Hydrogen-Bond Equilibrium and the Enthalpy and Entropy Relaxations in a Nonpolar State of Vitrified 2-Methyl-3-heptanol

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The spontaneous decrease of the enthalpy and entropy of the variously vitrified 2-methyl-3-heptanol, an octanol isomer which behaves like a nonpolar liquid as its molecular dipole vectors mutually cancel on intermolecular hydrogen bonding, has been studied by differential scanning calorimetry. The effect of annealing for different periods at a fixed temperature, and at different temperatures for a fixed period, has been investigated. The structural relaxation is close to exponential, and its characteristic time, in contrast with other glasses, does not increase with the annealing time. These characteristics are different from those found for other materials and correspond to a first-order rate of a chemical process or an exponential decay of the thermal functions. The exponential character and the low activation energy (=37.7 kJ/mol) of the process, which is comparable to the energy for the formation of two H-bonds and to the enthalpy (=36 kJ/mol) of ring dimerization data available in the literature, indicate that the enthalpy decrease observed on annealing is mainly a reflection of an increase in the concentration of the nonpolar ring dimers formed by H-bond association. The effect is attributed to the increase in the reaction quotient toward the equilibrium constant value of the intermolecular hydrogen-bond association reaction in the liquid's structure, as the fictive temperature decreases. The increase in the number of H-bonds and in the reaction quotient, as it approaches the equilibrium constant for the reaction, monomer ↔ ring dimer or lineardimer ↔ ring dimer, as well as the equilibrium concentration of the dimers, has been calculated from the enthalpy and entropy decrease observed on annealing. This is combined with a similar calculation from the dielectric data available in the literature. It is proposed that such effects occur also in materials with abundant H-bonding, as in hydrated proteins and carbohydrates and those in which ion association and isomerization reactions occur, and that the availability of configurational and conformational degrees of freedom is necessary for their occurrence. Hence, we introduce the terms for discussing spontaneous enthalpy and entropy decrease of an H-bonded glass in terms of a chemical fictive temperature corresponding to the H-bond and ion-pair formation.

Introduction

The vitrified state of a material is (i) thermodynamically metastable with respect to its crystalline state and (ii) usually kinetically unstable with respect to a lowest energy, equilibrium state of its metastable supercooled liquid. The first is observed when the glass crystallizes, and the second is observed by the slow, spontaneous approach of the state of a glass toward its equilibrium state. During the latter, the magnitudes of its enthalpy and entropy always decrease. But when the material densifies or dilates during this process, several other of its properties, particularly those whose magnitude is determined by the thermal activation over energy barriers, the frequency of vibrational modes, and electronic transition levels, also change, but in a direction determined by the volume change. The spontaneous change in these properties is referred to as structural relaxation or physical aging of a glass. Subsequent heating allows regain of the enthalpy, entropy, and other properties as the state of the material reaches a temperature where equilibrium tends to establish within the time scale corresponding to the heating rate. These effects constitute a wide variety of studies on amorphous polymers,[1−17] inorganic network and linear chain glasses,[18−23] metallic glasses,[24−26] biopolymers,[27−29] and molecular glasses.[30−33]

When molecules in a vitrified material chemically react, the exothermic reaction contributes to the loss of enthalpy,[34,35] and the dielectric properties change irreversibly.[36−38] In most cases, this effect is either negligible or absent because (a) the kinetics

of chemical reaction, which requires presumably a longer diffusion distance than for structural relaxation, is prohibitively slower than the kinetics of structural relaxation and (b) the chemical reaction in most cases kinetically freezes in on cooling at a temperature much higher than T_g, the glass-transition temperature for the same heating rate. Furthermore, on heating the glass, the enthalpy lost on chemical reaction, as well as changes in any other property on reaction, is not regained on rate heating in the same manner as they are regained for structural relaxation alone.

But when two energetically different chemical species exist in equilibrium with each other in the liquid, their equilibrium constant, K, changes on supercooling the liquid, and after the reaction itself has become diffusion-controlled, the equilibrium constant freezes in at a temperature where the rate of its change with temperature becomes comparable to the inverse of the cooling rate. The equilibrium concentration of the chemical entities involved at the temperature of structural freezing on a certain experiment's time scale is given by K at that temperature, but when the temperature at which the nonequilibrium state is kept is lower than this temperature, the quantity is formally seen as Q, the reaction quotient at that temperature, not as K. Q approaches K, as the annealing time approaches infinity, and Q = K, when the temperature at which the material is held is equal to its fictive temperature. The temperature at which the chemical equilibrium freezing occurs, or where K becomes formally Q, is usually close to T_g, at which the liquid's structure also freezes in. A recent review[39] on the time- and temperature-dependent features observed in the vibrational spectra of

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molecules dissolved in vitrifying solvents provides a discussion of the conformational changes in the molecules resulting from the change in the equilibrium constant for the conformational transitions.

Thus, a liquid's vitrified state has a frozen-in equilibrium defined by Q, which constitutes a third metastability, which is chemical in nature. It follows that the chemical state of a glass in such cases is kinetically unstable with respect to its Q, which spontaneously increases on annealing toward the ultimate, equilibrium value of $Q = K$ for an exothermic process. The decrease in the enthalpy and entropy of a glass would then correspond to two effects: (a) the increase in Q leading to the lowest chemical energy state corresponding to the equilibrium constant K and (b) the structural relaxation leading to the lowest structural energy state. The latter is a requisite for the former. The enthalpy and entropy loss due to the spontaneous increase in Q will be recovered on heating in the same manner as the enthalpy loss due to structural relaxation. Here we describe a study in which both changes occur on annealing, isothermally as well as on rate heating, but the increase in Q dominates the enthalpy and entropy loss. The observations are expected to be general and applicable to the already observed similar occurrence in hydrated DNA,[28,29] in proteins,[27,40−42] and in carbohydrates, where H-bond interactions are abundant, for ion associaton equilibrium and isomerization equilibrium in materials. As an example of this occurrence, we chose to study 2-methyl-3-heptanol, an octanol isomer in which H-bond association of the, initially, monomer state ultimately produces ring dimers, in which the dipole vectors cancel and reduce the static permittivity of the liquid to less than 2.5, comparable to the value for nonpolar liquids. Its virtually nonpolar state was discovered by Dannhauser[43] and later studied by several groups using different techniques.[33,44−47]

It is of course necessary that conformational and configurational rearrangements occur before a chemical reaction can occur. But, since the molecular diffusion distance in most cases is relatively long and therefore the apparent rate of a reaction is low, the fictive temperature for structural relaxation (for a given rate) is seen to be higher than that of the chemical reaction.[37] For chemical equilibrium that involves intermolecular H-bonding, however, the two may be the same or closely similar, because the distance of diffusion required for H-bonding between two molecules is relatively small. Thus, the fictive temperature for freezing of K would be close to that for the freezing of the structure on cooling, or the H-bond association fictive temperature and the structural (enthalpic) fictive temperature would be closely similar, with the possible implication that the enthalpy of the H-bond association reaction itself determines the enthalpy difference between the nonequilibrium glassy state and the equilibrium state at the same temperature. This of course would be strictly true if localized motions in the glassy state were absent and the vibrational contribution to the enthalpy did not change on further reaction or structural relaxation. That issue also will be discussed here.

Experimental Methods

2-Methyl-3-heptanol was donated to us by Prof. W. Dannhauser in March 1990. It was a purified sample from his extensive dielectric study,[43−45] which he had kept stored in a sealed container since 1966. It does not absorb moisture significantly, and its only impurities which could have been other octanol isomers were removed by fractional distillation under reduced pressure for earlier studies.[43−45] It was fractionally redistilled similarly again before use. Although its melting point is quoted as 188 K, it did not crystallize even on cooling

at 1 K/min to 100 K or keeping it near 180 K for 15 min. (This is not unusual in view of the well-known difficulty in crystallizing glycerol, whose freezing point is 293 K.) Its T_g for heating at 30 K/min rate is 161.5 K, and its calorimetric relaxation time is 84 s at 161.5 K.[33,48]

A differential scanning calorimeter (Model DSC 4 from Perkin-Elmer) was used. G. Sartor, who wrote the data acquisition and analysis software, had used it for earlier studies.[17,27] The instrument was calibrated with 1-octanol and distilled water. Aluminum pans were used to contain the sample with an aluminum lid to cover them, and helium was used as a purge gas. During the DSC scan of a sample, a baseline recorded with an empty pan was subtracted to remove any effects from the difference between the thermal capacity of the instrument's platinum holders for the pans. The thermal lag between the sample's temperature and the recorded temperature during the measurement was 2.1 K for heating at 30 K/min. The DSC scans shown in all the figures here are corrected for this thermal lag. The heating rate was chosen for consistency with our earlier studies and for enhancing the observed DSC features, particularly when earlier studies[22] have shown that the data obtained from this heating rate yield the same quantities as those obtained for 10 K/min heating rate.

