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# Study of the thermal behaviour of 1,3-propanediol and its aqueous solutions

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## Abstract

Differential scanning calorimetry was used to investigate the thermal behaviour of 1,3-propanediol and its aqueous solutions. The melting temperature of pure 1,3-propanediol and its melting heat were determined as 249 K and 11400 J $mol^{-1}$, respectively. The 1,3-propanediol–water phase diagram presented three types of behaviour on heating (following annealing), depending on composition: high alcohol–content mixtures that exhibited a eutectic and dissolution (equilibrium phases), intermediate mixtures that vitrified uniquely and high water-content solutions that showed a residual glass transition and dissolution but no eutectic. The fact that crystallization of the eutectic was not observed for high water-content solutions was discussed in terms of relatively strong interactions between water and alcohol in the liquid state, thus impeding crystallization of the alcohol. Computation of the congealing curve of water and the solubility curve of 1,3-propanediol, using the model of associated solutions, confirmed this hypothesis. Finally, a comparison between 1,3-propanediol and its isomer, 1,2-propanediol; was made; it was also discussed as to why the former crystallizes but not the latter. © 1998 Elsevier Science B.V.

*Keywords:* DSC; Glass/crystal; Propanediol; Water

## 1. Introduction

Alcohol–water systems have been the subject of numerous papers from both, a theoretical and a practical point of view (cryopreservation, for instance). The aqueous solutions of 1,2-propanediol [1,2] and of glycerol [3–9] have been extensively studied. On the other hand, 1,3-propanediol, a structural isomer of 1,2-propanediol, and its aqueous solutions have been studied in very few papers to our knowledge: thermal behaviour [10,11], thermodynamic data [12,13], dielectric studies [14,15], viscosity [16]. The aim of the present paper is to study the thermal behaviour of 1,3 propanediol and its aqueous solutions and to make a comparison with that of 1,2 propanediol and its aqueous solutions.

## 2. Experimental

A DSC Mettler TA 2000 B was used. It was standardized for temperature and heat flow using the temperatures and heats of melting of high purity metals and compounds [17]. The calorimeter was flushed with pure, dry argon.

1,3-Propanediol was purchased from Aldrich; its purity was 98% by mass. 1,2-Propanediol of purity >99% and 2-methyl 1,3-propanediol of purity >99% were also purchased from Aldrich. The samples were sealed in aluminium crucibles (40 μl). Masses were in

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the 20–35 mg range. They were quenched in liquid nitrogen, then placed in the calorimeter previously cooled at 130 K. DSC curves were recorded between 130 and 298 K using a heating rate of 2 K $\mathrm{min}^{-1}$. When the thermal behaviour of the pure alcohols was studied, their handling was done in a glove box under a dry inert atmosphere (argon).

The glass-transition temperature $T_g$ was taken as the inflection point of the calorimetric signal associated with the glass transition. The crystallization temperature $T_c$ was taken as the intersection of the slope of the exothermal crystallization event and the base line. The eutectic temperature was taken as the intersection of the slope of the eutectic endotherm and the baseline. The liquidus temperature $T_l$ was taken as the peak of the endothermal dissolution event. Annealing experiments were performed at peak temperature $T_{c,\max}$ of the crystallization exotherm.

## 3. Results

### 3.1. Thermal behaviour of 1,3-propanediol

Quenched 1,3-propanediol vitrified completely. Upon heating, partial crystallization occurred: the DSC curve exhibited glass transition, crystallization and melting. Annealing at the peak temperature $T_{c,\max}$ of the crystallization exotherm resulted in full crystallization of the sample. The subsequent DSC curve obtained upon reheating presented one endotherm corresponding to melting: the melting temperature was determined as 249 K (DSC purity method) and the heat of melting as 11 400 J $\mathrm{mol}^{-1}$ (150 J $\mathrm{g}^{-1}$).

The results are summarized in Table 1 along with those corresponding to 1,2-propanediol and also 2-methyl 1,3-propanediol. Crystallization of the latter liquids has not been observed.

