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STRUCTURAL EFFECTS IN THE ELECTROLYTES GLASS (LiCl)$_x$H$_2$O AND THE NUCLEATION OF METASTABLE PHASES


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Résumé - L'intérêt des électrolytes aqueux pour la compréhension de l'état vitreux est montré par la diffusion ou la diffraction de neutrons et par D.S.C. Sur deux gammes de compositions, le verre formé ne cristallise pas et un verre avec deux Tg différentes est obtenu. L'effet endothermique observé par D.S.C. pendant Tg, est attribué à un réarrangement du verre. L'effet thermique, se produisant dans le liquide très au-dessus de Tg, est probablement dû au réarrangement des molécules d'eau.

Abstract - The interest of aqueous electrolytes for the understanding of the glassy state is shown by neutron scattering or neutron diffraction and Differential Scanning Calorimetry (D.S.C.). In two ranges of composition the formed glass does not crystallize, and a glass with two different Tg is shown. The overshoot as observed by D.S.C. during Tg is attributed to a reordering of the glass. The thermal effect occurring in the liquid well above Tg is probably due to a rearrangement of the water molecules.

I - INTRODUCTION

Aqueous electrolytes are very interesting for the fundamental study of glass formation since they demonstrate a large variety of situations as a function of the nature of solute and its concentration (deep eutectics, multiple compounds, systems with two Tg's, strong undercooling of some liquidus lines...). These arise because of the competing forces between solvated ions and water. The experimental conditions are particularly favourable for Differential Scanning Calorimetry, and non equilibrium phase diagram lines are obtained at constant heating rates on quenched vitreous samples. Combined with neutron diffraction and small angle scattering, D.S.C. is effective for investigating the domains of glass and undercooled liquid metastability as well as the nucleation of microheterogeneities and the identification of the crystallization products (references 1, 2, 3, 4, 5, 6).

II - GLASS WITHOUT CRYSTALLIZATION

If we consider, for example the LiCl-H$_2$O phase diagram given in figure 1, there are two concentration ranges where strong undercooling of the liquidus is easily achieved and where a glass to liquid transition is observed at Tg on warming without crystallization, a conclusion confirmed by neutron diffraction.
These ranges of composition have been established by the metastable liquidus line. The ice line can be experimentally determined using the change in heat capacity during Tg and the thermal effect occurring when ice crystallizes. (figure 2) (reference 7).

The first glassy phase lies between the ice and the LiCl-3H2O branches, and the glass between the LiCl-5H2O and the LiCl-2H2O branches. These lines define two eutectics below the glass transition, the temperature being not yet determined. A transition is therefore expected in the vitreous state at low temperature. A possible explanation of this fact is that there is competition between the ions to create one of several crystalline phases in which the water molecules are incorporated. A stable crystalline phase is not formed because of the lack or excess of H2O molecules, so that the stable form is glassy state.

Figure 2 (LiCl,D2O 10%)

- Differences between neutron diffraction spectra at 140.4 K at different stabilization times and the spectra in the glassy state. (The glass being annealing 41 hours at 139 K).

- The structure of D2O ice (Ic) is given for identification.
III - REORDERING OF GLASS BELOW Tg

Tg and Tc have been measured as shown at x=10.9 (figure 3). A striking fact is that the D.S.C. shows no overshoot at Tg in the ranges where the glass does not crystallize. On the other hand, if the sample is annealed below Tg, the overshoot increases. At this concentration neutron diffraction shows that cubic ice is formed (figure 2). The same phenomena is observed at x=0.14 where no crystallisation occurs. The overshoot is then interpreted as being due to the destruction of the ordering of the glass.

Figure 3

IV - TWO Tg GLASS

Let us focus now on the concentrations between LiCl-5H2O and LiCl-3H2O which are well-defined compounds (9). Here two Tg's have been identified. They might have been produced by a phase separated solid but (i) the amplitude of the specific heat variation at each Tg is a function of concentration (see the DSC curve on figure 4 and the Tamman diagram on figure 5), and (ii) the absence of microheterogeneity revealed by neutron small angle scattering experiments seem to contradict this (8).

We are then left with two possibilities: either the initial glass goes to a phase separated undercooled liquid or to a liquid + glass mixture. This leads to a question: is Tg a single phenomenon or the sum of a number of transformation, physical or chemical, occurring in the glass or in the liquid?
V - LIQUID-LIQUID TRANSITION

The existence of two thermal effects (exo - endo) in the liquid phase near a peritectic line may represent a change in the arrangement of the liquid (figure 6). This is consistent with the interpretation of the thermal effect occurring at $T_g$. 
VI - CONCLUSION
A combination of careful calorimetric data and structural investigations lead to a wealth of information on these apparently complex systems: the system LiCl-H$_2$O has been well defined and it shows a great variety of behaviour.

The effect of impurities can be kept to a minimum, due to the simplicity of the compounds involved and to the ease of obtaining the glassy state. However, a proper description of the interaction between the hydration spheres is necessary if the detailed behaviour of the glassy state is to be fully understood.

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