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VITREOUS STATE DECOMPOSITION STUDY IN SOME AQUEOUS POLYALCOHOLS SOLUTIONS

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<u>Résumé</u> - Le but de ce travail est de présenter une étude expérimentale des conditions de stabilité de l'état vitreux obtenu après trempe à 77 K avec des solutions de glycérol et de 1,2-propanediol. Cette étude a été réalisée à l'aide de mesures de frottement intérieur et d'observations par diffusion aux petits angles et de diffraction des rayons X. En pratiquant des maintiens isothermes, il a été possible de mettre en évidence deux types de décomposition de cet état vitreux :

- une décomposition impliquant la formation de cristaux de glace avec trois domaines de température dans lesquels on a pu distinguer un processus de nucléation, un processus de nucléation et de croissance avec transformation de la glace cubique en glace hexagonale, un processus de coalescence des cristaux de glace hexagonale.

- une décomposition de l'état vitreux initial en deux phases vitreuses l'une ayant une concentration en eau plus élevée que l'autre.

<u>Abstract</u> - The aim of this work is to present an experimental study of the stability of vitreous state obtained after quenching at 77 K in the case of both aqueous glycerol and 1,2-propanediol solutions. This study has been performed by means of internal friction measurements and X ray observations, i.e., X ray diffraction and small angle X ray scattering. By means of annealing treatments, it has been possible to point out two mechanisms for the decomposition of vitreous state :

- first, involving ice crystallization with three temperature domains corresponding to (i) nucleation (ii) nucleation and growth (where cubic to hexagonal ice transformation occurs) (iii) Ostwald ripening mechanisms are evidenced.

- second, involving a vitreous state being decomposed into two vitreous phases having a different water concentration.

INTRODUCTION

Ice nucleation and crystallization process play a very important role in many circumstances. For instance, meteorological works (1,2) are concerned since precipitations in clouds are conditionned by the formation of ice nuclei on the top of clouds where the temperature is very low. On the other hand, cryobiologists are also concerned by these phenomena since ice crystallization during cooling or rewarming of living cells is generally considered as the most important factor of injury (3). In order to minimize this crystallization, cells are put into cryoprotective mixtures such as glycerol, dimethylsulfoxide (DMSO), or more complex alcohols solutions. The role of such solutes, is to lead, during cooling to a vitreous state for the whole solution (4). Boutron and Kaufmann (5) have proposed the definition of some criteria to characterize the stability of the vitreous state obtained after quenching. In previous works (6,7) two aqueous glycerol and 1,2-propanediol solutions have been studied by means of three different techniques : internal friction measurements, X ray diffraction and small angle X ray scattering. Four temperature ranges have been distinguished as nucleation, growth and Ostwald ripening are successively detected. The aim of this work is to study the various microstructures obtained in these different temperature ranges. The choice of alcohol-water system has been determined by the easiness with which it is possible to observe a given microstructural evolution.

EXPERIMENTAL TECHNIQUE

Experimental results here presented have been obtained with the three following techniques :

1) Internal friction measurements

Internal friction corresponds to an energy dissipation in a solid when it is submitted to cyclic stresses (8). In our measurements, an inverted torsional pendulum is used. A torque is applied to the specimen and the oscillation frequency is about 1 Hz. Measurements were performed during the decrease of the amplitude of oscillations by means of logarithmic decrement (9). Solutions studied are injected in a porous matrix (punice) which constitutes the specimen. This technique has been previously described (6). Specimens are quenched into liquid nitrogen and the measured maximum cooling rate is about 1000 K mn⁻¹. The inelastic behaviour of specimens is studied versus temperature from 77 K. The heating rate is about 0,3 K mn⁻¹.

2) Small angle X ray scattering (SAXS)

Small angle X ray scattering measurements have been made with an apparatus composed of : -a 12 KW generator with a copper rotating anode

- a monochromator which selects the K \propto ray (1,54 Å)

- a sample hold in which the specimen is introduced in the liquid state ; afterwards, the specimen is quenched to liquid nitrogen temperature, the cooling rate is about 250 K mn⁻¹. A temperature regulation maintain the sample at a given temperature found between 77 to 273 ± 2 K during 24 hours at least.

