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Rheological and dielectric behavior of milk/sodium carboxymethylcellulose mixtures at various temperatures

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Rheological and dielectric behavior of milk/sodium carboxymethylcellulose (Na-CMC) mixtures with 0–10 g/L Na-CMC were investigated from 15 °C to 55 °C. Shear viscosity and viscoelastic behavior of milk/Na-CMC mixtures are mainly controlled by Na-CMC. Raising temperature has an obviously influence on viscoelastic behavior of mixtures. Meaning, the interchain hydrogen bond interaction among Na-CMC chains and the hydrogen bond interaction between Na-CMC chains and water molecules change with temperature. At 55 °C, the viscoelastic behavior of mixture with 2.5 g/L Na-CMC is different from that of the others. That indicates temperature has a larger impact on chain conformation of Na-CMC at the mixtures containing lower Na-CMC concentration. The dielectric spectra show one relaxation caused by loosely bound counterions. With increasing temperature and Na-CMC concentration, the changes of relaxation time τ and dielectric increment $\Delta\varepsilon$ are critically relevant to the numbers of bound counterions and chain conformation of Na-CMC. The contribution of Na-CMC to the dc conductivity of mixtures notably changes at 45 °C. It reveals the free ion numbers and viscosity of bulk phase obviously changes at 45 °C. The results reveal the stability of mixtures reduce with increasing temperature.

1. Introduction

Most of processed dairy products, such as acidified milk drinks, low-fat dairy products and milk puddings et al., are produced from fresh milk or reconstituted milk. However, the fresh milk or reconstituted milk is very sensitive to pH, ion strength and temperature of the systems. Milk protein is readily aggregate as the pH value is close to the isoelectric point of the adsorbed protein, the ionic strength reaches a certain degree and/or the temperature above the denaturation temperature of protein [1]. The aggregate of milk protein will affect the sensory properties and consumer acceptability of processed dairy products. In order to improve the quality and shelf-life of dairy products, the polysaccharides, such as carrageenan [2–4], Na-CMC [5–9] and so on, are often added to fresh milk or reconstituted milk as stabilizer during processing.

Na-CMC is one of the most important anionic polysaccharides, used as viscosity modifier, thickener, emulsion stabilizer, and water-retention agent in food industrial. It plays an important role in the structure and stability of food systems, such as improving the water retaining capacity of emulsified sausage system [10], and the thermal stability of canned high-fat coconut milk by mixed with Montanox 60 (0.2–1.0% *w*/*v*) [11]. For dairy products, Na-CMC can improve the quality of buffalo milk [12], slow ice recrystallization of ice cream model systems by interaction with milk protein [13], and affect the viscoelasticity of milk [14,15]. Because Na-CMC can form entanglement dispersion networks and greatly improve the rheological properties of continuous phase. These properties depend on the chain conformations of Na-CMC [16,17].

There are many researches on the chain conformations of Na-CMC in aqueous solution by means of dielectric spectroscopy [18,19], rheology [20,21], small angle neutron scattering [22], etc. However, as a complex system, food contains carbohydrates, protein, fat, minerals and so on which, especially protein, may interact with Na-CMC. That affects the chain conformations of Na-CMC, and resulting in the changes of stability of food systems. As early as 1896, Beijerinck first reported phase separation phenomenon was observed in protein-polysaccharide mixture [23]. The phase behavior of protein-polysaccharide mixtures seemed to be of key importance for both the development of formulated foods and the improvement of conventional food processing [24]. Hence, it is significant to study the chain conformations of Na-CMC in the actual food systems and its interaction with food components, particularly protein.

It was reported that investigation of rheological behavior of polysaccharides contributes to predicting the structural changes of foods during manufacturing processes [25,26]. The effect of polysaccharides on the macroscopic characteristics of system also can be obtained by rheological measurement [27]. Therefore, using rheological measurement, we may be able to study macroscopic characteristics of food system and speculate the chain conformation changes of Na-CMC in the actual food systems.

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Furthermore, the ionic state in solution can influence the chain conformation of Na-CMC. The charge density of Na-CMC chains also has a direct effect on the macroscopic properties of the Na-CMC solutions. [28,29] These would influence the contribution of Na-CMC on the stability of system. It was reported the researches on dielectric and electric properties of systems can give a great deal of information on the movement, distribution and fluctuation of charges or the relaxation induced by the motions of dipoles and ions [30]. Hence, we can effectively study ionic state in Na-CMC solutions and speculate chain conformation changes of Na-CMC by dielectric relaxation spectroscopy.

