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Vitrification and crystallization in the $R(-)1,2$ -propanediol– $S(+)$ 1,2-propanediol system

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Abstract

Differential scanning calorimetry (DSC) was used to investigate the thermal behaviour of 1,2-propanediol enantiomers and to study the $R(-)1,2$ -propanediol– $S(+)$ 1,2-propanediol phase diagram. The melting temperature of the pure enantiomers was determined as 240 K and their melting heat as 8400 J mol^{-1} . The phase diagram exhibited two types of behaviour depending on composition: mixtures for which partial crystallization was observed and those in which no crystallization occurred. From the experimental results, a tentative equilibrium phase diagram is proposed. It is suggested that organic liquids for which crystallization is difficult or even impossible are mixtures of several molecular conformations. This is the case for racemic 1,2-propanediol. These liquids should be accounted for in phase diagrams.

Keywords: DSC; Enantiomers; Glass/crystal; 1,2-Propanediol; Racemic

1. Introduction

Organic liquids have been extensively studied in order to obtain a better insight into the vitrification process [1–4]. Some liquids will always crystallize when they are cooled. Others will systematically vitrify. Melting temperatures of many liquids are not known because their crystals have never been obtained.

The behaviour of glycerol, for example, in the liquid and solid states has been discussed in numerous papers [5–9]. Glycerol vitrifies easily when cooled. Its crystallization requires cooling for relatively long times at very low temperatures if it is pure

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[5, 10]. Seeding facilitates crystallization when glycerol is pure. However, crystallization is possible in the presence of suitable solvents even when glycerol is not very pure [11]. The crystal structure of glycerol was determined in [12]. Although the molecule can assume different conformations, the authors in [12] have shown that glycerol crystallizes in the $\alpha\alpha$ conformation.

1,2-propanediol is a chiral molecule because it possesses an asymmetrical carbon. As a result, it exists in two enantiomeric forms: $S(+)$ - and $R(-)$ 1,2-propanediol. Commercially available 1,2-propanediol is a racemic compound because it is an equimolar mixture of the two enantiomers. It has never been crystallized to our knowledge. Nevertheless, a melting temperature of 213 K has been reported in the literature [13]. Angell and Smith [2] have put forward the idea that crystallization cannot occur in racemic 1,2-propanediol because of the difficulty of the $S(+)$ 1,2-propanediol enantiomer fitting into the $R(-)$ 1,2-propanediol enantiomer crystal lattice, which precludes crystallization.

In the case of mixtures of enantiomers, three fundamental types of symmetrical equilibrium phase diagram can be distinguished, as was first described by Roozeboom [14] and comprehensively treated by Jacques et al. [15]; see Fig. 1:

(a) a diagram presenting two liquidus curves and a eutectic. The crystalline racemate ($x = 0.5$) is called a conglomerate and is a physical mixture of crystals of the two enantiomers. The conglomerate melts as if it were a pure substance because it is a eutectic;

(b) a diagram in which the crystalline racemate is an addition compound (this is called a racemic compound). In other words, it is a crystal in which the two enantiomers are present equimolarly in the crystal lattice. The racemate melts congruently;

(c) a diagram in which the pure enantiomers form a solid solution (of type 1, 2 or 3 in Fig. 1(c)). The racemate is designated as a pseudoracemate. This last case is seldom encountered.

Phase diagrams are indeed of great help in understanding crystallization and vitrification in liquids, because they allow the study of systems as a function of composition and temperature (or pressure). The glycerol–water [16–21] and racemic 1,2-propanediol–water [22, 23] systems, for example, have been extensively studied.

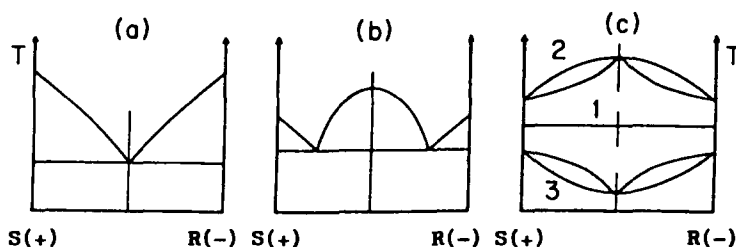


Fig. 1. Fundamental types of equilibrium phase diagram for enantiomer mixtures depending on the nature of the crystalline racemate ($x = 0.5$): (a) conglomerate, (b) racemic compound (addition compound), (c) pseudoracemate.

2. Materials and methods

A DSC Mettler TA 2000 B calorimeter was used. It was standardized for temperature and heat flow rate using the temperatures and heats of melting of high purity metals and compounds [24]. The calorimeter was flushed with pure, dry argon.

Racemic 1,2-propanediol (commercial 1,2-propanediol) was purchased from Aldrich; its purity was >99% by mass and it had density $d = 1.036$. *S*(+)1,2-propanediol and *R*(-)1,2-propanediol were purchased from Fluka and had a purity of >99%. The enantiomers are both optically active ($\alpha_D^{20} = 16.5 \pm 1^\circ$ and $\alpha_D^{20} = -16.5 \pm 1^\circ$ respectively) and have the same density $d_4^{20} = 1.036$. *S*(+)1,2-Propanediol was also purchased from Aldrich and had purity >99%. It is optically active ($\alpha_D^{20} = +16.6^\circ$) with density $d = 1.040$. No melting temperatures were given by the supplier. The water content in these compounds, as determined by Karl Fischer titration, was 0.01–0.04% by mass. 1,3-Propanediol of purity 98% was also purchased from Aldrich and 2-methyl-1,3-propanediol of purity >99% was obtained from Fluka in order to compare their thermal behaviour with that of the above compounds. A melting temperature of 246.1 K was given by the supplier for 1,3-propanediol but no melting temperature was given for 2-methyl-1,3-propanediol. The alcohols were handled in a glove box under a dry inert atmosphere (argon).

