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Experimental study on freezing of liquids under static magnetic field☆

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ABSTRACT

Freezing processes of several liquids under static magnetic field (SMF) less than 50 mT were investigated. Central temperature of liquid samples held in glass test tubes immersed in a liquid bath was measured and collected. Nucleation temperature and phase transition time were obtained from freezing curves. Normality tests were performed for nucleation temperature of these liquids with/without magnetic field and normality distributions were justified. Analysis of variances was carried out for nucleation temperature of these liquids with magnetic field flux density as the influencing factor. Results showed that no significant difference was found for deionized water with or without SMF. However, differences exist in 0.9% NaCl solution and 5% ethylene glycol solution with and without SMF. Nucleation temperature of 0.9% NaCl with SMF is lower than that without SMF, while its phase transition time is shorter than that without SMF. Nucleation temperature of 5% ethylene glycol with SMF is higher than that without SMF, while its phase transition time is not modified with SMF.

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1. Introduction

Freezing is one of the most important methods to preserve food and other perishable goods [1,2]. Freezing process is critical for maintaining quality and flavor of food. Taking liquid food as an example, freezing is usually divided into three stages [3], as shown in Fig. 1: (1) liquid cooling period (*a–b–c*), at this stage the food is cooled by releasing sensible heat until it reaches the nucleation point *c*. In some cases the temperature of the cooled liquid may be lower than its freezing temperature, and the difference between them is called degree of supercooling. In this supercooling period from *b* to *c*, liquid is unstable and nucleation may occur at any time [4]. The temperature at which nucleation starts is called nucleation temperature, i.e., the lowest temperature of liquid state (point *c*). (2) Phase transition period (*d–e–f*), during which latent heat is removed, nucleation happens and most of liquid turns into solid; the temperature from point *d* to *e* keeps constant, and is called freezing temperature. The temperature at point *f* is 5 °C lower than the freezing temperature. (3) Solid freezing period from point *f* to point *g*, during which temperature of frozen solid continues to drop and sensible heat is removed until the required temperature is reached. Freezing control is very important for preserving quality of frozen food, since the temperature course during solidification determines crystal growth and crystal structure inside frozen food [1,5]. As it is known, a quick and short freezing process produces small ice crystals, which will cause

less damages to cells, resulting in a better final quality after thawing of food products [5,6].

There are many studies on the new emerging freezing technology, such as impingement freezing [7,8], superchilling technology [9,10], pressure shift food freezing [11–13], ultrasound-assisted food freezing [14,15], freezing under electric field [16,17], radiofrequency-assisted freezing [18], and Magnetic Resonance-assisted Freezing (MRAF) [1,2, 15,19]. The MRAF is a new technology, also called as cell alive system (CAS) technology by some researchers; it preserves food and biology samples with better quality than other methods by using both magnetic and electric fields [20,21], but detailed information has not been disclosed yet. In CAS, a very weak magnetic field (0.01 mT) is applied to affect the freezing process of biological sample, flower or plant. The weak magnetic field will prevent ice from forming inside cells.

Magnetic field has been shown to affect particular water properties by physicists, such as heat capacity [22], refractive index [23], electrical conductivity [24], self-diffusion coefficient [25], viscosity and surface tension [26,27]. It has also been applied in many fields, such as waste water treatment, crystallization, and separation. [28]. However, few studies have been carried out on the effects of magnetic field to water freezing and the published research results are inconsistent. One paper reported that strong static magnetic field nucleated ice formation in 0.5 mL samples of distilled water, with a field strength of 0.5 T causing equilibrium freezing at 0 °C [29]. Another paper observed that containerless 6 mm globules of water levitated in an 18 T magnetic field supercooled to –10 °C before freezing [30]. Wowk [31] claims that it is questionable whether if a magnetic field less than 1 mT can promote or inhibit ice nucleation. He believed that there was no influence for static magnetic fields on freezing of bulk water away from surfaces.

