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# Composition dependence of the glass transition temperature: Application of Van Laar type equations to the glycerol -1,2-propanediol, glycerol - water and Se–GeSe$_2$ systems

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**Abstract**

The composition dependence of the glass transition temperature *Tg* was studied using differential scanning calorimetry for three different types of binary mixtures. The fit of the *Tg* curves versus composition with equilibrium thermodynamic equations has led to good agreement between experimental and theoretical curves. This surprising result was discussed in terms of molecular organizations in the glassy state.

*Keywords:* Chalcogenide; Equilibrium; Glass; Phase; Polyol; Water

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## 1. Introduction

Studies of the composition dependence of the glass transition temperature *Tg* have been performed on a variety of binary phase diagrams which include mixtures of polymers with plasticizers (lowering of *Tg*) and mixtures of alcohols with water. An empirical relation which has been successfully used in the fitting of the *Tg* curve in different types of binary mixtures was proposed by Jenckel and Heusch [1]:

$$Tg(w) = Tg_1(1-w) + Tg_2 w + K_w(1-w)w \quad (1)$$

where $w$ is the weight fraction of component 2, $Tg_2$ the $Tg$ of component 2, $Tg_1$ the $Tg$ of component 1 and $K_w$ an adjusting parameter. Eq. (1) can be rearranged into:

$$\frac{Tg(w) - Tg_2}{1-w} = -K_w(1-w) + [K_w + Tg_1 - Tg_2] \quad (2)$$

The slope of the graph $(Tg(w) - Tg_2)/(1-w)$ versus $(1-w)$ is equal to $-K_w$ and the intercept to $(K_w + Tg_1 - Tg_2)$. Knowing $Tg_2$ and $K_w$, $Tg_1$ can be determined.

For several systems, Eq. 1 is expressed as:

$$Tg(x) = Tg_1(1-x) + Tg_2 x + K_x(1-x)x \quad (3)$$

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where $x$ is the mole fraction of component 2 and $K_x$ an adjusting parameter.

A second type of empirical equation which has been applied in the fitting of $Tg$ versus composition is [2,3]:

$$Tg(w) = \frac{(1-w)Tg_1 + \mu w Tg_2}{(1-w) + \mu w} \qquad (4)$$

where $\mu$ is an adjusting parameter. Note that Fox [4] has proposed an equation analogous to Eq. (4) where $\mu$ is no longer an adjusting parameter but equal to $Tg_1/Tg_2$. The free volume model provides a theoretical basis for Fox's equation.

Equation (4) is also expressed as a function of mole fraction $x$ of component 2:

$$Tg(x) = \frac{(1-x)Tg_1 + CxTg_2}{(1-x) + Cx} \qquad (5)$$

where $C$ is an adjusting parameter.

Gordon and al. [3] derived an equation using the theory of configuration entropy as first presented by Gibbs and DiMarzio [5] and later Adam and Gibbs [6]. The latter equation gives the composition dependence of the glass transition temperature for binary mixtures which obey the laws of regular solutions:

$$Tg(x) = \frac{(1-x)Tg_1 + xTg_2\left(\dfrac{\Delta Cp_2}{\Delta Cp_1}\right)}{(1-x) + x\left(\dfrac{\Delta Cp_2}{\Delta Cp_1}\right)} \qquad (6)$$

where $\Delta Cp_1$ and $\Delta Cp_2$ are the heat capacity jump at the glass transition for component 1 and 2 respectively.

The aim of the present paper is a contribution to the investigation of the composition dependence of $Tg$ with emphasis laid on a new approach. The applicability of Eq. (1) and Eq. (6) (the most often used equations) to the experimental results in this paper will also be tested. Three systems will be studied: glycerol – 1,2-propanediol, glycerol – water and Se–GeSe$_2$. To our knowledge, the composition dependence of $Tg$ in the glycerol – 1,2-propanediol system is not known (the latter system is in fact a section in a ternary phase diagram since 1,2-propanediol, in the liquid state, is a racemic mixture of two enantiomers [7]). The viscosity of the glycerol – 1,2-propanediol system on the other hand has been studied by Huck and Nakheli [8] over 13 orders of magnitude. The glycerol – water system has been extensively studied [9–12]. Yannas [13], Rasmussen and MacKenzie [14], and Harran [11] used the equation of Jenckel and Heusch (Eq. 1) to fit the $Tg$ curve in the glycerol – water system. The glass transition temperature of water was estimated by extrapolation to zero solute concentration. For their part, Johari and al. [15] and Hallbrucker and Mayer [16] determined the onset glass transition temperature of water as 136 K using DSC. $\Delta Cp$ for water at the glass transition was estimated as 1.6 $JK^{-1}$ $mol^{-1}$ in [16]. Finally chalcogenides glasses and in particular, selenium and germanium mixtures (and their application to lithography), have been the subject of numerous studies [17,18].

## 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 [19]. The calorimeter was flushed with pure, dry argon.

Glycerol was purchased from Aldrich; its purity was 99.5 % by mass. 1,2-propanediol was purchased from Aldrich, its purity was > 99% by mass. Handling of 1,2-propanediol and glycerol was done in a glove box under a dry inert atmosphere (argon). The samples were sealed in aluminium crucibles (40 µl) and weighed inside the glove box. Masses were in the range from 20 to 35 mg. They were quenched in liquid nitrogen, then placed in the calorimeter previously cooled at 140 K. DSC curves were recorded between 140 K and 298 K using a heating rate of 2 K $min^{-1}$.

Se–GeSe$_2$ samples were prepared by Peyroutou and Peytavin in a previous work [18] and supplied to the laboratory. Germanium and selenium powders were from Aldrich (Aldrich gold label). Masses were in the range from 50–60 mg. DSC curves were recorded at a heating rate of 5 K$min^{-1}$. The temperature range studied was from 283 K–773 K.