The samples were sealed in aluminium crucibles (40 μ l) and weighed. Masses were in the range 15–30 mg. They were quenched in liquid nitrogen, then placed in the calorimeter previously cooled at 123 K. DSC curves were always recorded between 123 and 298 K using a heating rate of 2 K min^{-1} . Programmed cooling rates of 30 K min^{-1} were also used after annealing experiments performed at the peak temperature of the crystallization exothermal event.

The glass transition temperature T_g was taken as the inflection point of the change in 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 melting temperature T_m of samples as purchased from the supplier was taken as the intersection of the slope of the endothermal melting event and the base line. The melting temperature of the pure compounds was calculated using the method of purity determination by DSC [25–27]. Finally, the liquidus temperature T_l was taken as the peak of the endothermal dissolution event.

3. Results

3.1. Thermal behaviour of racemic 1,2-propanediol and of the enantiomers

The DSC curve of quenched racemic 1,2-propanediol is shown in Fig. 2. It shows a glass transition only. The glass transition temperature is 171.1 K and the change in specific heat capacity at T_g is 1.22 J $\text{K}^{-1} \text{g}^{-1}$. The DSC curve of quenched *S*(+)1,2-propanediol supplied by Aldrich is shown in Fig. 3(a). It exhibits glass transition, crystallization (exothermal event) and melting (endothermal event). The sample has totally vitrified after quenching, as the heat released in the exothermal event and

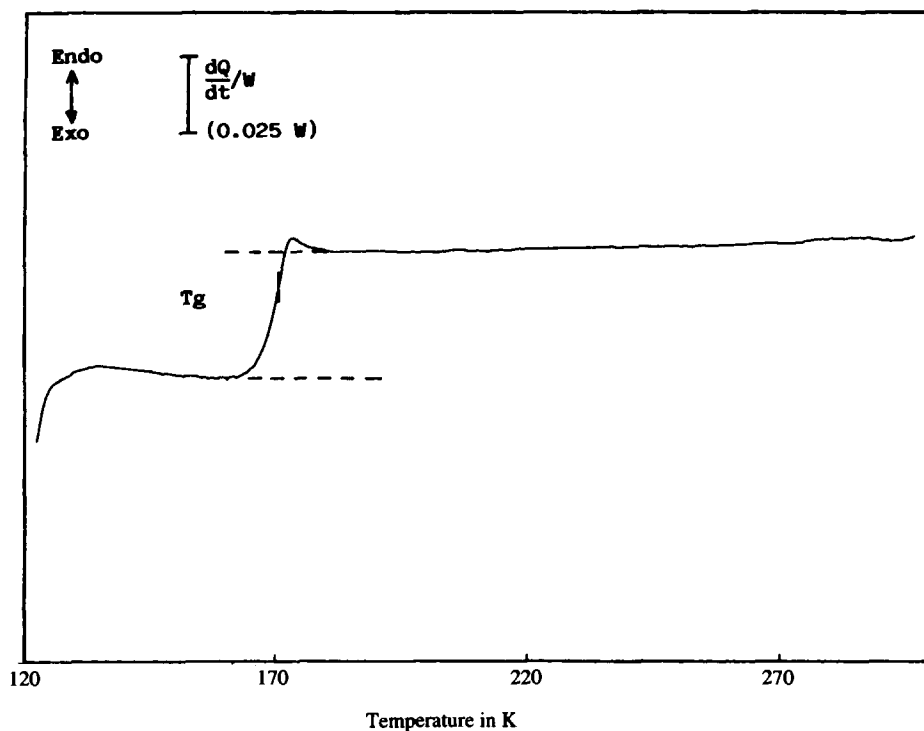


Fig. 2. DSC curve of quenched racemic 1,2-propanediol. Heating rate 2 K min^{-1} , $T_g = 171.1 \text{ K}$, glass transition temperature, $\Delta C_p = 1.22 \text{ J K}^{-1} \text{ g}^{-1}$, heat capacity change at T_g .

that absorbed in the endothermal event in the heating scan are equal ($\Delta H_1 = \Delta H_2 = 4900 \text{ J mol}^{-1}$) taking into account a repeatability of 3%. Annealing experiments at the peak temperature $T_{c \text{ max}}$ (225 K) of the crystallization exotherm were carried out to allow full crystallization to occur. After programmed cooling (30 K min^{-1}), and upon reheating, the DSC curve showed melting of the fully crystallized sample with an absorbed heat of 8400 J mol^{-1} (Fig. 3(b)). There was, however, a clear shoulder in the melting endotherm as though there were two non-separated endotherms, which for convenience we have called endotherm I and endotherm II.

The same experiments were run using the enantiomers purchased from Fluka (Fig. 4). A second endothermal event, with a much clearer resolution than in the previous case, appeared before the main endotherm (endotherm II) for both isomers after annealing at $T_{c \text{ max}}$ (217 K). An experiment was run with heating up to the end of endotherm I (235 K) in Fig. 4(b). Following programmed cooling, the final heating scan exhibits one endotherm with $T_m = 237 \pm 0.5 \text{ K}$ and $\Delta H_m = 8400 \text{ J mol}^{-1}$ for both isomers (Fig. 4(c)). Nevertheless, the calculation of the melting temperature of the pure compound in this last DSC curve, using the method of purity determination by DSC, yielded $T_m = 240 \text{ K}$. The results are summarized in Table 1.