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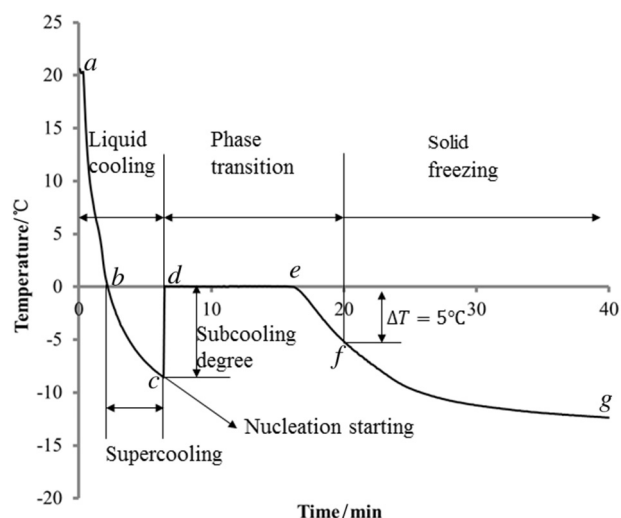


Fig. 1. Typical freezing curve of water.

Another study in Japan investigated food preservation using commercial freezers with a 0.5 mT magnetic field and found no better results [32]. Mok *et al.* [3] studied the influences of magnetic field alone and combination of both magnetic and electric field on the freezing process of 0.9% NaCl solution. The magnetic fields in their study are 480 mT and 50 mT. Their results showed that magnetic field alone can shorten phase transition time and produce uniform ice crystal patterns. Combination of magnetic field and electric field can further shorten the phase transition time and produces more round ice crystals. However, the authors did not provide the relationship between phase transition time and magnetic field flux density. In addition, the relationship between magnetic field flux density and the nucleation temperature is not provided either.

Strong magnetic field may harm cell properties and should not be used to preserve biological samples and fresh food. On the other hand, the existing study shows that very weak magnetic field (<0.5 mT) is not effective either [32]. However, weak magnetic field (>1 mT), may play a significant role in food freezing and biological sample preservation, as proved by Mok [3]. Weak magnetic field is also easy to obtain and cost less. Taking this into account, in this paper, the weak magnetic field is selected.

Ethylene glycol solution is often used as a cryoprotective agent in cryobiology. It will inhibit nucleation and growth of ice crystals by forming hydrogen bonds with water molecules [33]. Since magnetic field is proved to influence hydrogen bonds, it will affect freezing behavior of ethylene glycol solution, which may help us to improve the performance of ethylene glycol solution in cryopreservation. However, at present to the authors' knowledge, there is no research published on this aspect.

In this paper, the study will focus on the effect of static magnetic field (SMF) less than 50 mT on the freezing process of several liquids: deionized water, NaCl solution and ethylene glycol solution. The relationships between nucleation temperature, phase transition time and different magnetic field flux densities will be sought. The aim is to be able to control freezing process by applying an appropriate magnetic field.

2. Materials and Methods

2.1. Experiment system

As shown in Fig. 2, the experimental system is composed of a liquid bath, a data acquisition system, thermocouples, test tubes and permanent magnets. The test tube is made of glass, 18 mm $\times$ 180 mm, and 5 ml liquid sample for each test. The magnetic field is produced by

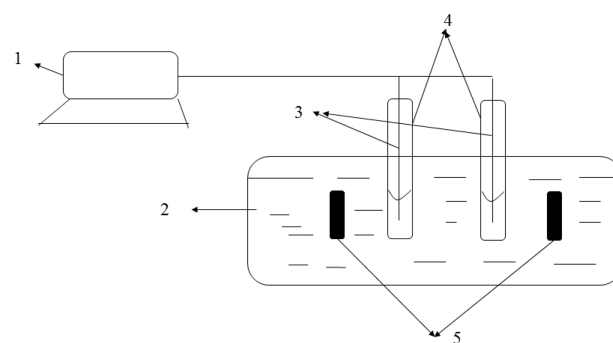


Fig. 2. Schematic diagram of experiment system. 1 – Data acquisition system, 2 – Liquid bath, 3 – Thermal Couples, 4 – Test tube, 5 – Magnets.

placing two permanent neodymium magnets (NdFeB, dimension 50 mm $\times$ 50 mm $\times$ 2 mm) on two sides of test tubes with opposite poles facing each other. The magnetic field flux density is adjusted by varying distance between the two magnets. The magnetic field flux density is measured by a Tesla meter (CH-1800, ± 0.001 mT). The temperature of the test samples and the temperature of liquid bath are measured by a K-type thermocouple (TT-K-30-SLE, ± 0.5 °C, Omega Engineering, Inc., Stamford, CT). Liquid bath is obtained by circulating calcium chloride solution with a mass concentration of 25.6% through a chiller and its temperature is kept constant at -16 °C.

