Rheological behaviour of salty and sweet soy sauces at sub-zero temperatures

Reidar Barfod Schüller and Elling-Olav Rukke

Norwegian University of Life Sciences, Faculty of Chemistry, Biotechnology and Food Science, 1432 Ås, Norway

ABSTRACT

Two different types of soy sauce were investigated at sub-zero temperatures, Kikkoman and ABC Sweet Soy Sauce. Kikkoman is a traditional low viscosity salty fermented soy sauce. The ABC Sweet Soy Sauce does not contain any water at all. It consists mainly of carbohydrates. The viscosity is high.

Kikkoman contains approximately 16.9% salt and exhibits a significant freezing point depression.

Figure 1. Kikkoman salty soy sauce.

The behaviour of the soy sauces were studied in rheometers, with both cone/plate and bob/cup measuring systems

The results show that Kikkoman soy sauce can be in thermodynamic non-equilibrium several degrees below the freezing point. The crystallization was observed in the rheometers. Tests show that the temperature at which crystallization starts depends on the shear rate for rotational flow.

The ABC Sweet Soy Sauce, containing 99% carbohydrates became very viscous at low temperatures, but it did not solidify. The sweet soy sauce did not exhibit a freezing point and the viscosity became very high at the lowest temperatures.

Figure 2. Soy sauce at -23 ºC in a glass just frozen as a result of agitation.

INTRODUCTION

Kikkoman, Figure 1, and ABC Sweet Soy Sauce. Kikkoman is a traditional low viscosity salty fermented soy sauce produced by Kikkoman Foods Europe B. V., Holland. The ABC Sweet Soy Sauce, imported by Scanesia AS, does not contain any water at all and consists mainly of carbohydrates. The viscosity is high.

Kikkoman contains approximately 16% salt and exhibits a significant freezing point depression. In addition, the sauce remained a liquid also below the freezing point if it was not agitated. Kikkoman sauce cooled to -23 ºC at rest was still a liquid, but as soon as it was stirred or agitated by rotating the glass, ice crystals formed, Figure 2.

Different commercial soy sauces can be found in grocery shops in Norway. The most common of these is the low viscosity salty fermented soy sauce that contain water. Another is the sweet soy sauce that does not contain any water at all.

Two soy sauces were selected, the Kikkoman salty soy sauce and a sweet soy sauce named ABC Sweet Soy Sauce.

Observations have shown that salty soy sauce does not freeze if left at rest in a deep freezer down to -23 ºC, but as soon as it is stirred or agitated, ice crystals form.

Both salty fermented soy sauce and sweet soy sauce have been made for centuries by traditional methods. Soy sauce is one of the world`s oldest condiments and it has been used in China for more than 2500 years. Soy sauce is made either by fermentation or by hydrolysis of the soybean. It is a dark brown liquid with a pleasant aroma, used primarily as flavouring agents for meat, poultry, fish, vegetables and rice1.

The preparation of soy sauce is known to involve the action of moulds, yeasts, and bacteria such as *Aspergillus oryzae*, *Zygosaccharomyces soya*, and *Lactobacillus* species.

Enzyme hydrolysis of soy protein may lead to enhanced solubility and thermal stability. A lot of research have been focused on optimizing the hydrolysis conditions of soy protein for enhanced solubility, thermal stability and bioactivity[2].

Denatured proteins, like most processed soy proteins, have exposed peptide bonds available for enzymatic cleavage. This phenomenon has been utilized in many research projects to improve physio-chemical and functional properties.

Changes in water solubility and rheological properties including dynamic shear, large deformation, and apparent viscosities of resulting hydrolysates have been determined and reported[3].

Increased solubility of amino acids and small peptides, will of course also contribute to a freezing-point depression when these hydrolysed products are dissolved in water or other aqueous solutions. Solubility of amino acids in water and aqueous solutions is also studied and reported based on the statistical associating fluid theory[4]. According to AnaSpec Inc. peptides shorter than five residues are usually soluble in water or aqueous buffer, except when the entire sequence consists of hydrophobic amino acids. Normally salt (HCl) prevent peptides to aggregate[5].

Salty fermented soy sauce contains normally about 16 -18% salt. Sweet soy sauce is a sweetened aromatic soy sauce with a dark colour, a thick syrupy consistency and a unique, sweet flavour due to the generous addition of palm sugar[1].