The glass transition temperature $Tg$ was taken as the inflection point of the calorimetric signal asso-

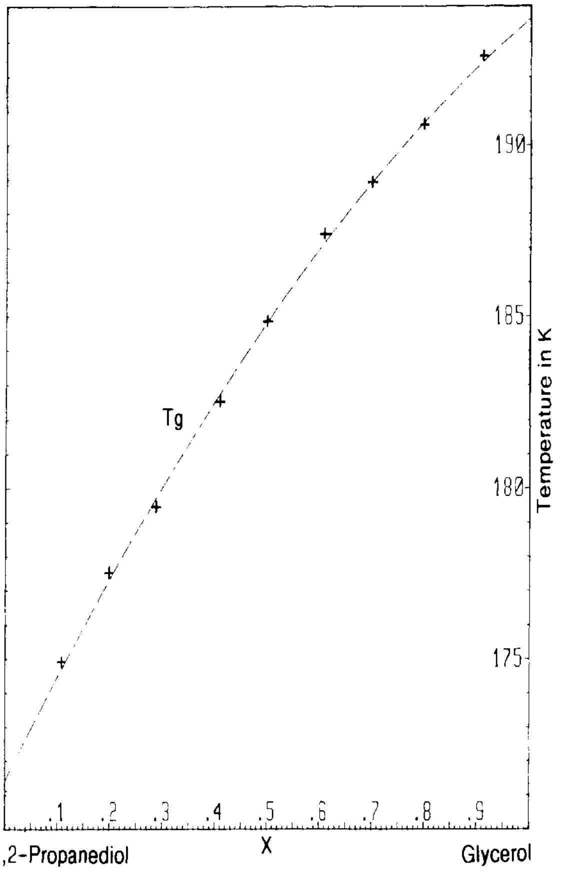

Fig. 1. $x$glycerol–$(1-x)$ 1,2-propanediol system illustrating $Tg$ versus composition. No sign of crystallization was observed (heating rate is 2 K min$^{-1}$ after samples were quenched).

ciated 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 liquidus temperature $T_l$ was taken as the peak of the endothermal dissolution event.

## 3. Results

### 3.1. Phase diagrams

#### 3.1.1. $x$ glycerol – $(1-x)$ 1,2-propanediol

The out of equilibrium $x$ glycerol–$(1-x)$ 1,2-propanediol phase diagram presented in Fig. 1 consists of a glass transition curve in the whole composition range. The glass transition curve is monotonous. No sign of crystallization was observed. The results are summarized in Table 1.

Table 1
$Tg$ as a function of composition in the $x$glycerol–$(1-x)$ 1,2-propanediol system

| Mole fraction $x$ of glycerol | $Tg$/K |
|---|---|
| 0 | 171.1 |
| 0.11 | 174.9 |
| 0.2 | 177.5 |
| 0.29 | 179.5 |
| 0.41 | 182.5 |
| 0.5 | 184.9 |
| 0.61 | 187.4 |
| 0.7 | 189.0 |
| 0.8 | 190.6 |
| 0.91 | 192.6 |
| 1.0 | 193.6 |

#### 3.1.2. $x$ glycerol – $(1-x)$ water

Figure 2 shows the out of equilibrium phase diagram illustrating $Tg$, $T_c$ and $T_l$. Lane's [20] equilibrium phase diagram is presented in full lines. The out of equilibrium diagram was classified into three regions according to the types of DSC curves:

- $0.3 < x \leq 1$: these solutions demonstrate a glass transition only. The $Tg$ moves to progressively lower temperatures as the water content increases.
- $0.1 < x \leq 0.3$: these solutions show a glass transition, crystallization and dissolution. The absolute values of crystallization and dissolution enthalpies are shown in Fig. 3. For $0.15 \leq x \leq 0.3$, crystallization and dissolution enthalpies are equal in the limit of experimental errors: $|\Delta_{\text{cris}}H| \approx \Delta_{\text{diss}}H$. Consequently, only a vitrified phase forms on quenching. For $0.1 < x < 0.15$, dissolution enthalpies are appreciably larger than crystallization enthalpies. This indicates that partial crystallization occurred on quenching.
- $0 < x \leq 0.1$: these solutions show a residual glass transition and dissolution. Crystallization occurred on quenching. On quenching, water congeals in equilibrium with a residual liquid which representative point follows the stable congealing curve. For