The sample kept in the instrument was cooled at the highest rate, which was found to be $\approx$150 K/min on calibration,[49,50] or at other rates, as noted in the text. The rate of heating for all DSC scans was 30 K/min, and 15−20 mg of the sample was used. The DSC output divided by the sample's mass remained the same for samples of different mass. This showed that the effect of the sample's mass on the measured values was negligible.

Results

To study the effects of annealing at different temperatures for a fixed annealing time, a sample of 2-methyl-3-heptanol was cooled from 193 to 103 K at 30 K/min and thereafter heated to a temperature, T_a, at 150 K/min, annealed for 5 min at T_a, cooled to 103 K at 150 K/min, and the DSC scan finally obtained during heating at 30 K/min. The annealing temperature, T_a, was chosen as 103, 145, 153, 157, 160, 162, and 168 K for different sets of experiments. The 5 min annealing at 103 K causes a vanishingly small loss of enthalpy, and so the samples kept for 5 min at 103 K are referred to as unannealed samples. The DSC scans obtained for this set of experiments are shown in Figure 1A. In the second set of experiments, the sample was cooled at 150 K/min and then annealed and studied in the same manner as that for Figure 1A. The corresponding DSC scans are shown in Figure 1B. The difference curves, which were obtained from the data in Figure 1A,B by subtracting the scan for the unannealed sample from the scan for the annealed sample, are shown in Figure 2A for the samples cooled from 193 K at 30 K/min and in Figure 2B for the samples cooled from 193 K at 150 K/min.

As a set of final experiments on vitrified 2-methyl-3-heptanol, the sample was cooled from 193 to 103 K at both 30 and 150 K/min, heated to 145 K at 150 K/min, annealed for a certain period at 145 K, cooled to 103 K at 150 K/min, and finally heated to 193 K at 30 K/min, during which its DSC scan was obtained. The annealing period, t_a, was 1, 2, 5, 7, 10, and 15 min at 145 K. The difference scan obtained by subtracting the scan for the annealed sample from the scan for the unannealed sample cooled at 30 K/min is shown in Figure 3.

The difference between the areas enclosed by two scans divided by the heating rate q is equal to the enthalpy recovered on heating, which should be the same as the enthalpy lost on
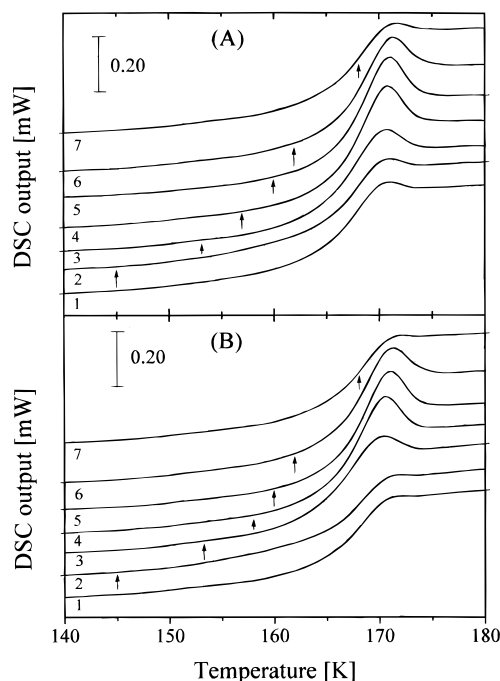
Figure 1. (top) DSC scans for 2-methyl-3-heptanol obtained by cooling the sample from 193 to 103 K at 30 K/min and annealing for 5 min at temperatures of 145 (curve 2), 153 (curve 3), 157 (curve 4), 160 (curve 5), 162 (curve 6), and 168 (curve 7), as marked by arrows. Curve 1 is for the unannealed sample. (bottom) Corresponding DSC scans for the samples obtained by cooling from 193 to 103 K at 150 K/min. The general procedure was as follows: the sample was cooled from 193 to 103 K at the desired rate, then heated to the annealing temperature, T_{ann}, at 150 K/min, kept at that temperature for a period t_{ann}, recooled to 103 K at 150 K/min, and scanned at 30 K/min from 103 to 193 K.

structural relaxation isothermally and/or on rate heating when no irreversible chemical reaction occurs during cooling, annealing, or heating. The area enclosed by similar plots but against the logarithm of temperature yields the entropy lost on structural relaxation isothermally and/or on rate cooling and heating. This was determined by measuring the area, as before,[17,27−28] of the endothermic peak in the difference curves seen in Figures 2 and 3.

Models for Structural Relaxation. Structural relaxation refers to the spontaneous approach of a disordered structure toward its lowest energy, disordered state by molecular rearrangement. The accompanying decrease in the enthalpy and entropy is a combined effect of two occurrences: (i) the loss of some (not all) of the configurational enthalpy and entropy as a result of structural rearrangement when long-range molecular motions have occurred within an unspecified degree of freedom in the disordered structure and (ii) the loss of the excess magnitude of a property determined by the molecular and atomic vibrations or electronic transitions (refractive index, which increases) over the value for the lowest energy state. The latter is due to the fact that the phonon frequencies change with change in the density, so that the enthalpy difference between the nonequilibrium and equilibrium glassy state is not only the difference due to the configurationally low-energy state but also the vibrationally different, less harmonic (low-energy) states of lower heat capacity. The results given in Figures 1−3 show generally how (a) the annealing temperature and (b) the annealing time of the sample vitrified by cooling at 150 and 30 K/min alter the configurational and vibrational contributions to the enthalpy and entropy in the glassy state. The decrease in these contributions on spontaneous structural relaxation is a consequence of a variety of local and long-range molecular motions, namely, rotations about the C−C and C−OH bonds
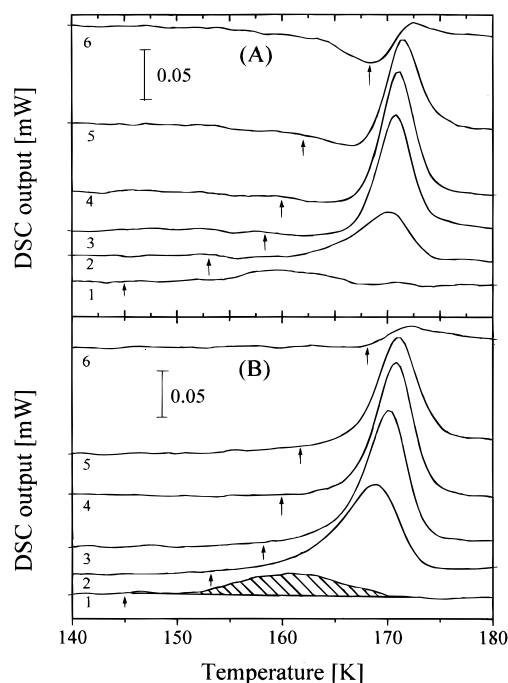

Figure 2. Difference curves for 2-methyl-3-heptanol obtained by subtracting the DSC scan of the unannealed sample from the DSC scan of the 5 min-annealed sample at different temperatures, which are marked by the arrows. The data in the top and bottom parts of the figures were obtained from the curves shown in the top and bottom parts of Figure 1, respectively. For example, curve 4 was obtained by subtracting curve 1 from curve 5 in Figure 1.
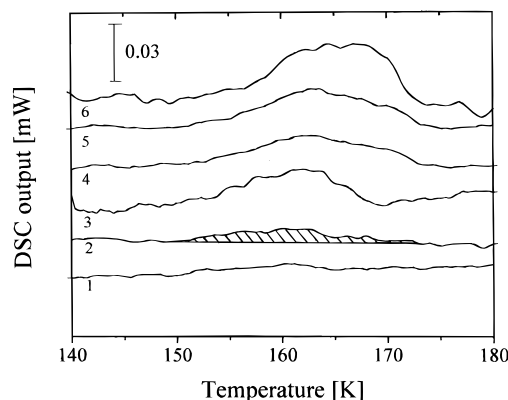

Figure 3. Difference curves for 2-methyl-3-heptanol obtained by subtracting the DSC scans of the unannealed sample from that of the annealed sample. The sample was cooled from 193 to 103 K at 30 K/min in all cases. For curves, 1, 2, 3, 4, 5, and 6 the time of annealing is 1, 2, 5, 7, 10, and 15 min at 145 K.

and displacement of the molecular segments or of molecules as a whole with respect to others. All of these motions occur in an intermolecular environment, including certain modes of segmental motions which may be conformational, if they involved only rotations about a covalent bond.

The phenomenon of spontaneous changes in the properties of a glass on annealing has been described in several review articles,[1,3,6,7,11−14,18,25] mostly in terms of physical aging, enthalpy and volume relaxations,[1−4,11−13,20] changes in the refractive index,[19] mechanical modulus,[2,12,13,51,52] and dielectric properties.[53,54] A variety of models have been developed for fitting to the various data on amorphous materials, but they all admit to the phenomenology of structural relaxation based upon the original observations of Winter-Klein[55] and Tool[56] and the formalisms by Narayanaswamy.[57] It was applied first by Moynihan and co-workers[18] to the DSC data of a variety of

substances, and algorithms for simulation of the data were developed by Berens and Hodge,[5] which they used for the DSC data on polymers.