- a linear detector associated with a minicomputer for the spectra recording. The beam is pin-hole collimated.

The minimum time for spectrum recording is about 5 minutes. The angular domain of investigation is between q = 0,03 to q = 0,4 Å⁻¹, where q is a wave-vector. Spectra were afterwards studied following a method previously described (10).

3) X ray diffraction

Diffraction observations are made by transmission with the same apparatus. It is possible to remove the linear detector along a large angular domain $(2\theta = \pm 60^{\circ})$ and for each detector position, the examined angular domain is about 20°. The detector position is exactly determined by use of a standard sample such as sulphur. Exposition times are about 30 s or more.

VITREOUS STATE FORMATION

For both aqueous glycerol and 1,2-Propanediol solutions quenched from room temperature to 77 K, the internal friction spectrum versus temperature exhibits two peaks in the case of intermediate concentration (about 50 % w/w) as shown by the figure 1.



These peaks may be related to vitreous transitions : the first peak corresponds to vitreous transition of a part of initial vitreous mixture obtained after quenching. During this transition, ice crystallization occurs and the solute concentration of the

Figure 1 Internal friction spectrum and period of pendulum oscillation versus temperature :

(a) 50 % (w/w) glycerol concentration

(b) 40 % (w/w) 1,2-propanediol concentration

vitreous residue increases. Then, the second peak is related to the vitreous transition residue. These experiments have been carried out for all the concentration range. Figure 2 shows that three concentration ranges have been evidenced : for the higher concentration, only one peak appears since a vitreous stable state is obtained for the whole solution. For the lower concentration the decomposition of the vitreous state occurs during cooling. And so, the second peak



is observed above. The intermediate cases have been described above and are studied more precisely now.

Figure 2 System glycerol-water 50 \$ (w/w) Evolution of the peak A and B temperature versus temperature :

- 🕷 peak A
- 🔺 and 🔹 peak B

The dashed line corresponds to values of Tg from reference (12).

VITREOUS STATE DECOMPOSITION BY ICE CRYSTALLIZATION

Three domains have been previously pointed out (7) :

- near the eutectic temperature, nucleation is difficult but, growth is easy. - close to 200 K, nucleation and growth occurs simultaneously and Ostwald ripening begins quickly.

- near about 170 K, only the nucleation process occurs and nuclei appear progressively and their dimension does not increase with time.

1) Near the eutectic temperature

In order to avoid ice crystallization during rewarming from 77 K to the final temperature, the mixture has been directly cooled from room temperature. Figure 3 shows the diffraction patterns obtained for the system glycerol-water (50% w/w).



The three peaks corresponding to hexagonal ice, i.e. $(001)_h$, $(002)_h$ and $(101)_h$ are clearly observed. The height of these peaks indicates that only hexagonal ice is formed during isothermal treatment. The ice microcrystal dimension is about 80 to 85 Å in these experimental conditions.

<u>Figure 3</u> System glycerol-water 50 % (w/w). Diffraction pattern obtained after cooling from room temperature to about 220 K and annealing treatment at this temperature (100 s). (without substraction of background).

2) <u>Close to 200 K</u>, the diffraction patterns obtained at 203 K in the case of the system glycerol-water (50% w/w) are plotted in figure 4. The first recording A shows the simultaneous presence of both cubic and hexagonal ice (60 and 40 % respectively). During Ostwald ripening, cubic ice disappears progressively. When hexagonal and cubic ice amounts are equal, the dimension of ice microcrystals is about 120 Å.

3) <u>Close to about 170 K</u>, the figure 5 shows the diffraction patterns obtained at 163 K in the case of the glycerol-water system (50 % w/w). The vitreous state illustrated by the figure 5 A is progressively decomposed (figure 5B and 5C) : a very large diffraction peak appears. This peak corresponds to a sum of three peaks : (111)_c, (002)_h and (100)_h. The amount of hexagonal phase remains constant during this annealing (about 30 %). In this case, the microcrystal dimension is about 50 Å.



