

Effect of Cetyldimethylbetaine Molecules on Agglomeration and Growth of Ice

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Certain surfactants with suitable brine, such as cetyldimethylbetaine with sorbitol, can inhibit agglomeration of ice particles and thus help disperse ice particles in ice/water slurries, and simultaneously reduce the drag of the slurry in pipes. In this study, the amount of cetyldimethylbetaine (surfactant) molecules remaining in the liquid phase of ice/water slurries was measured, and on the basis of these measurements, models explaining how cetyldimethylbetaine molecules affect ice to inhibit agglomeration of ice particles were proposed.

Certain surfactants with brine, such as poly(oxyethylene-sorbitan-monooleate) with sodium chloride (hereafter called Tween 80 system), cetyldimethylbetaine and sodium oleic acid with sodium chloride (betaine system), and cetyldimethylbetaine with sorbitol (betaine-sorbitol system), can inhibit agglomeration of ice particles and thus help disperse ice particles in ice/water slurries.^{1,2} Among such systems, the betaine-sorbitol system is the most effective in inhibiting crystal growth of ice and in dispersing ice particles in ice/water slurries,² although the mechanism remains unclear. In addition, both the betaine and betaine-sorbitol systems reduce the drag of ice/water slurries in pipes,² because the cetyldimethylbetaine (surfactant) molecules form the network structure of the thread-like micelles and thus reduce the drag.³ The amount of surfactant molecules that are neither adsorbed onto nor incorporated into the ice particles and thus remain in the liquid phase, determines the drag reduction performance, and therefore this amount needs to be accurately measured. In this study, first the amount of cetyldimethylbetaine molecules remaining in liquid phase in ice/water slurries containing the betaine and betaine-sorbitol systems was measured. Then, on the basis of the experimental results, models were proposed to explain how the betaine and betaine-sorbitol systems affect ice particles and to explain why the betaine-sorbitol system is more effective than the betaine system in inhibiting crystal growth and agglomeration of ice particles.

Sample solutions of the betaine system (2 g·L⁻¹ cetyldimethylbetaine, 2 g·L⁻¹ sodium oleic acid, and 0.2 mol·L⁻¹ sodium chloride) and the betaine-sorbitol system (2 g·L⁻¹ cetyldimethylbetaine and 0.2 mol·L⁻¹ sorbitol) were prepared in 0.5-L beakers. Each solution was cooled to between -2 and -6 °C in a cooling bath. When the solution temperature was below the melting temperature of ice, the solution was mechanically stirred to induce nucleation of ice, thus producing an ice/water slurry. The ice/water slurry was kept in the cooling bath for several hours to increase the ice fraction (defined as ice packing fraction, or IPF, in weight fraction percentage, wt %). IPF was measured by using a calorimeter. The procedures for ice production and IPF measurement were described in detail elsewhere.^{1,2} After the IPF was measured, the liquid phase of the ice/water slurry

was transferred to a separating funnel by using a pipette, and then a buffer solution (pH = 1), Orange II solution (0.1%), and chloroform were added to the separating funnel. The funnel was then shaken to separate the chloroform layer from the water layer. The chloroform layer, where Orange II had interacted with the cetyldimethylbetaine molecules, was separated from the lower part of the funnel, and then the absorbance of orange color was measured at 485 nm using a UV spectrophotometer. On the basis of the measured absorbance, the cetyldimethylbetaine concentration in the liquid phase was calculated from the known concentration of cetyldimethylbetaine.

The amount of cetyldimethylbetaine molecules adsorbed onto or incorporated into the solid phase (ice particles) was calculated by using the following equation:

$$m_s = m_0 - m_l = \{C_0 - C_l(1 - IPF)\}M_0 \quad (1)$$

where m_s is the mass of cetyldimethylbetaine adsorbed onto or incorporated into the ice particles, m_0 is the total mass of cetyldimethylbetaine, m_l is the mass of cetyldimethylbetaine in the liquid phase, C_0 is the initial cetyldimethylbetaine concentration, C_l is the measured cetyldimethylbetaine concentration in the liquid phase of the ice/water slurry, and M_0 is the total mass of the solution.

Figure 1 shows that m_s increased with increasing IPF for both the betaine and betaine-sorbitol systems, whereas m_l ($= m_0 - m_s$, where $m_0 = 1.0$ g) decreased. However, m_l was sufficiently large even at high IPF (around 30%) that drag of the ice/water slurry was reduced.² Figure 1 also shows that m_s of the betaine system was larger than that of the betaine-sorbitol system at the same IPF, although the difference was small.