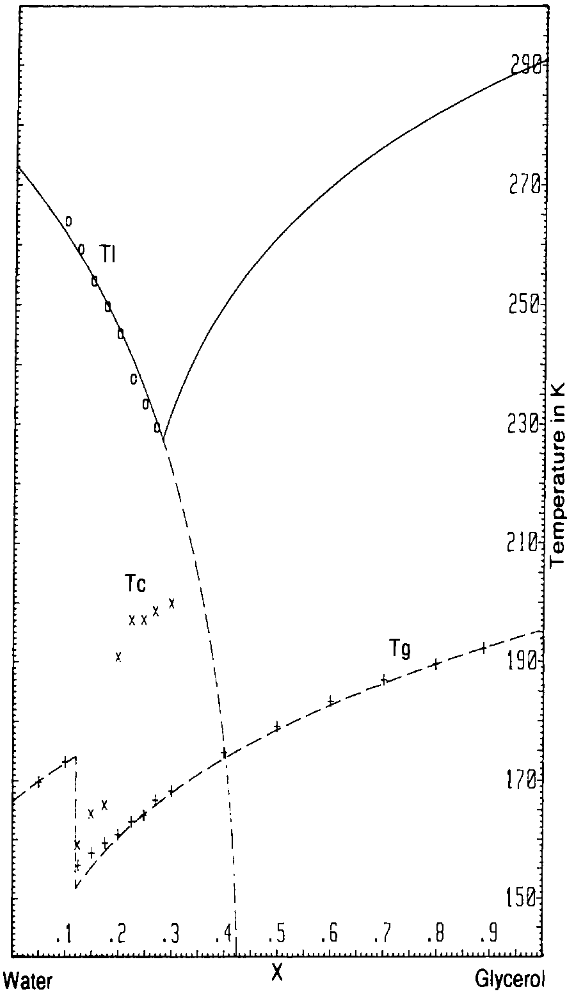

Fig. 2. $x$ glycerol–$(1-x)$ water system. $Tg$ is the glass transition temperature, $T_c$, the crystallization temperature and $T_l$ the liquidus temperature (heating rate is 2 Kmin$^{-1}$ after samples were quenched). Lane's equilibrium phase diagram is presented in full lines.

temperatures below the eutectic (226.6 K), the representative point of the residual liquid follows the metastable congealing curve (in dashed lines). Using the model of associated solutions [21], the congealing curve was defined as an equilibrium between ice and an ideal solution of water, glycerol and monohydrated glycerol. Note that the calculated congealing curve intercepts the $Tg$ curve for $x \approx 0.4$. The $Tg$ of the latter composition is practically equal to the $Tg$ corresponding to $x = 0.1$. This indicates that the ice ⇔ residual liquid equilibrium is virtually preserved until the vitrification of the residual liquid on cooling. Finally, a very weak exotherm (designed often as ante-melting in literature [9,10]) was observed on heating for $0 < x \leq 0.1$ solutions. It corresponds very likely to a minor supplementary crystallization [11].

*The results are summarized in Table 2.*

### 3.1.3. $x$ Se – (1-$x$) GeSe$_2$

The investigation was restricted to the study of the glass transition temperature as a function of composition. The results are shown in Fig. 4 and summarized in Table 3. The interesting feature of Fig. 4 is that the temperature range of the $Tg$ curve is very wide.

Note: in the following sections, the composition range for the $x$ glycerol–$(1-x)$ water system will be restricted to $0.15 \leq x \leq 1$, i.e., to solutions that vitrify completely on quenching.

### 3.2. *Fit of the Tg curve with the equation of Jenckel and Heusch*

The $(Tg(w) - Tg_2)/(1-w)$ versus $(1-w)$ graph (Eq. (2)) must be linear in order to fit the $Tg$ curve with Eq. (1). This was indeed the case for the glycerol – 1,2-propanediol and glycerol – water systems but not for the Se–GeSe$_2$ system. In Figs. 5 and 6 are shown the experimental and calculated $Tg$ curves as a function of the weight fraction w of glycerol for the glycerol – 1,2-propanediol and glycerol – water systems respectively. For the former system (Fig. 5), the best fit was found for $K_w = 6.3$ and $Tg_1$(1,2-propanediol) = 171 K (in perfect agreement with the experimental value). In the case of latter (Fig. 6), the best fit was found for $K_w = -46$ and $Tg_1$(water) = 145 K. This value of the $Tg$ for water is not in good agreement with that found by Rasmussen and MacKenzie (136 K) [14] who also used Eqs. (1) and (2) for aqueous solutions of glycerol. This is despite the fact that these authors used experimental conditions relatively "close" to ours (DTA with a heating rate of 5 Kmin$^{-1}$). One should note however that there is quite a large dispersion in the values of $Tg$ for water in literature. In the following sections, the measured onset $Tg$ of

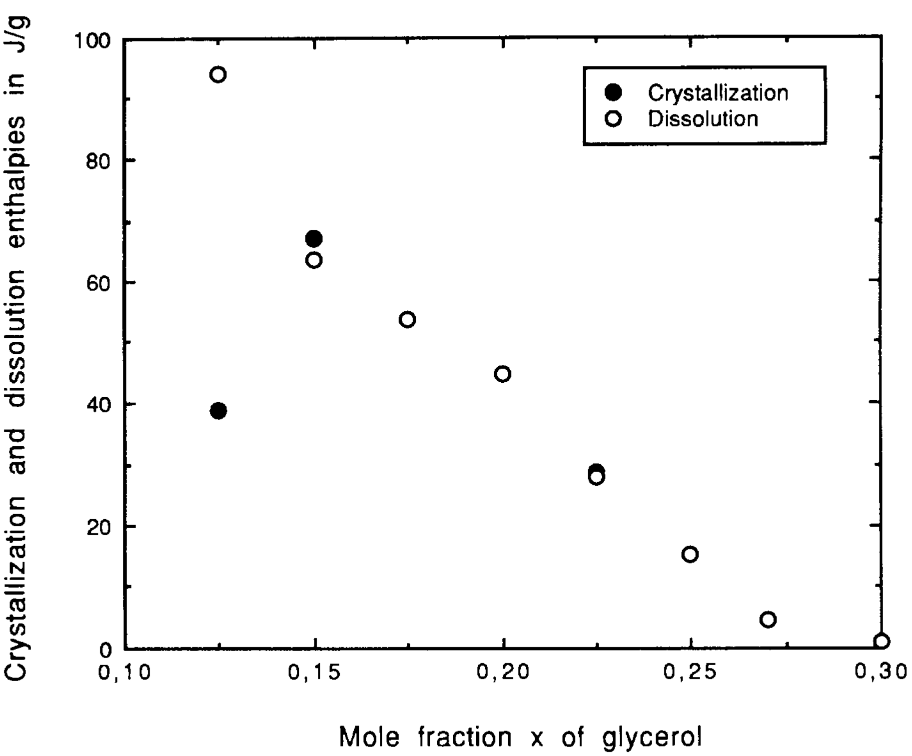

Fig. 3. Crystallization and dissolution enthalpies in the $x$glycerol–$(1-x)$ water system for solutions showing a glass transition, crystallization and dissolution on heating ($0.1 < x \leq 0.3$). For $0.15 \leq x \leq 0.3$, $|\Delta_{\mathrm{cris}}H| \approx \Delta_{\mathrm{diss}}H$ and only a vitrified phase forms on quenching. For $0.1 < x < 0.15$, $|\Delta_{\mathrm{cris}}H| < \Delta_{\mathrm{diss}}H$ and partial crystallization occurs on quenching.

water (136 K) as determined in [15] and [16] will be used.

