Corrigendum

Corrigendum to "Relaxational transitions and ergodicity breaking within the fluid state: the sugars fructose and galactose" [Thermochimica Acta 266 (1995) 9–30][1,2]

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The author wishes to make the following amendments to the above paper.

P.9, 3rd line:

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P.9, Footnote:

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P.9, 1. Introduction, 2nd sentence:

The viscosity, and the related relaxation processes such as dielectric relaxation and spin–lattice relaxation, exhibit monotonic variations [1] which are often [2] well described by the Vogel–Fulcher law in which the viscosity divergence temperature too can be predicted from purely thermodynamic data.

P.10, 1st full paragraph, 1st sentence:

Because the ergodicity–breaking in the latter case involves primarily the conformations of individual molecules, the system remains fluid at lower temperatures.

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[1] SSDI of original article: 0040–6031 (95)02551–0
[2] Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday

P. 10, Last sentence, 1st full paragraph:

The glass-like ergodicity breaking/restoring transitions we observe during cooling/heating in the present liquids could be called, on this basis, "superstructuring transitions" but in this paper we choose instead to simply designate them as EB transitions" (EB for ergodicity–breaking). They are closely related to, but much more prominent than, the interrupted Schottky anomaly observed first by Prof. Suga in his 1978 study of the plastic crystal system C12FC–CF2Cl. [5]

P. 10, last sentence:

While in linear chain representation, at least, they appear little different from the six-carbon molecule sorbitol which has been well studied and found to be more or less normal in its behaviour, except for a very broad dielectric relaxation spectrum, [2] their behavior is quite complex, as we will describe below.

P. 11, 5th full paragraph, 1st sentence:

Finally, in this introduction we stress the complications that may arise from the decomposition (finally caramelization) of sugar melts at "high" temperature, e.g., near their melting temperatures. The effects of dehydration and other decomposition can interfere.

P. 11, 6th full paragraph, 2nd sentence:

These decompositions consist of various dehydrations and fragmentations (see Ref. [11]).

P. 12, 2nd full paragraph, 2nd sentence:

The accuracy of the instrument was established by reproduction of the literature values for Al_2O_3 [14] and o-terphenyl [15] to within $2 \sim 3.5\%$ over temperature ranges 160 and 1000 K respectively.

P. 12, 5th full paragraph, 1st sentence:

Viscosities were measured with a Brookfield digital viscometer over the range 0.019 to 103 P.as.

P. 13, 1st full paragraph, 1st sentence:

^{13}C NMR spectra were obtained using a Gemini-300 NMR spectrometer (75.462 MHZ, 0.8 second acquisition time, 1200 repetitions) with either acetone-d_6 as the

internal standard and DMSO as the solvent or D_2O as the solvent and $DCCl_3$ as external standard.

P. 13, 2nd full paragraph, 2nd sentence:

However, these ^{13}C NMR spectra are not suitable for determining the relative conformer concentrations in crystals and melts because, as will be seen, there is little difference in ^{13}C NMR spectra between the solutions made from crystal starting material and the solutions made up from fresh melt, which indicates very fast tautomerizations in D_2O solution.

P. 15, Table 1, footnote a:

[a]Relaxed melt: the fresh melt was annealed at 372 K for 25 h.

P. 15, 2nd full paragraph, 1st sentence:

The spectra of D_2O solutions of the crystal, the fresh melt and the melt annealed at 372 K for 2.5 hours (i.e. relaxed melt) have identical peaks indicating that decomposition is negligible in these melts.

P. 17, 1st full paragraph, 3rd sentence:

Also T_{T_1} decreases as much as ~ 15 K and is smeared out so that T1 is no longer observable.

P. 17, 1st full paragraph, 4th sentence:

It is also noted that when the annealing temperature is below the glass transition temperature, e.g. at 273.2 K (TA9), the "overshoot" in the glass transition Cp increased in the normal manner while the higher temperature transitions remain unaffected.

P. 19, 1st full paragraph, 1st sentence:

(d)   There is a third small transition $T_3 (\Delta C_p \approx 7$ J $mol^{-1} K^{-1})$ at ~ 394 K in the melts which had experienced 5 separate heatings over ~ 140 K.