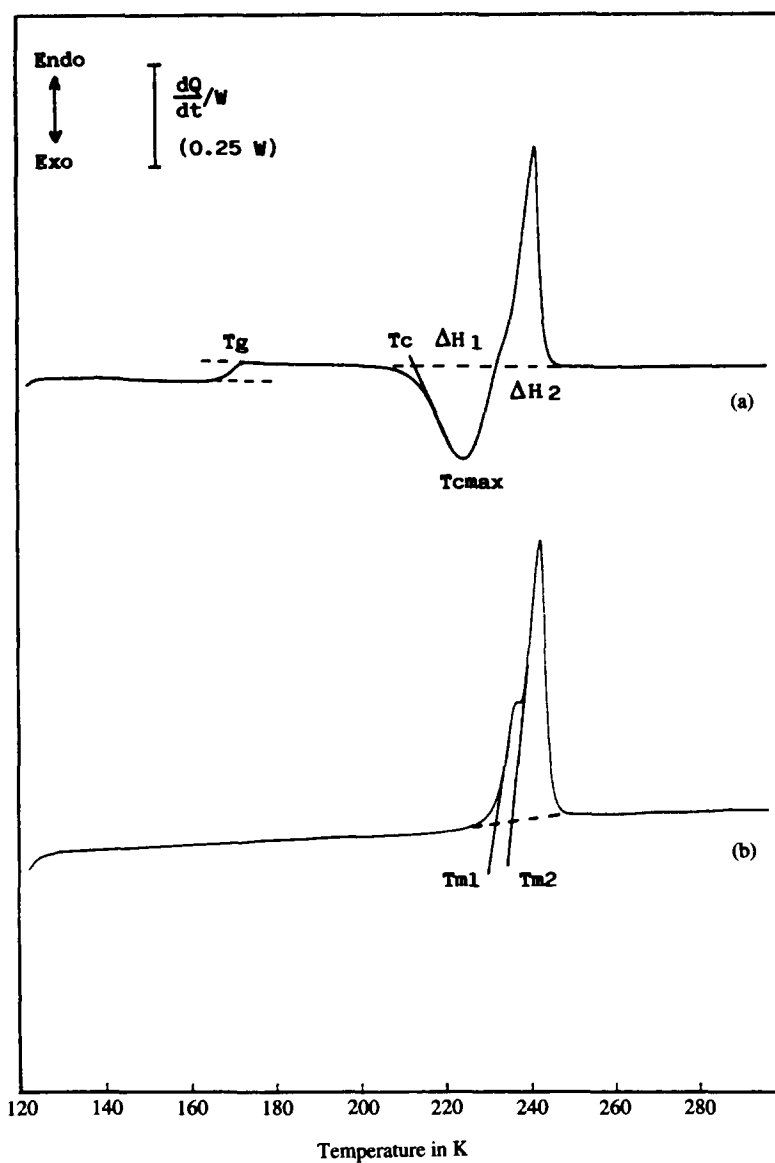


Fig. 3. DSC curves of S(+)-1,2-propanediol purchased from Aldrich: (a) heating scan at 2 K min^{-1} following quench. $T_g = 170.3 \text{ K}$, glass transition temperature; $\Delta C_p = 1.02 \text{ J K}^{-1} \text{ g}^{-1}$, heat capacity change at T_g ; $T_c = 213 \text{ K}$, crystallization temperature, $T_{cmax} = 225 \text{ K}$, peak temperature of crystallization; ΔH_1 , heat released during partial crystallization; ΔH_2 , heat absorbed during partial melting; $\Delta H_1 = \Delta H_2 = 4900 \text{ J mol}^{-1}$; (b) heating scan at 2 K min^{-1} following annealing at T_{cmax} . Two endotherms appear (I and II) characterized by temperatures $T_{m1} = 231.5 \text{ K}$ and $T_{m2} = 236 \text{ K}$ (programmed cooling rate is 30 K min^{-1}).

