

# ELECTRICAL CONDUCTIVITY OF WHEY PROTEIN DEPOSIT Xanthan Gum Effect on Temperature Dependency

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Protein-polysaccharide mixtures are widely used in the food industry as they play an essential role in the structure, texture and stability of many foodstuffs. The electrical conductivity is a key parameter in ohmic heating technology. The temperature dependence of the electrical conductivity of two fouling model fluids was studied at neutral pH, between 10°C and 100°C. The differences observed in the thermograms were attributed to the interaction between protein and xanthan gum molecules. The electrical conductivity of the deposit generated by ohmic heating of these model fluids was measured between 10°C and 120 °C. The marked differences between the conductivity of each deposit and the fluids could be related to observable differences in microstructure.

*Keywords:* electrical conductivity;  $\beta$ -lactoglobulin-xanthan gum interaction; ohmic heating technology; fouling.

## INTRODUCTION

The food industry and the dairy industry in particular are faced with a serious problem caused by the fouling of equipment during processing. The development of new technologies for continuous thermal food treatment is still of great industrial and scientific interest. Ohmic heating is a new technology where an electric current is passed directly through the product. Electrical conductivity is therefore a key parameter in this technology. Electrical conductivity is an intrinsic characteristic of all materials and depends on properties such as their composition, soluble salt fraction, electrolyte mobility and temperature (Benoit and Deransart, 1976; De Alwis and Fryer, 1992). Usually, electrical conductivity measurements are used to detect compositional variation and structural change in food products (Tsouli *et al.*, 1976; St-Gelais *et al.*, 1995; Zhuang *et al.*, 1997; Guerin *et al.*, 2004). Interest in the measurement of electrical conductivity has mainly focused on solid food particles (Mitchell and de Alwis, 1989; Halden *et al.*, 1990; Palaniappan and Sastry, 1991a). For liquids products, it has been demonstrated by several authors (Göft *et al.*, 1994; Palaniappan and Sastry, 1991b; Fryer and Li, 1993) that the electrical conductivity-temperature relationship is linear within a temperature

range of 20-100°C. The ohmic heating of liquid foods has not been studied in as much detail as that of solids and only a few reports have been published on the ohmic heating of non-fouling liquid foods (Ould Elmoktar, 1992; El Hajal, 1997; Marcotte, 1999). Recently Ayadi *et al.* (2004) have shown that continuous ohmic heating of whey protein solutions generates some deposit layers on the electrode surfaces. This deposit acts as an additional electrical resistance and over time it receives more and more electrical energy, causing its temperature to increase and consequently its electrical conductivity. The determination of the electrical conductivity-temperature relationship is very useful in understanding the link between thermo-electrical phenomena and the deposit layers.

In this paper, attention is drawn to the temperature-dependency of the electrical conductivity of two fouling model fluids formulated with  $\beta$ -lactoglobulin and their deposits, which are generated when they are ohmically heated.

## MATERIALS AND METHODS

### Model Fluids

Xanthan gum (Degussa E415, Texturant Systems; France) and whey protein powder (Protarmor 750; Armor protéines, France) were used to formulate the fouling model fluids.

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Two fouling model fluids were formulated: (i) an aqueous solution of native whey proteins (1 wt% of protein powder) and (ii) an aqueous mixed solution of native whey protein (1 wt%) and xanthan gum (0.2 wt%). The choice of these model fluids was based on the fact that the heat denaturation of  $\beta$ -lactoglobulin protein governs milk deposit formation when the temperature exceeds 75°C (Lalande *et al.*, 1985). The xanthan gum, a dairy product thickener, was added to modify the viscosity of the model fluid.

The model fluids were prepared with great care to ensure that their physical properties remained constant for all the tests. To prevent any change to the physical property, model fluids were prepared and stored at 4°C for 12 h before fouling experiments. Their density, specific heat and thermal conductivity were very close to those of water at  $7 < \text{pH} < 7.2$ . The protein-xanthan mixture fluid exhibited shear-thinning behaviour characterized by consistency  $k$  and flow index  $n$  given by:

$$n = 0.0023\theta + 0.234 \quad (1)$$

$$k = 6.78\theta^{-0.663} \quad (2)$$

where  $\theta$  is the temperature in Centigrade and  $k$  is in SI units as dictated by  $n$ . These parameters were obtained from regression of data collected over a temperature range of 20–80°C and shear rates from 0.4 to 700 s<sup>-1</sup>.