### 3.3. *Fit of the Tg curve with the equation of Gordon*

The fit of the *Tg* curves with Eq. (6) was not good for the three studied systems. Indeed, the calculated *Tg* curves depend strongly on the value of $\Delta Cp_2/\Delta Cp_1$. In the case of the glycerol – 1,2-propanediol system, the values of $\Delta Cp_1$(1,2-propanediol) and $\Delta Cp_2$(glycerol) are $67 \pm 7$ JK$^{-1}$mol$^{-1}$ and $79 \pm 8$ JK$^{-1}$mol$^{-1}$ respectively hence $\Delta Cp_2/Cp_1 = 1.18 \pm 0.24$. The fit of the *Tg* curve with the latter value was not satisfactory. In the case of the glycerol – water system, the difference between $\Delta Cp_1$(water) (1.6 JK$^{-1}$mol$^{-1}$ [16]) and $\Delta Cp_2$(glycerol) ($79 \pm 8$ JK$^{-1}$mol$^{-1}$) is such that the fitting becomes very questionable. Indeed, the fit of the *Tg* curve in the latter system was very poor. As for the Se–GeSe$_2$ system, the amplitudes of the change in heat capacity in the glass transition range were very weak. This didn't permit a reasonable determination of $\Delta Cp$ for Se and GeSe$_2$ (the calculation of $\Delta Cp$ (Se) from adiabatic calorimetry measurements in [22] gave 14 JK$^{-1}$mol$^{-1}$).

### 3.4. *Fit of the Tg curve with a Ln $x = f(1/Tg)$ function*

Experimental results were fitted with a Ln $x = f(1/Tg)$ equation. This type of equation usually define the thermodynamic conditions of the solubility of a solid in a liquid solution. The results are shown in Figs. 7, 8 and 9 for $x$ glycerol – $(1-x)$ 1,2-propanediol, $x$ glycerol – $(1-x)$ water and $x$ Se–

Table 2
Results relative to the $x$glycerol–$(1-x)$ water system

| Mole fraction $x$ of glycerol | $Tg$/K | $T_c$/K | $T_l$/K | $\Delta_{\mathrm{cris}}H/(\mathrm{J\,g^{-1}})$ | $\Delta_{\mathrm{diss}}H/(\mathrm{J\,g^{-1}})$ |
|---|---|---|---|---|---|
| 0.025 | 170.1 | – | – | – | 224 |
| 0.05 | 170.4 | – | 273 | – | 168 |
| 0.1 | 171.8 | – | 264.3 | – | 113 |
| 0.125 | 155.4 | 159.4 | 259.6 | −39 | 94 |
| 0.15 | 157.6 | 164.7 | 254.3 | −67.2 | 63.6 |
| 0.175 | 159.2 | 166.0 | 250.1 | −53.6 | 53.8 |
| 0.2 | 160.7 | 191.1 | 245.5 | −44.8 | 44.9 |
| 0.225 | 162.9 | 197.0 | 237.9 | −28.5 | 27.9 |
| 0.25 | 164.0 | 197.4 | 233.8 | −15.1 | 15.3 |
| 0.27 | 166.6 | 198.9 | 229.8 | −4.7 | 4.7 |
| 0.3 | 168.2 | 200.2 | ≈225 | ≈ −1 | ≈ 1 |
| 0.4 | 174.6 | – | – | – | – |
| 0.5 | 178.9 | – | – | – | – |
| 0.6 | 183.2 | – | – | – | – |
| 0.7 | 186.8 | – | – | – | – |
| 0.8 | 189.4 | – | – | – | – |
| 0.89 | 192.1 | – | – | – | – |
| 1 | 193.6 | – | – | – | – |

$Tg$: glass transition temperature
$T_c$: crystallization temperature
$T_l$: liquidus temperature
$\Delta_{\mathrm{cris}}H$: crystallization enthalpy
$\Delta_{\mathrm{diss}}H$: dissolution enthalpy

$(1-x)$GeSe$_2$ respectively. The graphs are appreciably linear for the three systems and the best fit is found for:

– $x$ glycerol – $(1-x)$1,2-propanediol

$$\mathrm{Ln}\,x = -\frac{3240}{Tg} + 16.8 \qquad (7.a)$$

– $x$ glycerol – $(1-x)$ water

$$\mathrm{Ln}\,x = -\frac{1507}{Tg} + 7.7 \qquad (7.b)$$

– for $x$ Se–$(1-x)$GeSe$_2$

$$\mathrm{Ln}\,x = \frac{1453}{Tg} - 4.3 \qquad (7.c)$$

### 3.5. *Fit of the Tg curves with Van Laar type equations*

The Van Laar equations define thermodynamic equilibrium between two ideal solutions (liquid – vapour or solid – liquid). In the following section, an attempt will be made to apply Van Laar type equations to the vitrification of a mixture of two components. In the present case, the solid phase would be a "vitrified" solid solution.