In the current study, the effects of temperature and Na-CMC concentrations on chain conformation of Na-CMC in milk were researched by rheology and dielectric spectroscopy. Such studies of Na-CMC addition to milk system would lead to a better understanding of the principles behind the instability of the mixture under conditions relevant to the development of dairy products. The study may be helpful in processing, evaluating and controlling the quality of dairy products containing Na-CMC.

2. Materials and methods

2.1. Materials

Skim milk powder was purchased at Coles (Australia, Sydney) and contains 35.20% protein, 52.80% carbohydrate(sugar), less than 4.00% fat, 0.45% Na^+, 1.69% K^+, 1.13% Ca^{2+}. Commercial grade of sodium carboxymethylcellulose (Na-CMC) (Solarbio, Beijing) was used as received. The sodium ion (Na^+) content was reported as 0.065–0.085 in weight by the manufacturer.

2.2. Sample preparation

Reconstituted milk stock solution of 300 g/L solids was prepared by dissolving skim milk powder in deionized water under gentle stirring at 25 °C for 2 h, then seal and overnight at 4 °C to ensure complete hydration. Na-CMC stock solution (20.0 g/L) was obtained by mixing Na-CMC powder and deionized water under intensively shearing at 25 °C for 3 h, followed by seal and storage at 4 °C overnight to allow complete hydration. Milk/Na-CMC mixtures were prepared by mixing the Na-CMC stock solution with reconstituted milk stock solution, deionized water at the Na-CMC concentrations from 2.5 to 10.0 g/L and milk concentration of 150 g/L solids, then the mixtures were stirred for 1.5 h to allow sufficiently mixing.

2.3. Rheological measurements

Small deformation oscillatory measurements (frequency sweeps) of milk/Na-CMC mixtures were performed on an MCR 302 rheometer (Anton Paar, Graz, Austria) equipped with Couette geometry (bob diameter 24 mm, cup diameter 26 mm, bob height 25 mm). Temperatures were controlled by means of a Peltier system. Steady shear viscosity measurements were carried out on the shear rate range from 1 to 1000 s^{-1} at 25 °C. Small deformation oscillatory measurements of storage modulus (G′) and loss modulus (G″) were taken between 0.1–62.8 rad/s at different temperatures (15–55 °C, in steps of 10 °C) and a constant strain of 1%. Strain sweep tests at 1 Hz at the studied concentrations were previously conducted to determine the linear viscoelasticity range of strain.

2.4. Dielectric measurements

Dielectric measurements were performed in the frequency range from 49 Hz to 110 MHz at temperatures from 15 to 55 °C/10 °C by HP 4294A precision impedance analyzer (Agilent Technologies) with concentrically cylindrical platinum electrodes cell [31]. The applied alternating field was 500 mV. The temperature of samples was controlled by a circulating thermostatic water jacket. The raw experimental data, capacitance C_x and conductance G_x, were corrected by stray capacitance (C_r), cell constant (C_l), and residual inductance (L_r) according to Schwan method [32,33]. They are determined with three standard substances (pure water, ethanol and air) and KCl solution of varying concentrations. Then the corrected data of capacitance Cs and conductance Gs at each frequency were converted into permittivity and conductivity according to equations $\varepsilon = C_s/C_l$ and $\kappa = G_s\varepsilon_0/C_l$ (ε_0 is the permittivity of vacuum).