2.2. Sample preparation and test procedure

The liquid samples tested are deionized water, 0.9% mass concentration NaCl solution, and 5% mass concentration water glycol solution (phase transition temperature = -1.4 °C). Deionized water is bought from the market and measured by 100 ml graduate cylinder (E1 ml). The NaCl (Analytical Reagent, AR) is measured by an analytical balance (E0.0001 g, Ohaus, EX324ZH). Ethylene glycol used is AR, with purity $>99.5\%$, measured by 5 ml graduated cylinder (E 0.1 ml). For each test, 5 ml liquid sample is put into the glass test tube. Then it is placed into a thermostat box for 2 h before experiments for temperature stabilization to make sure that the test samples are starting at the same temperature. The temperature of the thermostat box is kept at (20 ± 0.5) °C. When 2-hour stabilization period is reached, the test tube is taken out of the thermostat box quickly and immersed into the liquid bath and fixed in a sample holder. Then the freezing process starts. The temperature of the sample is measured by a K-type thermal couple placed at the center of the test sample. Data is collected via a data acquisition system (Agilent 34970A) and transferred into a computer. The magnetic field flux density is measured before each test since it will not change during experiments. For each magnetic field flux density, at least triple tests were carried out.

2.3. Data processing methods

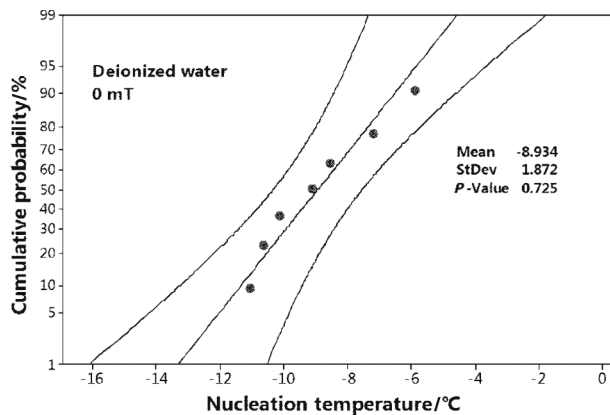
Microsoft Excel was employed for statistical analysis of experiment data. Normality test and Analysis of Variance (ANOVA) were performed. Mean phase transition time and nucleation temperature were computed and compared.

3. Results and Discussion

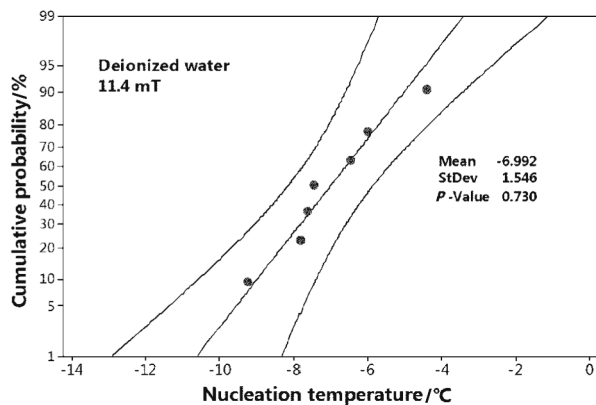
3.1. Normality test and ANOVA

Nucleation is a stochastic event, and nucleation temperature at which nucleation starts must follow a normal distribution. However, when magnetic field is applied, it may deviate from the normal distribution. In order to check on this, the cumulative probability plot vs. nucleation temperature for deionized water, 0.9% NaCl and 5% glycol solution

is shown in Figs. 3–5 for both without magnetic field and with magnetic field of 11.4 mT. The Anderson–Darling normality tests [34] were also carried out on these data and results are also presented in Figs. 3–5. When P value for the Anderson–Darling normality test is greater than 0.05, normal distribution is verified. When P value equals 1, it means perfect normal distribution.



(a) Without magnetic field



(b) With 11.4 mT magnetic field

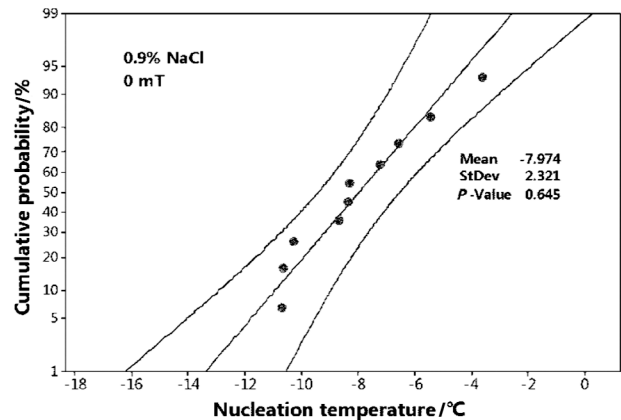
Fig. 3. Normal cumulative distribution with 95% confidence interval (two curved lines on both sides) of nucleation temperature of deionized water frozen in test tube (a) without magnetic field, and (b) with 11.4 mT magnetic field.