Figure 3. Soy sauce at sub-zero temperature in the CC27 bob/cup system. A thin oil layer is placed on surface of the sauce to prevent dilution from water originating from the surrounding air.

METHODS

Samples

The soy sauces were purchased from grocery shops in Norway. The composition of the chosen soy sauces are shown in Table 1.

Table 1. Composition of soy sauces per 100 ml as declared by the manufacturers.

	Kikkoman	ABC Sweet Soy Sauce
Energy (kJ)	325	1790
Fat (g)	0.0	1.5
Carbohydrates (g) of which is sugar	3.2 0.6	99.2 81.0
Fibre (g)	0.0	1.5
Protein (g)	10.0	2.5
Salt (g)	16.9	5.4
Water	70.2	0.0
pH	4.68	-

Measurements were also conducted on a reference fluid being distilled water with 16.9 g/100 ml added NaCl. Salt (42.25 g) was weighed and placed in a bottle which was filled with distilled water to a total volume of 250 ml.

Rheological methods

The behaviour of the soy sauces were studied in a MCR301 rheometer. A CP50-1 cone/ plate system was used for the Kikkoman sauce and a PP08 system was used for the very viscous sweet soy sauce. Cooling to -25 ^{0}C was done at different shear rates.

A UDS200 rheometer from Anton Paar with a CC27 bob/cup measuring system was also used in the experiments. A Peltier TEZ 150P controlled the temperature, and the cooling fluid to the Peltier was supplied from a Lauda Ecoline RE 204 fitted with an E200 controller. The set point of the cooling fluid, which was a water - Glycol solution, was -10 ^{0}C.

The rheometer was run at constant shear rate (50, 150, 250 or 500 1/s) while the temperature was reduced at a rate of 1 ^{0}C/minute starting at 0 ^{0}C. Freezing was detected by a sudden increase in shear stress. When the shear stress exceeded 20 Pa, the rotation was programmed to stop and the temperature was increased to 0 ^{0}C at the maximum rate of the Peltier. The sequence was then repeated several times, generating multiple measurements of freezing point. An oil layer was placed on top of the soy sauce to prevent water diluting the sauce since ice deposited on the metal surfaces of the Peltier and some of this melted when the temperature was increased to 0 ^{0}C.

RESULTS AND DISCUSSION

Viscosity measurements

The viscosity increased as the temperature was reduced as shown in Figure 4. Values for the salt Kikkoman soy sauce viscosity at room temperature, found in the literature[6], show variations between 1.6 to 3.6 mPas. In these experiments the viscosity became much higher, up to 50 mPas at a temperature of -23 ^{0}C.

The sweet soy sauce hade much higher viscosity, increasing to more than 600 Pas at -20 ^{0}C.

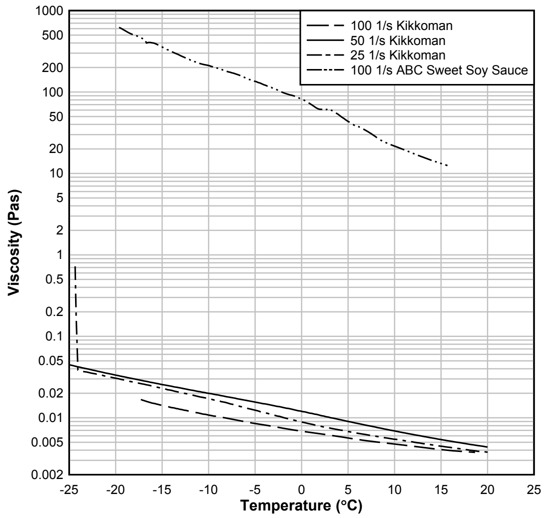

Figure 4. Viscosity measurements of the soy sauces versus temperature.

The viscosity of the sweet soy sauce was more than 4 decades higher than the salty soy sauce at the lowest temperatures.

Freezing point

The freezing point of the salty soy sauce containing 16.9w% NaCl at low shear rates was as low as -28 ºC. The freezing point of distilled water with 16.9 g/100 ml NaCl added was measured to be approximately -15 ºC.

The freezing point of a pure 16.9 wt% NaCl solution is according to Bodnar[7] 19.5 ºC. For saturated brine the value is -23.2 ºC at a salinity of 21.2 wt%. Other impurities will in addition also contribute to the freezing point depression.

