Measurement of the induction time of water freezing

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It has been found that the freezing of water involves an induction period which can be affected by surface-active compounds.

It is known that many heterogeneous processes can be preceded by an induction period. As a rule, these induction periods can be shortened or prolonged by appropriate additives. For example, the induction periods of scaling (deposition of mineral salts, such as calcium carbonate and sulfate, barium sulfate, *etc.*),[1–3] cathodic deposition of metals and alloys,[4,5] pitting of metals[6–8] and the formation of gas hydrates[9,10] can be affected by adding various compounds, known as inhibitors of the corresponding processes. This possibility is of considerable theoretical and practical importance as it enables one to control the rates of the above processes by adding relatively small amounts of inhibitors without affecting the thermodynamics of the processes ('kinetic inhibition').

Water freezing is a well-studied process of great importance in nature and technology (where it is usually an undesirable process which is combated by various methods, *e.g.* in the fight against icing and in creating antifreezes for diverse cooling systems). The freezing of water is usually combated by the thermodynamic method, *i.e.* by decreasing the equilibrium freezing point by the addition of considerable amounts (up to 50% or even more) of various organic or inorganic compounds (glycols, alkaline and alkaline-earth metal chlorides, *etc.*). It is also known that the drop in the freezing point of water can be changed by the addition of a small of a surfactant, *e.g.* sodium dodecylsulfate.[11] However, in some cases it would be sufficient just to retard water freezing by slowing down the nucleation of ice crystals (*i.e.* by creating an induction period). As far as we know, such an approach to the study of ice formation has not been reported.

As a heterogeneous process, ice nucleation and growth should be affected by the adsorption of surfactants on ice seeds and on growing crystals. Although Nechaev and co-authors[12,13] found that an ice surface has a negative charge at pH > 3, its properties (*e.g.* its hydrophobicity) are as yet unclear. Thus, it is unclear what type of additives adsorbed on such surfaces can effectively prevent water freezing and ice nucleation. Therefore, it was of interest to test whether the process of interest is actually affected by different types of surfactant. These experiments should determine the induction time as a measure of the process kinetics. Therefore, the purpose of the present study was to propose a simple method for estimating the induction time of water freezing and to find out what type of chemical compounds affect this process.

For this purpose, we elaborated a simple set-up (Figure 1). The set-up consists of a glass cell cooled with a cryostat; the cell is equipped with a thermometer, a thermocouple connected to a X–Y recorder, a magnetic stirrer and an inlet for inserting an ice seed crystal.

The measurements were conducted as follows. The cell was filled with an aqueous–organic liquid (20 v/v % aqueous DMF) with mp −6.5 °C. Circulation of the heat-carrying liquid and the magnetic stirrer were started, and the temperature of the liquid was monitored using the thermometer. When −7.0 °C, *i.e.*, 0.5 °C below the freezing point of the reference solution, was reached, the recording the thermocouple signal *versus* time was began, and an ice seed crystal was simultaneously introduced. After a period depending on the solution composition, ice nucleation occurred, which could be observed by the appearance of flaky crystals of ice in the solution (which became rather turbid) and by a temperature increase observable both on the thermometer and on the 'thermocouple signal–time' plot (Figure 2*a*). Under the conditions chosen, the induction time (from the introduction of the seed crystal till the start of the temperature rise) in the non-inhibited (reference) solution was 10±1 s.

Several organic compounds belonging to different classes of surfactants were tested as potential ice nucleation inhibitors using the above approach. The results are listed in Table 1.

