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THE USE OF DSC TO STUDY THE KINETICS OF HETEROGENEOUS AND HOMOGENEOUS NUCLEATION OF ICE IN AQUEOUS SYSTEMS

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ABSTRACT

Differential scanning calorimetry (DSC) combined with sample dispersal in the form of an emulsion can be successfully used as a tool for studying kinetics of both homogeneous and heterogeneous nucleation of ice in an aqueous sample. Adding freeze-dried *Pseudomonas syringae* as an ice nucleant into the filtered aqueous system before preparing the emulsion proved to be a method for inducing uniform controllable heterogeneous nucleation. Exotherms associated with the heterogeneous and homogeneous events in scanning occur at characteristic temperatures. The kinetics of both heterogeneous and homogeneous nucleation in the same sample have been studied by an isothermal hold procedure. Kinetic analysis of the individual peaks yields consistent kinetic constants. The parameters describing the temperature dependence of the nucleation kinetics are different for the heterogeneous and homogeneous nucleation processes. There is a linear relationship between freezing point depression and the reduction of nucleation temperatures associated with sucrose addition.

INTRODUCTION

Nucleation of ice in an aqueous system can either be homogeneous, in which the ice phase is initiated by water molecules spontaneously combining together to form an ice embryo, or heterogeneous, in which ice embryos grow on the catalytic surface of foreign particles. Homogeneous nucleation occurs at lower temperatures than heterogeneous nucleation.

Most kinetics studies for nucleation have investigated homogeneous nucleation [1,2] although it is believed that heterogeneous nucleation is predominant and more important in food and living materials [3,4]. There are two main difficulties in studying the kinetics of heterogeneous nucleation: firstly, it is technically difficult to obtain a uniform population of the available, natural, foreign particles suspended in the aqueous systems; and secondly, in order to obtain reliable kinetic results, a statistically reliable method is required. According to Vali and Stansburry [5], the statistical reliability of each observed freezing event changes as different numbers of

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drops (samples) are measured. Therefore in kinetic studies of heterogeneous nucleation, large numbers of independent samples are needed.

Franks et al. [1] and Michelmore and Franks [2] used differential scanning calorimetry (DSC) together with sample dispersal as an emulsion to study the homogeneous nucleation of aqueous solutions of propylene glycol and hydroxyethyl starch. The method is based on the fact that the heat released on freezing of each aqueous droplet in the emulsion is measured by DSC. This can then be correlated to the number of droplets frozen. The method appears to be simple, less time-consuming and gives better statistical results as the freezing of 10^6–10^7 drops will be observed within one DSC run.

In our studies we attempted to determine the feasibility of studying the behavior of heterogeneous and homogeneous nucleation of ice in water and in sucrose solutions by applying thermal analysis. It is difficult to study the heterogeneous nucleation caused by natural foreign particles preexisting in the water or aqueous solution because they induce heterogeneous nucleation randomly and they are present in variable amounts; therefore, our strategy was to induce a uniform heterogeneous nucleation in the sample by inseminating it with the bacterial ice nucleant, *Pseudomonas syringae*. Many investigators [6,7] have shown that this bacterium can induce a well-defined range of heterogeneous nucleation events. Once the feasibility of using this method was demonstrated the next step was to quantify the kinetics of the heterogeneous and homogeneous nucleation processes in each sample and to identify any parallels between both nucleation processes.

MATERIALS AND METHODS

We applied the combined techniques of droplet emulsions and DSC. As the emulsion was placed in a DSC and cooled at a finite rate, nucleation and the crystallization of water in the droplets should result in the evolution of latent heat. Because ice crystal growth is rapid compared to nucleation, the rate of the latter phenomenon may be assumed to equal that of droplet freezing and can be calculated from the heat of crystallization that is liberated [1]. These heats of crystallization were observed as exothermic peaks in the DSC thermogram. Exothermic peaks corresponded to heterogeneous nucleation events for drops containing ice nucleants (*P. syringae*) and to homogeneous nucleation events for the drops containing no ice nucleants.

Emulsions of water or sucrose solution dispersed with freeze-dried *P. syringae* were prepared in silicone oil containing 5% SPAN 65 (sorbitan tristearate) as an emulsifier. Emulsions were prepared to contain 1 : 3 water to silicone oil (w/w). The emulsion dropsize calculated from approximately 300 drops, was controlled so as to be in the 5–10 μm diameter range. Droplet size distributions were determined by measuring droplet diameters from photomicrographs of the diluted emulsion sample.