There are at least nine different models, either empirical or based on a particular concept, and all seem to fit satisfactorily the DSC data. The equations needed for fitting are based on the description of (i) enthalpy,[18] (ii) configurational entropy,[58,59] (iii) distribution of relaxation times,[60,61] (iv) defects diffusion,[13,62] (v) distribution of free volume,[63] (vi) fractal lattice fluctuation,[64] (vii) a multiparameter description known as the KAHR model,[3,4] (viii) a different multiparameter description given by Rekhson,[65] and (ix) a density fluctuation interpolation model.[66] The fitting of the models to data requires four self-consistent parameters, but their values for a particular relaxation are not measurable by independent methods. Also, it is found[12] that the values of the parameters required to fit the DSC data differ remarkably from the values that fit the dielectric, mechanical, refractive index, or volume relaxation data. (The latter two are distinguished because the Lorentz−Lorenz equation for electronic polarizability that relates the refractive index with the molar volume is itself only approximately valid for both liquids and solids, as for example, for water and for ice, for which accurate refractive index and density data are available.) This may be rationalized on the grounds that the regions of the spectra probed by different techniques differ, as do the molecular groups and size of the molecular regions in a material. Furthermore, the choice of the empirical parameters used for fitting the nine formalisms differ, even when the models provide an acceptable simulation of the same experimental data. So, it seems that there is a need for caution in deducing molecular information from the parameters of these model fittings. These models are undoubtedly most useful for predicting the consistency of behavior of the same material during aging and for a comparative analysis of different materials.

There are also several limitations to the use of such models. First is the assumption needed for the convenience of data analysis that the slope of T_f against T plot (which is used to define a dimensionless C_p[5]) for the equilibrium state of a glass remains constant on changing its temperature, thus implying that the entropy of an equilibrium glass when extrapolated in such a manner will become equal to the entropy of a crystal at T_K or T_2, the temperature at which the area enclosed by the C_p plots of the equilibrium liquid and of the crystal in a ln T plane, from T_K to the melting point, will be equal to the entropy of freezing of the liquid. Such an extrapolation of entropy was originally conjectured by Kauzmann[67] in the interest of further analysis of the thermodynamics of a supercooled liquid, not to suggest that this paradoxical situation could be fundamentally sound. Even over a narrow range of temperatures, C_p ($=dT_f/dT$) does not remain constant for all materials. For some, C_p decreases with temperature near T_g, as for *o*-terphenyl, and for others it increases, as for 1-butene.[68] There is a further weakness in assuming that C_p of a glass increases linearly with the temperature, because an increase in the contributions to C_p from anharmonic vibrations and localized molecular motions (referred to as the Johari−Goldstein relaxation) in a glass cause its C_p−T plots to increase in slope progressively more as T_g is approached. In summary, the temperature dependence of C_p needs to be extrapolated to fit the model, and that becomes difficult when the C_p−T plots are curved.

Second, the most important parameter, β, the asymmetric distribution of relaxation times, is taken to remain constant with t_a and T_a, in all the above nine models, although it is acknowledged that it is expected to change. Recent stud-

ies,[23,30,32] however, show that this is not the case and thus confirm a 30-year-old finding by Douglas[69] that β changes with t_a.

Third, the Kauzmann situation[67] for the extrapolated entropy of a supercooled liquid becoming equal to that of a crystal at T_K or T_2, which is the basis of several models based on the Adam−Gibb's resolution of the Kauzmann situation in terms of the complete loss of configurational entropy at T_K,[58,59] neither is anticipated on fundamental grounds nor is observed. An alternative was discussed in a recent paper,[68] but in terms different from those of Simon[70] and of several others,[71−74] where it was concluded that the entropy of a thermodynamically equilibrium state of a disordered solid will remain above that of the crystalline state on cooling the solid toward 0 K, because the former contains contributions from anharmonicity of phonons[71] and from the volumetrically nonequivalent sites occupied by the atoms or molecular segments in the disordered structure.[68] Nevertheless, the nine different model fittings still seem adequate over a narrow temperature range of the glass−liquid transition, because the combined effect of these approximations seem to be insignificant in comparison with the errors in the DSC scans, even if it is allowed that some structural relaxation must occur in all experiments because the heating rate is never high enough to avoid it completely.

In view of these issues, we use an alternative approach in which the observed properties are analyzed without the use of a model. This has a further advantage in that it yields an insight into the thermodynamics rather than a comparison between the validity of various models. In this approach, which was first used for understanding the thermodynamic data on hydrated DNA,[29] the irreversible decrease in enthalpy on annealing, $d\Delta H_a$, is written as the sum of several contributions:

$$d\Delta H_a = \left(\frac{\partial \Delta H_a}{\partial T_a}\right)_{t_a,q,q_c} dT + \left(\frac{\partial \Delta H_a}{\partial t_a}\right)_{T_a,q,q_c} dt_a +$$
$$\left(\frac{\partial \Delta H_a}{\partial q_c}\right)_{T_a,t_a,q} dq_c + \left(\frac{\partial \Delta H_a}{\partial q}\right)_{T_a,t_a,q_c} dq \quad (1)$$

where $d\Delta H_a$ is the difference between the enthalpy of the material before and after the annealing experiment, and all other notations are as defined before. (The prefix Δ is used to maintain that the quantities determined by experiments are $H − H(0\ K)$ and $S − S(0\ K)$, and not the absolute values of H and S.) The first term on the right-hand side of eq 1 represents the enthalpy loss with respect to the temperature for constant annealing time, t_a, the heating rate, q, and the cooling rate, q_c, and the second term represents this loss with respect to t_a, for constant q, q_c, and the annealing temperature, T_a. The third term represents the enthalpy loss over a certain temperature range with respect to the cooling rate for constant t_a, T_a, and q, and the fourth term represents the enthalpy loss with repect to the heating rate for constant t_a, T_a, and q_c. The plots in Figures 1 and 2 show the magnitude of the first term, and those in Figure 3 show the magnitude of the second term. Because q_c and q for a set of experiments are kept constant, the magnitudes of the third and the fourth terms are zero.

The corresponding decrease in the entropy is

$$d\Delta S_a = \left(\frac{\partial \Delta S}{\partial T_a}\right)_{t_a,q,q_c} dT + \left(\frac{\partial \Delta S_a}{\partial t_a}\right)_{T_a,q,q_c} dt_a + \left(\frac{\partial \Delta S_a}{\partial q_c}\right)_{T_a,t_a,q} dq_c +$$
$$\left(\frac{\partial \Delta S_a}{\partial q}\right)_{T_a,t_a,q_c} dq \quad (2)$$

where the terms have the same meaning as in eq 1. The two

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equations describe how H and S of a chemically stable disordered solid in storage would decrease if its temperature during the storage period fluctuated at a certain rate. The corresponding change in the free energy is given by

$$d\Delta G_a = d\Delta H_a - T_a\,d\Delta S_a \qquad (3)$$

which is related to the values in eqs 1 and 2. We discuss the DSC results as changes in the various terms in eqs 1–3 using the data given in Figures 1–3.

Calculations of the $d\Delta H_a$, $d\Delta S_a$, and $d\Delta G_a$ Coefficients. The coefficients of eqs 1–3 were calculated by a method proposed by Lagasse[75] and used by Fransson and Backstrom[30] and others,[17,21,27–29] i.e., by determining the area between the DSC scans for the annealed and the unannealed samples or, alternatively, from the area under the endothermic peak in the difference scan, as illustrated in Figure 3. The area under the broad peak in the difference curve in, for example, Figures 2 and 3 gives the enthalpy regained on heating. This should be equal to the enthalpy lost on isothermal annealing, and if any dip, like an exothermic feature, in the scan appears prior to the appearance of the broad peak, the area of the dip should be included. This is a well-known observation when the heating rate is slower than the cooling rate and has been reviewed by Hodge[6] for the enthalpy relaxation of the vitrified polymers. The appearance of this dip is an indication of a further enthalpy loss as a result of structural relaxation *during* the heating of the sample. It appears when T_a is such that the characteristic relaxation time of the material is less than that which corresponds to the inverse of the heating rate. The area of the broad peak plus the area of the exothermic dip is equal to the true decrease in ΔH and ΔS during the annealing before scanning began.