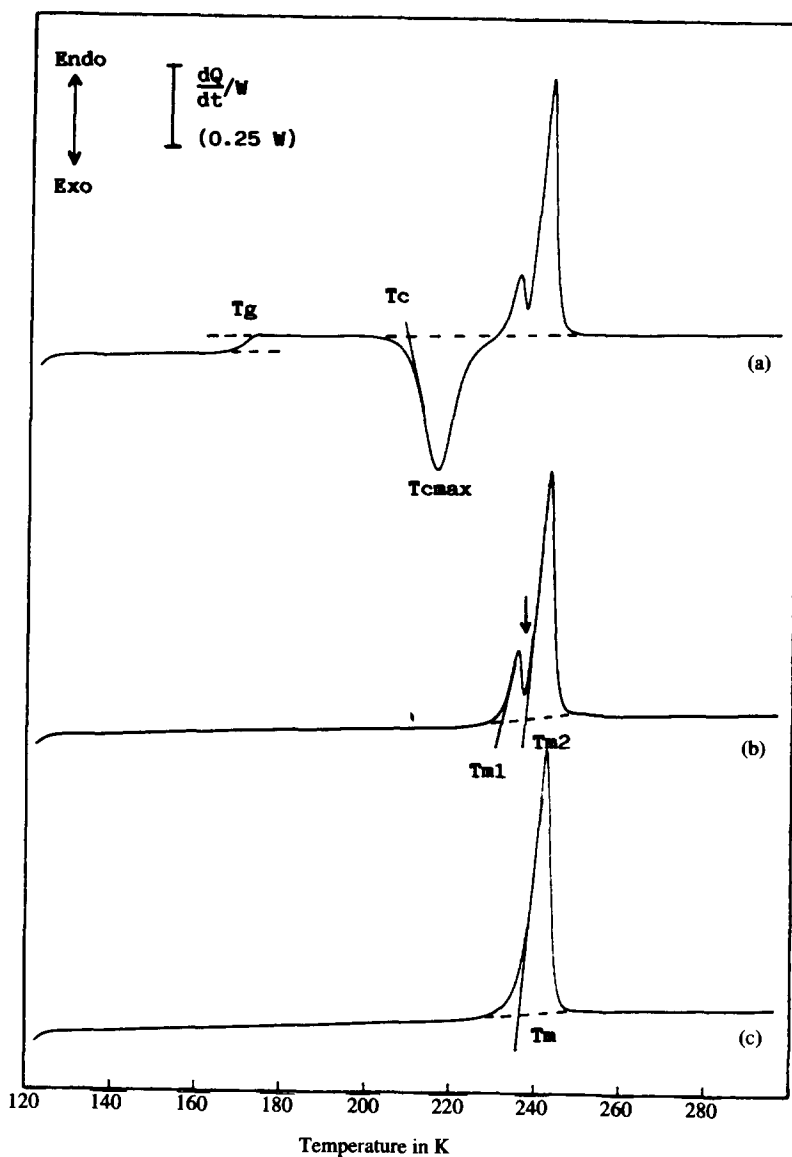


Fig. 4. DSC curves of *S*(+)-1,2-propanediol purchased from Fluka (same DSC curves as for *R*(-)-1,2-propanediol): (a) heating scan at 2 K min^{-1} following a quench. $T_g = 171.3 \text{ K}$, glass transition temperature; $\Delta C_p = 1.28 \text{ J K}^{-1} \text{ g}^{-1}$, heat capacity change at T_g ; $T_c = 209 \text{ K}$, crystallization temperature; $T_{cmax} = 217 \text{ K}$, peak temperature of crystallization; (b) heating scan at 2 K min^{-1} following annealing at T_{cmax} . Two endotherms appear (I and II) characterized by temperatures $T_{m1} = 232 \text{ K}$ and $T_{m2} = 237 \text{ K}$; (c) DSC curve upon reheating (2 K min^{-1}) after interruption of heating scan in (b) at the end of endotherm I (\downarrow). Only one endotherm is observed with melting temperature $T_m = 237 \text{ K}$ (programmed cooling rate 30 K min^{-1}).

Table 1
Thermal behaviour of racemic 1,2-propanediol and of the enantiomers

	(1)					(2)		(3)	(4)	(5)
	T_g /K	ΔC_p /(J K ⁻¹ g ⁻¹)	T_c /K	T_m /K	T_{m2} /K	T_m /K	T_{m2} /K	T_m /K	T_m /K	ΔH /(J mol ⁻¹)
Racemic PD 1,2 Aldrich	171.1	1.22	—	—	—	—	—	—	—	—
S(+) PD 1,2 Aldrich	170.3	1.02	213	—	235	231.5	236	—	—	8400
S(+) PD 1,2 Fluka	171.3	1.28	209	231	237	232	237	237	240	8400
R(-) PD 1,2 Fluka	171.3	1.10	208	231.5	237	231	237	237	240	8400

(1) Heating scan following a quench.

(2) Heating scan following annealing at T_{max} .

(3) Heating scan after interruption of the previous heating scan (2) at the end of endotherm I.

(4) Melting temperature as determined by the DSC purity method.

(5) Heat absorbed in heating scans (2) and (3).

Key: T_g , glass transition temperature (± 0.4 K); ΔC_p , heat capacity change at T_g (± 0.10 J K⁻¹ g⁻¹); T_c , crystallization temperature (± 0.5 K); T_m , T_{m2} , temperatures characterizing endotherm I and II respectively (± 0.5 K); T_{m1} , melting temperature (± 0.5 K in (3)); ΔH , heat absorbed in heating scans (2) and (3) (3% repeatability).

Heating rate 2 K min⁻¹, programmed cooling rate 30 K min⁻¹.

It is interesting to note that the absorbed heat in the final DSC curve (Fig. 4(c)) is equal to that absorbed for endotherm I + endotherm II (Fig. 4(b)).

3.2. Phase diagram

S(+)-1,2-Propanediol and *R*(-)-1,2-propanediol from Fluka were used for the construction of the phase diagram. The composition range studied was $0 \leq x \leq 0.5$, where x is the mole fraction of the (-)-enantiomer. As the phase diagrams of the enantiomers are symmetrical relative to $x = 0.5$, the thermal behaviour in the whole composition range $0 \leq x \leq 1$ can be deduced.

Fig. 5 represents the out of equilibrium phase diagram, illustrating T_g and T_l (liquidus temperature) after annealing experiments were carried out on quenched samples exhibiting crystallization. The out of equilibrium diagram was classified into two regions according to the types of DSC curves, namely, ones that demonstrate a residual glass transition and dissolution and ones that show glass transition only. In Fig. 6 is shown a typical DSC curve demonstrating a residual glass transition and dissolution ($x = 0.045$).

