

Cryogenic Characteristics and Relaxation Polarization Mechanism of NaCl Aqueous Solutions

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Abstract- In this paper, the crystallization and relaxation of NaCl aqueous solutions at low temperatures were studied by differential scanning calorimetry (DSC) analysis and dielectric analysis. From DSC analysis, the three-phase composite ice structural model consisting of pure ice, salty ice, and amorphous ice after the liquid-solid phase transition of NaCl aqueous solution under low temperature is established. The conversion rate of pure ice decreases monotonically with the increase of solution concentration. From dielectric analysis, the relaxation time of water molecules in composite ice decreases significantly at first and then increases slightly with increasing concentration, while the relaxation activation energy increases significantly at first and then decreases slightly. This is due to the damaging effect of ions on hydrogen bonds between water molecules and the interaction between anions and cations. This study can provide theoretical support and experimental basis for cryopreservation technology of biomaterials controlled by electromagnetic field.

Keywords: Bio-dielectrics; ice crystallization; NaCl solution; dielectric properties; relaxation polarization.

I. INTRODUCTION

In recent years, many scholars have devoted themselves to improving the long-term cryopreservation efficiency of biomaterials with the assistance of electromagnetic fields, in order to achieve low damage or even non-damage cryopreservation effect [1-2]. Biological tissues are mainly composed of water molecules, biological macromolecules and a large number of charged ions. Mechanical crushing damage and solute effect caused by ice crystals generated inside and outside cells at low temperatures are the main factors of cryoinjuries [3]. Previous studies have shown that the effect of cryopreservation can be directly affected by controlling the nucleation and growth of ice crystals in the freezing process of biomaterials by electromagnetic field [4]. At present, the research on the effect of cryopreservation controlled by electromagnetic field is mainly based on the observation of ice crystal size in microscopic observation pictures. Although this method is intuitive and easy to operate, it is easy to be influenced by the subjective judgment of the observer, and it is inconvenient to calculate quantitatively. Moreover, it reflects a relatively macroscopic experimental phenomenon and does not help to explore the interaction between electromagnetic field and water molecules in biomaterials at low temperatures. Therefore, further research is needed to accurately characterize and evaluate the crystalline morphology of water molecules in frozen biomaterials and to clarify the corresponding electromagnetic response at low temperatures.

In this paper, NaCl aqueous solutions with different concentrations were used as experimental samples. By combining dielectric analysis and differential scanning calorimetry (DSC) analysis, the crystallization and relaxation characteristics at low temperatures were obtained by quantitative calculation, and the relationship between composition structure and dielectric properties of NaCl aqueous solutions after cryopreservation was revealed.

II. MATERIALS AND METHODS

A. Preparation of NaCl Aqueous Solutions

Define the concentration ratio β , where $\beta = 1$ represents the molality of physiological saline $b_{NS} = 1.552 \times 10^{-4}$ mol/g and $\beta = 0$ refers to deionized water. Deionized water with a resistivity of 18.2 M Ω -cm and analytically pure NaCl powder were used to prepare NaCl aqueous solutions with molality of $c = \beta \cdot b_{NS}$ ($\beta = 0, 0.5, 1, 2, 4$). The effect of salt ions on solution volume is ignored.

B. DSC Method

DSC curves were measured by a Mettler Toledo DSC822e analyzer and 40 μ L standard aluminum crucibles. For each measurement, a 4 μ L sample was taken with a pipette gun. Each kind of solution was measured three times and the average value was obtained. The temperature control program was as follows: holding for 2 minutes at 10°C, cooling down to -60°C at a rate of 3°C/min, holding for 5 minutes, and then heating up to 10°C at a rate of 3°C/min.

Since the supercooling phenomenon may result in great errors for quantitative analysis by using cooling DSC curves, and the difference of crystallization among samples with different concentrations can be directly reflected through rewarming melting curves, the rewarming DSC curves are selected for quantitative analysis.

C. Measurement and Characterization of Dielectric Properties

Dielectric properties were measured using a Novocontrol Concept 80 broadband dielectric spectrum measurement system. The parallel plate liquid sample cell BDS1308 was used as the measuring electrode. Each sample was cooled from 10°C to -60°C and scanned every 2°C for a dielectric spectrum with a frequency range of 0.5Hz~5MHz and an effective voltage of 1V.

Considering the existence of long-range conductance, the expression of relative complex permittivity is as follows [5]:

$$\epsilon_r = \epsilon_r' - i\epsilon_r'' \quad (1)$$

where

$$\varepsilon_r' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2}, \quad (2)$$

$$\varepsilon_r'' = \frac{\sigma_{DC}}{\varepsilon_0 \omega} + \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2}. \quad (3)$$

In equation (3),

$\varepsilon_{r1}'' = \sigma_{DC}/(\varepsilon_0 \omega)$ is the direct current component corresponding to the long-range conductance and $\varepsilon_{r2}'' = (\varepsilon_s - \varepsilon_\infty) \omega \tau / (1 + \omega^2 \tau^2)$ is the alternating current component.