### 3.2. Out of equilibrium x1,3 propanediol–(1−x)water phase diagram

The out of equilibrium $x$1,3 propanediol–$(1-x)$ water phase diagram shown in Fig. 1 presents different thermal behaviour, depending on the mole fraction $x$ of 1,3-propanediol:

1. $0.75 \leq x < 1$: Quenched solutions demonstrated glass transition, crystallization and dissolution. Annealing experiments performed at $T_{c,\max}$ allowed for a eutectic phase to form (for $0.75 \leq x \leq 0.95$). The case of $x=0.8$ is presented in Fig. 2. For the latter composition, crystallization of the whole sample did not take place even after annealing. Indeed, note the presence (Fig. 2) of a residual glass transition followed by a minor supplementary crystallization of the eutectic. At higher temperatures, melting of the eutectic occurs ($T_E \approx 206$ K) and is followed by dissolution.
2. $0.3 < x < 0.75$: These solutions only vitrified. No sign of crystallization was observed even after annealing.
3. $0.1 < x \leq 0.3$: Quenched solutions showed glass transition, crystallization and dissolution. Annealing at $T_{c,\max}$ did not result in the crystallization of a eutectic phase. Instead, only crystallization of water took place. An example is given in Fig. 3 for $x=0.2$: after annealing, the subsequent DSC curve upon reheating presented a residual glass transition, a weak exotherm (SC) corresponding to a minor supplementary crystallization of water, the events termed ante-melting ($T_{AM}$) and incipient melting ($T_{IM}$) (see Section 3.3 for the discussion about their definition and their possible nature), followed by dissolution.
4. $0 < x \leq 0.1$: These solutions demonstrated a residual glass transition and dissolution. This means that

Table 1
Thermal behaviour of the pure alcohols

| | $T_g$ [a]/K | $T_c$/K | $T_m$/K | $T_m$ [b]/K | $\Delta H$/(J $\mathrm{mol}^{-1}$) | $T_m$ [c]/K |
|---|---|---|---|---|---|---|
| 1,3 PD | 150.4 | 195 | 245.6 | 246 | 11400 | 249 |
| 1,2 PD | 171.1 | — | — | — | — | — |
| 2-methyl 1,3 PD | 167.0 | — | — | — | — | — |

[a] Heating scan following a quench.
[b] Heating scan following annealing at $T_{c,\max}$.
[c] Melting temperature as determind by the DSC purity method: $T_g$, glass transition temperature; $T_c$, crystallization temperature; $T_m$, melting temperature; and $\Delta H$, melting heat.