P. 19, 1st full paragraph, 2nd sentence:

This is seen much more clearly in more slowly scanned samples as Fig. 7, below.

P. 20, 1st full paragraph, 1st sentence:

Fig. 9. shows the heat capacities of α-D-galactose in the following states: (i) the crystal, (ii) the fresh melt and (iii) the melts with the thermal histories specified in the figure legend.

P. 22, 2nd full paragraph, 3rd sentence:

The initial viscosities ($\eta(0)$) marked on the graph were obtained by the extrapolation of the low temperature viscosities shown in Fig. 11.

P. 24, 1st full paragraph, 4th sentence:

The solution exhibits the same annealing effects on T_g and on the EBT_2 transition temperature as seen in the anhydrous systems.

P. 25, 1st full paragraph, 4th sentence:

We now discuss the sources of complexity in molten fructose in the order: decomposition, initial equilibrium, and temperature dependent equilibrium.

P. 25, *4.1 Effects of decomposition*, 2nd sentence:

In this respect it is fortunate that, according to the ^{13}C NMR, shown in Fig. 2, decomposition can be almost completely avoided if temperatures above that of the initial melting point (278 K) are avoided for times greater than a few minutes, since even heating at 374 K for six hours showed minimal development of new NMR peaks.

P. 25, *4.2 Tautomerization and the initial melt equilibration process*, 2nd sentence:

While this latter is the lowest energy form, differing from the next lowest energy form, β-furanose, by ≈ 11.2 kJ mol^{-1}, [16] it only constitutes 70% of the molecules in a D_2O solution at 303 K, or 60% of a fresh fructose melt at 378 K.

P. 26, 1st paragraph, 2nd sentence:

The enthalpy absorbed in the equilibrium process at 373.8 K seen in Fig. 10 amounts to 13.9 Kj mol^{-1}, and corresponds to the part of the total process that was left incomplete after fusion at 378 K, and temperature equilibrium at 373.8 K.

P. 26, *4.3 Tautomerizations and heat capacity anomalies*, 3rd sentence:

Such equilibria should give rise to distinct two-state heat capacity contributions to the total observed quantity.

P. 26, *4.3. Tautomerizations and heat capacity anomalies*, 4th sentence:

These have been extensively discussed in connection with interpretation of the glass transition itself [34–36], for which they prove instructive, though usually unsatisfactory [36].

If we have two distinct structural states in equilibrium

$$A \Leftrightarrow B, \hspace{6cm} \text{2(a)}$$
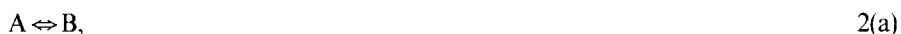
(with changes in thermodynamic quantities, ΔH, ΔV, ΔS), then

P. 27, 1st line:

where [36]

P. 27, 1st sentence through to and inclusive of 5th sentence:

When ΔS is zero this heat capacity increment is small at all temperatures, and maximizes at 3.76 J mol^{-1} K^{-1} (Schottky anomaly) at a temperature which is determined by ΔH. An example in the heat capacity literature of glass-forming systems is that of cis-trans isomerism in the molecule CFC12-CFC12 in its plastic crystal phase reported by Prof. Suga and coworkers [5]. This occurs at 130 K with a ΔC_p of 1.1 J (mol K^{-1}) which is even less than the 3.76 J mol^{-1} K^{-1} expected for the theoretical case in which ΔS is zero. The anomaly observed by Suga and coworkers shows a time dependent effect like our cases demonstrating that the lower part, including the maximum, of the Schottky heat capacity was hidden by kinetic arrest.

While the case studied by Prof. Suga shows a smaller excess heat capacity than expected, much larger values than the ideal Schottky anomaly value are possible. For instance, if ΔS in Eq. 2(e) is large, the whole process is compressed in temperature, and the heat capacity at the maximum which appears then at a lower temperature, can be greatly increased. [36] An extreme case of the latter effect is provided by the denaturation of proteins where the process is so compressed that it appears like a first order transition. In such a case, the range of temperature is small enough that no kinetic arrest occurs at the lower end. We see the EB anomalies, T_2, in fructose and galactose as intermediate cases of this two-state equilibration in which the lower part of the process becomes kinetically arrested.