A Perkin–Elmer DSC-2C with a thermal data analysis unit was used in this study. The calorimeter was fitted with an Intracooler II subambient accessory and a dry box. The DSC head and the dry box were purged continuously with dried nitrogen.

Emulsion samples between 2 and 5 mg (small quantities were analyzed to achieve rapid thermal equilibration) were put in a sealed aluminum pan. An empty pan was used as a reference. The pattern of nucleation was evaluated by scanning mode while the kinetic study of the nucleation processes was monitored using the isothermal mode of DSC operation at several temperatures.

To evaluate the temperature dependence of kinetics, temperatures must be accurately known. Temperature calibration based on the ice–water melt at 273.2 K used the methods described by Michelmore and Franks [2] for both isothermal and scanning modes.

Scanning experiment

The sample was cooled from 280 to 200 K at a rate of 1.25 K min^{-1}. The differential heat flow signal from this mode indicated the range of both heterogeneous and homogeneous nucleation temperatures.

Isothermal experiment

The sample was rapidly cooled to a temperature T_1, 3 K above the temperature of interest (T_2). After an equilibration period, the sample was then subjected to a temperature jump to T_2 to permit determination of the nucleation rate at this temperature. Data were collected until the baseline was steady. The instrumental transients were determined by repeating the T_1 to T_2 drop with an already frozen sample. This gave data which can be subtracted from the initial trace. Because nucleation is a first-order kinetic process, J at temperature T_2 could be calculated from a plot of $\ln(dq/dt)_t/(dq/dt)_{t_0}$ of the corrected trace against time.

RESULTS AND DISCUSSION

Figure 1 represents thermograms of cooling scans of water and 15% sucrose solution emulsions. Each thermogram exhibited two distinct exotherms. The first, A, at higher temperature resulted from the crystallization of the droplets containing the bacterial ice nucleant, *P. syringae* which induces heterogeneous nucleation at a higher temperature. The second exotherm, B, resulted from the homogeneous nucleation of ice in the remaining unseeded droplets. The sharpness of the exotherm associated with heterogeneous nucleation showed that a well-defined heterogeneous nuclea-

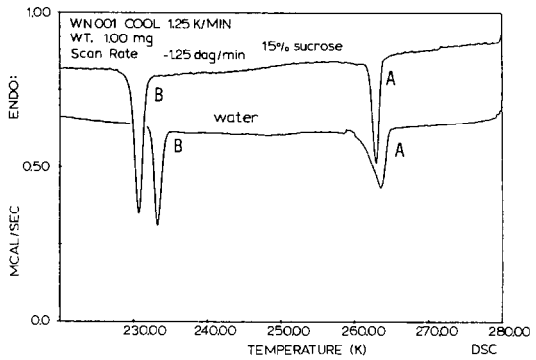

Fig. 1. Cooling scans of water and 15% sucrose solution.

tion process can be successfully induced in a significant portion of the emulsion droplets.

The minima of both peaks refer to the temperatures of the maximum effective nucleation rates and were consistent in repeat scans and with repeat samples (Table 1). The temperature of the maximum effective heterogeneous nucleation rate in water was around 263.6 K which is the active temperature for the majority population of *P. syringae* [8]. Our DSC method allows for the study of nuclei active at lower temperatures, in contrast to the cold plate method [6] which shows the nuclei active at higher temperatures. The individual drop size for the cold plate method is large enough that even the less common high-temperature active nuclei are probably contained in each drop. Thus the sample freezes before its population of more common lower temperature active nuclei can have an effect, unless the nucleant sample is diluted such that some drops have only the lower temperature active nuclei. In an emulsion, on the other hand, each nucleant can occupy a separate drop.