On the basis of these results, how the betaine and betaine-sorbitol systems affect ice particles in ice/water slurries can be explained as follows. Crystal growth and agglomeration of ice

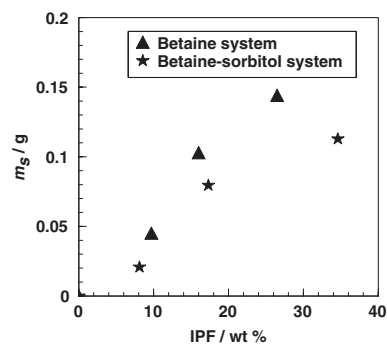


Figure 1. Mass of cetyldimethylbetaine molecules (m_s) adsorbed onto or incorporated into ice particles as a function of ice fraction (IPF).

particles are affected not by cetyldimethylbetaine molecules incorporated into ice, but by those adsorbed onto ice surfaces, because crystal growth and agglomeration of ice particles are dominated by interfacial phenomena. Therefore, the ratio Nad/A , where Nad is the number of cetyldimethylbetaine molecules adsorbed onto the ice surfaces and A is the total surface area of the ice particles, can be used as an index of the inhibition of crystal growth and agglomeration of ice particles; the larger the Nad/A ratio, the higher the effectiveness in inhibiting crystal growth and agglomeration. Previously reported experiments² show that, compared with the betaine system, the betaine–sorbitol system is more effective in inhibiting agglomeration of ice particles and thus dispersing ice particles in ice/water slurries, and consequently, increasing the total surface area of ice particles;² namely, $Nad_B/A_B < Nad_{BS}/A_{BS}$ and $A_B < A_{BS}$, therefore, $Nad_B \ll Nad_{BS}$, where subscript B represents the betaine system and BS represents the betaine–sorbitol system. Figure 1 shows that the difference in the number of cetyldimethylbetaine molecules adsorbed onto or incorporated into the ice particles between the betaine and betaine–sorbitol systems was not significant; namely, $(Nad_B + Nin_B)$ is approximately equal to $(Nad_{BS} + Nin_{BS})$, where Nin is the number of the surfactant molecules incorporated into the ice particles. Therefore, based on previously reported experiments² and on Figure 1, $Nin_B \gg Nin_{BS}$.

On the basis of these results, Figure 2 schematically shows an “interaction” model that explains how the betaine and betaine–sorbitol systems affect ice particles in ice/water slurries by describing the interactions between the surfactant molecules and ice particles. For both systems, cetyldimethylbetaine molecules can be adsorbed onto the ice surfaces after nucleation of ice (Figure 2). In the betaine system, however, Nad_B/A_B is not large enough to inhibit crystal growth and agglomeration of ice particles. Eventually, most of the adsorbed molecules will be incorporated into the ice particles during crystal growth and agglomeration (Figure 2a). In contrast, in the betaine–sorbitol

system, Nad_{BS}/A_{BS} is large enough to inhibit crystal growth and agglomeration of ice particles, and thus no significant crystal growth and agglomeration occur after initial growth following the nucleation of ice, but instead further nucleation occurs because of continuous cooling of an ice/water slurry. Therefore, in the betaine–sorbitol system, most of the adsorbed molecules will not be incorporated into the ice particles (Figure 2b).

The effect of the betaine and betaine–sorbitol systems in inhibiting crystal growth and agglomeration of ice particles is similar to that of antifreeze proteins (AFPs).⁴ Because of the Kelvin effect caused by adsorption of AFP molecules onto ice surfaces, AFPs can completely inhibit crystal growth of ice at temperatures even below the melting temperature of ice.⁵ However, when the AFP solution temperature is lower than the freezing temperature at which ice crystals start to grow, the AFP molecules no longer inhibit crystal growth of ice because they are incorporated into ice crystals.⁶ The interaction model (Figure 2), therefore, does not contradict the interpretation of the function of AFPs, although there is no evidence that the betaine and betaine–sorbitol systems used here affect ice crystals in the same manner as AFPs.

Another model that explains the effect of the betaine–sorbitol system on ice crystals is that the network structures of the micelles existing in the solutions affect crystal growth and agglomeration of ice. Spatial confinement caused by three-dimensional network structure in polymer gels can prevent crystal growth of ice also by the Kelvin effect.⁷ The network structure of micelles in the betaine–sorbitol system might also cause the same effect as that in polymer gels, thus inhibiting the crystal growth and agglomeration of ice. In this network-structure model, the betaine–sorbitol system exhibits the Kelvin effect without adsorption of the cetyldimethylbetaine molecules onto ice surfaces.

The function of sorbitol in the betaine–sorbitol system would be explained as follows. The difference in inhibiting crystal growth and agglomeration of ice between the betaine and betaine–sorbitol systems indicates that sorbitol molecules play an important role in the inhibition. In the interaction model (Figure 2), sorbitol might increase Nad/A and decrease Nin . In the network-structure model, sorbitol might increase the complexity of the network structure of the micelles.

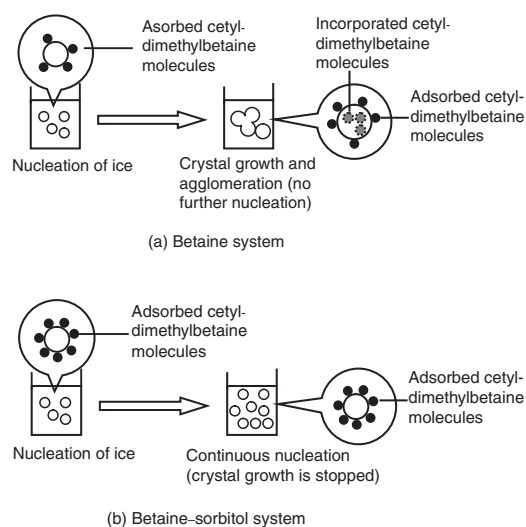


Figure 2. Model describing interaction between cetyldimethylbetaine (surfactant) molecules and ice particles in ice/water slurries.

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