It is evident that most of the compounds tested only slightly affect the induction time. For example, the charge of the surfactants do not play a very significant role: both non-ionic (oleic acid, propylene glycol), anionic (oleate) and cationic species (Katamin surfactant) do not increase, or even decrease, the induction time *t*. However, there are compounds that change *t* to a considerable extent. For example, the cationic surfactant γ-aminopropyltriethoxysilane had practically no affect *t* at 1 g dm^{-3}, but higher concentrations were more effective (Figure 2). The increase in *t* observed with this compound is accompanied by one more effect: far fewer ice flakes appear, and the subsequent temperature rise occurs much more slowly. It is possible that the ability of such compounds to form polymolecular adsorption layers in the

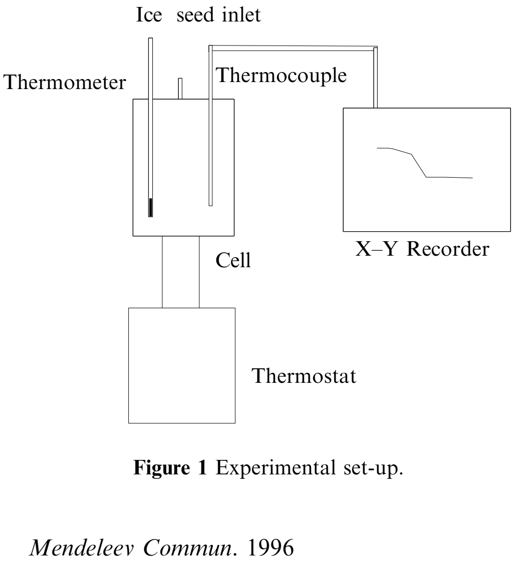

Figure 1 Experimental set-up.

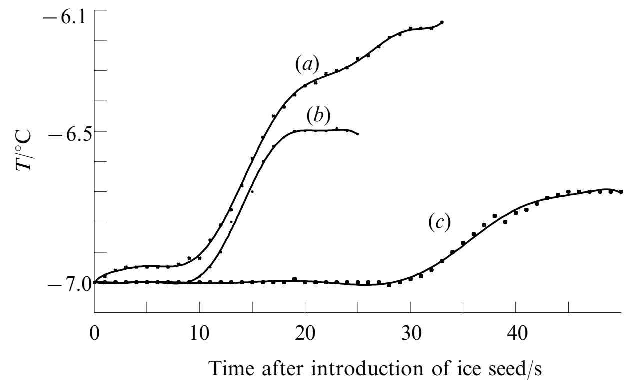

Figure 2 Effect of the surfactant γ-aminopropyltriethoxysilane on the temperature–time dependencies during ice nucleation with (*a*), 0 (reference solution); (*b*), 1; (*c*), 10, g dm^{-3} of surfactant.

Table 1 Induction time t of water freezing.

Compound	Concentration/g dm^{-3}	t/s
Reference solution	0	10±1
Reference solution + hexane	$0+10^a$	10±1
Sodium oleate	1	10±1
Oleic acid	1 (insoluble)	10±1
Oleic acid + hexane	$1+10^a$	9±1
Non-ionic OP-10 surfactant	1	9±1
(oxyethylated phenols)	10	10±1
Katamin-AB (cationic)	1	9±1
	10	8.5±1
Polypropylene glycol (non-ionic)	1	8±2
γ-Aminopropyltriethoxysilane	1	11±2
	5	16±3
	10	~30
Primary amines C_{10-17}	10^a	15±5
Primary amines C_{10-17} + hexane	$10+10^a$	35±9
Tributylamine + hexane	10^a	23±3
Dicyclohexylamine + hexane	10^a	32±5
Lignosulfonates (anionic)	10	10±1

[a] Emulsion.

presence of water,[14,15] which make the surface hydrophobic and hinder ice seed growth, plays a positive role in this case.

It is interesting that several compounds belonging to the one class, namely aliphatic amines, also markedly increase the induction time of water freezing (Table 1). They are effective at rather high concentrations and mainly in the presence of a non-aqueous solvent, hexane, which forms a second phase. Formation of polymolecular adsorption layers is also possible in this case, and incorporation of aliphatic hydrocarbons in them seems to increase the hydrophobic action of the film.

Thus, the accelerated procedure proposed by us has shown that certain additives can significantly affect the kinetics of ice nucleation. This procedure allows screening of compounds affecting the rate of ice nucleation by measurement of the induction time.

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