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Short communication

Examination of the concentration dependence of T_g of binary aqueous solutions

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Abstract

We present Differential Scanning Calorimetry (DSC) results of rapidly quenched samples of the aqueous solutions of glycerol, propylene glycol and ethylene glycol along with some of their oligomers over a wider concentration. We have critically examined the concentration dependence of glass transition temperature (T_g) of these mixtures. Our results indicate that the Gordon–Taylor equation is not the correct description of the situation. The implication of this finding on the determination of T_g of bulk water from the binary solution data, is discussed.

Keywords: Differential Scanning Calorimetry (DSC); Glass transition; Aqueous solutions; Water

1. Introduction

The glass transition temperature (T_g) of a liquid is defined as the temperature where the co-operative motion of the molecules of liquid freeze-out kinetically during supercooling. This temperature can be easily identified in Differential Scanning Calorimetry (DSC) as a step-like change in the base line or specific heat C_p. In case of a bad-glass forming liquid, T_g can be determined either by vapour quenching method (or by hyperquenching of tiny droplets [1]) which yields a cooling rate of 10^6–10^7 K/s. [2], or by the extrapolation of T_g of the liquid mixture with a suitable solvent [3–5]. In all the above references the extrapolation was done using the well-known Gordon–Taylor equation (or its equivalents) [6] as:

$$T_g(x_w) = \frac{T_{g2} \cdot x_w + T_{g1} \cdot k \cdot (1 - x_w)}{x_w + k \cdot (1 - x_w)} \qquad (1)$$

to obtain the T_g ($= T_{g2}$) of water ($x_w = 1$), where x_w is the weight fraction of water in the solution; T_{g1}, T_{g2} are the T_g s of the components of the mixture. The above equation in terms of the mole fraction x_m of the second component (which in the present case is water) can be written as [6]:

$$T_g(x_m) = \frac{T_{g2} \cdot x_m + T_{g1} \cdot C \cdot (1 - x_m)}{x_m + k \cdot (1 - x_m)} \qquad (2)$$

In the above equation, C is related to k by the expression $C = k \cdot \gamma$ where $(1 - \gamma)$ is the ratio of the molecular weight of water (component 2) to the molecular weight of component 1. For many substances, the excess specific heat ΔC_p of the liquid over the corresponding crystalline state varies as T^{-1}, and this approximation leads to the thermodynamic identity that $C = \Delta C_{p1}(T_g)/\Delta C_{p2}(T_g)$. For all cases where ΔC_{p1} and ΔC_{p2} are constant, one expects to find a monotonic change in T_g with x_w or x_m.

Suga and co-workers [7,8] have observed that in a simple molecular liquid T_g thus measured was invariant for the vapour deposited and liquid quenched samples; and interestingly enough it also agrees with the extrapolated value from binary data using Eq. (1). On applying Eq. (1)(or its equivalent expressions [6]) the T_g of the aqueous solutions extrapolate to ≈ 138 K [10–12] and this value is believed to be the T_g of bulk water. Coincidentally, this value agrees more or less with the DSC data taken on hyperquenched water droplets [1,12]. Since then, this has become a topic of discussion in literature [11–16]. However, in an article, Angell and coworkers [17] have hypothesized that it is probably located in the temperature range 165–175 K, based on analysis of the calorimetric data on hyperquenched

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glassy water, which otherwise would project its properties as anomalous if the T_g is accepted as 138 K. Since then, it has become a topic of larger debate in literature [18–27]. However, very recently some articles have appeared [28–31] supporting Angell's view where [30,31], T_g of water has been predicted to be 162 ± 1 K from the extrapolation of the binary solution data using Eq. (1)(see Fig. 9 of Ref. [30] and Fig. 2 of Ref. [31]), favouring the above hypothesis. These authors have measured T_g of the aqueous solutions of propylene glycol (PG) and its oligomers viz., polypropylene glycols (PPGs) using DSC, where the T_g data was recorded up to a weight fraction of water ($x_w \leq 0.5$ only). However, our experimental observations shown in this communication on the same substances indicate that Eq. (1) is not a good description of the temperature ($T-$) dependence of T_g of aqueous solutions, and the implications of the failure of Eq. (1) in the context of water are discussed below.