$d\Delta H_a$ was determined from the difference in the DSC signal of the annealed and unannealed sample plotted on a linear temperature scale, and $d\Delta S_a$ was determined from the area of the difference curves plotted on a logarithmic temperature scale. The decrease in ΔH and ΔS on annealing was thus determined also at different T_as, and this decrease is plotted against T_a in Figure 4. Since only the difference in the magnitudes of ΔH and ΔS is known, the curves for the annealed state of 2-methyl-3-heptanol vitrified by cooling at 150 and 30 K/min are shown to have the same value at 157 K. This temperature is to be seen as a reference point for all the changes in the magnitudes of ΔH and ΔS at other temperatures in a given ΔH and ΔS curve, as well as between the different curves at a fixed temperature. In Figure 4, the curve labeled 1 is for the sample vitrified by cooling at 150 K/min and curve 2 is for that vitrified by cooling at 30 K/min. Curves 3 and 4 correspond to the state of the samples vitrified by cooling at 30 K and 150 K/min, respectively, and thereafter annealing for 5 min at 157 K. Each set of four curves show the effects of annealing, and altogether they show the net effect of structural relaxation (a) during cooling, (b) during isothermal annealing at 157 K, and (c) during heating to $T > T_g$. The difference between the curves vanishes above 175 K, where metastable, supercooled 2-methyl-3-heptanol reaches its state of thermodynamic equilibrium on heating at 30 K/min. Above 175 K, the sample's properties are time-invariant at 30 K/min heating rate and independent of the thermal history.

Discussion

(a) Effect of Annealing Temperature. The magnitude of the first term on the right-hand side of eqs 1 and 2, or the effect of T_a is indicated by the manner in which the area under the
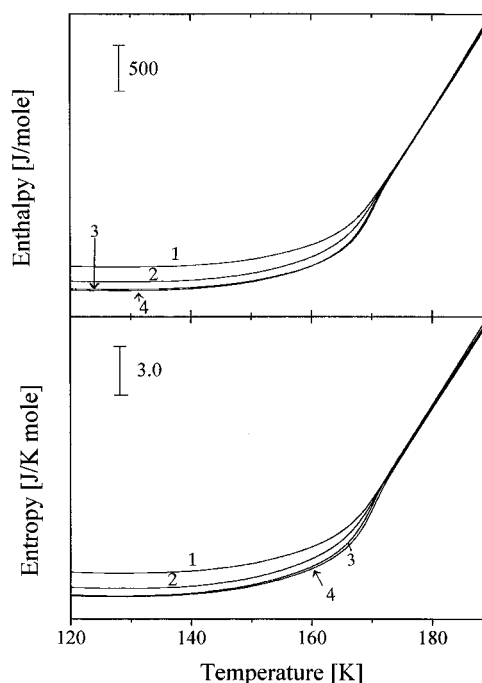

Figure 4. (top) Difference in the enthalpy of 2-methyl-3-heptanol before and after annealing for 5 min at 157 K. Curve 1 is for the state obtained by cooling at 150 K/min and curve 2 for that obtained by cooling at 30 K/min. Curve 3 is for the former state after annealing for 5 min at 157 K and curve 4 for the similarly annealed, latter state. (bottom) the corresponding entropy change is shown. The data were taken from the corresponding curves in Figure 1.

peaks seen in Figures 1 and 2 changes with T_a. When the vitrified samples are annealed at selected T_as for a fixed period of 5 min, $d\Delta H$ and $d\Delta S$ reach a maximum value with increase in T_a, as seen in Figure 6, which is consistent with the earlier observations on polymers[76,77] This value is more for the sample vitrified by cooling at 150 K/min than for the sample vitrified by cooling at 30 K/min, as anticipated, because the kinetically frozen-in ΔH and ΔS are more in the former case than in the latter. The ratio of the values is 1.64 ± 0.02 for both H and S.

In a plot of $d\Delta H$ and $d\Delta S$ against T_a, as seen in Figure 6, a peak appears, because for low T_as, the characteristic relaxation time, τ, is exceedingly long so that the decrease in ΔH and ΔS is too small to be measurable. As T_a is increased, τ decreases rapidly such that at each T_a there is a progressive decrease in ΔH and ΔS until the point of inflection in the sigmoid-shape part on the left-hand side of the peak in Figure 6 is reached. At still higher T_a, $\Delta H_a = [\Delta H(t_a=0) - \Delta H(t_a\rightarrow\infty)]$ and $\Delta S_a = [\Delta S(t_a=0) - \Delta S(t_a\rightarrow\infty)]$, where 0 and ∞ in parentheses refer to t_a, themselves decrease and become zero as T_g is approached. Thus, the shape of the plot in Figure 6 is determined by two processes: (i) a kinetically limiting process that increases the spontaneous H and S loss as T_a is increased and (ii) a thermodynamically limiting process that decreases ΔH_a and ΔS_a as T_a is increased. The peaks in $d\Delta H_a$ and $d\Delta S_a$ appear at a T_a when effect (ii) begins to control the thermal consequences of the annealing process.

As for hydrated DNA,[29] we analyze the data in terms of the equations

$$\partial\Delta H_a(t_a,T_a) = \Delta H_a(T_a)\left[1 - \exp\left\{-\left(\frac{t_a}{\tau(T_a)}\right)^{\beta}\right\}\right] \qquad (4)$$

$$\partial\Delta S_a(t_a,T_a) = \Delta S_a(T_a)\left[1 - \exp\left\{-\left(\frac{t_a}{\tau(T_a)}\right)^{\beta}\right\}\right] \qquad (5)$$
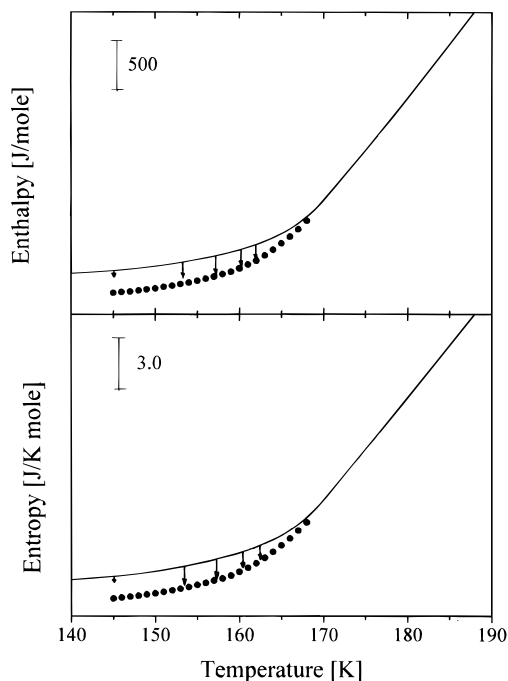
Figure 5. Enthalpy and entropy of 2-methyl-3-heptanol is plotted against the temperature. Also plotted is the loss of enthalpy and entropy that occurred on annealing for 5 min at different temperatures. Length of the arrows gives the magnitude of this loss. The dashed line is the extrapolated value of the enthalpy and entropy at formally infinite time of annealing, i.e., when the equilibrium metastable state has been reached. The sample was cooled at 150 K/min. The data are taken from Figures 1 and 2, where details are given.
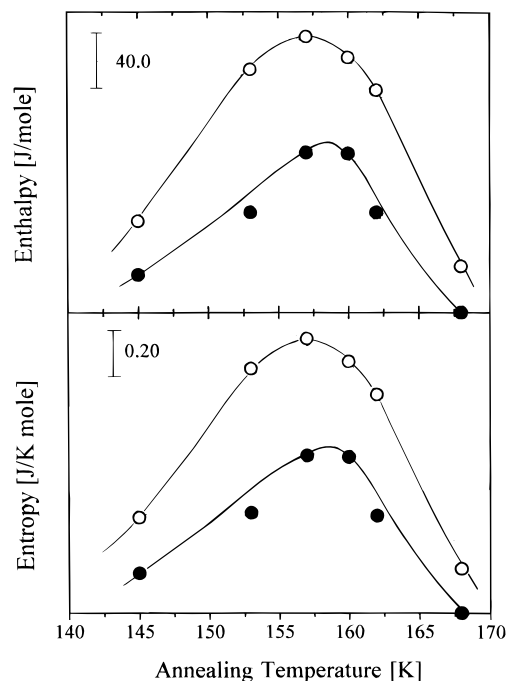

Figure 6. Enthalpy and entropy lost on structural relaxation of 2-methyl-3-heptanol annealed for 5 min at different temperatures is plotted against the annealing temperature. The two curves in each section are for the states obtained after cooling at 150 K/min for (i) and 30 K/min for (ii). The data are taken from the curves in Figures 1 and 2.