Under our conditions, the concentration dividing these two regions is $x = 0.125$. For this composition, heat released during crystallization and heat absorbed during dissolution in the heating scan following a quench were $< 76 \text{ J mol}^{-1}$ (1 J g^{-1}). Following annealing at $T_{c_{\max}}$, the second heating scan showed a residual glass transition and dissolution with an endothermal heat effect of 3200 J mol^{-1} . For $0 < x \leq 0.125$, the annealing experiments did not lead to crystallization of the whole sample, as was the case for the enantiomers, since a residual glass transition was detected (down to $x = 0.02$) followed by dissolution. For $0.125 < x \leq 0.5$, no sign of crystallization was observed on heating after a quench nor on heating after annealing experiments had been carried out. The annealing experiments were performed in the temperature range corresponding to crystallization peaks for $0 < x \leq 0.125$ (221–226 K).

3.3. Thermal behaviour of 1,3-propanediol and 2-methyl-1,3-propanediol

Quenched 1,3-propanediol partially crystallizes on heating, as in the case of the enantiomers. Annealing experiments at $T_{c_{\max}}$ were required to crystallize the whole sample. The melting temperature, as determined from the DSC curve, is $246 \pm 0.5 \text{ K}$. The determination of the melting temperature of pure 1,3-propanediol using the purity method gave 249 K (the alcohol had a purity of 98% by mass as purchased from the supplier). Crystallization, on the other hand, was not observed for 2-methyl-1,3-propanediol. The results are summarized in Table 2.

4. Discussion

1,2-Propanediol enantiomers have a melting temperature of 240 K, as determined by the DSC purity method, and their melting heat was determined as 8400 J mol^{-1} . The splitting into two of the melting endotherm (Figs. 3(b) and 4(b)) led us, in a first stage,

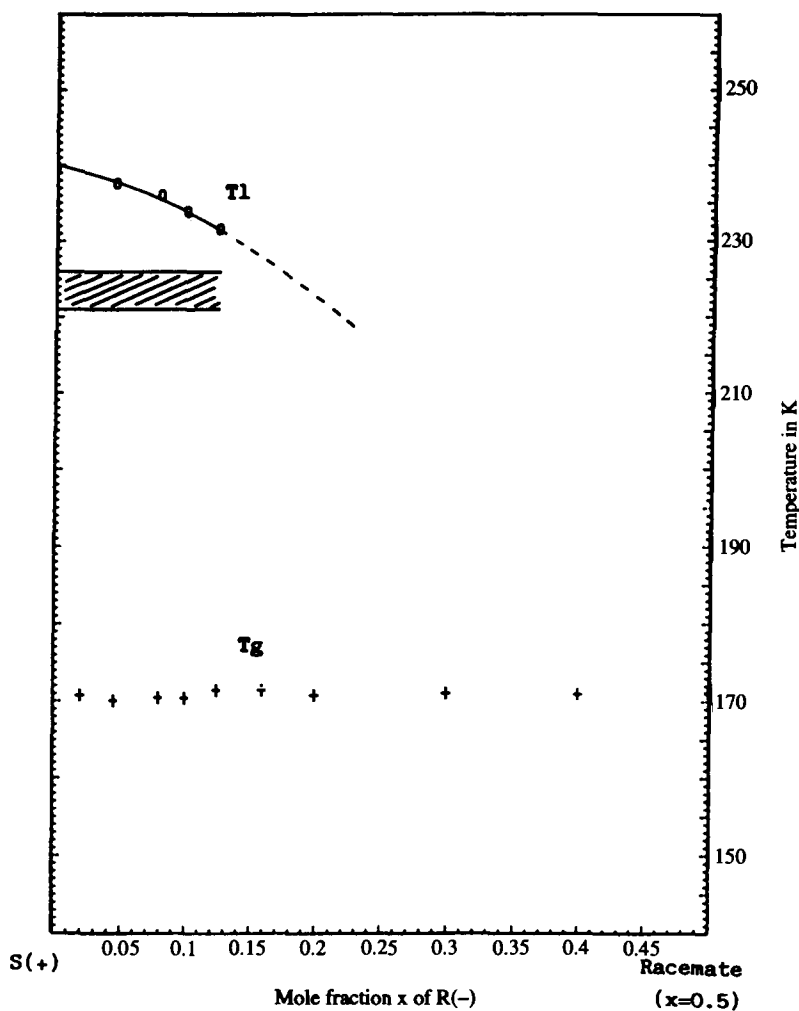


Fig. 5. Out of equilibrium $R(-)$ -1,2-propanediol- $S(+)$ -1,2-propanediol phase diagram for $0 \leq x \leq 0.5$ (x is the mole fraction of $R(-)$ -1,2-propanediol) as obtained following annealing at $T_{c_{max}}$. T_g is the glass transition temperature, T_l is the liquidus temperature. Two types of behaviour: for $0 < x \leq 0.125$, glass transition and dissolution are observed; for $0.125 < x \leq 0.5$, only glass transition is observed. (-----) extrapolation of liquidus curves; (▨▨▨▨) annealing temperature range for quenched samples (221–226 K).