Figure 4 Système Glycerol-Water 50% (W/W). Diffraction patterns obtained after rewarming at 203 K during isothermal annealing treatment. A: 50 s B: 200 s

C: 1500 s D: 4000 s.

J 1500 S D 14000

Τ,



Figure 5 Système Glycerol-water 50 % (w/w). Diffraction paterns obtained after :

- A : quenching at 77 K
- B : rewarming to 163 K and annealing treatment during 2000 s.
- C : annealing treatment during 6 hours at 163 K.

(without substraction of background).

DECOMPOSITION OF VITREOUS STATE INTO TWO VITREOUS PHASES

In the case of aqueous 1,2-propanediol-water solution (40 % w/w) a new vitreous state decomposition mechanisms have been point out. Figure 6 shows the evolution of the diffraction pattern obtained during an annealing at 163 K. The amorphous ring is progressively transformed and after about one hour, two rings are clearly observed.



Figure 6 System 1,2-Propanediol 40% water 60 % (w/w). Diffraction patterns obtained at 163 K. A : After quenching to 77 k After annealing treatment at 163 K : B : 19 mn ; C : 58 mn ; D : 840 mn D : 860 mn at 163 K followed by a rewarming to about 180 K.

This fact is in accordance to the shift of the amorphous ring to higher angle when the water concentration increases. Thus, it may be concluded that, at this temperature, the mixture is decomposed into two vitreous phase. In order to differentiate this vitreous decomposition phenomenon from ice crystallization phenomenon as previously described, this annealed mixture has been rewarmed to 180 K. At this temperature, ice crystallization occurs (figure 5E). The principal diffraction peak appears between the two amorphous ring.

A small angle X ray scattering experiment has been carried out in a way to determine the dimension of these two vitreous phases. From this experiment, it is possible to say that (i) no precise interface exist between these two phases. (ii) the microstructure may be described as a concentration fluctuation with a wave length of about 23 Å (determined from the position of the scattering ring).

DISCUSSION AND CONCLUDING REMARKS

The values of thermodynamical parameters of cubic and hexagonal ices are very close (11). The interfacial energy δ_h and the bulk energy change ΔG_v^h are slightly higher than respectively δ_h and ΔG_v^c . Moreover it has been demonstrated (7) that the ratio $\Delta G_v^c / \Delta G_k^h$ decreases as temperature increases. So in agreement with experimental data the following analysis can be made :

- when ice crystals are big enough, hexagonal ice constitutes the final and stable phase (see for example Ostwald ripening phenomenon).

- during nucleation these two phases can be formed simultaneously but closer T_E the decomposition is produced, easier the hexagonal phase is formed (following the decrease of the ratio $\Delta G_v c / \Delta G_v h) \cdot$

- on the contrary when the temperature decomposition decreases, the crystal nuclei become smaller and cubic ice formation becomes preponderant.

- when the nuclei become very small, interfacial energy is preponderant. In order to minimize this one, undistinct interface formation is necessary, as indicated by spinodal decomposition theory. So concentration fluctuations are observed. Their amplitude is sufficiently important to say that the initial mixture is decomposed in two vitreous phases. This fact is really observed in the case of the 1,2-propanediol-water system.

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COMMENTS

P. BOUTRON

Have you compared qualitatively and quantitatively your X-ray observations of two amorphous phases in wholly amorphous 1-2 propanediol solutions with the calorimetric glass transition analysis by Mac Farlane in Cryo-Letters ?

Answer :

It is not possible to compare our results to those of Mac Farlane. In fact, due to the relatively low cooling rate used by this author, the mixture obtained after quenching is not wholly amorphous. X-ray experiments carried out with the same concentration show that it is impossible to avoid ice formation even with a quicker cooling rate than that used by Mac Farlane. So, direct comparison are difficult.