from Ramanamurti et al. [28]. An extrapolation of the linear regression was made, assuming a Vogel–Fulcher–Tamman behavior for these aqueous solutions. The activation energy E^* is determined as a function of the temperature T_0 and converted to E^* as described by Rajagopal et al. [27] via $E = E^*/\beta$. The variations in the activation energies E and A as a function of T_0 for $\tau(T)$ and for the viscosity data intersect at a particular temperature $T_0 = 100$ K for an activation energy of 433 K. For these parameters, the extrapolated viscosity of 60% w/w ethylene glycol at the onset of the glass transition (≈ -130°C) from the data of Ramanamurti et al. [28], is equal to 4×10^9 Poise, which is close to the anomalous viscosities observed by Angell for organic glass-forming liquids at around 10^{10} Poise at the glass transition [11, 12]. The determination of T_0 with only the best fit with the calorimetric data is therefore not sufficient and needs to be complemented with other experimental results.

For higher temperatures, the more rapid decrease of $\tau(T)$ represents a quicker achievement of the relaxation than that predicted from the lowest temperatures as β remains constant. This shows that either the difference $H(T; t = 0\,\text{min}) - H(T; \text{infinite})$ has been overestimated or the nucleation processus has artificially increased the rate of the relaxation. The second explanation will be investigated in more detail later.

The direct isothermal method results show that $\tau(T)$ varies in a similar way as for the indirect isothermal method. However, for the values of the exponent β, $\tau(T)$ increases very quickly to values above 1. This means that another phenomenon is increasing the rate of energy release during the isothermal exposure. This is consistent with the hypothesis of nucleation overlapping the relaxation of the glassy state.

All the previous analyses concerning the indirect isothermal method have been made on the linear parts of the variations of $\ln(-\ln(\phi(T, t)))$ versus $\ln(t)$ concerning the different temperatures T. Experimentally, as this temperature T increases above -135°C, $\ln(-\ln(\phi(T, t)))$ reaches a plateau and sometimes decreases. As reported in Fig. 10, this is a good reason for assuming that some nucleation is occurring. As the annealing time increases above that of reaching the plateau, the subtraction between the reference and the experimental thermograms shows that the specific heat of the liquid decreases slightly, as expected as crystallization occurs in the liquid. The combination of the decrease in the specific heat and of the decrease in the amount of glassy matter in the sample might also change the baseline in the determination of the variation of the excess enthalpy and entropy for the glassy state for the indirect isothermal method.

CONCLUSIONS

The glass transition for 60% w/w ethylene glycol in water has been analyzed by two different complementary methods involving calorimetry and thermal treatments. Indirect and direct isothermal methods allow the determination of the kinetics parameters for the Kohlrausch–Williams–Watts response function.

The method of subtracting a reference thermogram for the analysis and calculation of relative thermodynamics functions gives good relative data which can be combined for the determination of the glass transition dynamics. The assumption of the basal line is done only once for the reference curve. The only uncertainty is therefore reduced to its minimum effect after the right energy and temperature calibrations are taken into account.

The determination of the parameters for the Kohlrausch–Williams–Watts response function ϕ are not defined very easily by calorimetry and complementary data: longer experiments are needed to achieve the determination of T_0 and, therefore, the activation energy A.

The present results lead to different questions which cannot be answered here, such as the relationship between the nucleation and the relaxation of the glassy state, or how to correlate these isothermal results with the non-isothermal data represented by the direct thermograms during warming. Complementary investigations are needed for a better understanding of the behavior of the glassy state from 60% w/w ethylene glycol in water.

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REFERENCES

1 G.M. Fahy, D.R. MacFarlane, C.A. Angell and H.T. Meryman, Cryobiology, 21 (1984) 407.
2 P. Boutron and P. Mehl, J. Phys. C, 48 (1987) 441.
3 P. Boutron, in D.E. Pegg and A.M. Karow (Eds.), The Biophysics of Organ Cryopreservation, NATO ASI Series, Series A: Life Sciences, Vol. 147, Plenum Press, New York, 1987, pp. 201–236.
4 D.R. MacFarlane and M. Forsyth, Cryobiology, 27 (1990) 345.
5 C.A. Angell and Y. Choi, J. Microsc., 141 (1985) 251.
6 P.M. Mehl, Thermochim. Acta, 27 (1989) 187.
7 P.M. Mehl, Cryobiology, 27 (1990) 378.
8 R.J. Williams, P. Mehl and D.L. Carnahan, in C.Th. Smit-Sibinga, P.C. Das and H.T. Meryman (Eds.), Cryopreservation and Low Temperature Biology in Blood Transfusion, Kluwer Academic, Boston, 1989, pp. 71–86.
9 J.T. Dickinson, L.C. Jensen and M.R. McKay, J. Vac. Sci. Technol., A4 (1986) 1648.
10 G.N. Chapman and A.J. Walton, J. Appl. Phys., 54 (1983) 5961.
11 C.A. Angell, Pure Appl. Chem., 63 (1991) 1387.
12 C.A. Angell, J. Non-Cryst. Solids, 131–133 (1991) 13.
13 O.S. Narayanaswamy, J. Am. Ceram. Soc., 54 (1971) 491.
14 S. Rekhson, J. Non-Cryst. Solids, 95/96 (1987) 131.
15 K.L. Ngai and G.B. Wright (Eds.), Relaxations in Complex Systems, National Technical Information Service of U.S. Department of Commerce, Arlington, VA, 1984.

16 C.T. Moyhinan, P.B. Macedo, C.J. Montrose, P.K. Gupta, M.A. DeBolt, J.F. Dill, B.E. Dom, P.W. Drake, A.J. Easteal, P.B. Elterman, R.P. Moeller, H. Sasbe and J.A. Wilder, Ann. N.Y. Acad. Sci., 279 (1976) 15.
17 C.T. Moynihan and A.V. Lesikar, Ann. N.Y. Acad. Sci., 371 (1981) 151.
18 C.T. Moyhinan, S.N. Crichton and S.M. Opalka, J. Non-Cryst. Solids, 131–133 (1991) 420.
19 M.T. Clavaguera, J. Therm. Anal., 35 (1989) 1787.
20 M.T. Clavaguera, Thermochim. Acta, 148 (1989) 261.
21 K. Hofer, E. Mayer and I.M. Hodge, J. Non-Cryst. Solids, 139 (1992) 78.
22 G.B. McKenna and C.A. Angell, J. Non-Cryst. Solids, 131–133 (1991) 528.
23 J.B. Ott, J.R. Goates and J.D. Lamb, J. Chem. Thermodyn., 4 (1972) 123.
24 S.R. Nagel and P.K. Dixon, J. Chem. Phys., 90 (1989) 3885.
25 C. Sandu and R.K. Singh, Thermochim. Acta, 132 (1988) 89.
26 K.L. Ngai, J. Non-Cryst. Solids, 131–133 (1991) 80.
27 A.K. Rajagopal, K.L. Ngai and S. Teitler, J. Non-Cryst. Solids, 131–133 (1991) 282.
28 M.V. Ramanamurti, P.V.S.S. Prabhu and S.L. Bahadur, Bull. Chem. Soc. Jpn., 49 (1986) 2341.