3. Results and discussions

3.1. Rheological behavior of milk/Na-CMC mixtures

3.1.1. Effects of Na-CMC concentrations on shear viscosity

Fig. 1a shows the shear viscosity as a function of shear rate for milk and milk/Na-CMC mixture with 2.5–10.0 g/L Na-CMC at 25 °C. As shear rate increases, shear viscosity of pure milk is very low and basically unchange, and it is considered a Newtonian fluid. Fernndez-Martin [34], and Wayne and Shoemaker [35] also reported that milk and evaporated milk behave as Newtonian fluid. However, shear viscosity of milk/Na-CMC mixtures decrease with increasing shear rate, exhibiting shear thinning behavior. That is similar to that of CMC aqueous solution reported by several researchers [36,37]. It was reported that lactose molecules make little contribution to the viscosity of milk, while the proteins and fat globules have an important influence in the structure and overall behavior of dairy products [38]. Thus, in this work, the viscosity of milk is controlled by proteins, especially casein micelles. And under neutral pH conditions, both casein micelles and Na-CMC chains in milk are negatively charged. Between them, they are mainly dominated by electrostatic repulsion and cannot form electrostatic complex. It was also reported by X.H. Yang and W. L. Zhu that when dissolve CMC in water before adding salt, the salt has little influence in the viscosity of solution [39]. In summary, the shear viscosity of milk/Na-CMC mixtures mainly depend on Na-CMC, and almost unaffected by the protein and salt in milk. And the Na-CMC chains can not only form hydrogen bonds with water molecules but also entangle each other to form network structure, which hinder the flow and result in an increase in viscosity. However, when the system is subjected to shear stress, the winding Na-CMC chains are oriented and stretched, and entangle network structures are destroyed, then leading to a decrease in viscosity. [40]

As expected, the viscosity of milk/Na-CMC mixtures increases with increasing Na-CMC concentration. Because the water molecules and hydrophilic OH and COONa groups of Na-CMC chains can form hydrogen bonds, the hydrophilic OH and COONa groups also can form intrachain and/or interchain hydrogen bonds [41]. That has a great impact on the viscosity of the solution, especially the interchain hydrogen bonds [42]. And as Na-CMC concentration increases, the more hydrogen bonds formed, which increases the interaction force between molecules and results in an increase in viscosity. In order to better compare the effect of Na-CMC concentration on viscosity of milk/Na-CMC mixtures, we fitting the experimental data in Fig. 1 with Eq. (1) and obtain the zero-shear viscosity η_0.

$$\eta(\gamma) = \eta_\infty + (\eta_0 - \eta_\infty)\left(1 + (\tau\gamma)^a\right)^{n-1/a} \quad (1)$$

where $\eta(\gamma)$ represents the dynamic viscosity of the solution, η_∞ is infinite shear viscosity. τ indicates characteristic time, n is flow index without dimensionless, a is a dimensionless exponent which determines the transition between the first Newtonian plate and the power law zone. Then, based on $\eta_{sp} = (\eta_0 - \eta_s) / \eta_s$ (η_s is solvent viscosity), we calculate the specific viscosity as showed in Fig. 1b. The power law exponent for low Na-CMC concentration systems data is 1.99, which is compare well the best fit power law exponent for entangled regimes (1.7 ± 0.2) [22].

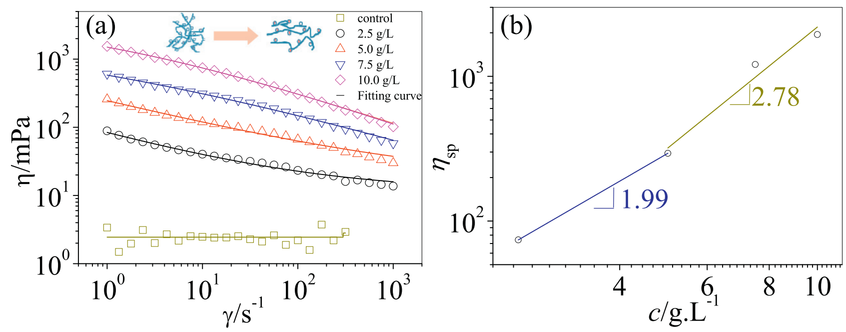

Fig. 1. At 25 °C, (a) shear viscosity as a function of shear rate for milk and milk/Na-CMC mixtures with 2.5–10 g/L Na-CMC. (b) Specific viscosity as a function of concentration for milk/Na-CMC mixture. The symbols represent experimental data, and lines are fitting curves.

It indicates that the Na-CMC concentrations used in this work are all in entangled regimes.