to assume that endotherm I was due to the presence, in non-negligible quantities, of the opposite enantiomer in a given enantiomer, thereby leading to the existence of a eutectic in the solid state. If this were the case, the amplitude of endotherm I should have increased when the mole fraction x of $R(-)$ -1,2-propanediol in mixtures increased in the range $0 < x \leq 0.125$ in the phase diagram (Fig. 5). Because this is not observed, the hypothesis is unlikely to be true. Although the origin of endotherm I has still to be

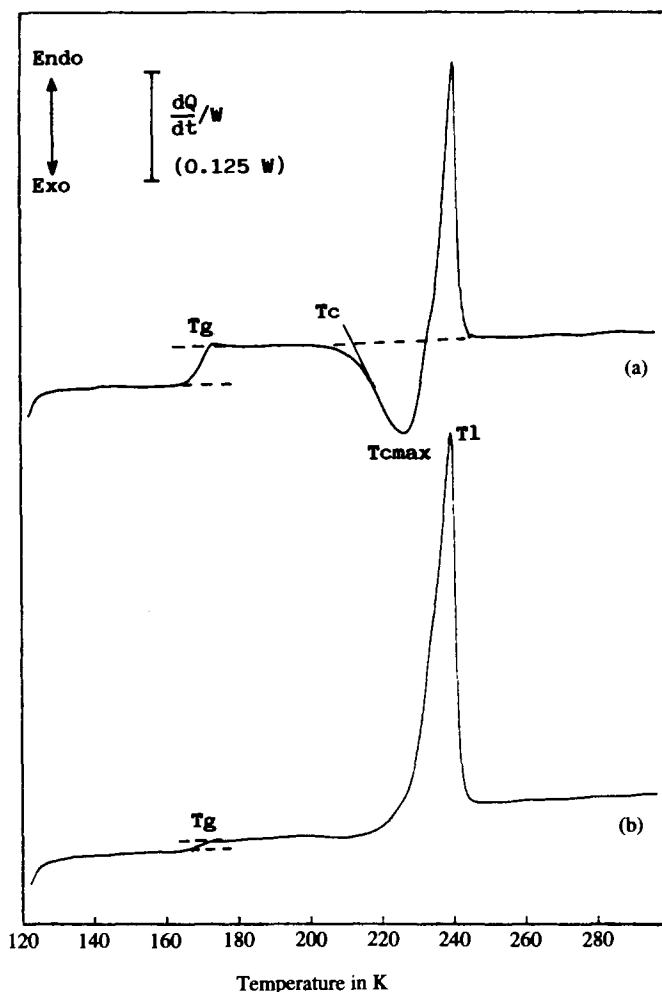


Fig. 6. DSC curve of $x = 0.045$ mixture (x is the mole fraction of $R(-)$ -1,2-propanediol): (a) heating scan at 2 K min^{-1} following a quench. $T_g = 171.0 \text{ K}$, glass transition temperature; $\Delta C_p = 1.29 \text{ J K}^{-1} \text{ g}^{-1}$, heat capacity change at T_g ; $T_c = 212 \text{ K}$, crystallization temperature; $T_{cmax} = 226 \text{ K}$, peak temperature of crystallization; (b) heating scan at 2 K min^{-1} following annealing at T_{cmax} . $T_g = 170.0 \text{ K}$, residual glass transition; $\Delta C_p = 0.34 \text{ J K}^{-1} \text{ g}^{-1}$, heat capacity change at T_g ; $T_l = 236.5 \text{ K}$, liquidus temperature of the dissolution event (programmed cooling rate 30 K min^{-1}).

clarified, it is likely that impurities present in the enantiomers (other than the opposite enantiomer) should be considered in order to explain its nature.

In the phase diagram in Fig. 5, crystallization of the (+)-enantiomer only is observed for $0 < x \leq 0.125$, and hence partial crystallization occurs. Part of the sample does not crystallize and vitrifies at low temperatures (Fig. 6). For $0.125 < x \leq 0.5$, no crystallization takes place even when annealing experiments are performed in the temperature

Table 2
Thermal behaviour of racemic 1,3-propanediol and 2-methyl-1,3-propanediol

	(1)		(2)				(3)
	T_g/K	$\Delta C_p/(\text{J K}^{-1} \text{g}^{-1})$	T_c/K	T_m/K	T_m/K	$\Delta H/(\text{J mole}^{-1})$	T_m/K
1,3 PD	150.4	0.87	195	245.6	246	11400	249
2 methyl 1,3 PD	167	1.03	–	–	–	–	–

(1) Heating scan following a quench.

(2) Heating scan following annealing at $T_{c_{\max}}$.

(3) Melting temperature as determined by the DSC purity method.

Key: T_g , glass transition temperature (± 0.4 K); ΔC_p , heat capacity change at T_g ($\pm 0.10 \text{ J K}^{-1} \text{ g}^{-1}$); T_c , crystallization temperature (± 0.5 K); T_m , melting temperature (± 0.5 K in (2)); ΔH , melting heat (3% repeatability).

Heating rate 2 K min^{-1} , programmed cooling rate 30 K min^{-1} .

range 221–226 K (peak crystallization temperatures on heating for $0 < x \leq 0.125$). This means that neither nucleation of the enantiomers nor that of an addition compound has taken place for $0.125 < x \leq 0.5$. In other words, no embryos have been able to attain the critical size needed to observe spontaneous crystal growth from nuclei.