On the data analysis, in order to eliminate the influence of conductance produced by the interaction between inevitably introduced impurity particles and electrodes in the low frequency band, the equation (2) is derived [6]:

$$\frac{\partial \varepsilon_r'}{\partial \ln \omega} = \frac{-2}{\varepsilon_s - \varepsilon_\infty} \left(\frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2} \right)^2 = \frac{-2}{\varepsilon_s - \varepsilon_\infty} (\varepsilon_{r2}'')^2, \quad (4)$$

$$-\frac{\partial \varepsilon_r'}{\partial \ln \omega} \propto (\varepsilon_{r2}'')^2. \quad (5)$$

Both ε_{r2}'' and $-\partial \varepsilon_r' / \partial \ln \omega$ have maximum values at relaxation frequency $\omega_m = 2\pi f$, and the peak of $-\partial \varepsilon_r' / \partial \ln \omega$ is sharper and easier to distinguish. With the help of MATLAB programming, the cubic spline fitting of measured ε_r' data ensures its second-order continuous derivability, thus the relaxation time $\tau = 2\pi / \omega_m = 1/f$ can be calculated.

III. RESULTS AND DISCUSSIONS

A. Structural Model of the Composite Ice

Fig. 1 shows the rewarming DSC curves of NaCl aqueous solutions with different concentrations after refrigeration. For $\beta = 0$, only one typical melting peak of single substance appears, which is caused by pure water solid-liquid phase transition. This corresponding crystalline form is defined as "Pure Ice" (abbreviated as PI). For $\beta > 0$, two peaks appear. The high temperature peak is the melting peak of pure ice. The peak position gradually moves to the low temperature direction as the concentration ratio increases, which is consistent with the law of freezing point depression. The low temperature peak is a eutectic peak caused by the phase transition of a mixture of salt ions and water molecules. The peak size increases with increasing concentration, but the peak position is basically unchanged, indicating that this kind of mixture has a fixed composition. Therefore, the corresponding crystalline morphology of the low temperature peak is defined as "Salty Ice" (abbreviated as SI). In addition, there should be a small number of unstable, long-range disordered amorphous water molecules, which is defined as "Amorphous Ice" (abbreviated as AI).

Thus, the "Composite Ice" is defined as the mixture of pure ice, salty ice and amorphous ice formed by frozen NaCl aqueous solution. Combined with the microscopic observation of frozen NaCl aqueous solution by W. Sun and Y.H. Ma [7-8], the structural model of the composite ice is established as shown in Fig. 2.

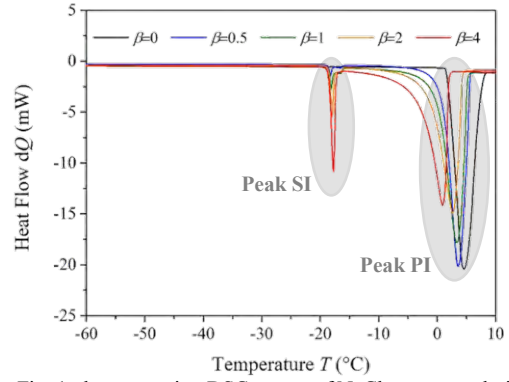


Fig. 1. the rewarming DSC curves of NaCl aqueous solutions

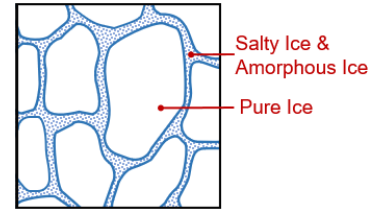


Fig. 2. the structural model of the composite ice

B. Conversion Rate of Pure Ice

Define the conversion rate of pure ice η as the percentage of water molecules frozen into pure ice after solution freezing:

$$\eta = \frac{\Delta Q_{PI}}{\Delta Q_{H_2O}} \times 100\%, \quad (6)$$

where ΔQ_{PI} and ΔQ_{H_2O} are the fusion heat of pure ice after freezing NaCl solution and deionized water with the same volume respectively, which are obtained by integrating the corresponding melting peaks in DSC curves.