From Fig. 3(a) and (b), it can be seen that nucleation temperature of deionized water fits normal distribution well with or without magnetic field. P values for the Anderson–Darling normality test under these two conditions are almost equal. This means that magnetic field does not change the stochastic behavior of nucleation and it still follows normal distribution.

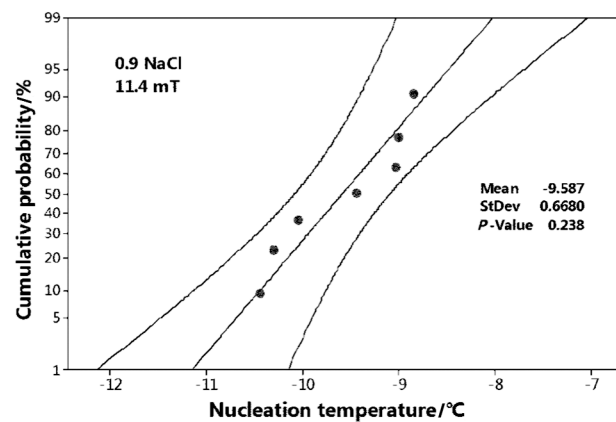
From Fig. 4(a) and (b), it shows that nucleation temperature of 5% NaCl solution also follows normal distribution with or without magnetic field. P value for 11.4 mT magnetic field is 0.238, less than that without SMF, but is greater than 0.05 required for normal distribution test.

Normality tests are also performed for 5% ethylene glycol solution and results are shown in Fig. 5(a) and (b). Nucleation temperature of 5% ethylene glycol also follows normal distribution with or without magnetic field.

After it is confirmed that nucleation temperature of all three liquids is normally distributed, ANOVA was carried out for these data with SMF flux density as the influencing factor. ANOVA results for deionized water at different SMF flux density show that there is no significant difference among different groups (P value = 0.106 greater than required 0.05). This means that nucleation of deionized water is not



(a) 0.9% NaCl solution frozen in test tube without magnetic field



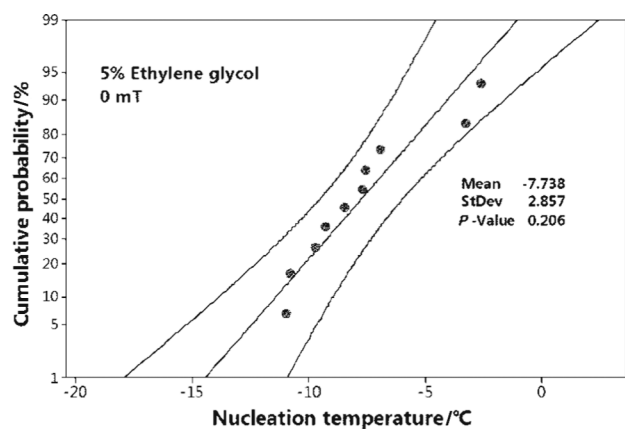
(b) 5% NaCl solution frozen in test tube with 11.4 mT magnetic field

Fig. 4. Normal cumulative distribution with 95% confidence interval (two curved lines on both sides) of nucleation temperature of (a) 0.9% NaCl solution frozen in test tube without magnetic field, and (b) 5% NaCl solution frozen in test tube with 11.4 mT magnetic field.

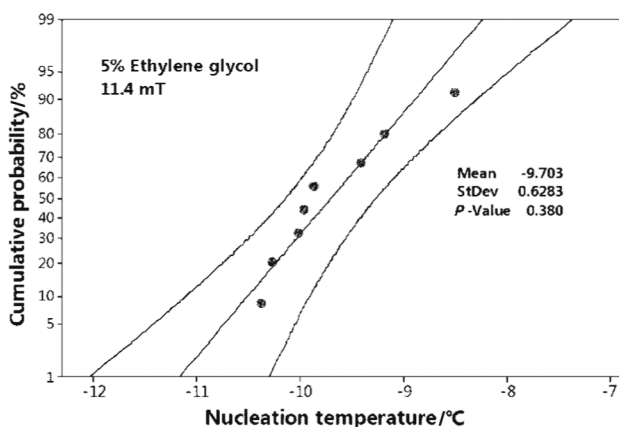
notably influenced by SMF in the current study. However, both 0.9% NaCl and 5% ethylene glycol were influenced by SMF, and P values are 0 and 0.041 respectively.