From the experimental results, two equilibrium phase diagrams have been envisaged. If the racemate ($x = 0.5$) were a conglomerate in the equilibrium phase diagram as described in the introduction, (Fig. 1), it would be possible to calculate the eutectic temperature from the melting heat and the melting temperature of the enantiomers using the simplified classical Schröder–Van Laar equation (Eq. (1)). The validity of Eq. (1) is based mainly upon the condition of the ideality of the enantiomer mixtures in the liquid state and their immiscibility in the solid state.

Eq. (1) is written as follows

$$\ln x = \frac{\Delta H_f^E}{R} \left(\frac{1}{T_f^E} - \frac{1}{T} \right) \quad (1)$$

where x is the mole fraction of the more abundant enantiomer, T is the liquidus temperature of the mixture, T_f^E and ΔH_f^E are the melting temperature and melting heat of the pure enantiomer and R is the gas constant.

The calculation for $x = 0.5$ yields a eutectic temperature $T_E = 206$ K. This temperature is close to the hypothetical melting temperature 213 K as reported in [13] for racemic 1,2-propanediol. The equilibrium phase diagram in the composition range $0 \leq x \leq 1$ would be the one drawn in Fig. 7 with the liquidus curves calculated using Eq. (1). However, crystals of the (+)-enantiomer do form in mixtures with $0 < x \leq 0.125$ and hence crystals of the (–)-enantiomer should also form at $T \leq T_E$. In other words, the equilibrium phase diagram should have been obtained for $0 < x \leq 0.125$ in Fig. 5. Instead, only crystallization of the (+)-enantiomer takes place in this composition range and no eutectic is observed. Consequently, the equilibrium phase diagram in Fig. 7 is unlikely.

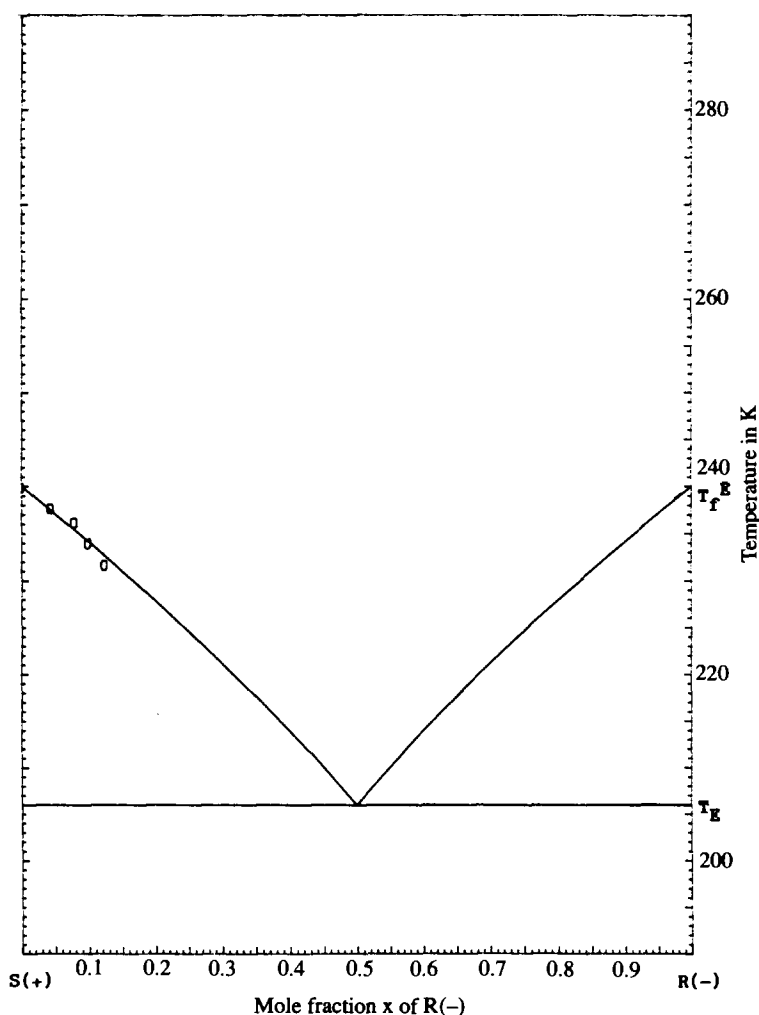


Fig. 7. Tentative $R(-)$ -1,2-propanediol- $S(+)$ -1,2-propanediol equilibrium phase diagram where the racemate ($x = 0.5$) is a conglomerate (x is the mole fraction of $R(-)$ -1,2-propanediol). Experimental liquidus temperatures are indicated by (O). The liquidus curves are calculated using Eq. (1) in the text, $T_m^E = 240$ K, melting temperature of the enantiomers; $T_E = 206$ K, eutectic temperature calculated using Eq. (1) in the text.

A more reasonable equilibrium phase diagram would be one of the type drawn in Fig. 8 for $0 \leq x \leq 1$. In this diagram, the liquidus curves of the enantiomers are limited to the ones observed experimentally, and the racemate is an addition compound. This would point to the existence of a possible eutectic in the equilibrium phase diagram for $x \approx 0.125$ (or $x = 0.875$) and $T \approx 232$ K. Experimentally, no crystallization of the racemate is observed. As a result, a vitrification domain is seen for $0.125 < x < 0.875$ ($E_S E_R$). For the same reason, no eutectic is observed for $0 < x \leq 0.125$ or $0.875 \leq x < 1$.