where $\tau = \tau_0 \exp(E^*/RT_a)$, τ_0 being the preexponential factor, E^* the activation energy, and R the gas constant. (Note that the use of the Arrhenius equation for τ here implies that its value does not increase with t_a, an aspect confirmed in section b.) Conditions for which $d\Delta H_a(t_a,T_a)$ and $d\Delta S_a(t_a,T_a)$ reach their
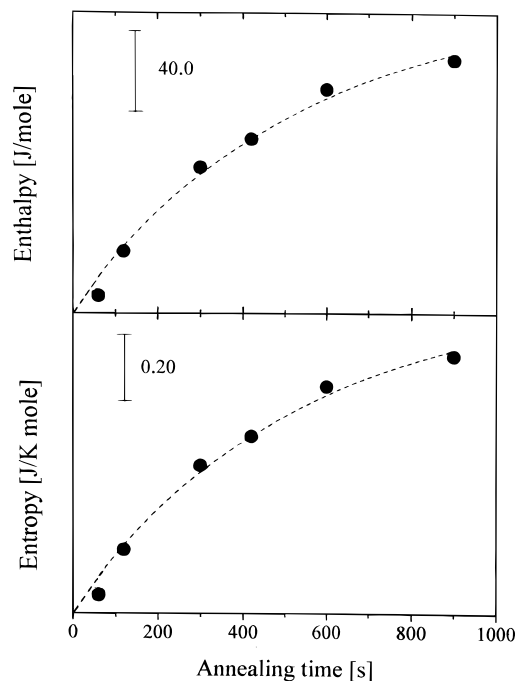
Figure 7. Enthalpy and entropy lost on structural relaxation of 2-methyl-3-heptanol annealed at 145 K is plotted against the annealing time. The curves in each section are for the states obtained after cooling at 150 K/min.

peak values are given by

$$-\frac{\partial \ln \Delta H_a(T_a)}{\partial T_a} = \frac{\beta t_a^{\beta} E^*}{\tau^{\beta} R T_{peak}^2} \tag{6}$$

$$-\frac{\partial \ln \Delta S_a(T_a)}{\partial T_a} = \frac{\beta t_a^{\beta} E^*}{\tau^{\beta} R T_{peak}^2} \tag{7}$$

By combining eqs 4 and 6 and eqs 5 and 7

$$T_{peak} = \left(\frac{\beta t_a^{\beta} E^*}{-\tau^{\beta} R[\partial \ln \Delta H_a(T_a)/\partial T_a]}\right)^{1/2} \tag{8}$$

$$T_{peak} = \left(\frac{\beta t_a^{\beta} E^*}{-\tau^{\beta} R[\partial \ln \Delta S_a(T_a)/\partial T_a]}\right)^{1/2} \tag{9}$$

for the temperature of the peak for both the enthalpy and entropy loss.

The enthalpy and entropy loss data were then analyzed in terms of eqs 4–9 by using the extrapolated values $\Delta H_a(T_a)$ and $\Delta S_a(T_a)$ for a fixed annealing temperature and different t_as from Figures 3 and 7. This analysis gave $E^* = 37.7$ kJ/mol and $\beta = 0.93$ for the enthalpy and entropy loss of the samples vitrified by cooling at both 150 and 30 K/min, as was expected, but the τ_0 values differed. For the former state, $\tau_0 = 21$ ps, and for the latter, $\tau_0 = 37.8$ ps. The curves calculated from these parameters are also shown in Figure 7. The agreement between the calculations and the data seems to indicate that β for 2-methyl-3-heptanol is relatively independent of t_a and T_a and that its τ varies in an Arrhenius manner. For comparison, the distribution of dielectric relaxation times is much broader,[43−46] with β less than 0.5, even at a much higher temperature of 216 K.

(b) Effects of Annealing Time. The spontaneous decrease in ΔH and ΔS determined from the areas of the broad peaks in

Figure 3 is plotted against the annealing time in Figure 7. The data may be described by eqs 4 and 5 for fixed T_a, as seen from the plots in Figure 7, when both τ and β are assumed to remain constant with increasing t_a. The parameters are $\Delta H_a = 164$ J/mol and $\Delta S_a = 0.99$ J/(mol K), $\tau = 558$ s, and $\beta = 0.93$ for the sample vitrified by cooling at 150 K/min and annealed at 145 K. The corresponding values for τ and β for the sample vitrified by 30 K/min could not be determined because of the poor accuracy of the data, but the other quantities are $\Delta H_a = 146$ J/mol and $\Delta S_a = 0.86$ J/(mol K). The lower values for the 30 K/min cooling rate are an indication of the decrease in fictive temperature on the frozen-in enthalpy and entropy, as is also evident in Figure 4. Recently, O'Reilly and Hodge[78] have observed that for polymers β increases toward unity when the sample is DSC scanned at a slower rate, i.e, when enthalpy relaxation occurs during the course of heating or that the fictive temperature, T_f, defined as the temperature at which the state of a system is kinetically stable and is in a thermodynamic equilibrium,[56,57] is lower. Alternatively stated, β will decrease if T_f remains high, contrary to that observed here where β is high when T_f is high.

(c) Characteristics of Structural Relaxation. The high value for β, of 0.93 ± 0.02, and the annealing time-independent, Arrhenius behavior of the τ for 2-methyl-3-heptanol are certainly unusual among liquids, particularly when the β that fits the DSC scan is only 0.45.[33] It is worth noting that annealing experiments on hydrated DNA[29] have yielded $\beta = 0.6 \pm 0.1$ and an Arrhenius dependence of τ, even when the DSC scan for hydrated DNA was too broad to fit such a high value of β, by the usual method of analysis.[5,6,18,22] These observations also differ from the generally found, annealing-time-dependent τ in the DSC experiments[5,6,18] for organic polymers and molecular glasses, where τ increases with t_a, as the fictive temperature, T_f, decreases with t_a, according to the Narayanaswamy equation[57]

$$\tau = A \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right] \quad (10)$$

where Δh^* is the activation energy, A is a parameter equal to τ when both T and T_f are formally infinity, and $x < 1$ is an empirical parameter referred to as the nonlinearity parameter. For $x = 1$, τ is independent of T_f or t_a. This means that for 2-methyl-3-heptanol and for the earlier studies of hydrates DNA[29] $x = 1$.

Alternatively, when the change in T_f with t_a is small, the second term in the brackets in eq 10 may remain nearly constant (at say magnitude C) with t_a, from the beginning of the annealing experiment and

$$\tau = A \exp\left[\frac{x\Delta h^*}{RT} + C\right] \quad (11)$$

This may yield a t_a-independent τ when t_a is short or T_a is low, but when t_a is long, as in the isothermal annealing experiments, T_f must decrease substantially, as would also be the case when T_a is increased and t_a kept constant. There may even be a third situation when T_a and T_f are close to each other, i.e, when the H and S plots against the temperature have a high slope. This will reduce eq 11 to the approximate form

$$\tau = A \exp\left[\frac{\Delta h^*}{RT}\right] \quad (12)$$

This last situation will make the apparant C_p ($=$dH/dT or dT_f/dT) overshoot very high and observable only when the instrument's time constant is relatively small. This situation

corresponds to $x = 1$ and $\beta = 1$, for which the simulated scans for 10 K/min heating rate have shown such large overshoots.[5] But, such a large overshoot is not observed on heating 2-methyl-3-heptanol at 30 K/min, as seen in Figure 1 here, and in the DSC scans elsewhere.[33] Given this inconsistency between the values of x and β that fitted the DSC scan[33] and those observed here, we conclude that eq 10, which is valid for most materials, is not valid for 2-methyl-3-heptanol and for DNA. Our studies of beef proteins,[41] gluten,[42] and other octanols (unpublished) also show this to be the case.

In 1994, Hodge[6] suggested that the enthalpy relaxation time can also be *approximated* by an equation of the type $\tau(t_a) = \tau(t_a=0)t_a^{\mu}$ where μ ($=1 - \beta$) is a shift factor deduced from the mechanical compliance data of polymers and applied to the enthalpy relaxation data. He pointed out to us that since τ as observed here remains constant with t_a, the implication is that μ must be zero or that β should be close to unity, which is indeed observed. Thus, it seems that if this approximation were tenable, a discussion of τ in terms of the nonlinearity parameters and eqs 10–12 will be unnecessary.

The loss of H and S on annealing a glass is interpreted in terms of physical effects, mainly as the loss of configurational contribution plus a negligible loss of vibrational contribution when the sample densifies. The densification on aging or annealing also causes τ to increase, as it does on isothermal compression. Hence, τ increases with increase in t_a or decrease in T_f, which leads to the nonlinearity of the relaxation process parametrized in terms of $x < 1$ in eq 10. If annealing were to cause dilation, as is expected for glassy water,[79] τ may decrease with t_a or (decrease in) T_f, and x will exceed unity. But if annealing had a negligible or no effect on volume, τ will remain constant with changing t_a or T_f, and x will be unity. It is not certain whether the density of 2-methyl-3-heptanol decreases on annealing as the population of bulkier ring dimers relative to the chain dimers and monomers[43,44] increases or whether it remains constant if the density decrease on the formation of ring dimers were partly compensated for by a density increase on structural relaxation of the material as a whole, containing the monomers, dimers, etc., species. The latter occurrence may account for x, but in view of the observation that both β and x for 2-methyl-3-heptanol are close to unity, it seems necessary that a second source of enthalpy and entropy loss be considered.