When there are several possible two-state exchanges there may the same number of anomalies to be seen (not by their contributions to all the excess C_p, which are board,

but by their different couplings to the viscosity). Their strengths will depend not only on the ΔS values, but also on the mole fractions of tautomer free to participate. Of the possible equilibria mentioned above only those involving pyranose⇌furanose conversions have DH values sufficient to appear in the temperature range of the present anomalies, and the entropy change would have to be very large to account for the magnitude of the C_p jump.

P. 27, 1st full paragraph, 2nd sentence:

For ΔH about 12 kJ mol^{-1}, the excess C_p would maximize only at 700 K, but a not unreasonable ΔS value of 30 J mol^{-1} K^{-1} would drop the T_{max} to below 400 K, and raise the $C_{p,max}$ into the range observed.

P. 27, 1st full paragraph, 3rd sentence:

Then, in the viscous medium, the crossing of the barrier between the two states may be impeded and, as in the case described by Suga and co-workers [5] a fraction of the "excited state" (species B) molecules surviving at the lower temperature during cooling, could then become kinetically trapped in the B state, and ergodicity would be broken for lower temperatures.

P. 27, 1st full paragraph, 4th sentence:

The less prominent T1 and T3 anomalies could be related to the αp-βf and αp-αf exchanges which, by different couplings to the viscosity, could fall out of equilibrium at different temperatures.

P. 27, 2nd full paragraph, 3rd sentence:

Then on subsequent upscanning at the normal rate, the extra lost enthalpy is regained in a narrow range of temperatures where the re-equilibration time becomes commensurate with the scanning rate– as is well-known in glass transition phenomenology. The range will be broader in the present case because the temperature is well above T_g, and as a result, the relaxation time will be less temperature-dependent [37].

P. 27, 3rd full paragraph, 2nd sentence:

In the latter case, it is found that, for annealing near T_g, the lower the annealing temperature the higher the temperature of onset of the subsequent heat capacity jump [38, 39].

P. 27, 3rd full paragraph, 4th & 5th sentences:

This effect could be due to the fact that the state of tautomer equilibrium does not directly control the relaxation time as the configurational entropy of the glass controls its relaxation time, see Eq. 1. The entropy of tautomerization is only one component of the total configurational entropy which is already quite high at TT2. On the other hand, the effect could also be related to partial decomposition in view of the heating limit having been set too high (410 K) in this series of measurements.

P. 28, 2nd full paragraph, 1st sentence:

To assist the discussion we show, in Fig. 15, the relation of the time scales we have measured for the slow enthalpy and viscosity relaxations to the shear relaxation times derived from the viscosity data by means of the Maxwell equation.

P. 28, Equation (3):

$$\eta = G_\infty \tau_s \tag{3}$$

P. 28, 2nd full paragraph, 2nd & 3rd sentences:

It is interesting then to put on the diagram the relaxation times for the T_2 process based on the notion that when a process begins to come back into equilibrium from the non-ergodic state during a DSC scan at 10 K min^{-1}, the relaxation time of the process is 102s. (40,41) Using datta from the scans of Fig. 6 at 10 K/min and Fig. 7 at 3K/min, we obtain the points denoted p = A4f in Fig. 15.

P. 28, 2nd paragraph, 4th sentence:

Rather than falling on the line of slow enthalpy and viscosity relaxation as might have been expected, they fall at somewhat shorter times and exhibit a different slope. Furthermore, the plot slopes, though highly uncertain, are respectively, too small and too large to interpret in terms of solvent-controlled relaxation.

P. 28, 5th sentence:

It is not clear to us at this time whether this difference reflects our incomplete understanding of the phenomenology or a non-simple relation between the source of the isothermal relaxations and the source of the slow degree of freedom responsible for the heat capacity jump. The galactose data are not discussed here, but the phenomenology is so similar to that of fructose, that similar isomer equilibria must be involved.

P. 29. Before *Reference*:

Acknowledgements

References

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