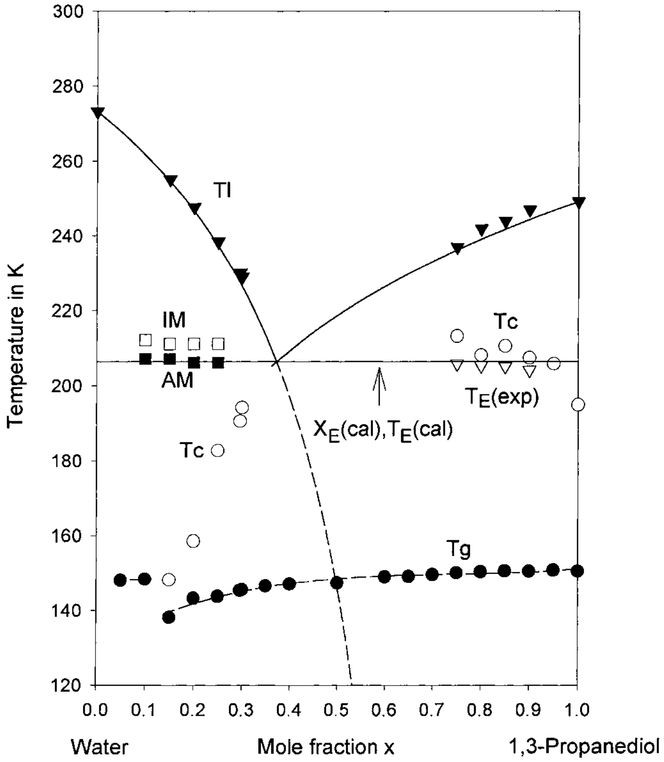

Fig. 1. $x$1,3-Propanediol–(1−$x$)water system. Quenched samples: $T_g$, glass transition temperature; $T_c$, crystallization temperature; and $T_l$, liquidus temperature (heating rate 2 K $\mathrm{min}^{-1}$). Annealed samples: $T_{E(exp)}\approx206$ K, experimental eutectic temperature, $T_{E(cal)}\approx207$ K, calculated eutectic temperature, $x_{E(cal)}\approx0.36$, calculated eutectic composition ($T_{E(cal)}$ and $x_{E(cal)}$ were calculated as the intersection of the two computed liquidus curves (full line) using the model of associated solutions (see text)), $T_{AM}\approx206.5$ K, ante-melting temperature, $T_{IM}\approx213$ K, incipient melting temperature (heating rate, 2 K $\mathrm{min}^{-1}$ after samples were annealed at $T_{c,max}$).

water congeals on quenching in equilibrium with a residual liquid whose representative point follows the stable congealing curve (solid line in Fig. 1). For temperatures below the eutectic, the representative point follows the metastable congealing curve (dashed line). Using the model of associated solutions [18], the congealing curve was computed as an equilibrium between ice and an ideal solution of water, 1,3-propanediol and (1,3-propanediol$_{0.65}$–water$_{0.35}$) species (for comparison, the solubility curve of 1,3-propanediol was calculated as the pure solubility curve). It should be noted that the congealing curve intercepts the $T_g$ curve for $x\approx0.5$. In other words, the residual liquid which vitrifies on quenching for $0<x\leq0.1$ has a composition $x\approx0.5$.

### 3.3. Ante-melting (AM) and incipient melting (IM)

In this study, the ante-melting (AM) and incipient-melting (IM) events were observed in the case of $0<x<0.1$ solutions as well as annealed samples for $0.1<x\leq0.25$ solutions (Fig. 3). For $0<x<0.1$, the amplitude of these events were too small to permit a reasonable determination of the associated temperatures. These events occurred at almost constant temperatures: $T_{AM}\approx206.5$ K and $T_{IM}\approx213$ K (Fig. 1). $T_{AM}$ is surprisingly close to the experimental eutectic temperature $T_E\approx206$ K as obtained for high 1,3-propanediol-content solutions ($0.75\leq x<1$). One could think that this would point to AM and IM being an "aborted" formation of a eutectic phase. This is not very likely however, as will be seen in the following.