3.1.2. Effects of temperatures on viscoelasticity

Representative dynamic elastic modulus (G′) and viscous modulus (G″) as a function of frequency for (a) milk and (b) milk/Na-CMC mixture with 2.5 g/L Na-CMC are plotted in Fig. 2, only for the temperatures of 15 °C, 35 °C and 55 °C, to show the results more clearly. For milk (Fig. 2a), the G′ is much less than G″ and the temperature has little effect on both moduli within the entire frequency range and tested temperatures. Meaning the microstructure of milk is basically unchange within the test temperature range. Because G′ and G″ is mainly controlled by the proteins of milk [38], the concentration of proteins in the tested milk is low, and there is no aggregation between proteins, thus the viscosity predominates in milk. Besides, it was reported that heating has little impact on the casein micelles at temperatures less than 100 °C, and whey proteins do not unfold and denature at temperatures less than 60 °C [43]. Therefore, milk proteins tend to aggregate with increasing temperatures, but no aggregation occurs over the tested temperatures. For milk/Na-CMC mixtures, there is no electrostatic complex formation between casein micelles and Na-CMC. And elastic modulus (G′) and viscous modulus (G″) of milk/Na-CMC mixtures are also controlled by Na-CMC. A decrease in both moduli G′ and G″ is observed with increasing temperature over the entire frequency range (Fig. 2b). Meaning the interchain hydrogen bonds between CMC chains reduce, and the hydrogen bonding between CMC chains and water molecules also decreases. At 15 °C and 35 °C, low frequency G′ is larger than G″, namely elasticity is the dominant property of milk/Na-CMC. However, at 55 °C, the G′ is smaller than G″ over the entire frequency range, exhibiting liquid-like behavior. That indicates the long-term stability of milk/CMC mixture decrease with increasing temperature. Probably because raising temperature induces chain conformation changes of Na-CMC. Because at room temperature, milk/Na-CMC mixtures are dominated by ion-binding, hydrogen bond and electrostatic repulsion rather than hydrophobic interactions and electrostatic attraction [39]. However, rising temperature would enhance hydrophobic interactions, while weaken ion-binding and hydrogen bonds interactions. And the Na-CMC chains become more and more hydrophobic, then they have the tendency to form clusters at higher temperature. Hence, the contribution of Na-CMC to viscoelasticity and stability of milk/Na-CMC mixtures decreases.

3.1.3. Effects of Na-CMC concentrations on viscoelasticity

Fig. 3 presents the profiles of elastic modulus G′ and viscous modulus G″ from frequency sweep test of milk and milk/Na-CMC mixtures with 2.5–10.0 g/L Na-CMC at temperature (a) 25 °C and (b) 55 °C. At 25 °C and 55 °C, both moduli are increase with Na-CMC concentration. Meaning more entangled network structures formed among CMC chains and more hydrogen bonding formed between CMC and water molecules with increasing Na-CMC concentration. At 55 °C, lower frequency G′ is less than G″ for all milk/CMC mixtures, indicating the stability reduces. However, it can be observed in Fig. 3b that the moduli (G′ and G″) of the milk/Na-CMC mixture with 2.5 g/L Na-CMC is different from the others at 55 °C. That is the G″ is more than G′ at the whole frequency range. Meaning the microstructure of mixture with 2.5 g/L Na-CMC is different from that of the others. That may be due to the dynamics of Na-CMC chains in milk and the stochastic effect of temperature. As Na-CMC chains become more hydrophobic, they tend to collapse and form clusters at higher temperature. For milk/Na-CMC mixtures with lower Na-CMC concentrations, few coupling points exist in entangled network structures. And the Na-CMC chains collapse completely and its interaction with water sharply weakens, leading to a decrease in viscosity. There may be very few entangled network structures, resulting in a sharp decrease in elasticity. However, as Na-CMC concentration increases, the coupling points of extended entangled network increase. The Na-CMC chains also tend to collapse and form clusters, but there is still entangled network structure. And at middle frequency region, Na-CMC chains cannot emerge from the entanglements, causing tension in the Na-CMC chain segments between the coupling points, thus showing an elastic behavior.

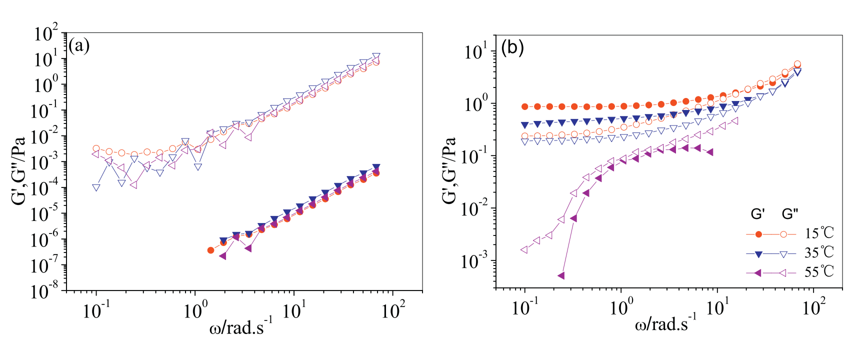

Fig. 2. Elastic and viscous moduli(G′ and G″) as a function of frequency for (a) milk and (b) milk/Na-CMC mixture with 2.5 g/L Na-CMC at 15 °C, 35 °C and 55 °C.