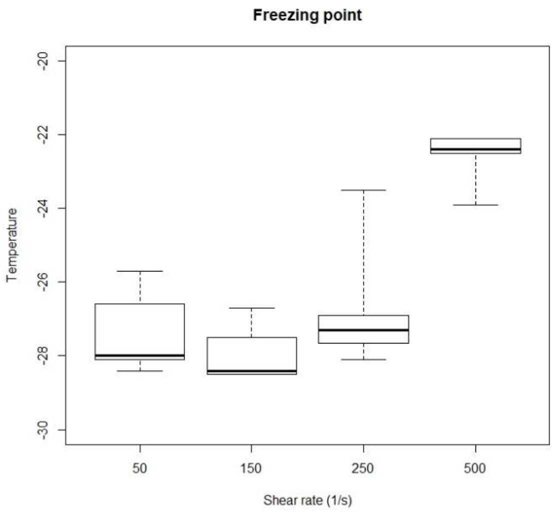

Figure 5. Box diagram showing freezing point of Kikkoman soy sauce versus shear rate.

The presence of the dissolved hydrolysed proteins is believed to be the main cause of the reduced freezing point temperature, which is almost 10 degrees below the freezing point of salt water with the same salt concentration.

The presence of the hydrolysed proteins is also reflected in the pH value of the Kikkoman soy sauce; pH = 4.68.

Also, the measurements show that the freezing point is a function of the shear rate. A larger shear rate tends to increase the freezing temperature as seen in Figure 7. The number of repetitions for the shear rates 50, 150, 250 and 500 1/s were 5, 4, 15 and 6. The same effect is seen for distilled water with 16.9 W% added NaCl as seen in Figure 6, which is based on 14 repetitive measurements at each shear rate. A comparison is shown in Figure 7. The freezing temperature of Kikkoman soy sauce at a shear rate of 500 1/s was significantly different (ANOVA, Tukey 95%) from freezing temperature at lower shear rates. Likewise, the freezing temperature of the salt water at 50 1/s was significantly different from the higher shear rates.

The sweet soy sauce did not contain any water so freezing was not an issue for this product.

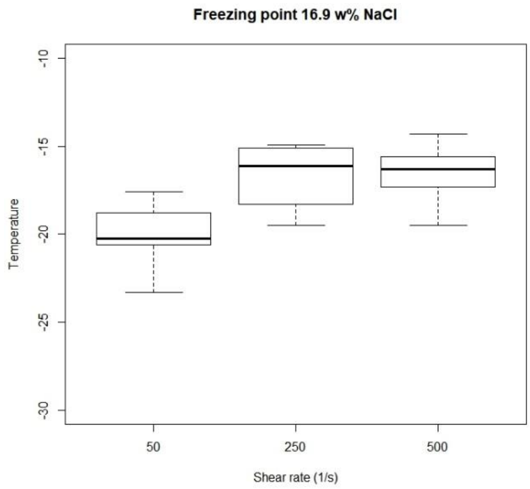

Figure 6. Box diagram showing freezing point of distilled water with 16.9 w% NaCl versus shear rate.

CONCLUSIONS

The results of this study are summarized as follows:

- The viscosity of both salty and sweet soy sauce increases as the temperature is decreased.

- The viscosity of sweet soy sauce is 4 decades higher than the salt soy sauce.
- The salty soy sauce freezes at a temperature well below the freezing point of distilled water with the same salt concentration.
- High shear rates seem to increase the freezing point.

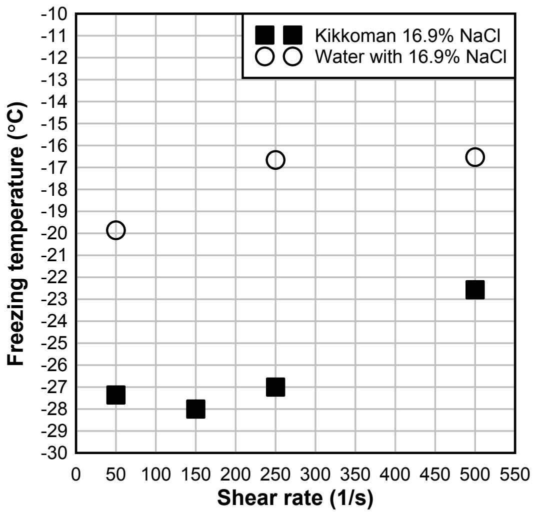

Figure 7. Freezing point versus shear rate for Kikkoman and distilled water both with 16.9 g/100 ml NaCl.

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