2. Experimental

The water used in the study was of HPLC quality from Merck (India); ethylene glycol (EG) (LR grade, 99% pure, S.D. Fine Chem. Ltd., India); propylene glycol (PG) (AR, 99.5%, Sisco Research Labs., India); glycerol (99%, Qualigens Fine Chemicals, India); polypropyleneglycol (PPG) 400 (Alfa Aesar, USA); polyethyleneglycol (PEG) 200, 400, 600 (synthesis grade, Merck India; and PEG 6000 (synthesis grade, Loba Chemie, India). All the liquids are further purified through distillation before use. The DSC measurements were taken on the above solutions using PerkinElmer Sapphire DSC with a quench cooling accessory. The DSC cell was calibrated for two temperatures: one for the melting temperature of Indium (429.78 K) and the other for the solid-solid transition of cyclohexane (186.09 K). The cooling rate obtainable with the use of quench cooling accessory is less than $20^\circ\ \text{min}^{-1}$ due to the design of the DSC cell and hence it does not allow us to measure T_g s for $x_w > 0.5$. This method of using the quench cooling accessory is hereafter would be referred to as normal quench cooling or NQC. In order to increase the cooling rates, we dipped the crimped sample pans directly into liquid nitrogen with the help of a very thin forceps with a plastic handle, to form 100% glass. This procedure gives an average cooling rate of $\approx 800^\circ\ \text{min}^{-1}$ [11]. In the following discussion this method would be referred to as fast quench cooling or FQC in order to distinguish it from NQC. This sample pan was then introduced into the DSC cell whose temperature was maintained at 103 K. The sample was then equilibrated for 10 min before heating it at a rate (q) of $10^\circ\ \text{min}^{-1}$.

3. Results and discussion

The T_g s of pure samples as measured by DSC for a heating rate of $10^\circ\ \text{min}^{-1}$are: 172.5 K for PG, 199.5 K for PPG 400, 191.9 K for glycerol, 157.9 K for EG, 188.5 K for PEG 200, 200.3 K for PEG 400, 205.3 K for PEG 600 and 209.9 K for PEG 6000. The DSC scans thus taken using FQC method for PG solutions are shown in Fig. 1, where one can notice that solutions with higher x_w values always crystallize to cubic ice upon heating above T_g. This procedure using FQC allowed us to obtain the T_g values for an additional range of $0.5 \leq x_w \leq 0.675$, not obtainable in the procedure adopted by Cerveny et al. [30,31]. However, this procedure also fails for $x_w > 0.65$ where crystallization is always faster than the above cooling rate. Shown in Fig. 2 are the $T_g s$ obtained by NQC and FQC methods for PG and its oligomers along with that of the data obtained for EG and glycerol, where the latter set of data are shown seperately as Fig. 2(a) for the sake of clarity. The reader may see that the present data on glycerol-water (which is one of the most widely studied system) agree well with the that of Slade and Levine [32], Ablett et al. [33], Rasmussen and MacKenzie [10], and Inaba and Andersson [27] by taking into account the heating rates involved. For solutions of EG and glycerol Eq. (1) gives satisfactory fits as shown in Fig. 2(a) but the corresponding T_g ($= T_{g2}$) of water is about 137.4 K with a large uncertainity of ±6 K. Shown in Fig. 2(b) is the T_g data of the aqueous solutions of PG and its oligomer PPG400 where one can see that if Eq. (1) is fitted to the data for $x_w \leq 0.5$, then the experimental points for $x_w > 0.5$ do not follow Eq. (1). Hence, we see that Eq. (1)(with fixed value for the parameter k), doesn't give a correct picture of the variation of T_g with x_w.

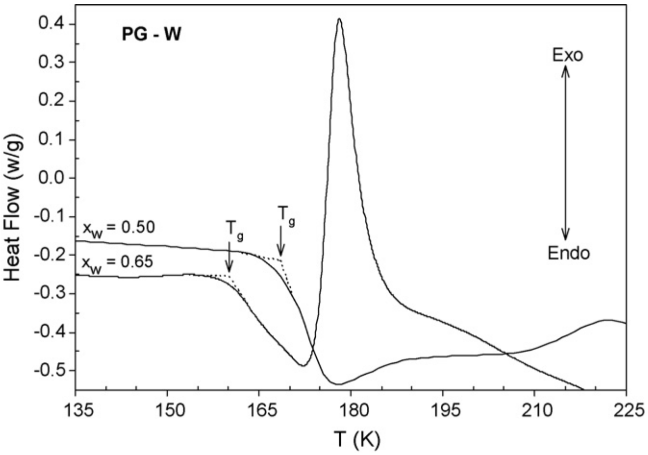

Fig. 1. DSC scans of glasses formed by fast quenched PG-W solutions for a heating rate of $10^\circ\ \text{min}^{-1}$. The sample weights are 17.9 mg for $x_w = 0.5$ and 9.36 mg for $x_w = 0.65$, respectively. Note that the latter crystallizes to cubic phase just above T_g, where T_g is the onset of the glass transition process, determined using the standard DSC analysis software supplied along with the instrument.