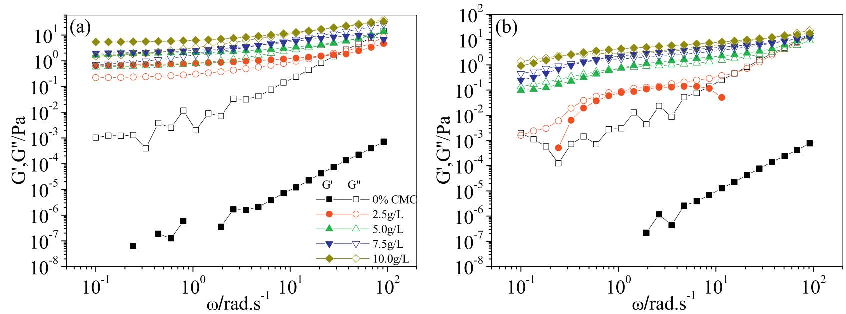

Fig. 3. Frequency dependence of elastic and viscous moduli (G′ and G″) for milk/Na-CMC mixtures with 0–10.0 g/L Na-CMC at temperature (a) 25 °C and (b) 55 °C.

3.2. Dielectric behavior of milk/Na-CMC

3.2.1. Dielectric analysis

To better describe the dielectric properties of the system, the experimental data were fitted by Eq. (2) to obtain the dielectric parameters (or relaxation parameters) that characterize the dielectric relaxation behavior. The Eq. (2) is Cole-Cole equation which containing one dielectric relaxation and electrode polarization (EP) term $A\omega^{-m}$.

$$\varepsilon* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+(j\omega\tau)^\beta} + \frac{\kappa_{dc}}{j\omega\varepsilon_l} + A\omega^{-m} \quad (2)$$

where $\Delta\varepsilon(=\varepsilon_l-\varepsilon_\infty)$ is dielectric increment, ε_l and ε_∞ are low and high frequency limit of permittivity respectively. $\tau(\tau=1/2\pi f_0, f_0$ is characteristic frequency) is relaxation time, κ_{dc} is dc conductivity. β is the parameter representing the distribution of relaxation time. After removing the *EP* no dielectric relaxation is observed in pure milk. But an obvious dielectric relaxation was observed near MHz in milk/Na-CMC mixtures as shown in Fig. 4. The characteristic frequency is similar to the report by T. Radeva [44]. And there's a little difference from the reported by D. Truzzolillo [19]. This may be the result of the difference in M and concentration of Na-CMC samples. We speculate the dielectric relaxation in this study may be caused by loosely bound counterions which fluctuate in the correlation length of Na-CMC chains.

Base on the counterion wave theory reported by Ito et al., [45,46] the dielectric increment Δε caused by counterion fluctuations can be explained as follows.

$$\Delta\varepsilon \sim \frac{n_L\alpha_e}{\varepsilon_0} \sim \frac{n_L e^2 d^2}{\varepsilon_0 KT} \propto n_L d^2 \quad (3)$$

where α_e and n_L represent the electrical polarizability and the number concentration of the loosely bound counterions respectively, ε_0 is the vacuum permittivity, *e* is the elementary charge, *d* is the fluctuation length of bound counterions, *K* is the Boltzmann constant, and *T* is the absolute temperature. Since, the loosely bound counterion fluctuates within the range of *d,* relaxation time τ is given

$$\tau \sim \frac{d^2}{2D} \quad (4)$$

where *D* is the diffusion constant of counterions.