The conversion of pure ice decreases monotonically with the increase of concentration ratio, as shown in Fig. 3, which implies that the addition of salt ions hinders the formation of pure ice. However, when $\beta > 0.5$, the curve drops more gently, indicating the decrease of this ability of salt ions. This may be due to the non-ignorable interaction between anions and cations weakening the effect of the ion on the water molecules, since ions in solution can only be considered to exist independently when the solution concentration is less than about 0.1 mol/L for 1:1 electrolyte solution (i.e., $\beta = 0.64$ for NaCl solution) [9].

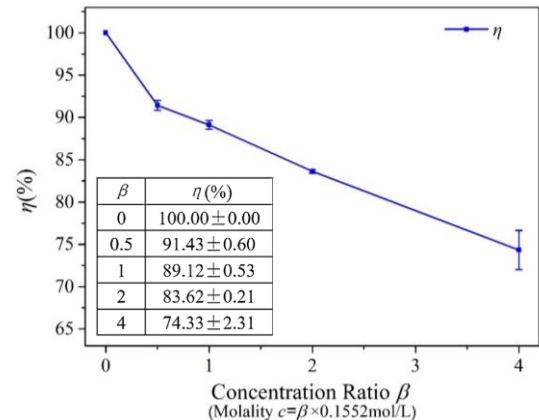


Fig. 3. the conversion rate of pure ice

C. Dielectric Characteristics of Composite Ice

Fig. 4 shows the dielectric spectra of pure ice and composite ice at -30°C and -60°C for $\beta = 0, 1$, and 2. It can be seen that both pure ice and composite ice exhibit relaxation polarization in the measured frequency range, and the relaxation frequency moves toward the low frequency direction as the temperature decreases.

The relaxation frequency of pure ice appearing at 1.24kHz to 5.88kHz is caused by the dipole polarization of water molecules. The relaxation polarization frequency of composite ice in the range of 2.59kHz to 19.32kHz is of the same order of magnitude. Therefore, it is considered as the relaxation polarization of water molecules in pure ice and amorphous ice.

The relaxation frequency of composite ice is higher than that of pure ice. This is due to the destructive effect of hydrogen bonds between water molecules by ions in solution, which inhibits the entry of water molecules into the crystal lattice of pure ice, resulting in the decrease of pure ice and the increase of amorphous ice.

In addition, the real part of the dielectric constant of composite ice is a diagonal line in the frequency range below 100Hz, and $-\partial\epsilon_r'/\partial\ln\omega$ also increases obviously at low frequency, with a value two orders of magnitude higher than that of pure ice. Since the effect of conductivity has been eliminated for $-\partial\epsilon_r'/\partial\ln\omega$, it can be inferred that there is another relaxation polarization phenomenon in the lower frequency range belonging to the thermal ion polarization caused by ions in salty ice.

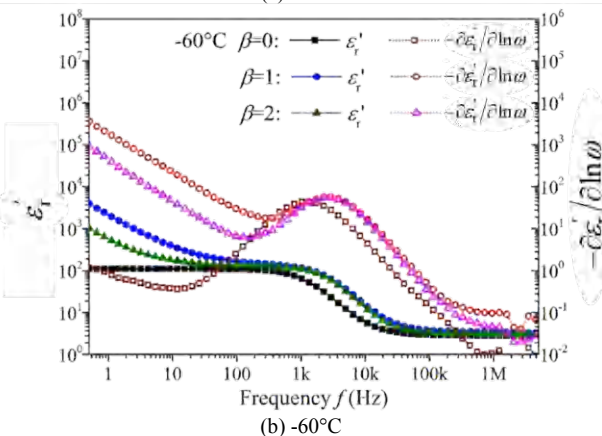
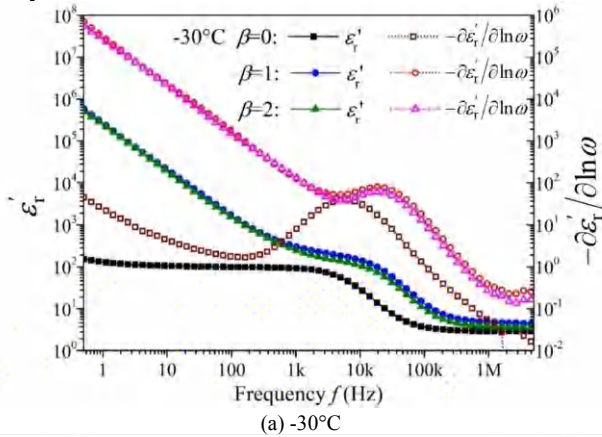


Fig. 4. dielectric spectra of pure ice and composite ice

D. Relaxation Time and Activation Energy

According to dielectric spectra, the relaxation time τ of composite ice at different concentrations and temperatures can be obtained. Combined with the Arrhenius formula, the relaxation activation energy E_a of composite ice can also be calculated. The solid line in Fig. 5 is $\ln\tau-1/T$ linear fitting with Adj. R-Square above 99.5%. This confirms the previous inference that the relaxation process of composite ice in the measurement range is a single relaxation process of water molecules.