3.2. Effect of magnetic field on nucleation temperature and phase transition time of deionized water

Fig. 6 exhibits that nucleation temperature of deionized water at different SMF may be lower or greater than that without SMF. Even though Cai *et al.* [26] pointed out that water is more stable after magnetic treatment with less molecular energy and more activation energy. However, the SMF used in their study is 0.50 T. In the Monte Carlo simulation of liquid water in a magnetic field, Zhou *et al.* [22] concluded that a significant change in the internal energy and heat capacity occurred when a magnetic flux density about 0.2 T is applied. Their results also showed that there is no substantial changes when the SMF is less than 0.05 T. Pang and Shen [24] used 0.4 T SMF and found out that dielectric constant and resistance of water is reduced. The influence on hydrogen bonding between water molecules is responsible for all the changes of physical properties when SMF is present. More hydrogen bonds are formed and water clusters become larger after magnetic treatment [22,24,26]. All the above studies used a much higher SMF than the current one (less than 0.05 T), which may explain that hydrogen bonding between water molecules are not affected by small SMF (less than



(a) Without magnetic field



(b) With 11.4 mT magnetic field

Fig. 5. Normal cumulative distribution with 95% confidence interval (two curved lines on both sides) of nucleation temperature of 5% ethylene glycol solution frozen in test tube (a) without magnetic field, and (b) with 11.4 mT magnetic field.

50 mT) applied in the current study. Hence supercooling degree and energy required for water nucleation did not change either under small SMF.

Effect of SMF on phase transition time of deionized water is not obvious, indicated by Fig. 7. It agrees with the above ANOVA analyses that SMF did not make big difference on nucleation temperature of deionized water. Another point is that the lower nucleation temperature is not corresponding to the shorter phase transition time. The reason is that there are many factors except nucleation temperature which

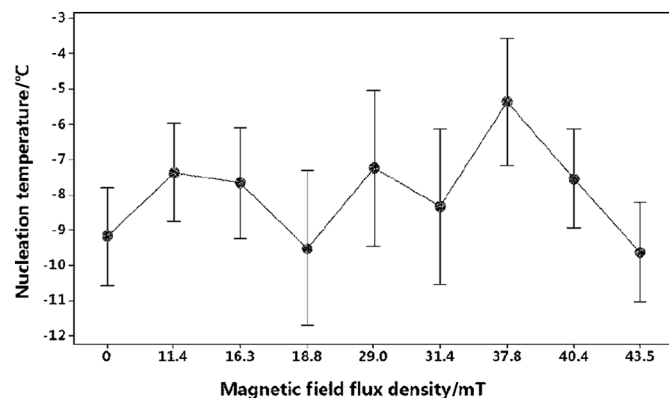


Fig. 6. Nucleation temperature of deionized water vs. magnetic field flux density.

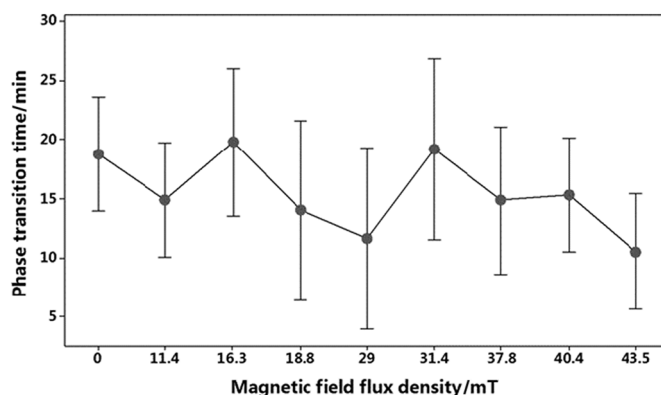


Fig. 7. Phase transition time of deionized water vs. magnetic field flux density.

influences the phase transition process, such as water viscosity, thermal conductivity, heat capacity and activation energy, etc. The phase transition process, in which latent heat is released constantly and ice nucleus keeps growing, is basically a heat transfer process. Nucleation temperature only determines the starting temperature of nucleation and the size of initial ice nucleus, but not the later phase transition. Therefore nucleation temperature alone cannot determine how the phase transition proceeds.

