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Crystallisation of undercooled aqueous solutions: Experimental study of free dendritic growth in cylindrical geometry

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Abstract

This paper reports a study of crystallisation kinetics in small volumes of undercooled water–MPG (monopropylene glycol) mixture. The experimental cell is a vertical cylinder (height 5 mm, diameter $2r_e = 7.5$ mm); its bottom section is closed by a Plexiglas disc that transmits light from the lower part of the cylinder to a high-speed digital camera. Photographic recordings allow the determination of the crystal growth rate. When the antifreeze mass fraction is below 25 wt%, crystallisation is clearly divided into two stages: the growth of dendritic crystals in the undercooled solution followed by the passage of the interdendritic solidification front. Dendrite growth induces a sudden temperature increase in the mixture, while the passage of the interdendritic solidification front determines the time at which sensible heat effects again predominate. The results show that the dendrite growth rate is an increasing function of the degree of undercooling and a decreasing function of the antifreeze mass fraction.

Keywords: Dendrites; Freezing; Undercooling; Solidification; Phase transition; Aqueous solution; Antifreeze

1. Introduction

Water–antifreeze mixtures are widely used as secondary refrigerants in refrigeration and air-conditioning systems, thus minimizing the quantity of environmentally harmful primary refrigerants and confining them to a restricted area. Monopropylene glycol (MPG) is one of the most commonly used antifreezes, either in liquid solution or in two-phase liquid–ice mixture as a phase-change secondary refrigerant. This latter technique raises the possibility of exploiting the latent heat of ice to increase the apparent heat capacity of the mixture, thus improving the overall efficiency of the system. Understanding the phenomena involved during the process of crystallisation of these aqueous solutions is useful in preventing the bursting of pipes [1] and in controlling ice production in heat exchangers, an issue particularly relevant to systems that produce ice starting from an undercooled solution [2].

The objectives of this paper are to synthesise information of the literature about the freezing mechanisms of water–antifreeze mixtures and to complement them with an experimental study of crystallisation kinetics in undercooled water–MPG mixtures. This study is restricted to small volume samples in a cylindrical geometry and we focus on the dependence of dendrite growth rate on undercooling degree and on antifreeze mass fraction.

Section 2 gives a brief outline of the physics of crystallisation of undercooled solutions. The experimental set-up is described in Section 3 and the results obtained for the global solidification process are detailed in Section 4. The dependence of dendrite growth rate on undercooling degree and on antifreeze mass fraction is discussed in Section 5, and conclusions are given in Section 6.

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Nomenclature

c_p	mass heat capacity ($\mathrm{J\,°C^{-1}\,kg^{-1}}$)
L_f	latent heat of solidification ($\mathrm{J\,kg^{-1}}$)
r	radius (m)
t	time (s)
T	temperature (°C)
x	mass fraction ($\mathrm{kg\,kg^{-1}}$)
y	relative position (%)
ΔT	degree of undercooling (°C)

Greek symbol

v	velocity of dendrites growth ($\mathrm{mm\,s^{-1}}$)

Subscripts

a	antifreeze
c	beginning of crystallisation
e	external (wall)
eq	thermodynamic equilibrium
f	freezing
i	initial
l	liquid
r	relative
s	solid

2. Freezing mechanism of undercooled solutions

Experimental and theoretical work on solidification since the 1950s have been analysed and summarised by Müller-Krumbhaar and Kurz [3], Papon et al. [4] or Huppert [5]. Crystallisation is a phase-transition phenomenon, governed by the laws of thermodynamics, heat transfer, and kinetics, that proceeds in two stages: nucleation and crystalline growth. Nucleation is the formation of microstructures of a new solid phase in the liquid one. Crystalline growth follows by the addition of molecules or particles on the interface separating the liquid and the most recently formed crystals. Thus, diffusion in the liquid phase of the solidifying compound is one of the most significant phenomena involved in crystallisation. Heat diffusion also has a very important role because crystallisation calls into play the latent heat of solidification. Finally, particle aggregation at the liquid–solid interface depends on interfacial tension [4].

Considering solidification of an initially liquid aqueous solution, one can obtain the curves for temperature vs. time shown on the right-hand side of Fig. 1 (for a 15 wt% monopropylene glycol–water mixture). The graph on the left-hand side of Fig. 1 represents the evolution of temperature and composition of the liquid and solid phases in the MPG–water phase diagram, assuming that they are in thermodynamic equilibrium. Note that, considering the small temperature range we are interested in, the solute always remains in liquid phase and the solidus is assumed strictly vertical [5]. The liquid–solid transition can be divided into four stages [1,6]:

- Between *a* and *b*: sensible cooling stage during which the mixture remains liquid in a thermodynamically stable state; the temperature is above that of solid–liquid equilibrium $T_{eq}(x_{a,i})$ [1].
- Between *b* and *c*: sensible cooling stage during which the mixture is undercooled in a thermodynamically unstable state described as metastable. The temperature is below the solid–liquid equilibrium temperature $T_{eq}(x_{a,i})$.
- Between *c* and *d*: steep temperature increase between T_c and the maximum temperature of crystallisation T_{mc}. This temperature increase characterises the return to thermodynamic equilibrium accompanied by latent heat release associated with ice formation. As for most of aqueous solutions, the vertical solidus in the MPG–water phase diagram (Fig. 1) implies that the solid phase is exclusively made of ice crystals [1,5]. Note that, due to the increase in solute concentration in the residual liquid (linked to the appearance of ice), the maximum temperature of crystallisation of binary mixtures is necessarily below the solid–liquid equilibrium temperature of the initial mixture $T_{eq}(x_{a,i})$ [7].
- Between *d* and *e*: the mixture is still cooled through the vessel walls. The temperature variations are small due to the high apparent heat capacity of the solidifying solution. Then (after point *e*), the mixture is almost completely solidified and sensible effects again predominate: the apparent heat capacity is low and the temperature decrease is steep [8].

2.1. Undercooling

Most liquids crystallise only if they pass through an undercooled state [4], which corresponds to the persistence of liquid, free of solid crystals, at temperatures below the transition point T_{eq} defined by the liquidus (between *b* and *c* in Fig. 1). In the undercooled state, some nuclei of the solid phase appear in the liquid, but they are not large enough to induce crystal growth in the entire system. Once a nucleus reaches the critical size, crystallisation occurs at a temperature T_c below T_{eq}. The degree of undercooling is defined as the difference between these two temperatures (1)

$$\Delta T = T_{eq} - T_c \tag{1}$$

Values of T_c are controlled by stochastic phenomena and depend on sample volume, presence of foreign bodies, thermal history and cooling rate [9,10].

The influence of solutes on aqueous mixture undercooling is not clearly known. We observe that liquid antifreezes like MPG (monopropylene glycol) or MEG (monoethylene glycol) can prevent nucleation, probably by limiting inter-