The solid lines in Fig. 6 are the curves of the relationship between relaxation time and concentration ratio at -30°C , -40°C , -50°C , and -60°C , and the dotted line is the curve of the relationship between relaxation activation energy E_a and concentration ratio. All these lines have obvious slope changes at $\beta = 0.5$.

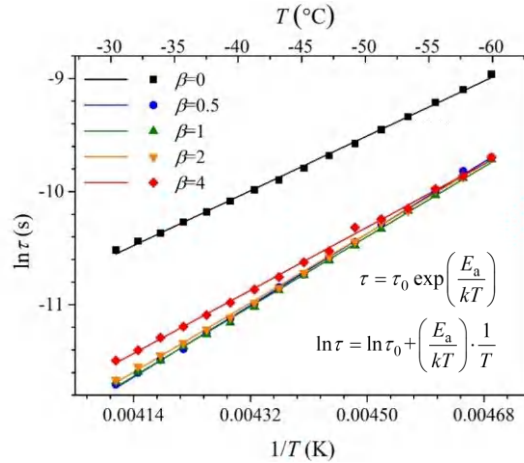


Fig. 5. $\ln\tau-1/T$ linear fitting

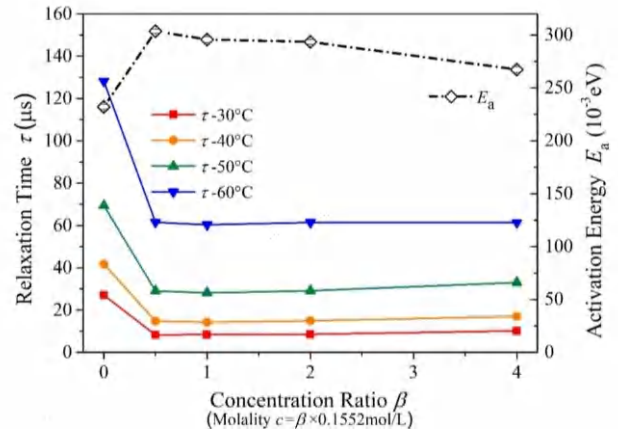


Fig. 6. Variation of relaxation time and activation energy with concentration

For $0 < \beta < 0.5$, the relaxation time of composite ice decreases significantly with the addition of ions. The destructive effect of salt ions on hydrogen bonds between water molecules leads to more amorphous ice, and the relatively small interaction force between water molecules in amorphous ice makes the polarization more easily, so the relaxation time becomes shorter.

For $\beta > 0.5$, the relaxation time gradually increases with increasing concentration. Although the destruction of hydrogen bonds caused by ions still dominates, the non-negligible

interaction between anions and cations weakens the ability of ions to destroy hydrogen bonds between water molecules, resulting in a slight increase in relaxation time.

Contrary to the relaxation time, the relaxation activation energy of composite ice increases significantly at first and then decreases slowly with the increase of concentration. Overall, the relaxation polarization of water molecules in composite ice needs to overcome a larger barrier than that in pure ice due to the binding effect of ions on water molecules, while the non-negligible ion-to-ion interaction gradually reduces the barrier when the concentration ratio is large enough ($\beta > 0.5$).

IV. CONCLUSIONS

In this paper, DSC analysis and dielectric analysis were carried out on NaCl aqueous solution samples with different concentration ratios, and the following conclusions were drawn:

1) The phase transition of NaCl aqueous solution at low temperatures constitutes a three-phase composite ice structure consisting of pure ice, salt ice, and amorphous ice. The conversion rate of pure ice decreases monotonically with the increase of concentration ratio.

2) In the temperature range from -30°C to -60°C , for pure ice, the relaxation polarization frequency of water molecules ranges from 1.24kHz to 5.88kHz. For composite ice, the relaxation polarization frequency of water molecules ranges from 2.59kHz to 19.32kHz, and the thermal ion relaxation exists in a lower frequency range below 0.5Hz.

3) The addition of ions destroys the hydrogen bonds between water molecules, which makes the relaxation activation energy of composite ice significantly enhanced and the relaxation time significantly shortened compared with pure ice. However, when $\beta > 0.5$, the interaction force between ions is non-ignorable, so that the relaxation activation energy decreases slowly and the activation energy of relaxation time increases slightly with increasing concentration.

The study on the crystallization and relaxation of sodium chloride aqueous solutions at low temperatures in this paper is expected to provide theoretical and experimental basis for further exploration of electromagnetic field controlled cryogenic refrigeration technology for biomaterials.

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