### Fouling Experiments

The experimental pilot-plant used to generate fouling in the ohmic cells is shown in Figure 1. Firstly, the fluid was preheated from 4 to 75°C using a conventional plate heat exchanger, then heated from 75°C to 100°C in the ohmic

heater (fouling generation) and finally the model fluid was cooled via a tubular heat exchanger. The ohmic heater was made up of five ohmic cells, three of them ensuring heating and the two side cells ensuring electric insulation and the recovery of leakage currents. Each cell can be compared to a rectangular channel (length = 240 mm, width = 75 mm and thickness = 15 mm), the electrodes constituting side surfaces. Several fouling experiments were carried out in order to monitor fouling in the ohmic cells for varying durations (3, 4 and 6 h).

After each fouling test, the ohmic cells were dismantled and a sample of wetted deposit was scraped off, in order to measure its electrical conductivity.

### HPLC Analysis

The native  $\beta$ -lactoglobulin concentration in fouling model fluids, before heat treatment, was measured by HPLC system (Kontron, Zurich, Switzerland). The temperature of the column was maintained at 30°C by a HPLC column thermostat (John Chromatography, model 7971, France). The separations were performed on a reversed-phase analytical column C<sub>4</sub> (250 × 4.6 mm), with 300 Å pore diameter and 5 µm particle size (Allteck, France).

An aqueous solution of ultra-pure  $\beta$ -lactoglobulin was prepared at concentrations of 1, 2.5, 5, 7.5 and 10 g l<sup>-1</sup> using milliQ water and a freeze-dried and crystallized lactoglobulin containing the two genetic variants A and B (Sigma-France). The fouling model fluid samples were reduced and injected into the column by an automatic injector (Schenkon, Switzerland). HPLC analyses were carried out three times for each sample.

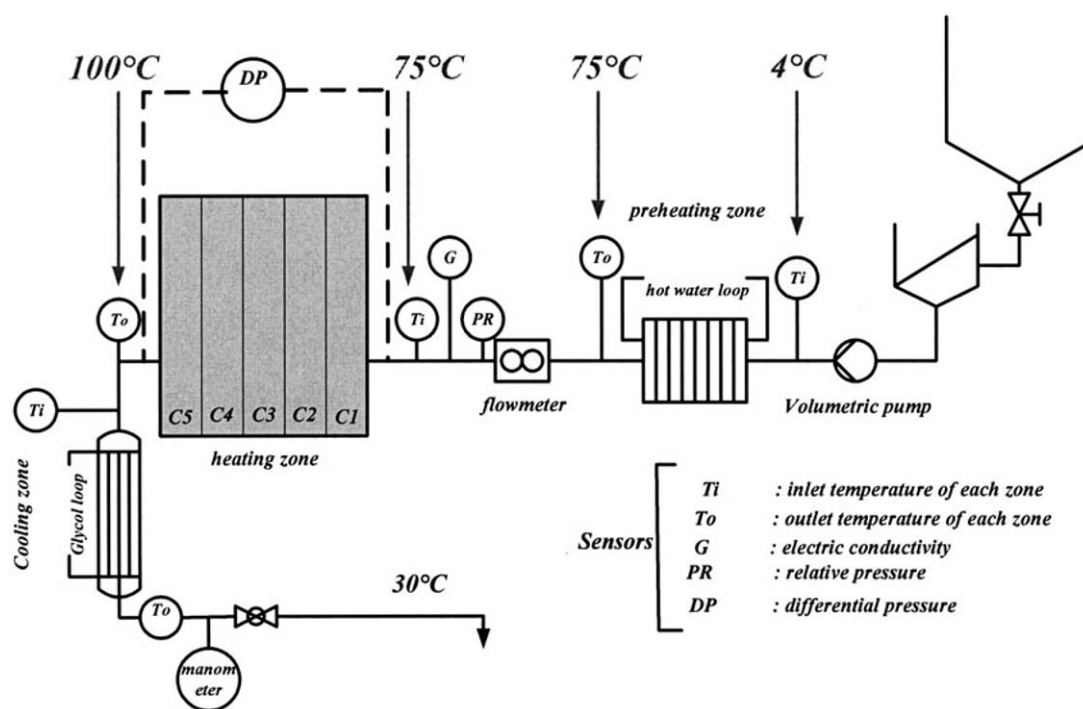


Figure 1. Fouling deposit generation in the ohmic cells: pilot plant test rig.