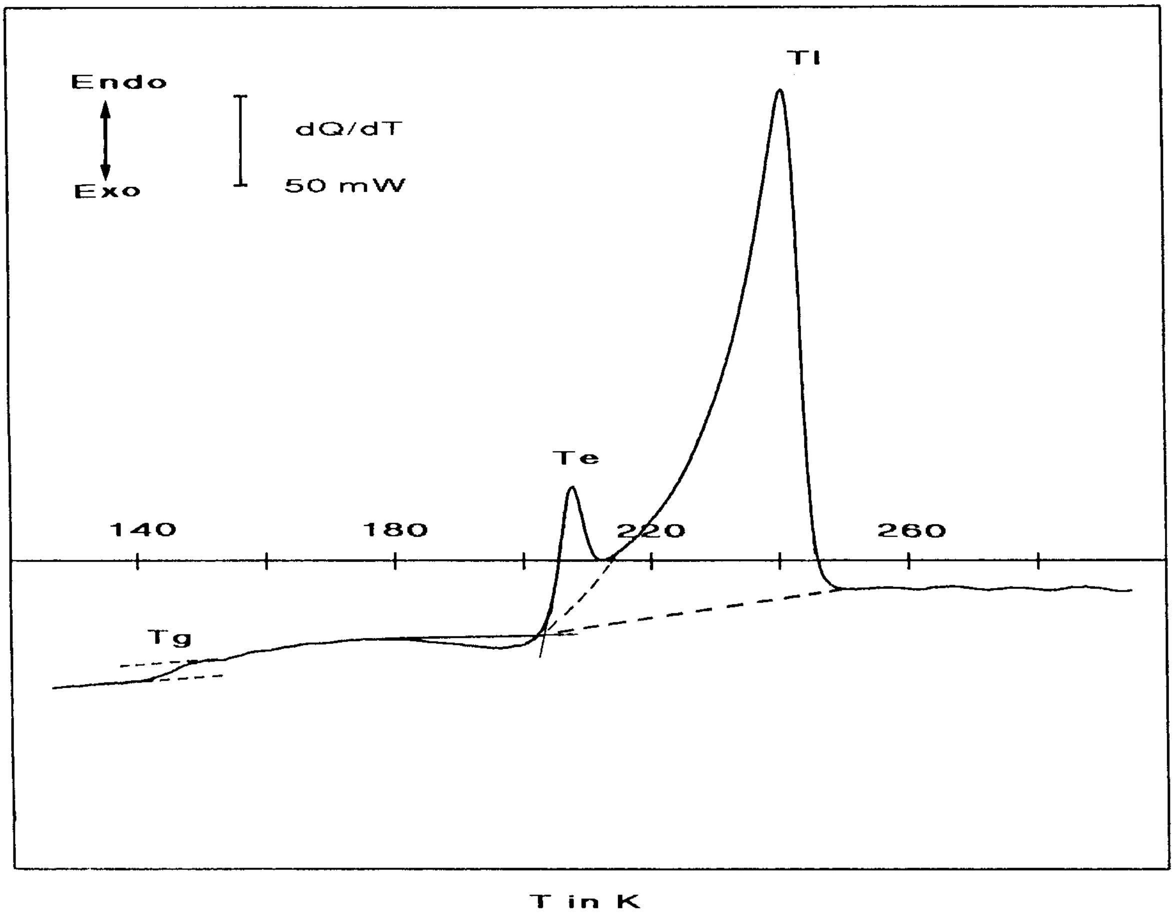

Fig. 2. DSC curve of an $x$=0.8 solution ($x$, mole fraction of 1,3-propanediol) following annealing. $T_g$=148.5 K, residual glass transition; $T_E$=206 K, eutectic temperature; and $T_l$=242 K, liquidus temperature. Note the very weak crystallization exotherm (of the eutectic) before melting of the eutectic.

The events termed AM and IM, as was originally designated by Luyet and Rasmussen [4], have been the subject of numerous discussions and many interpretations were advanced about their nature. Rasmussen and Luyet [5] propose that AM is a relaxation process at the interface between ice crystals and the residual solution similar to that in the bulk of the amorphous solution undergoing glass transition. Bohon and Conway [6] think of these events as a secondary glass transition. A study by Harran [7] would rather indicate that AM is an exothermic event corresponding to a minor supplementary crystallization of water which has not occurred on cooling for high water-content solutions (the representative point of the residual liquid would leave the metastable congealing curve on cooling before vitrification of the residual liquid at lower temperatures; upon heating, the representative point of the residual liquid would rejoin the metastable congealing curve by a small deposit of ice). A study by us [9] on the thermal behaviour of water-rich glycerol solutions would tend to reinforce this hypothesis: annealing experiments at $T_{AM}$ resulted in slightly higher $T_g$s (the residual liquid is more concentrated in glycerol) and the absence of AM on the subsequent heating curve (IM being always present). In this view, IM is probably the beginning of the dissolution endotherm.

In this study, the existence of both SC and AM (Fig. 3) was observed on several DSC curves of annealed samples in the domain $0.1<x\leq0.25$. Note