For a mixture of two components that vitrifies, the Van Laar type equations would be:

$$y_1 = \frac{e^{\lambda_2}-1}{e^{\lambda_2}-e^{\lambda_1}} \quad x_1 = e^{\lambda_1}\frac{e^{\lambda_2}-1}{e^{\lambda_2}-e^{\lambda_1}} \qquad (8.a)$$

$$y_2 = \frac{e^{\lambda_1}-1}{e^{\lambda_1}-e^{\lambda_2}} \quad x_2 = e^{\lambda_2}\frac{e^{\lambda_1}-1}{e^{\lambda_1}-e^{\lambda_2}} \qquad (8.b)$$

with

$$\lambda_1 = \frac{\Delta H_1}{R}\left[\frac{1}{T} - \frac{1}{Tg_1}\right] \qquad (8.c)$$

$$\lambda_2 = \frac{\Delta H_2}{R}\left[\frac{1}{T} - \frac{1}{Tg_2}\right] \qquad (8.d)$$

In Eqs. (8.a)–(8.d), $x_1$ and $x_2$ would represent the mole fraction of components 1 and 2 in the vitrified solid phase and $y_1$, $y_2$, the mole fraction of compo-

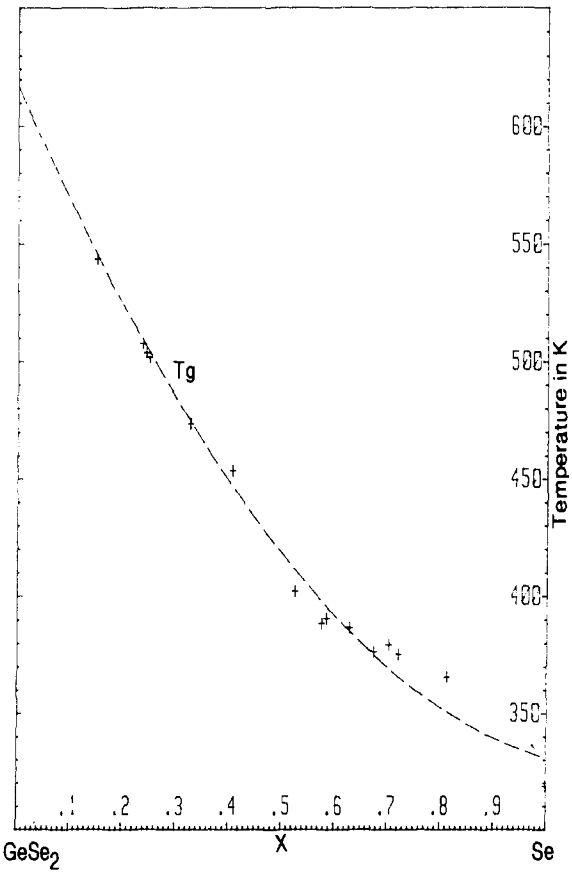

Fig. 4. $x$Se–(1 − $x$)GeSe$_2$ system illustrating $Tg$ versus composition (heating rate is 5 Kmin$^{-1}$).

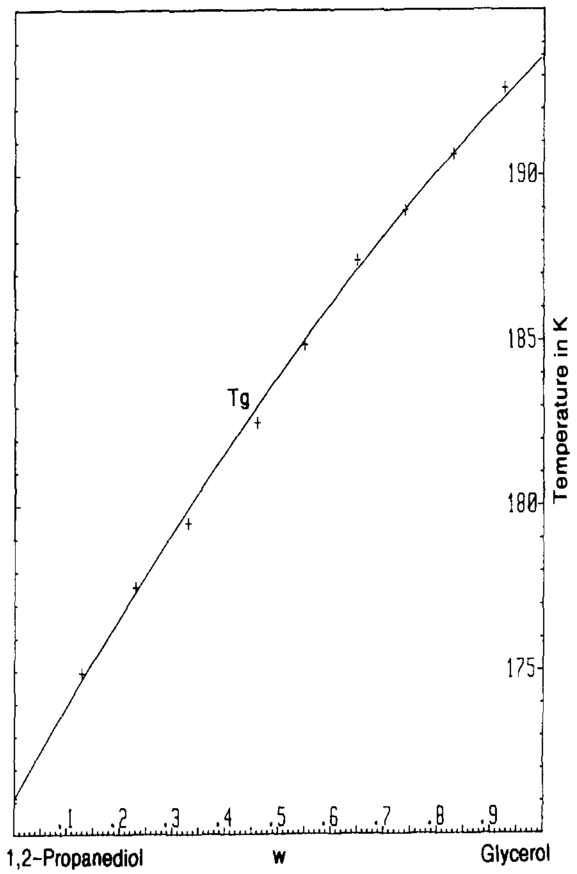

Fig. 5. Fit of the $Tg$ curve (+) with the equation of Jenckel and Heusch (Eq. 1) in the $w$glycerol–(1 − $w$) 1,2-propanediol system ($w$ is the weight fraction of glycerol).