Because the static dielectric permittivity of 2-methyl-3-heptanol liquid is less than 2.5 near 200 K,[43] Dannhauser had concluded that H-bonded ring dimers, in which the dipole moments of the two monomers involved are canceled by their opposing vectors, are formed in the liquid.[42–44] Cooling shifts the monomer + monomer $\leftrightarrow$ ring dimer and/or chain dimer $\leftrightarrow$ ring dimer equilibrium to predominantly ring dimers in the liquid, and thus its permittivity approaches that of a nonpolar liquid. The reaction quotient $Q = C_{dimer}/[C_{monomer}]^2$ or $Q' = C_{ring\ dimer}/C_{chain\ dimer}$ of the H-bond association reaction increases on cooling.[43,44] Its value ceases to increase on supercooling 2-methyl-3-heptanol through its T_g or that the population of monomers, chain dimers, and ring dimers becomes frozen in at T_g. The population of chain dimers is less in the vitrified state, or Q is less when the cooling rate is high and more when it is low. Hence, its vitrified state is kinetically unstable with respect to two factors: (i) the ultimate reaction equilibria corresponding to the constant K, toward which Q increases spontaneously under isothermal conditions as well as on rate heating, and (ii) the ultimate structure toward which the packing of the various species tends, as for ordinary glasses and polymers. The enthalpy loss is then equal to the sum of the heat released on (i) the ring dimerization reaction and (ii) the structural relaxation

of the vitrified state. Since the chain dimer ↔ ring dimer reaction is a first-order reaction, $\beta = 1$, i.e., the enthalpy and entropy loss increases with the inverse exponential of the reaction time, which is equal to t_a here. The process is expected to follow the Arrhenius equation, independent of t_a, because although the reaction is diffusion controlled it occurs in a medium whose density changes negligibly with the annealing time.

The increase in Q on annealing is given by

$$-RT\Delta \ln Q_a = \Delta G_a = \Delta H_a - T\Delta S_a \qquad (13)$$

where all terms are as defined before. By using $\Delta H_a = 164$ J/mol and $\Delta S_a = 0.99$ J/(mol K) the sample vitrified by 150 K/min cooling and annealed at 145 K, $\Delta G_a = -20.45$ J/mol and $\Delta Q_a = 1.017$. By using $\Delta H_a = 140$ J/mol and $\Delta S_a = 0.86$ J/(mol K) for the sample vitrified by 30 K/min cooling and annealed at 145 K, $\Delta G_a = -15.3$ J/mol and $\Delta Q_a = 1.012$.

It is noteworthy that similar isothermal annealing studies of glycerol by Fransson and Backstrom[30] and of glycerol and propylene glycol by Oguni and co-workers[32] have shown that (a) β changes with t_a, an observation that prevented Douglas[69] from developing the stretched exponential function for relaxation in the glassy state, and (b) β increases with the magnitude of ΔH_a, i.e., it is more for a rapidly vitrified sample than for a slowly vitrified one. We propose that the enthalpy relaxation behavior of glycerol and propylene glycol is not anomalous but is due to the heat evolved as more H-bonds form and densify the network or linear chain structures in their glassy state. In these cases, the density increases on the bond formation, which causes x to be less than one or τ to depend on t_a.

For most chemical reactions in highly viscous polymers or in the glassy state of aqueous, ionic solutions, it is generally assumed that the probability of diffusion of the reacting groups, or molecules, becomes too slow to allow a significant chemical reaction over the annealing time. This is usually the case when the reaction kinetically freezes in at a viscosity much lower (and temperature much higher) than that where the liquid's structure freezes in, both on the same time scale. But studies on polymerization[34-38] of a network forming thermoset polymer have clearly shown that even at a temperature 20 K or more below the calorimetric T_g, chemical reactions occur and predominate the effects of structural relaxation, as observed by dielectric measurements[36-38] and by the increase in the T_g[34,35] of the network polymer itself. Recent studies[80] have shown an increase in the ion-pairs population by ion association in vitrified aqueous solution. For 2-methyl-3-heptanol, the diffusion distance needed to allow one chain dimer to form one ring dimer is expected to be much less than that needed to allow two reacting groups in polymers and dilute solutions. Consequently, the reaction freezing and structural freezing in 2-methyl-3-heptanol are expected to occur at temperatures close to each other, as is also expected for other alcohols and hydrated proteins rich in hydrogen bonds.

(d) Fictive Temperatures and the Reaction and Structure Freezing. On the basis of the above given discussion, the decrease in H and S due to a chemical reaction on isothermal annealing may be seen as analogous, in its kinetic and thermodynamic manifestations, to the decrease in H and S of a glass on its structural relaxation. Therefore, it seems reasonable to extend the concept of fictive temperature to a chemically metastable state, i.e., that the chemical fictive temperature $T_{f,chem}$ is higher when 2-methyl-3-heptanol is vitrified by rapid cooling than when it is vitrified by slow cooling, just as the structural fictive temperature, T_f, of a chemically stable glass is higher when it is vitrified by rapid cooling.[56]
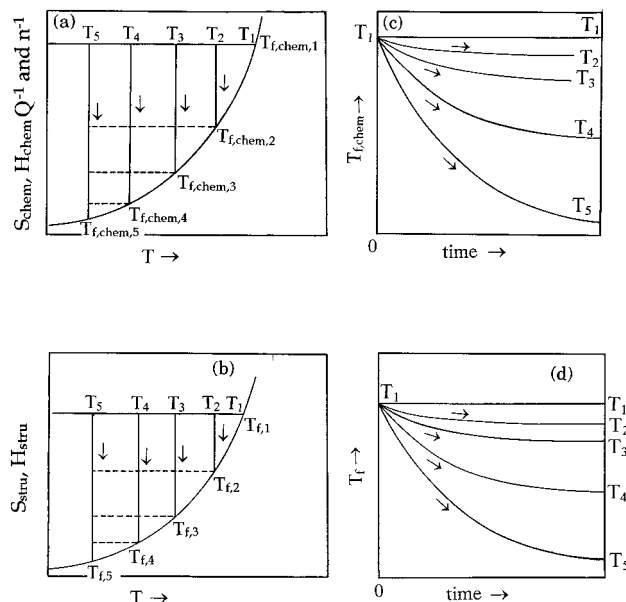

Figure 8. Illustration for the chemically metastable state (frame a), in which the chemical equilibrium constant Q and the number of H-bonds, n, have become frozen in on cooling and for the structurally metastable state (frame b). Both are shown to be approaching the equilibrium state during which H and S decrease, but Q and n increase on annealing the chemically metastable state. The illustration in frame c is for the decrease in the chemical fictive temperature on reaction during annealing and frame d for the decrease in the usual fictive temperature on structural relaxation, as the equilibrium state is approached in both cases.

In the illustration in Figure 8a, the decrease in H and S of a chemically unstable state is shown by dashed lines and of a chemically stable state by full lines. The equilibrium line indicates the variation of H and S when the state has reached its equilibrium at that temperature, both chemical and structural. The equilibrium line for chemical reaction is curved because chemical equilibrium constant varies with the inverse exponential of the reciprocal temperature and H-bond formation is an exothermic process. The equilibrium line for the structural state is curved, because of the requirement that anharmonicity of vibrations will keep the enthalpy of a glass, devoid of a configurational contribution, above that of a crystal as 0 K is approached[71] and that an equilibrium disordered state at 0 K should have an energy different from an equilibrium crystal state.[68] (Note that this requirement alone precludes the extrapolation that produces the Kauzmann situation.) Vertical lines in Figure 8 show irreversible decreases in the H and S with time as the metastable liquid's nonequilibrium state approaches its equilibrium state on the curved line. $T_{f, chem}$ and T_f are the temperatures at which a horizontally extended line starting from any point on the vertical (dashed) line after a time t_a cuts the equilibrium (curved) line. Thus the plots in Figure 8 illustrate the irreversible changes on dimerization in one case and structural relaxation in the other which decrease the fictive temperature in both cases, from the initial $T_{f,chem,1}$ at $Q(t_a=0)$ to $T_{f,chem,5}$ at $Q(t_a \rightarrow \infty)$ or from $T_{f,1}$ at $\Delta H(t_a=0)$ to $T_{f,5}$ at $\Delta H(t_a \rightarrow \infty)$.

The plots in Figure 8b illustrate how $T_{f,chem}$ decreases with increase in Q or the dimers population, while approaching isothermally the chemical equilibrium state, and those in (d) illustrate the well-known behavior on the annealing of a glass, i.e., the rate at which its T_f decreases with t_a is proportional to the T_f's deviation from the actual temperature, and the proportionality factor depends upon both T_f and T.[18,56,57] This time may be nanoseconds for a liquid at high temperatures and many years for a glass at low temperatures.