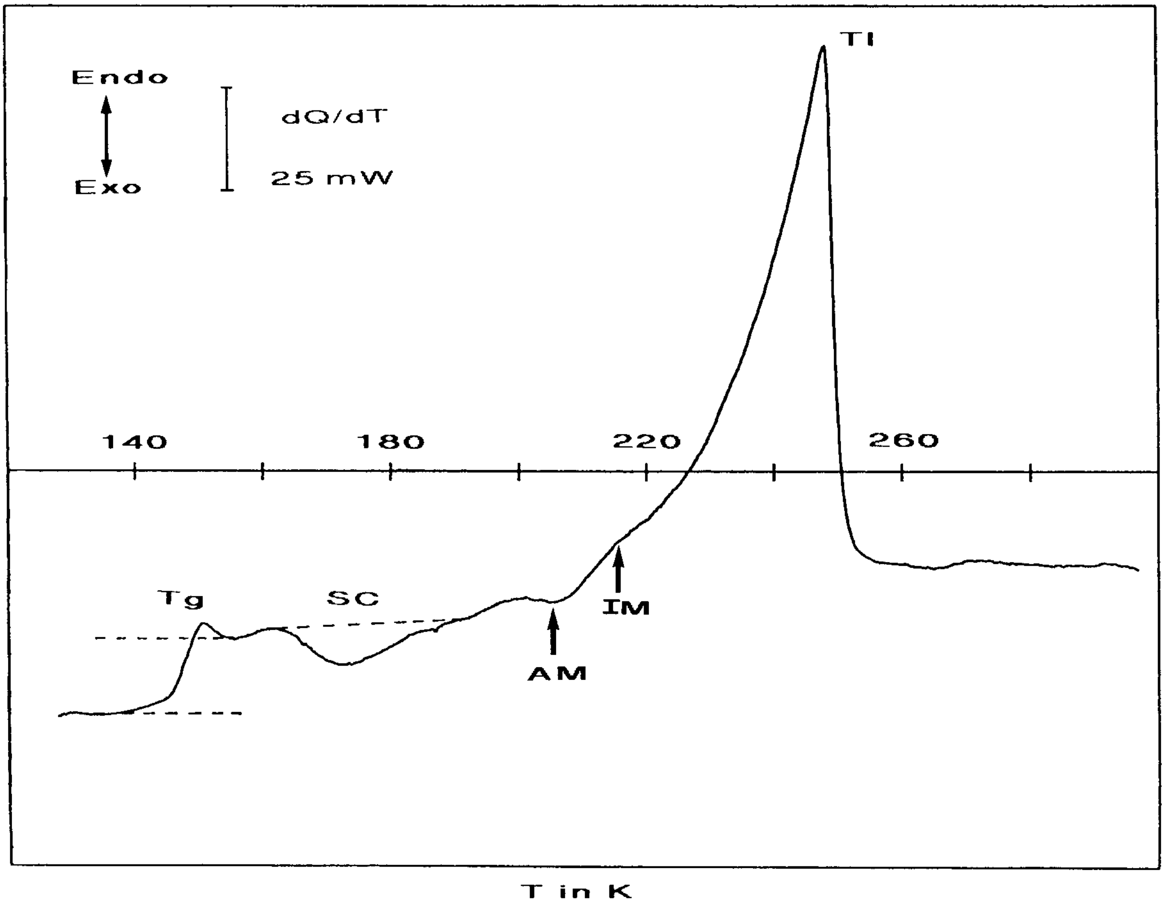

Fig. 3. DSC curve of an $x$=0.2 solution ($x$, the mole fraction of 1,3-propanediol) following annealing. $T_g$=148.3 K, residual glass transition; SC, a minor supplementary crystallization of water, AM, ante-melting (206 K); IM, incipient melting (214 K); and $T_l$=242 K, liquidus temperature. No formation of a eutectic was observed.

that these two events are not incompatible since SC would correspond to a minor crystallization of water that has not occurred during the annealing times that were used, and AM to a small deposit of ice that brings the representative point of the residual liquid on the metastable congealing curve as was advanced by Harran [7]. Supplementary studies are required, however, to better understand these events and no further speculation will be made here about their origin.

### 3.4. Dissolution enthalpies

The dissolution enthalpies $\Delta H_{\text{diss}}$ determined after annealing are presented in Fig. 4. In the case of $0.75 \leq x < 1$ solutions, $\Delta H_{\text{diss}}$ were calculated using the dashed baseline in Fig. 2. Note that if the $\Delta H_{\text{diss}}$ vs. $x$ curves in Fig. 4 are fitted with linear regressions in the domains limited to $0.15 \leq x \leq 0.3$ and $0.75 \leq x < 1$, the intersection composition corresponding to $\Delta H_{\text{diss}} \approx 0$ would be $x_E \approx 0.33$. Although the latter composition is close to the calculated eutectic $x_E \approx 0.36$ and $T_E \approx 207$ K (intersection of the two computed liquidus curves), one can think that this is fortuitous rather than having a real significance. Indeed, the rigorous way to calculate $x_E$ is using the Tamman method (which was not possible to apply here since high water-content solutions do not present a eutectic).