### Microscopy Analysis

Dry samples of the deposit were broken with a razor blade to reveal their internal structure. The sample was coated with about 40 nm of gold–palladium by cathodic spreading in a Polaron E5100 coater. Sample observations and photomicrography were performed on a Hitachi S-3000N scanning electron microscope (SEM), operating at low voltage in order to give good resolution of the delicate structures and avoid charging phenomena.

### Electrical Conductivity Measurement

The temperature dependence of each fluid's electrical conductivity was measured online within a temperature range of 10–100°C. An industrial sensor was used for measuring conductivity. This sensor was composed of a four-pole cell measurement, integrated Pt 100 platinum resistance probes to measure temperature at the measurement point (Kemotron, S/N 28160; Germany) and an automatic compensation system for temperature (Knick, Stratos 2401 Cond). The electrical conductivity sensor was calibrated over the range 0–10 mS cm<sup>-1</sup> using standard solutions.

The deposits' electrical conductivity–temperature relationship was determined using the direct current method over the temperature range 10–120°C (Figure 2). The voltage was applied to the sample placed between two platinum electrodes. Two sensors were used to measure the applied voltage and the resulting current intensity. A J-type thermocouple, placed through the sample, was used to measure the temperature of the sample (the thermocouple was coated in Teflon to avoid Joule heating). The values of deposit electrical conductivity  $\sigma$  were calculated using the following equation:

$$\sigma = \frac{d}{A} \cdot \frac{I}{U} \quad (3)$$

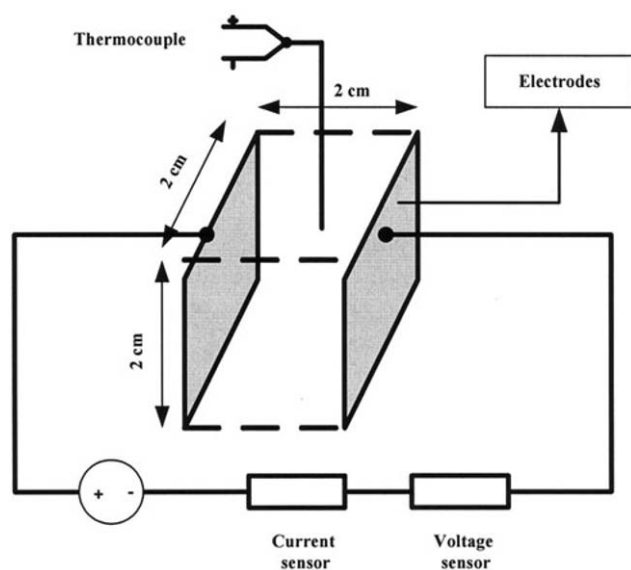


Figure 2. Experimental configuration for measurement of deposit electrical conductivity.

where  $A$  is the cross-section area of the measured surface,  $d$  is the thickness of the deposit sample in the direction of measurement,  $U$  is the voltage applied and  $I$  is the measured current intensity.

In order to avoid any structural changes in the deposit at higher temperatures (e.g. drying), the measurement of the deposit's electrical conductivity was carried out as follows:

- the conductivity measurement system was placed in an incubator under a water-saturated atmosphere (to prevent drying phenomena at high temperature);
- the incubator temperature was adjusted to the required value;
- when the required temperature was reached, the voltage was applied to the sample and instantaneous values of the current intensity were collected for the conductivity determination.

Conductivity measurements were carried out three times for each sample and the relative error was less than 5% in all cases.