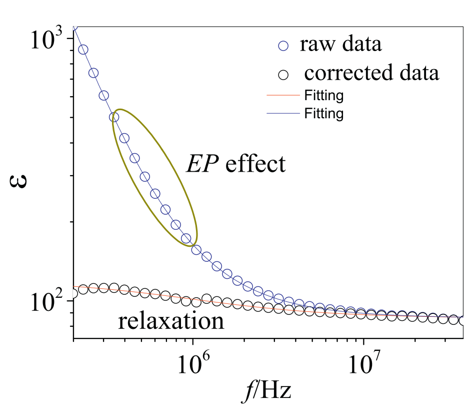

Fig. 4. Dielectric spectra of Na-CMC-milk mixture with 2.5 g/L Na-CMC at 15 °C. The blue circle and blue line are the uncorrected raw data and best total fit with EP, respectively. The black circle and red line are corrected raw data and best total fit without the EP, respectively.

3.2.2. Temperature dependence of dielectric parameters

Fig. 5 shows the temperature dependence of (a) relaxation time τ and (b) dielectric increment Δε for milk/Na-CMC mixtures with different Na-CMC concentrations in the best fitting. Based on Eq. (4), the τ is proportional to d^2/D. The relaxation time τ is found to decrease with increasing Na-CMC concentration (see Fig. 5a). Because as concentration increases, Na-CMC chains entangle with each other, and more entangled network like structure emerges, leading to a decrease in *d* and an increase in *D*. And τ also decreases with temperature. Because solvent quality seems to decrease with increasing temperature, and resulting in enhanced intermolecular and intramolecular associations [47]. That lends to a decrease in *d*. Besides, raising temperature has the effect of increasing on *D*. These two reasons would lead to a reduction in τ.

It is found that the dielectric increment Δε increases with increasing Na-CMC concentration showed in Fig. 5b. That maybe indicates the effect of Na-CMC on n_L is larger than the *d* in the concentration range we studied. Because according to Eq. (3), Δε is also proportional to $n_L d^2$. And it was reported that the n_L is proportional to the polymer concentration, while the *d* is inversely proportional to the polymer concentration [48]. The Δε is found to decrease with increasing temperature, meaning the change of n_L induced by heating is less than that of d^2/T. Because ionic solvation of counterions decreases with increasing temperature, leading to an increment in counterion bound to polyion chains [49–51]. That would lead to n_L increased. And with increasing temperature, the d^2/T is reduce. In summary, with increasing temperature and Na-CMC, the changes of τ and Δε are critically relevant to chain conformation change of Na-CMC.

3.2.3. Temperature dependence of dc conductivity

Fig. 6a shows the temperature dependence of dc conductivity (κ_{dc}) for milk and milk/Na-CMC mixture with 2.5–10.0 g/L Na-CMC. It shows the κ_{dc} of the mixtures increases with increasing temperature. For milk, the conductivity is mainly caused by its soluble salt fraction. The contribution of proteins is negligible and lactose does not conduct current [52]. Thus, the κ_{dc} of milk increase may be caused by the diffusion coefficient of soluble salt free counterions increased with increasing temperatures. However, for milk/Na-CMC mixtures, the contribution of soluble salt in milk to the κ_{dc} of all milk/Na-CMC mixtures is basically the same. The differences in κ_{dc} among the milk/Na-CMC mixtures are mainly due to Na-CMC. Thus, when discussing the

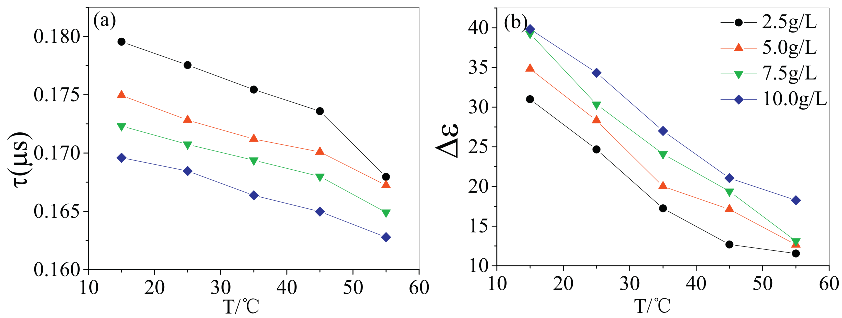

Fig. 5. Temperature dependence of (a) relaxation time τ and (b) dielectric increment $\Delta\varepsilon$ for milk/CMC mixtures.

κ_{dc} of milk/Na-CMC mixtures, we only from the point of view of Na-CMC.