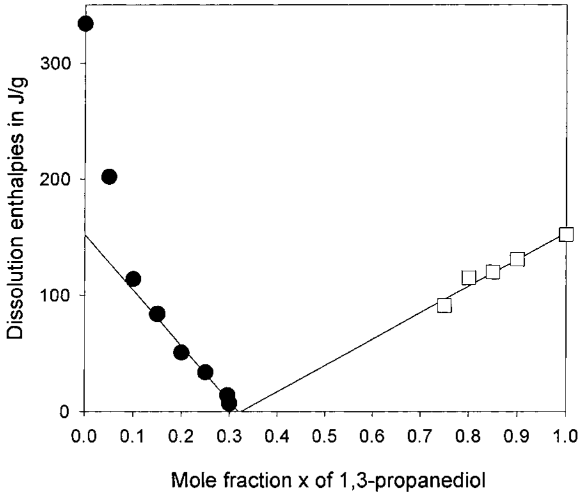

Fig. 4. Dissolution enthalpies $\Delta_{\text{diss}}H$ in the $x$1,3-propanediol–(1−$x$)water system after annealing experiments were performed: (●) high water-content solutions; and (□) high alcohol-content solutions. If the $\Delta H_{\text{diss}}$ vs. $x$ curves are fitted with linear regressions in the domains limited to $0.15 \leq x \leq 0.3$ and $0.75 \leq x < 1$, the intersection composition ($\Delta H_{\text{diss}} \approx 0$) would be $x_E \approx 0.33$. Although the latter composition is close to the calculated eutectic ($x_E \approx 0.36$), this is fortuitous rather than having a real significance (see text).

## 4. Discussion and conclusion

1,3-Propanediol crystallizes contrary to 1,2-propanediol and 2-methyl 1,3-propanediol. 1,3-Propanediol is a symmetric molecule which can only present conformers of rotation. 1,2-Propanediol, on the other hand, is a racemic liquid equimolarly composed of two enantiomer molecular forms [19,20]. The presence of the two enantiomers prevents nuclei formation and/or crystal growth. In the case of 2-methyl 1,3-propanediol, crystallization may be sterically hindered by the presence of the methyl group. The difficulty to crystallize could also be due to the presence of the methyl group leading to the existence of different molecular conformations. One must also keep in mind that these hydrogen-bonded liquids are hygroscopic: the presence of even small traces of water (despite having worked in a glove box) can impede crystallization.

As a consequence, annealing of aqueous solutions of 1,3-propanediol in the $0.75 \leq x < 1$ domain results in the crystallization of 1,3-propanediol and of a eutectic phase (contrary to aqueous solutions of 1,2-propanediol for which crystallization of the alcohol was never observed [1,2]). On the other hand, high water-content solutions do not demonstrate crystallization of a eutectic even when annealing experiments are performed. We see two possible reasons for this:

- for high water-content solutions, 1,3-propanediol molecules may be sterically hindered by water molecules from forming crystal nuclei; and
- it is possible that the alcohol–water interactions in the liquid state are stronger for high water-content solutions than for solutions which are rich in alcohol. This would be confirmed by the computation of the congealing curve (model of associated solutions [18]) as an equilibrium between ice and an ideal solution of water, 1,3-propanediol and 1,3-propanediol(0.65)–water(0.35) species (two molecules of 1,3-propanediol for one molecule of water) whereas the 1,3-propanediol solubility curve was calculated as the pure solubility curve. As a result, the alcohol molecules would be "freer" to form crystal nuclei for high alcohol-content solutions ($0.75 \leq x < 1$).

Finally, $0.3 < x \leq 0.75$ solutions did not show any sign of crystallization even after annealing experiments were carried out. The viscosity argument often advanced (in the case of glycerol–water solutions, for example) as an explanation cannot hold here since $0.75 \leq x < 1$ solutions (more viscous) do crystallize. Apart from "steric" reasons, another possible explanation is that this domain of composition corresponds to a "well" of vitrification as was observed for aqueous solutions of the electrolytes LiCl and $MgCl_2$ among others [21–23]. If this was the case, the equilibrium phase diagram would be more complicated than the one drawn in Fig. 1 (full lines) and would necessarily present at least one definite compound in the domain $0.3 < x \leq 0.75$. The metastable congealing curve and 1,3-propanediol solubility curve would then probably intersect for temperatures below $T_g$ as was observed in [21–23].

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