Vitrified 2-Methyl-3-heptanol

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The increase in the number of H-bonds on annealing is related to the enthalpy and entropy of the dimerization reaction by $\Delta n_{H-bond} = d\Delta H(t_a)]/\Delta H°$ or $d\Delta S(t_a)]/\Delta S°$, where $\Delta H°$ and $\Delta S°$ are the enthalpy ($=36$ kJ/mol) and entropy ($=113.6$ J/(mol K) at 298 K) of the monomers $\leftrightarrow$ ring dimer reaction. Thus, the scale of 500 J/mol in Figure 4A also corresponds to 28 mmol of H-bonds formed, and the scale of 3 J/mol in Figure 4B corresponds to 53 mmol of H-bonds for the monomers $\leftrightarrow$ ring dimer equilibrium and the same amounts if $\Delta H°$ and $\Delta S°$ for the linear dimer $\leftrightarrow$ ring dimer equilibrium were half of the above given values. Hence, the increase in the number of H-bonds on annealing, $\Delta n_{H-bond} = 9$ mmol from $\Delta H_a = 164$ J/mol in Figure 7 and 17.4 mmol from $\Delta S_a = 0.99$ J/mol, from the above given values of $\Delta H°$ and $\Delta S°$ for both equilibria. The inconsistency between the two values of Δn_{H-bond} is likely to be due to our use of $\Delta S°$ value at 298 K instead of the value at 157 K, as earlier studies have conclusively shown that $\Delta S°$ increases on decreasing the temperature because the plots of ln Q ($= -((\Delta H° - T\Delta S°)/RT))$ against $1/T$ are curved toward the axis at low temperatures. Thus, it seems that the above-given disagreement between the Δn_{H-bond} values, although significant, does not invalidate our conclusions.

It should be stressed that part of the annealing effect may well be a consequence of structural relaxation of the overall, chemically equilibrated state at any instant characterized by a fixed Q or the composition during the annealing. Nevertheless, the equilibrium curve for structural relaxation itself will change when Q changes spontaneously, so that the recovery of H and S on heating will contain contributions from both (a) the attainment of a chemical equilibrium at a higher temperature and (b) the recovery of the equilibrium structure corresponding to the composition, as determined by the value of Q at each temperature. The net effect is that the kinetics of the structural relaxation changes not only because T_f decreases but also because the equilibrium curve that defines T_f itself changes. The effects observed here seem predominantly due to an increase in Δn_{H-bond}, or Q, on isothermal annealing and thereafter on its decrease at higher temperatures during the rate heating when the rate of H-bond breaking and re-forming becomes comparable to the rate of change of temperature.

One more aspect of the H-bond equilibrium needs be mentioned here. Because a chemical reaction is represented by a two-site model according to which the population of two energetically different states vary with temperature—this is also the case with the thermodynamics of point defects equilibrium in crystals known since 1921[81]—part of the decrease in C_p on supercooling the liquid should be attributed to the kinetic freezing in of the chemical equilibrium, particularly near T_g. Its magnitude is given by[81]

$$\Delta C_p = (\Delta H°/RT^2)[n \ln n - (1 - n) \ln(1 - n)] \quad (14)$$

where n, the fraction of dimers in this case, is given by

$$n = (1 + \exp[(\Delta H° - T\Delta S°)/RT])^{-1} \quad (15)$$

R and $\Delta H°$ ($=36$ kJ/(mol K)[43,44]) and $\Delta S°$ ($=113.6$ J/(mol K)) are as defined before. This gives $n = 9.28 \times 10^{-8}$ and ΔC_p of 0.197 J/(mol K) at 165 K (the midpoint of the T_g endotherm[33]) and an unreasonably high maximum in ΔC_p of 396.3 J/(mol K) at 310.4 K. The conditions at which the latter two features appear are given by eq 15, when $\Delta H°$ and $\Delta S°$ remain constant with T, but when they vary with T, these conditions are determined by both eqs 14 and 15. If $\Delta S°$ decreases with increase in T, the maximum shifts towards higher temperatures and its height increases because a decrease of $\Delta S°$ decreases n

for a given T. As $\Delta S°$ has been found to increase with decrease in temperature,[43-46] it seems appropriate to calculate the value of $\Delta S°$ that would yield ΔH_a of 164 J/mol at 145 K. For monomer $\leftrightarrow$ ring dimer equilibrium, this value is 203.49 J/(mol K) at 145 K ($\Delta H°$ remaining at 36 kJ/mol) and $n = 0.0091$ ($\Delta n_{H-bond} = 18.2$ mmol). For linear dimer $\leftrightarrow$ ring dimer equilibrium, $\Delta S°$ is 85.15 J/(mol K) at 145 K ($\Delta H°$ remaining at 18 kJ/mol) and $n = 0.0182$ ($\Delta n_{H-bond} = 36.4$ mmol). Assuming that $\Delta H°$ and $\Delta S°$ remain constant on heating from 145 to 165 K, ΔC_p is 396 J/(mol K) in the former case and 72.1 J/(mol K) in the latter case. The expected decrease in $\Delta S°$ on heating will change ΔC_p according to eqs 14 and 15. So, even without further analysis of these conditions, it is apparent that reasonable values of ΔC_p at T_g, ΔH_a, and ΔS_a may be obtained for a fixed value of $\Delta H°$, and reasonable, and temperature-variant, values of $\Delta S°$. A detailed discussion of this effect and of the related equations for the physical aging process are beyond the scope of this article and will be discussed in the context of another study on alcohols and proteins.

Conclusions

The loss of enthalpy and entropy on annealing an alcohol is due to two effects: (i) increase in the equilibrium constant involving H-bonded species as reactants and products and (ii) structural relaxation, i.e., an approach of the structure as a whole, containing the various H-bonded species, toward the equilibrium state. The effects of a chemical change during the annealing of a vitrified solid have been difficult to study because the enthalpy and entropy lost during such a change are not regained on heating the sample, but it is practical to do such studies when concentration of the chemical species is determined by a temperature-dependent equilibrium. H-bond association, isomerization (boat–chair configurations), or ion association equilibrium in a liquid may be kinetically frozen in by its vitrification, and these may constitute freezing in of a chemical reaction, for which a description in terms of a chemical fictive temperature may be useful. It is conceivable that some of the enthalpy and entropy loss on annealing of the vitrified ionic materials, H-bonded polymers, and hydrated biopolymers is due to the increase in the chemical quotient toward the equilibrium constant. A discussion of this effect on the thermodynamics of biopolymers will be published separately.

References and Notes

(1) Kovacs, A. J. *Fortschr. Hochpolym.-Forsch.* **1963**, *3*, 394.
(2) Kovacs, A. J.; Stratton, R. A.; Ferry, J. D. *J. Phys. Chem.* **1963**, *67*, 152.
(3) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M. In *Structure of Non-Crystalline Materials*; Gaskell, P. H., Ed.; Taylor & Francis: London, 1977; p 153.
(4) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, A. R. *J. Polym. Sci., Polym. Phys.* **1979**, *17*, 1097.
(5) Berens, A. R.; Hodge, I. M. *Macromolecules* **1982**, *15*, 756, 562.
(6) Hodge, I. M. In *Relaxation in Complex Systems*; Ngai, K. L., Wright, G. B., Eds.; Office of Naval Research: Washington, DC, 1983; p 65; *J. Non-Cryst. Solids* **1994**, *169*, 211; *Science* **1995**, *267*, 1945.
(7) O'Reilly, J. M. In *Structure and Properties of Amorphous Polymers*; Walton, A. G., Ed.; Elsevier: Amsterdam, 1980; p 165.
(8) Prest, W. M.; Roberts, F. J., Jr. *Ann. N. Y. Acad. Sci.* **1981**, *67*, 371.

(9) Sasabe, H.; Moynihan, C. T. *J. Polym. Sci.* **1978**, *16*, 1447.

(10) Adachi, K.; Kotaka, K. *Polym. J. (Tokyo)* **1982**, 14, 959.

(11) Plazek, D. J.; Berry, G. C. In *Glass Science & Technology*; Uhlmann, R., Kreidl, N. J., Eds.; Academic Press: New York, 1986; Vol. 7, Chapter 7, p 363.

(12) McKenna, G. B. In *Comprehensive Polymer Science*; Booth, C., Price C., Eds.; Pergamon: Oxford, 1989; Vol. 2, Chapter 10, p 311.

(13) Perez, J. *Physique et Mecanique des Polymeres Amorphes*; Lavoisier, Tec & Doc.: Paris, 1992.

(14) O'Reilly, J. M. In *Critical Reviews in Solid State and Materials Science*; CRC: Boca Raton, FL, 1987; Vol. 13, p 259.

(15) Wang, H. S.; Wang, T. T. *J. Appl. Phys.* **1981**, *52*, 5898.

(16) Roe, R.-J.; Curro, J. J. *Macromolecules* **1983**, 16, 428.

(17) Sartor, G.; Mayer E.; Johari, G. P. *J. Polym. Sci., Polym. Phys. B* **1994**, *32*, 683.