Table 3
$Tg$ as a function of composition in the $x$Se–(1 − $x$)GeSe$_2$ system

| Mole fraction $x$ of Se | $Tg$/K | Mole fraction of Se | $Tg$/K |
|---|---|---|---|
| 0 | 623.7 | 0.576 | 387.7 |
| 0.151 | 543.6 | 0.585 | 389.9 |
| 0.237 | 506.9 | 0.629 | 385.7 |
| 0.243 | 503.1 | 0.674 | 376.5 |
| 0.249 | 501.1 | 0.703 | 379.1 |
| 0.326 | 473.1 | 0.721 | 375.1 |
| 0.407 | 453.1 | 0.813 | 365.2 |
| 0.525 | 401.6 | 1 | 318.1 |

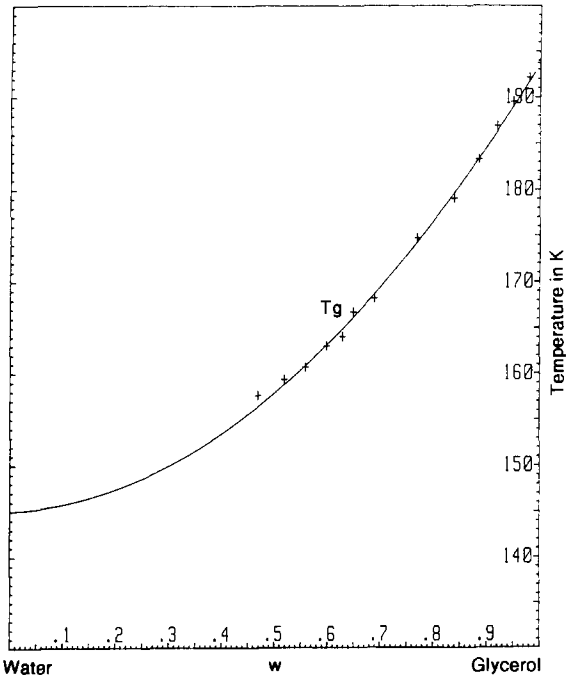

Fig. 6. Fit of the $Tg$ curve (+) with the equation of Jenckel and Heusch (Eq. 1) in the $w$glycerol–$(1 - w)$ water system ($w$ is the weight fraction of glycerol).

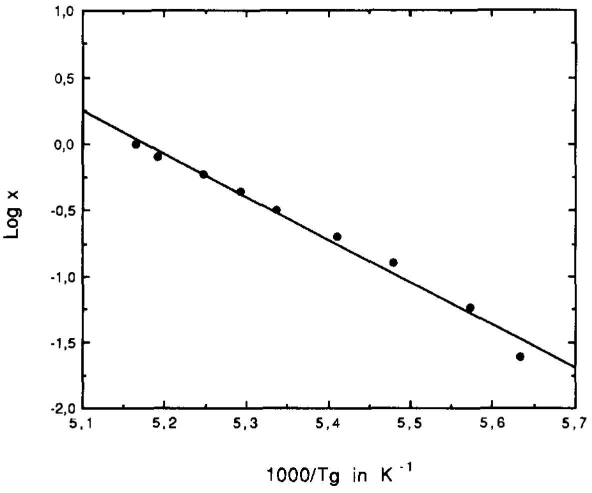

Fig. 7. Fit of the $Tg$ curve with a Ln $x = f(1/Tg)$ function in the x glycerol - (1-x) 1,2-propanediol system. The best fit was found for Ln $x = -(3240/Tg) + 16.8$.

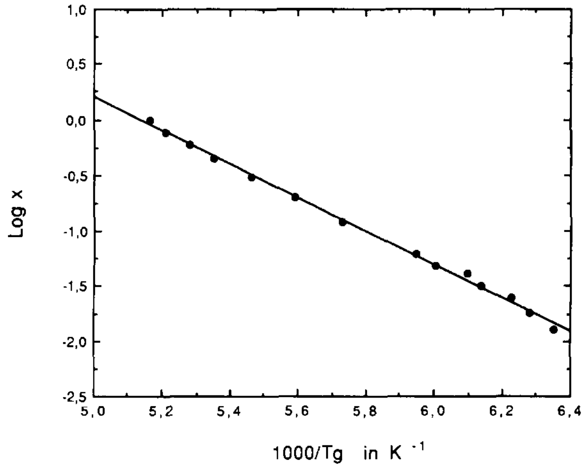

Fig. 8. Fit of the $Tg$ curve with a Ln $x = f(1/Tg)$ function in the $x$glycerol–$(1 - x)$ water system. The best fit was found for Ln $x = -(1507/Tg) + 7.7$.

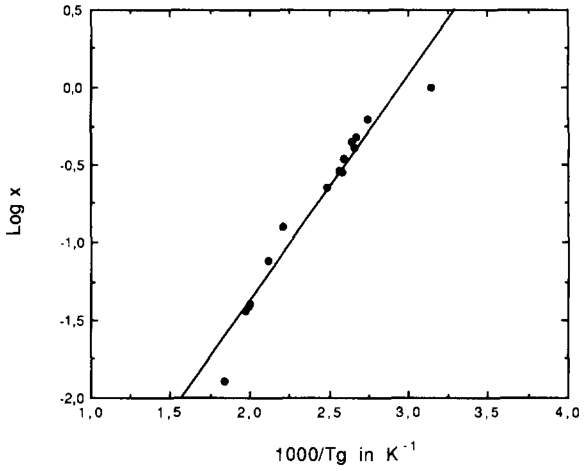

Fig. 9. Fit of the $Tg$ curve with a Ln $x = f(1/Tg)$ function in the $x$Se–$(1 - x)$GeSe$_2$ system. The best fit was found for Ln $x = (1453/Tg) - 4.3$.

nents 1 and 2 in the liquid phase. $Tg_1$ and $Tg_2$ are the glass transition temperatures of components 1 and 2. $R$ is the gas constant and $\Delta H_1$, $\Delta H_2$ would be the change in enthalpy in the glass transition range for components 1 and 2. The value of $\Delta H$ for glycerol was taken from previous measurements performed in the laboratory [23] on the glass transition of glycerol by step heating DSC. The study showed that the glass transition of glycerol involves two contributions to the apparent heat capacity:

– a change in true heat capacity from that of the liquid to that of a solid (glass) on cooling (or the opposite on heating)