## RESULTS AND DISCUSSION

### Temperature Dependency

#### Fouling model fluids

The temperature dependency of the electrical conductivity of the two fouling model fluids is shown in Figure 3. A linear effect of temperature was observed, which has been reported previously in the literature for several liquid foods. For temperatures over 35°C, the electrical conductivity of the aqueous protein–xanthan mixture was higher than that of the protein solution. This electrical conductivity behaviour could be explained by the presence of interaction between xanthan gum and  $\beta$ -lactoglobulin molecules (Laneuville *et al.*, 2000; Bryant and McClements, 2000; Hemar *et al.*, 2001). Figure 4 confirms this fact fairly well. Indeed, the chromatograms obtained from the two fouling model fluid samples, before heat treatment, are very different. The quantity of free native  $\beta$ -lactoglobulin

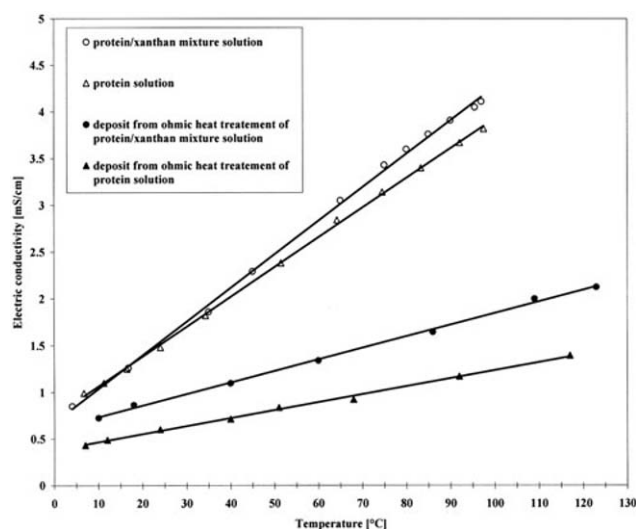


Figure 3. Fluid electrical conductivity versus temperature. Solid line shows regressed linear model.

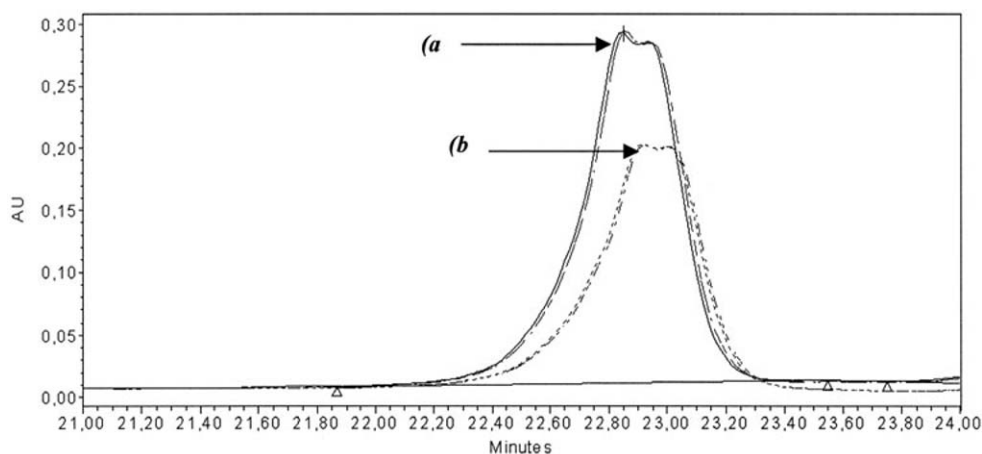


Figure 4. Zoom and superposition of native  $\beta$ -lactoglobulin peaks: (a)  $\beta$ -lactoglobulin solution; (b)  $\beta$ -lactoglobulin-xanthan gum mixture.

in the protein-xanthan mixture ( $3.784 \pm 0.05 \text{ g l}^{-1}$ ) is less than that in the protein solution ( $7.690 \pm 0.05 \text{ g l}^{-1}$ ). The presence of such a protein-xanthan complex does not significantly change the electrical conductivity of the aqueous mixture in the lower temperature region ( $5\text{--}35^\circ\text{C}$ ), but as the temperature increases from  $35$  to  $100^\circ\text{C}$  the electric conductivity of the aqueous protein-xanthan mixture becomes larger. Samant *et al.* (1993) and Shu *et al.* (1996) reported that the factors affecting the protein-polysaccharide complex characteristics are the protein-to-polysaccharide ratio, pH, total solids content and especially temperature. Laneuville *et al.* (2000) reported that heat treatment of a protein-polysaccharide mixture could favour a second aggregation and lead to a gritty texture. Adding a polysaccharide can prevent excessive protein aggregation by minimizing protein-protein interactions, either by shielding actively charged groups or by lowering the collision rate between molecules. These changes to the complex structure and the protection of active charged groups could explain the difference between the evolution of the two fluids' electrical conductivity across the  $35\text{--}100^\circ\text{C}$  temperature range.