3.3. Effect of SMF on nucleation temperature and phase transition time of 0.9% NaCl

Fig. 8 reveals the way nucleation temperature varies with SMF for 0.9% NaCl solution. It tells that all the nucleations occur at lower temperature when SMF is applied, though the trend is not linear. The lowest nucleation temperature when SMF is applied is 3 °C lower than that without SMF. This is different from deionized water for which SMF does not affect much on its nucleation temperature. The reason may be associated with ions in the NaCl solution. The mobility of ions (Na^+ and Cl^-) is enhanced and hence the diffusion coefficient is increased when SMF is applied. The diffusion process of water molecules will hinder the formation of nucleus, and hence lower the nucleation temperature [25].

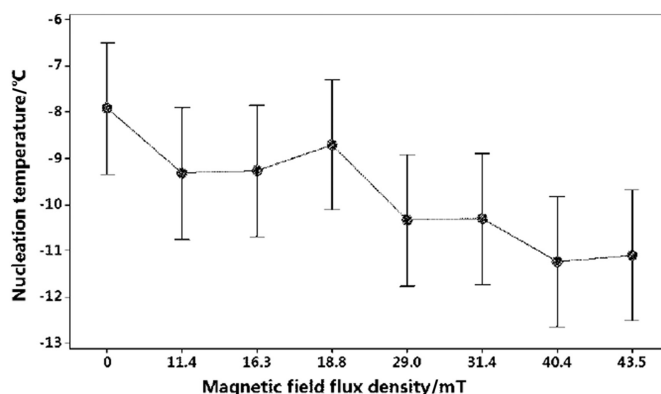


Fig. 8. Nucleation temperature of 0.9% NaCl vs. magnetic field flux density.

Effect of SMF on phase transition time of 0.9% NaCl solution is substantial, as indicated in Fig. 9. All the phase transition time at different SMF is less than that without SMF. It may attribute to the enhanced diffusion coefficient under SMF, which promotes heat transfer once nucleation starts. However, the shortened phase transition time does not vary with SMF flux density in a linear trend. This means that the way SMF affects phase transition time of 0.9% NaCl solution is complex. On average,

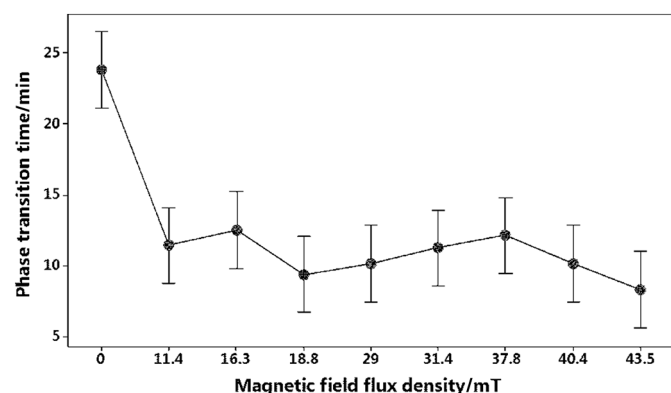


Fig. 9. Phase transition time of 0.9% NaCl vs. magnetic field flux density.

the phase transition time is shortened about 55.3% compared with no SMF. Since Na^+ and Cl^- ions are widely existed in many foods, it is concluded that SMF will impact freezing process of these foods.

3.4. Effect of magnetic field on nucleation temperature and phase transition time of 5% ethylene glycol

Fig. 10 displays that nucleation temperature of 5% ethylene glycol mixture varies with magnetic field flux density. The nucleation temperature is higher when SMF is employed, compared with that without SMF. However, the change is not following the same trend as magnetic field flux increases. To the best of the authors' knowledge, no study was found on how SMF affects the nucleation temperature of ethylene glycol solution. Further theoretical studies are needed to understand this behavior. Here it is postulated that the influence on hydrogen bonds within ethylene glycol molecules by SMF caused this behavior. It is known that hydrogen bond is formed between two $-\text{OH}$ s for an ethylene glycol molecule, therefore, it may be strengthened by external SMF which inhibits molecule's rotation and vibration at supercooling stage and promotes growth of ice nucleus. Hence critical radius will be reached at higher temperature with SMF than without SMF, and the nucleation temperature is raised. This is contrary to 0.9% NaCl solution, which may come from different compositions of these two solutions, ions vs. molecules. However, similar to deionized water, the phase transition time is not directly related with nucleation temperature; i.e., the lowest nucleation temperature is not corresponding to the shortest phase transition time, as shown in Fig. 11. The highest nucleation temperature occurs at SMF 29 mT, but the shortest phase transition occurs at SMF 43.5 mT.