To better understand the contribution of Na-CMC to the dc conductivity of milk/Na-CMC mixtures at different temperature, we calculated the increment in κ_{dc} of milk/Na-CMC mixtures by adding Na-CMC. Fig. 6b shows the increment in κ_{dc} of milk/Na-CMC mixtures by adding Na-CMC as a function of temperature. The increment in κ_{dc} is found to increase with increasing temperature. It may be mainly caused by a temperature-induced an increment in velocity of the ions in milk/Na-CMC mixtures at higher temperatures [49]. It is also observed that raising temperature leads to an increase in increment in κ_{dc} with a slope changed at 45 °C. That may be interpreted as the chain conformation change of Na-CMC. Because as temperature increases, the ionic solvation of counterions decreases and the condensation of counterion on polyion chain increases, resulting in a decrease in the fraction of uncondensed counterions [49,50]. And chain conformations of Na-CMC may be change from an extended random network structure to collapsed state. That also leads to a significant decrease in viscosity, and consequently to velocity of the ions increases significantly. It's also interesting to found that the slope changed of milk/Na-CMC mixture with 2.5 g/L Na-CMC are obviously larger than that of other systems at 45 °C. It may be explained as the change of ions number and viscosity. Mitsumata et al. [53] reported that degree of swelling of hydrogels increase with increasing the degree of dissociation. At lower Na-CMC concentration, the more counterions may bound to the CMC polyion chain. Degree of collapse of Na-CMC chain is greater, and resulting in a greater degree of viscosity reduction. However, at higher Na-CMC concentration, Na-CMC chains interpenetrate to form domains by reducing its electric charges, within which a finite fraction of counterions can be trapped [50,54]. And compare to lower Na-CMC concentration, the reduction in total amount of counterion in bulk phase may be greater at higher Na-CMC concentration. It was reported that stability and thickening of Na-CMC in dairy products are mainly determined by its formation of extended random network structure [26]. Stability and thickening of Na-CMC will be weaken as its chain conformation tend to collapsed state. Therefore, the Na-CMC may not be suitable for improving the thermal stability of milk under neutral conditions.

3.3. Microstructure of milk/Na-CMC mixtures

To summarize the rheological and dielectric properties of milk/Na-CMC mixtures, a schematic illustration representing the microstructure of milk/Na-CMC mixtures and chain conformations of Na-CMC in milk is given in Fig. 7. Under neutral pH, both Na-CMC and milk proteins are negatively charged, and they repulse each other and con not form electrostatic complexes. Besides, no denaturation of milk protein occurred within the test temperature range [43]. Thus, the microstructure of milk/Na-CMC mixtures is dominated by Na-CMC. At lower temperature, Na-CMC chains are exhibiting the extended random entangled network structure with few coupling points due to the electrostatic repulsion among Na-CMC chains, leading to an increase in viscosity and contributing to the stability of milk/Na-CMC mixture. However, raising temperature diminishes ionic solvation of counterions, leading to an increase in counterion bound to the polyion chains [49]. And the chain conformation of Na-CMC changes to collapsed state, decreasing the viscosity and weakening the stability. At low Na-CMC concentration, few coupling points exist in entangled network structure. With increasing temperature, Na-CMC chains completely collapse and almost without intermolecular interaction, resulting in a significantly reduction in viscosity. And due to gravity, CMC and casein may not distribute evenly in the water. The stability of mixtures is obviously weakened. However, as Na-CMC concentration increases, Na-CMC chains form a network-like structure with many coupling points by more interchain hydrogen bonds. And some casein micelles may be trapped in the entangled network structure. Although, with increasing temperature, the chain conformation of Na-CMC also tends to change from extended to collapsed state at higher concentration. There is still intermolecular interaction among Na-CMC chains, and entangled network structure, such which still plays a crucial part in maintaining the stability of mixtures. Therefore, we consider the Na-CMC, especially low Na-CMC concentration,