Shown in Fig. 3 are the T_g s thus measured for various solutions of ethylene glycol (EG) and its oligomers i.e. polyethylene glycols(PEGs). The T_g values change monotonously with x_w for $0.0 \leq x_w \leq 0.675$ towards lower values of T_g and based on our experience with simple liquids [3,7,8] we expect all the curves to converge to a temperature located around 136 K. Since the specific heat of supercooled water is an anomalous [34] and also because Eq. (1) does not describe the data well, it is not clear whether this behaviour will still be maintained at much higher concentrations of water. (The Brekner equation [35] also doesn't describe the data well, although it is a better fit than Eq. (1)).

Since Eq. (1) fails to describe the data for $x_w > 0.5$ of solutions of PG, PPGs and PEGs as shown in Figs. 2(b) and 3, the corresponding T_{g2} ($= T_g$ of water) of the fits (for data $x_w \leq 0.5$)

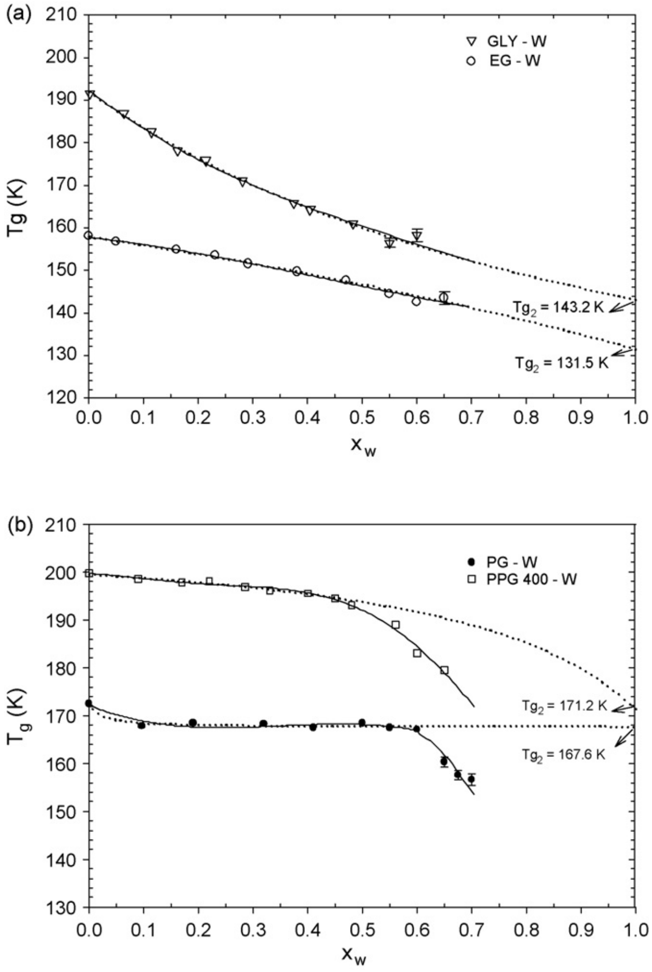

Fig. 2. Variation of T_g of aqueous solutions of (a) glycerol and EG and (b) PG and PPG 400, with x_w. The dashed lines correspond to Eq. (1) for $x_w \leq 0.5$ and the thick lines are guide to the eye. Indicated in the figure by arrows are the corresponding values of T_g (water) in Eq. (1){for $x_w \leq 0.5$}.

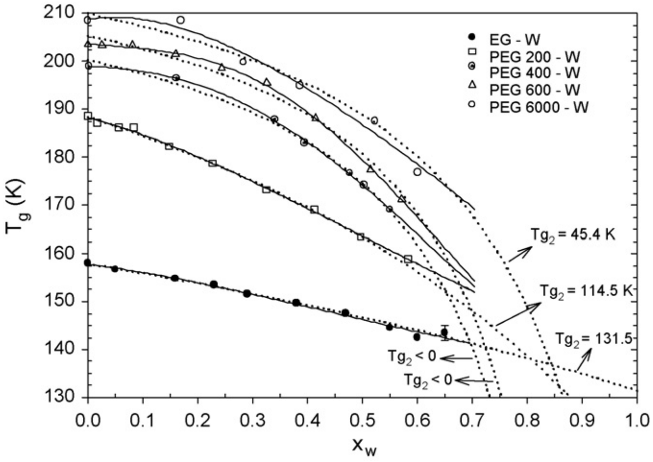

Fig. 3. Variation of T_g of various aqueous solutions of EG and its oligomers with x_w. The dotted lines are fits to Eq. (1) for $x_w \leq 0.5$ and the thick lines are guide to the eye.