– a temperature and time dependent enthalpic effect $\Delta H$ (configurationel or excess heat capacity) very likely due to molecular associations. $\Delta H$ was estimated as 460 J mol$^{-1}$ (5 J g$^{-1}$). A simulation of the calorimetric signal, in good agreement with experimental results, was made assuming the following equilibrium transformation of molecular associations in the glass transition range:

$$A_n \rightleftarrows nA$$

with $A_n$ associations or clusters of the A species (A representing a molecule of glycerol for example). It is the formation (cooling) and destruction (heating) of the associated species in the glass transition range that involves an enthalpic effect $\Delta H$. In this view, the concentration (or size) of associated species (clusters) in the glass transition range on cooling would be such that the congealing of the structure of the liquid occurs leading to the obtaining of a solid (glass) at lower temperatures (this would explain the change of true heat capacity from that of a liquid to that of a solid since degrees of freedom have been frozen in). On heating, the progressive destruction of these molecular associations takes place in the glass transition range.

In the present study, the values of $\Delta H$ for 1,2-propanediol and water are not known, thus representing fitting parameters in Eqs. (8.a)–(8.d). As for the $x$Se–$(1-x)$GeSe$_2$ system, the value of $\Delta H$ for selenium was chosen arbitrarily and that for GeSe$_2$ chosen to give the best fit. In Figs. 10, 11 and 12 are shown the experimental $Tg$ curves and the calculated "solidus" and "liquidus" curves using Eqs. (8.a)–(8.d) for the $x$ glycerol $-(1-x)$ 1,2-propanediol, $x$ glycerol–$(1-x)$ water and $x$ Se–$(1-x)$GeSe$_2$ systems respectively. Harran's results are also presented in the case of the $x$ glycerol–$(1-x)$ water system and fitted with Eqs. (8.a)–(8.d) (the latter author used a heating rate of 20 K min$^{-1}$ hence a $Tg$ curve shifted to higher temperatures compared to our results).

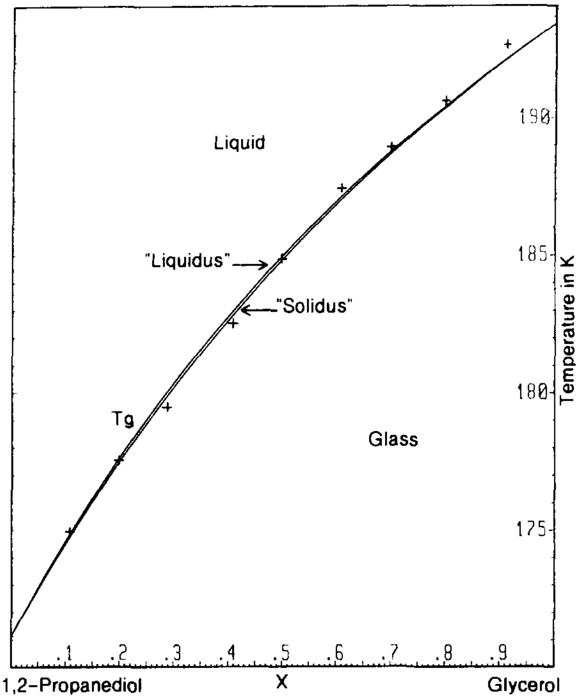

Fig. 10. Fit of the $Tg$ curve (+) with Van Laar type equations (Eqs. (8.a)–(8.d)) in the $x$glycerol–$(1-x)$ 1,2-propanediol system. Theoretical curves were calculated using: $Tg_1$(1,2-propanediol) = 171.1 K, $Tg_2$(glycerol) = 193.6 K, $\Delta H_1$(1,2-propanediol) = 250 J mol$^{-1}$ (fitting parameter), $\Delta H_2$(glycerol) = 460 J mol$^{-1}$ (taken from [23]).

## 4. Discussion

The equation of Jenckel and Heusch (Eq. (1)) is empirical with $K_w$ representing a fitting parameter rather than a parameter with a physical significance. Eq. (1) has been largely used in literature and will not be discussed further here. Eqs. (8.a)–(8.d) usually define thermodynamic equilibrium between a solid solution and a liquid solution while Eqs. (7.a)–(7.c) give the solubility of a solid in a liquid solution. These sets of equations surprisingly seem to lead to very satisfactory agreement between experimental and theoretical $Tg$ curves as a function of composition. Note that Koos [24] has given the following relation between $Tg$ and the mean bonding per atom m in the case of $x$Se–$(1-x)$Ge glasses:

$$Tg = \exp(3.42\,\mathrm{m} - 3) \qquad (9)$$

Equation (9) has a somewhat similar form to Eqs. (7.a)–(7.c). If the application of Eqs. (7.a)–(7.c) or (8.a)–(8.d) to glasses has indeed a possible meaning, then the results suggest that the studied glasses obey thermodynamic equilibrium laws. More particular-