The temperature of the maximum effective homogeneous nucleation rate of the water sample was around 233.3 K which agreed well with the results

TABLE 1

DSC results

	Temp of max. eff. nucleation rate		Equilibrium freezing point (K)
	Heterogeneous (K)	Homogeneous (K)	
Water	263.6	233.3	273.2
15% sucrose	262.8	230.5	272.1
20% sucrose	260.8	227.4	271.7
35% sucrose	258.3	223.7	269.7
50% sucrose	249.3	212.1	265.7

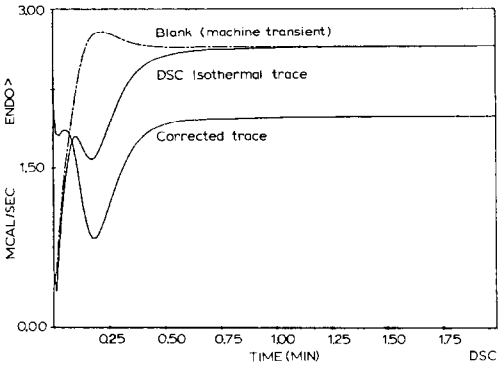

Fig. 2. Isothermal experiment, heat output after temperature drop.

reported by Rasmussen and Mackenzie [9]. Homogeneous nucleation events also occurred as there are more droplets in the emulsion than heterogeneous nuclei. The number of droplets without heterogeneous nuclei increased as drop size decreased. Our experiment showed that if the average drop size is less than 5 μm diameter, the majority of the drops would nucleate homogeneously. To obtain reliable quantitative results the average drop size should not exceed 10 μm in diameter [4]. Since we wish to have similar proportions of populated and unpopulated droplets in order to study both nucleation processes in the same sample, we require sample drop sizes from 5 to 10 μm, a narrower range than is usually considered appropriate for the study of homogeneous nucleation. With the size range of 5–10 μm diameter and the quantity used in a DSC pan (2–5 mg), more than 10^7 drops are observed during cooling. This number of independent samples should be large enough for the ice nucleation rate to be reliably measured as a function of temperature.

Figures 2 and 3 represent sample data of isothermal nucleation measurements on water. From Fig. 2, the corrected heat output (dq/dt) provided a

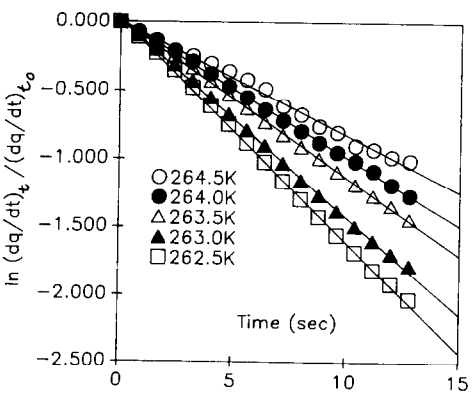

Fig. 3. Isothermal nucleation data for water at heterogeneous nucleation temperatures.

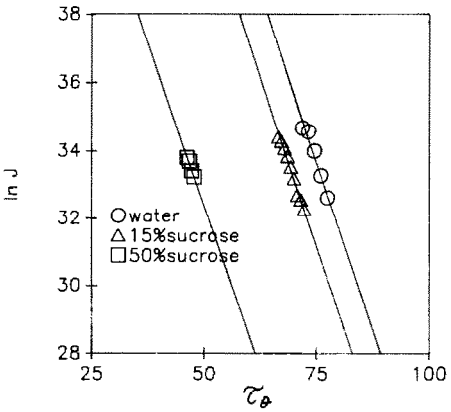

Fig. 4. Homogeneous ice nucleation rate in water and sucrose solutions as a function of τ_θ.

measure of the rate of ice nucleation. As nucleation is considered a first-order kinetic process, the nucleation rate per unit volume, J, for both heterogeneous and homogeneous nucleation at a specific temperature could be calculated from a plot of $\ln(dq/dt)_t/(dq/dt)_{t_0}$ versus time (Fig. 3). The linearity of this plot confirmed that both nucleations are indeed first-order kinetic processes.

From these data, we can determine the effect of temperature on the rate of nucleation. Classical kinetic theory for homogeneous nucleation suggests that

$$J = A \exp(B\tau_\theta)$$

where A and B are constants characteristic of the aqueous phase and τ_θ is a function of reduced temperature (θ).

$$\tau_\theta = \frac{1}{\theta^3(1-\theta)^2}$$

in which $\theta = T/T_f$ and T_f is the equilibrium freezing temperature (K) of the aqueous droplet [1].