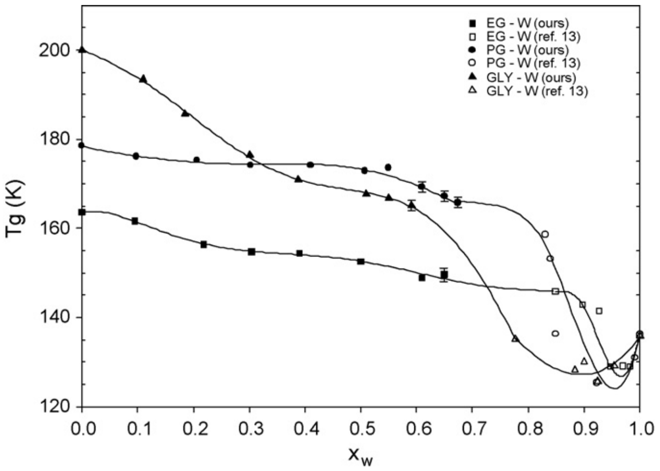

Fig. 4. Variation of T_g of aqueous solutions of EG, PG and Glycerol with x_w over the complete concentration range $0.0 \leq x_w \leq 1.0$. The data (shown by open symbols) for $0.75 \leq x_w \leq 1.0$ corresponds to the hyperquenched solutions taken from Fig. 8 of Ref. [13]. The thick lines are guide to the eye.

to Eq. (1) do not give consistant values as shown in those figures. If we go by our experience with the simple liquids [3–5,7,8] where the T_g of the solution varies monotonously with x_w, it is rather tempting to expect that all the curves of Figs. 2 and 3 would converge smoothly to a T_{g2} value of about 136 K.

In view of the experience of Suga and coworkers [7,8] with normal liquids, it is tempting to get the correct behaviour of T_g versus x_w curves over the entire concentration range $0 \leq x_w \leq 1.0$ by clubbing the data of normally cooled binary liquids with the corresponding hyperquenched liquid data. For this purpose, we have chosen three cases, viz. aqueous solutions of glycerol, EG and PG for which the T_g values (for $q = 30$ K/min) at higher water concentrations were taken by Hofer et al. [13,14] with their hyperquenching method. We have depicted our T_g values measured for $q = 30$ K/min in Fig. 4 along with the data of Hofer et al. [13]. Interestingly, both the sets of T_g agree well with each other within the experimental uncertainity of ±2 K, and follow the same pattern. The T_g values of solution thus measured are invariant for the hyperquenched droplets and liquid quenched samples, and interestingly enough, the liquid data shown in Fig. 4, for $0.0 \leq x_w < 1.0$ do not extrapolate to the T_g of water in a simple manner. There is a minimum in the curves of T_g versus x_w on the water rich side which was attributed by Hofer et al. [13] due to a breakdown of structure peculiar to water. Another alternative explanation that can be offered here is based on the predicted [34] anomalous temperature dependence of the specific heat (C_p) of water which needs to be taken into account in the formulation of Eq. (1). According to Ref. [6], the adjustable parameter k in Eq. (1) is equal to C/γ where C is identified for a particular mixture as the ratio of the corresponding $\Delta C_{pl}(T_g)$ [6] and hence, Eq. (1) or Eq. (2) is bound to fail in the case of water as the basic assumption that ΔC_p of the supercooled liquid varies as T^{-1} is no more valid. To account for the minima in Fig. 4, the parameter k has to be concentration dependant [13]. It is also important to take in to account of the fact that the anomalous properties including C_p of water gradually vanish on addition of another component [9,36,37] and water behaves normally for larger addition of the component. Therefore, it is no surprise that Eq. (1) is valid only for $x_w \leq 0.5$ and fails for higher values of x_w.

4. Conclusions

In essence, the evidence presented through Figs. 2–4, suggest that Eq. (1)(or equations that are similar to it [6]) do not appear to give a correct description of the concentration dependence of T_g of aqueous solutions and therefore, the conclusions arrived at on use of Eq. (1) by Cerveny et al. in Refs. [30,31] are erroneous. As demonstrated in Fig. 4, the glass transition temperature data obtained using different quenching techniques merge smoothly, implying that T_g of bulk water in all probability is located in the range 136–138 K. This point needs to be taken seriously in the context of the controversy surrounding the T_g of water. The failure of Eq. (1) in the case of binary solutions of water could partially, be due to an anomalous temperature dependence of the specific heat (C_p) of water [34] and its removal on addition of another component [36,37] which need to be taken into account in Eq. (1) in which case the adjustable parameter k becomes concentration dependent.

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