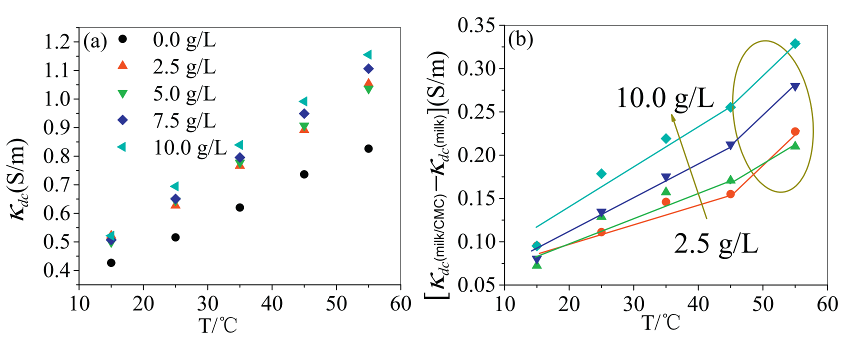

Fig. 6. (a) dc conductivity(κ_{dc}) for milk and milk/Na-CMC with 2.5–10.0 g/L Na-CMC and (b) the increment in κ_{dc} of milk/Na-CMC mixtures by adding Na-CMC as a function of temperature.

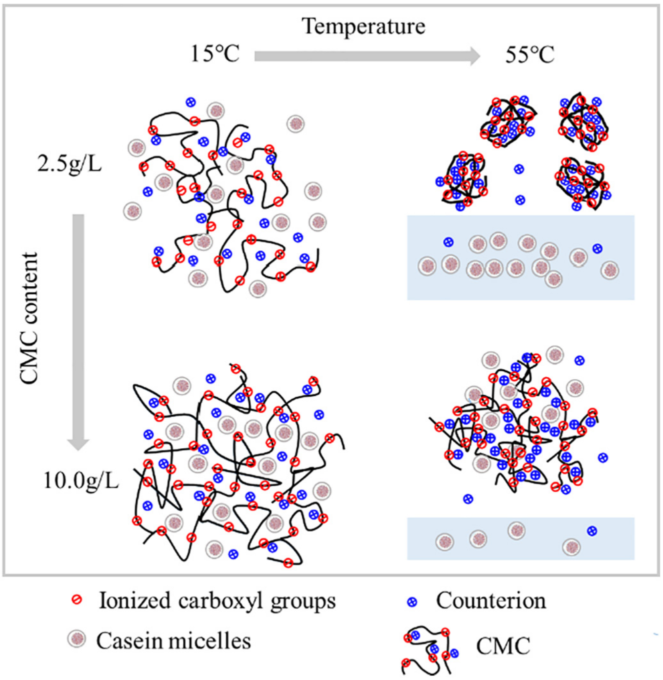

Fig. 7. Influence of temperature and Na-CMC concentrations on the microstructure of milk/Na-CMC mixtures.

is not applicable to improve the thermal stability of milk system under neutral pH conditions.

4. Conclusion

Rheological and dielectric properties of milk/Na-CMC mixtures at different temperatures have been investigated to clarify chain conformation of Na-CMC in milk. The G′ and G″ of milk/Na-CMC mixtures at low frequency are found to decrease with increasing temperature. Because raising temperature diminishes counterions solvation and increases counterion condensation on the polyion chain, resulting in weaken in interaction between Na-CMC chains and water. However, in the milk/Na-CMC mixture with 2.5 g/L Na-CMC, the G′ is smaller than G″ over the entire frequency range at 55 °C, this is different from the other systems. That can be explained as follows: at low Na-CMC concentration, chain conformation of Na-CMC changes to collapsed state and almost without intermolecular interaction at 55 °C. And with increasing concentration, more Na-CMC chains entangle with each other and form a network like structure even in 55 °C.

The dielectric spectra of milk/Na-CMC mixtures show one relaxation, which is caused by loosely bound counterions, in the experimental frequency range. With increasing Na-CMC concentration, the relaxation time τ decrease and dielectric increment Δε increase, meaning Na-CMC chains entangle with each other. The τ and Δε decrease with increasing temperature, indicating the temperature induced Na-CMC chains changes to collapsed state. Raising temperature leads to an increment in κ_{dc}, which may be caused by a temperature-induced increase in the speed of ions at higher temperatures. The contribution of Na-CMC to the dc conductivity of mixtures notably changes at 45 °C. That reveals when raising temperature to 45 °C, the free ion numbers and viscosity of bulk obviously changes.

The thickening and stability of Na-CMC are closely related to its chain conformation. This work may contribute to the production, processing, research and development of dairy products containing Na-CMC. Besides, the dielectric properties of materials play an important role in dielectric heating. This work may also provide useful information for dielectric heating in food industry.

Acknowledgments

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