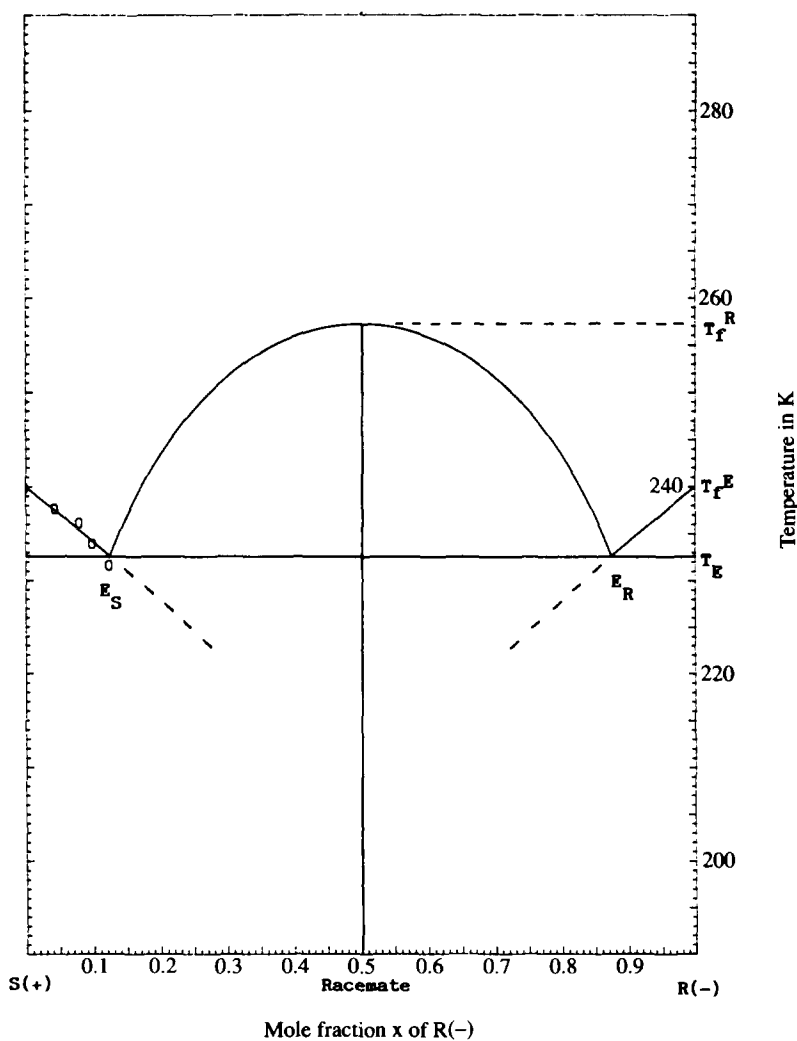


Fig. 8. Tentative $R(-)$ 1,2-propanediol– $S(+)$ 1,2-propanediol equilibrium phase diagram where the racemate ($x = 0.5$) is an addition compound (x is the mole fraction of $R(-)$ 1,2-propanediol). Experimental liquidus temperatures are indicated by (○). The liquidus curves are calculated using Eqs. (1) and (2) in the text. $T_f^R = 257$ K, melting temperature of the racemate using Eq. (2) and the same melting heat as for the enantiomers; $T_f^E = 240$ K, melting temperature of the enantiomers; $T_E = 232.6$ K, eutectic temperature.

For temperatures below the hypothetical eutectic temperature T_E , a metastable thermodynamic equilibrium exists between the crystalline enantiomer and a liquid with a composition given by the extrapolation of the liquidus curves to low temperatures (dashed lines in Fig. 8).

An estimation of the melting temperature of the racemate was made using the Prigogine and Defay liquidus curve equation [28] (Eq. (2)), which is applicable for

phase diagrams in which an addition compound forms (the validity conditions of the latter equation are the same as those for Eq. (1)). Using the eutectic temperature $T_E = 232.6$ K as determined by Eq. (1) for $x = 0.125$ (or $x = 0.875$) and the same melting heat as for the enantiomers yields a congruent melting temperature of 257 K.

Eq. (2) is written as

$$\ln 4x(1-x) = \frac{2\Delta H_f^R}{R} \left(\frac{1}{T_f^R} - \frac{1}{T} \right) \quad (2)$$

where x is the mole fraction of one of the enantiomers, T is the liquidus temperature of the mixture, T_f^R and ΔH_f^R are the melting temperature and melting heat of the racemate and R is the gas constant.

The tentative equilibrium phase diagram in Fig. 8 is drawn using the liquidus curves as calculated by means of Eqs. (1) (for $0 < x \leq 0.125$ and $0.875 \leq x < 1$) and (2) (for $0.125 < x < 0.875$).

5. Conclusion

Crystallization of many liquids is difficult or even impossible. Indeed, the melting temperatures of many liquids are not known. A possible explanation is that these liquids are in fact mixtures of several molecular conformations. This is the case for racemic 1,2-propanediol. Consequently, the nature of these liquids has to be accounted for in phase diagrams. For example, 2-methyl-1,3-propanediol does not crystallize whereas 1,3-propanediol does. It is possible that, in the case of the former compound, the presence of the methyl group leads to the existence of different molecular conformations. This would make its crystallization difficult. In the same way, if a study of glycerol shows that conformations other than the $\alpha\alpha$ conformation in which it crystallizes are present in significant quantities in the liquid phase, this would explain why its crystallization is difficult and undercooling or seeding is required. Consequently, a deeper knowledge of the configurational/conformational structure of liquids will undoubtedly help in better understanding why many liquids do not crystallize and hence only vitrify at low temperatures.

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