(18) Moynihan, C. T.; Macedo, P. B.; Montrose, C. J.; Gupta, P. K.; Debolt, M. A.; Dill, J. F.; Dom, B. E.; Drake, P. W.; Easteal, A. J.; Eltermann, P. B.; Moeller, R. A.; Sasabe, H.; Wilder, J. A. *Ann. N.Y. Acad. Sci.* **1976**, *279*, 15.

(19) Macedo, P. B.; Napolitano, A. *J. Res. A. NBS* **1967**, *71A*, 231.

(20) Boesch, L.; Napolitano, A.; Macedo, P. B. *J. Am. Ceram. Soc.* **1970**, *53*, 148.

(21) Hofer, K.; Perez, J.; Johari, G. P. *Philos. Mag. Lett.* **1991**, *64*, 37.

(22) Pascheto, W.; Parthun, M. G.; Hallbrucker, A.; Johari, G. P. *J. Non-Cryst. Solids* **1994**, *171*, 182.

(23) Hanaya, M.; Nakayama, M.; Oguni, M. *J. Non-Cryst. Solids* **1994**, *172*, 608.

(24) Chen, H. S. *J. Appl. Phys.* **1981**, *52*, 1868; *J. Non-Cryst. Solids* **1981**, *46*, 289.

(25) Greer, A. L.; Spaepen, F. *Ann. N.Y. Acad. Sci.* **1981**, *371*, 218.

(26) Egami, T. *Ann. N.Y. Acad. Sci.* **1981**, *371*, 38.

(27) Sartor, G.; Mayer, E.; Johari, G. P. *Biophys. J.* **1994**, *66*, 249.

(28) Rudisser, S.; Hallbrucker, A.; Mayer, E. *J. Phys. Chem.* **1996**, *100*, 458.

(29) Rudisser, S.; Hallbrucker, A.; Mayer, E.; Johari, G. P. *J. Phys. Chem. B* **1997**, *101*, 266.

(30) Fransson, A.; Backstrom, G. *Int. J. Thermophys.* **1987**, *8*, 352.

(31) Takeda, K.; Yamamuro, O.; Suga, H. *J. Phys. Chem. Solids* **1991**, *52*, 607.

(32) Fujimore, H.; Adachi, Y.; Oguni, M. *Phys. Rev. B* **1992**, *46*, 14501.

(33) Sartor, G.; Hofer, K.; Johari, G. P. *J. Phys. Chem.* **1996**, *100*, 6801.

(34) Choi, I.; Plazek, D. J. *J. Polym. Sci., Polym. Phys.* **1986**, *24*, 1303.

(35) Plazek, D. J.; Frund, Z. A., Jr. *J. Polym. Sci., Polym. Phys.* **1990**, *28*, 431.

(36) Mangion, M. B. M.; Johari, G. P. *J. Polym. Sci., Polym. Phys.* **1990**, *28*, 71; **1991**, *29*, 437.

(37) Sidebottom, D.; Johari, G. P. *Chem. Phys.* **1990**, *147*, 205. Hofer, K.; Johari, G. P. *Macromolecules* **1991**, *24*, 4978.

(38) Mangion, M. B. M.; Wang, M.; Johari, G. P. *J. Polym. Sci., Polym. Phys.* **1992**, *30*, 445.

(39) Fishman, A. I.; Stolov, A. A.; Remizov, A. B. *Spectrochim. Acta* **1993**, *49A*, 1435.

(40) Green, J. L.; Fan, J.; Angell, C. A. *J. Phys. Chem.* **1994**, *98*, 13780.

(41) Sartor, G.; Johari, G. P. *J. Phys. Chem.* **1996**, *100*, 10450.

(42) Johari, G. P.; Sartor, G. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4521.

(43) Dannahauser, W. *J. Chem. Phys.* **1968**, *48*, 1911, 1918.

(44) Johari, G. P.; Dannhauser, W. *J. Phys. Chem.* **1968**, *72*, 3273.

(45) Johari, G. P.; Dannhauser, W. *J. Chem. Phys.* **1968**, *48*, 5114, 3407; **1969**, *50*, 1862.

(46) Hofer, K.; Johari, G. P. *J. Chem. Phys.* **1991**, *95*, 2020.

(47) Vij, J. K.; Scaife, W. G.; Calderwood, J. G. *J. Phys. D* **1978**, *11*, 545; **1981**, *14*, 373.

(48) Johari, G. P.; Goldstein, M. *J. Chem. Phys.* **1971**, *55*, 4245.

(49) Sartor, G.; Hallbrucker, A.; Mayer, E. *Biophys. J.* **1995**, *67*, 2679.

(50) Sartor, G.; Mayer, E. *Biophys. J.* **1995**, *67*, 1724.

(51) Cavaille, J.-Y.; Etienne, S.; Perez, J.; Monnerie, L.; Johari, G. P. *Polymer* **1986**, *27*, 682.

(52) Muzeau, E.; Cavaille, J.-Y.; Vassoile, R.; Perez, J.; Johari, G. P. *Macromolecules* **1992**, *25*, 5108.

(53) Johari, G. P. *Ann. N.Y. Acad. Sci.* **1976**, *279*, 117; *J. Chem. Phys.* **1982**, *77*, 4619.

(54) Pathmanathan, K.; Johari, G. P.; Faivre, J.-P.; Monnerie, L. *J. Polym. Sci., Polym. Phys.* **1986**, *24*, 1589.

(55) Winter-Klein, A. These, Paris, 8 Juillet, 1938; *J. Am. Ceram. Soc.* **1943**, *26*, 189.

(56) Tool, A. Q. *J. Am. Ceram. Soc.* **1946**, *29*, 240.

(57) Narayanaswamy, O. S. *J. Am. Ceram. Soc.* **1971**, *54*, 691.

(58) Scherer, G. W. *J. Am. Ceram. Soc.* **1984**, *67*, 504; *Relaxations in Glass and Composites*; Wiley: New York, 1986.

(59) Hodge, I. M. *Macromolecules* **1987**, *20*, 2897.

(60) Agarwal, A. *J. Polym. Sci., Polym. Phys.* **1989**, *27*, 1449.

(61) Cumbrera, F. L.; Munoz, A. *Thermochim. Acta* **1992**, *196*, 137.

(62) Perez, J. *Polymer* **1988**, *29*, 483.

(63) Chow, T. S. *Macromolecules* **1984**, *17*, 2336; *Adv. Polym. Sci.* **1992**, *103*, 149.

(64) Chow, T. S. *Macromolecules* **1992**, *25*, 440.

(65) Rekhson, S. M. *J. Non-Cryst. Solids* **1986**, *94*, 68.

(66) Rotiashvilli, V. G.; Nekhoda, A. R.; Irzhak, V. I.; Rozenberg, B. A. *J. Polym. Sci., Polym. Phys.* **1984**, *22*, 1041.

(67) Kauzmann, W. *Chem. Rev.* **1948**, *43*, 219.

(68) Johari, G. P.; Perez, J. *Mol. Phys.* **1994**, *83*, 235. The plus sign between the two terms in eq 2 should read minus.

(69) Douglas, R. W. In *Proceedings of the 4th International Congress on Rheology, Providence, RI*; Lee, E. H., Ed.; Wiley: New York, 1965; pp 3−27; *Br. J. Appl. Phys.* **1966**, *17*, 435; see also: Majumdar, C. K. *Solid State Commun.* **1971**, *9*, 1087.

(70) Simon, F. E. *Ergbn. Exact. Naturwiss.* **1930**, *9*, 244.

(71) Johari, G. P. *Philos. Mag.* **1981**, *41*, 41.

(72) Gutzow, I. *Wiss. Ztschr. Friedrich-Schiller-University Jena, Math., Nat. R.* **1979**, *28* H2/3, 243; In *Disordered Systems and New Materials*, Conf. Proc. Varna, Bulgaria; Borissov, M., Kirov, N., Vavrek, A., Eds.; World Scientific: Singapore, 1989, p 11.

(73) Stillinger, F. H. *J. Chem. Phys.* **1988**, *88*, 7818.

(74) Wittman, H.-P. *J. Chem. Phys.* **1991**, *95*, 8449.

(75) Lagasse, R. R. *J. Polym. Sci., Polym. Phys.* **1982**, *20*, 279.

(76) Illers, K. H. *J. Makromol. Chem.* **1969**, *127*, 1.

(77) Petrie, S. E. B. *J. Polym. Sci. A2* **1972**, *10*, 1255.

(78) O'Reilly, J. M.; Hodge, I. M. *J. Non-Cryst. Solids* **1991**, *131*, 451.

(79) Johari, G. P.; Fleissner, G.; Hallbrucker, A.; Mayer, E. *J. Phys. Chem.* **1994**, *98*, 4719.

(80) Fleissner, G.; Hallbrucker, A.; Mayer, E. *J. Phys. Chem.* **1995**, *99*, 8401.

(81) Schottky, W. *Phys. Z.* **1921**, *22*, 1; **1922**, *23*, 9.