Figures 4 and 5 illustrate the plot of $\ln J$ versus τ_θ for homogeneous and heterogeneous nucleation processes for water, 15% and 50% w/w sucrose solution respectively. It appears that linear plots were obtained for homogeneous and heterogeneous nucleation which indicates that the classical theory is applicable to our data. A comparison of results obtained from homogeneous nucleation of emulsions with and without sucrose added are shown in Fig. 4. The plots $\ln J(\tau_\theta)$ are all parallel. It is clear that adding sucrose changes the temperature dependence of the nucleation rate. At a given temperature, adding sucrose lowers the nucleation rate. Figure 5 shows a comparison for heterogeneous nucleation. The patterns here were different from those of homogeneous nucleation. For the emulsion of water and a low

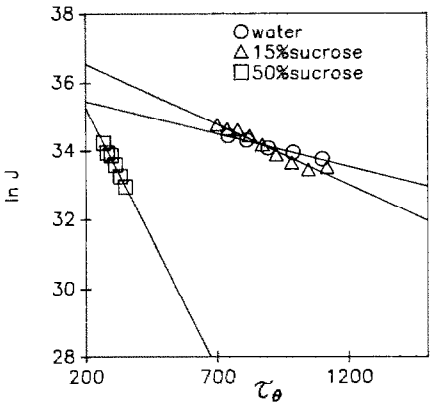

Fig. 5. Heterogeneous ice nucleation rate in water and sucrose solutions as a function of τ_θ.

concentration of sucrose (15%), there was no obvious difference in $\ln J(\tau_\theta)$ plots. However, when the concentration of sucrose increased (50%), there was a change in slope. Both the rate of change of J with τ_θ and the reduced temperature for any given J were altered. It appears that there is a concentration dependent interaction between the ice nucleant and the sucrose molecules. This suggests that the site for nucleation is hydrophilic in nature. Table 2 shows the values of A and B for water, 15% and 50% w/w sucrose solutions analysed by our method.

As can be noted from Table 1, there was a reduction of the temperature of heterogeneous (ΔT_{het}) and homogeneous (ΔT_{hom}) nucleation associated with the addition of sucrose. It seems appropriate to combine them with the solute-induced depression of freezing point (ΔT_m). Figure 6 shows that there is a linear relationship between freezing point depression and the reduction of heterogeneous and homogeneous nucleation temperature associated with sucrose addition. The relation is in the form

$$\Delta T_{het} \quad \text{or} \quad \Delta T_{hom} = k\,\Delta\,T_m$$

Studies of homogeneous nucleation [9] have found that k falls typically in the range of 1–2. The values of k from our experiment were correlated to

TABLE 2

Constants A and B for water and sucrose solutions

	A ($sec^{-1}\ m^{-3}$)		B	
	Hetero	Homo	Hetero	Homo
Water	3.71×10^{15}	3.32×10^{27}	1.92×10^{-3}	0.396
15% sucrose	1.50×10^{16}	3.10×10^{26}	3.53×10^{-3}	0.397
50% sucrose	4.43×10^{16}	2.24×10^{22}	1.53×10^{-2}	0.382

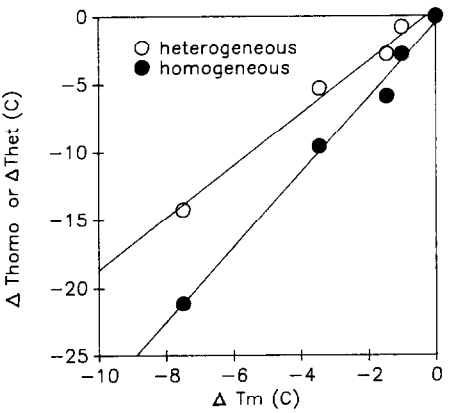

Fig. 6. The reduction of heterogeneous and homogeneous nucleation temperature as a function of freezing point depression in sucrose solutions.

the previous studies, i.e. 2 and 3 for heterogeneous and homogeneous nucleation respectively.

CONCLUSION

Thermal analysis, combined with sample emulsification of seeded samples allows for the study of both homogeneous and heterogeneous nucleation kinetics. The temperature dependence of nucleation kinetics is of the form predicted by classical theory. The constants are different for homogeneous and heterogeneous nucleation. There is a linear relationship between freezing point depression and the reduction of nucleation temperatures associated with sucrose addition.

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