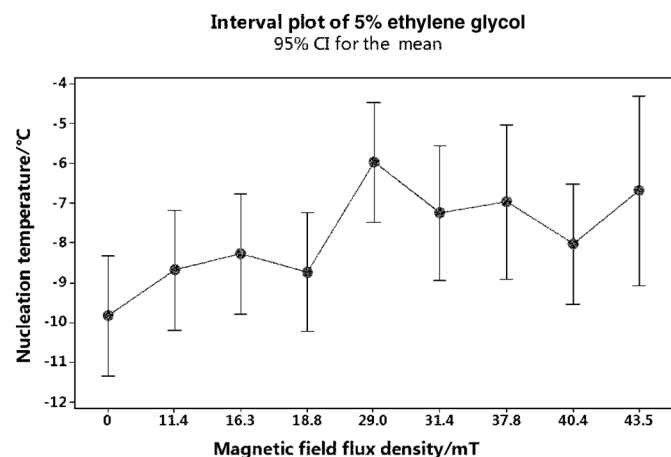


Fig. 10. Nucleation temperature of 5% ethylene glycol vs. magnetic field flux density.

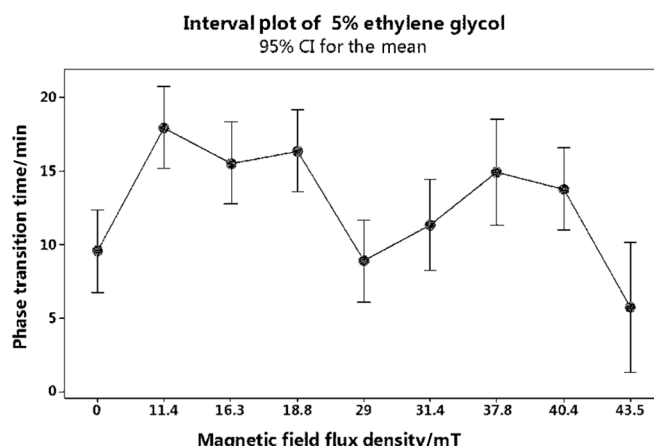


Fig. 11. Phase transition time of 5% ethylene glycol vs. magnetic field flux density.

Effect of SMF on phase transition time of 5% ethylene glycol is significant, as depicted in Fig. 11. Contrary to 0.9% NaCl solution, when small magnetic field is applied, the phase transition time of 5% ethylene glycol shows a cyclic behavior with a decreasing amplitude. It first rises and then drops as magnetic field increases. When SMF is less than 29 mT, the phase transition time with SMF is longer than that without SMF. However, when SMF is greater than 29 mT, the phase transition time with SMF is less than that without SMF. The behavior of its phase transition time is different from its nucleation temperature (Fig. 8). This again means that lower nucleation temperature not necessarily results in shorter phase transition time. There are many other factors which influence the phase transition process. More research is needed on this aspect.

4. Conclusions

In the present study, freezing processes of deionized water, 0.9% NaCl solution and 5% ethylene glycol solution under different SMF were studied. Nucleation temperature and phase transition time were obtained. Normality tests were performed for nucleation temperature. ANOVA of nucleation temperature was carried out to check influences of different SMF flux densities. It was concluded that:

- Nucleation temperature follows normal distribution with or without SMF for deionized water, 0.9% NaCl and 5% ethylene glycol solution.
- Nucleation temperature and phase transition time of deionized water are not significantly influenced by SMF, but 0.9% NaCl solution and 5% ethylene glycol solution do.
- Nucleation temperature of 0.9% NaCl with SMF is lower than that without SMF, while its phase transition time is 55.4% shorter than that without SMF on average.
- Nucleation temperature of 5% ethylene glycol with SMF is higher than that without SMF, while its phase transition time may or may not shorter than that without SMF.

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