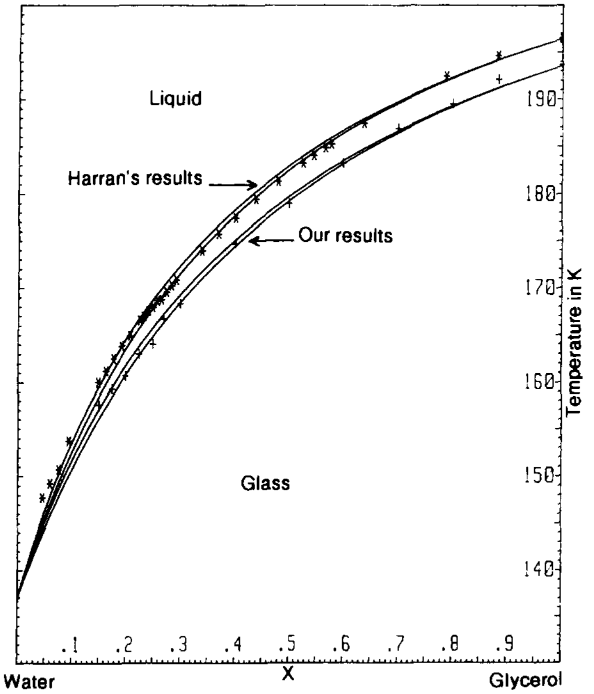

Fig. 11. Fit of the $Tg$ curves with Van Laar type equations (Eqs. (8.a)–(/8.d)) in the $x$glycerol–(1 − $x$) water system: With our results (+), the theoretical curves were calculated using: $Tg_1$ (water) = 136 K (taken from [15,16]), $Tg_2$(glycerol) = 193.6 K, $\Delta H_1$(water) = 108 J mol$^{-1}$ (fitting parameter), $\Delta H_2$(glycerol) = 460 J mol$^{-1}$ (taken from [23]). With Harran's [11] results (∗), the theoretical curves were calculated using: $Tg_1$(water) = 136 K ([15, 16]), $Tg_2$(glycerol) = 196.5 K, $\Delta H_1$(water) = 96 J mol$^{-1}$ (fitting parameter), $\Delta H_2$ (glycerol) = 460 J mol$^{-1}$ [23].

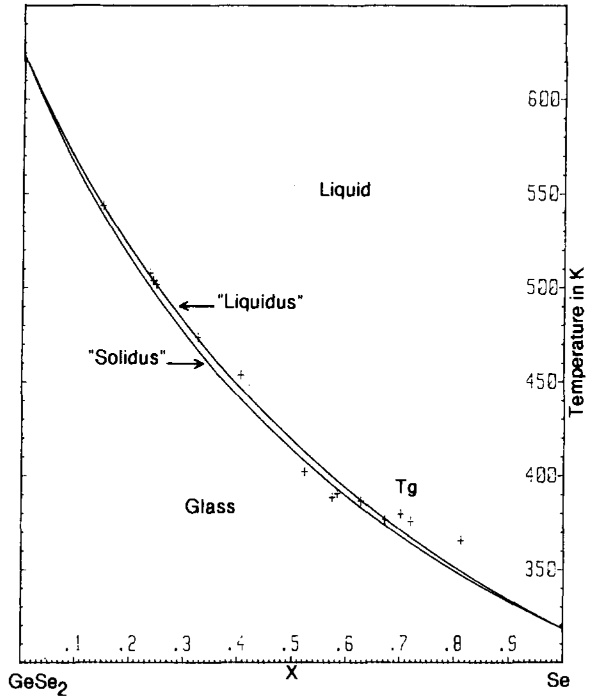

Fig. 12. Fit of the $Tg$ curve (+) with Van Laar type equations (Eq. (8.a)–(8.d)) in the $x$Se–(1 − $x$)GeSe$_2$ system. Theoretical curves were calculated using: $Tg_1$(GeSe$_2$) = 623.7 K, $Tg_2$(Se) = 318.1 K, $\Delta H_1$(GeSe$_2$) = 400 J mol$^{-1}$ (arbitrarily chosen value), $\Delta H_2$(Se) = 430 J mol$^{-1}$ (fitting parameter).

ly, Eqs. (8.a)–(8.d) imply that, on cooling a liquid mixture of two components that doesn't crystallize, a temperature dependent equilibrium occurs between the liquid and very likely organized molecular species (molecular associations or clusters) in the glass transition range resulting in vitrification at lower temperatures. This progressive "phase transition" would have to be in reality, not only temperature dependent, but also time dependent (kinetics) since glass transition is highly dependent on cooling and heating rates. Schwartz [25] showed for example, from experimental results on cooling and using thermomechanical analysis on polymer materials, that the extrapolation of cooling and heating rates to zero rate gives the same glass transition temperature $Tg$. This could also reveal a thermodynamic equilibrium in the glass transition range between liquid phase and glassy phase. Because $Tg$ in this work was determined after quenching and heating at 2 Kmin$^{-1}$, it is clear that the temperature dependant equilibrium is shifted because of kinetic effects. A more rigorous approach would have been to use the $Tg$ corresponding to zero cooling and heating rates (by extrapolation) in the fitting with Eqs. (7.a)–(7.c) and (8.a)–(8.d).

Note that the idea of molecular organizations in the glassy state was already introduced by Tammann in 1933 [26] and more recently by Hoare [27] who, through a computer simulation, studied the thermodynamic and mechanical stability of amorphous packings (clusters). The latter author has put forward the idea that the glass transition on heating may be considered as the "melting" of amorphous clusters present in the glassy state. The small size of these clusters ($\approx 100$ units) would cause the lowering of the "melting" temperature (due to surface phenomena) of what would be the "bulk" from "$T_m$" to $Tg$. One can think that "melting" occurs, in fact, in a temperature range (glass transition range) because of a distribution in the size of clusters. Hoare's view partially joins the percolation theories of the glass transition [28].

## 5. Conclusion

The application of equations defining thermodynamic equilibrium between a solid solution and a liquid solution on one hand and the solubility of a solid in a liquid solution on the other to the vitrification of different binary mixtures has led to good agreement between experimental and theoretical $Tg$ curves as a function of composition. More particularly, the results obtained with Van Laar type equations point to a possible temperature dependent thermodynamic equilibrium between liquid phase and glassy phase in the glass transition range. In this view, the origin of glass would be thermodynamic with an important kinetic component. This does not fit in however with the current trends on glass transition whereby glass is described as solely kinetic in origin.

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