#### Deposits

Figure 3 shows the electrical conductivity of the deposits generated by the ohmic heating of each fouling model fluid.

As with the model fluids, a linear effect of temperature on the deposits' electrical conductivity was observed. However, the electrical conductivity values of the deposits were markedly lower than those of the fluids. This low deposit electrical conductivity has a practical significance for the linking of fouling layers and thermo-electric phenomena during the fouling build-up. Indeed, when electricity is applied to a series of materials (electrode-deposit-fluid-deposit-electrode), the Joule effect is strongest in the material which has the highest conductivity (fluid).

Whereas the fluid conductivities were quite similar, there is a significant difference between the deposits' values. The microstructure of the deposit layers, as determined by scanning electron microscopy (Figure 5), reveals that the deposit generated by heating the protein solution is less fibrous than that generated by heating the protein-xanthan solution. This observation is in agreement with the observations of Laneuville *et al.* (2000), who reported that during protein-xanthan gum complexation the globular protein bonds along the xanthan molecule backbone produce fibrous complexes. The structural difference between the two deposit layers could explain the difference between the evolution and the values of the electrical conductivity. Generally, when a protein solution is heated, protein molecules partially unfold and then aggregate to form a three-dimensional network that entraps water through capillary forces (Mulvihill and Kinsella, 1987). The

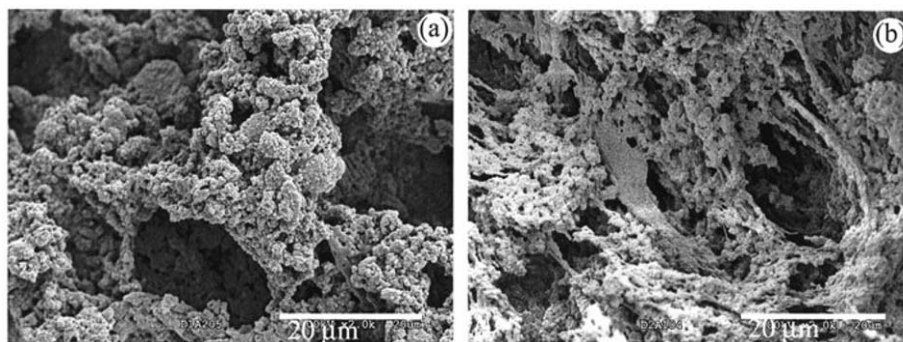


Figure 5. SEM observations of deposit generated by ohmic heating of: (a) protein solution; (b) protein-xanthan mixture solution.



Table 1. Parameters of the linear electrical conductivity models [equation (4)].

Sample	$\sigma$ at 25°C (S m <sup>-1</sup> )	$\alpha$ (S m <sup>-1</sup> c <sup>-1</sup> )	$r^2$
$\beta$ -Lactoglobulin solution (1 wt%)	0.155	0.0032	0.998
$\beta$ -Lactoglobulin-xanthan mixture solution (1 wt% protein + 0.2 wt% xanthan gum)	0.1562	0.0036	0.996
Deposit from ohmic heating of $\beta$ -lactoglobulin solution (1 wt%)	0.058	0.0009	0.993
Deposit from ohmic heating of $\beta$ -lactoglobulin-xanthan mixture (1 wt% protein + 0.2 wt% xanthan gum)	0.0898	0.0013	0.997

presence of xanthan gum reinforces this three-dimensional structure and makes it more porous and more water will be entrapped by capillary action and consequently a higher electrical conductivity is observed.

### Temperature-Electrical Conductivity Relationships

The electrical conductivity of the model fluids and their deposits were empirically modelled as a linear function of temperature, using the value at 25°C as a reference conductivity ( $\sigma_{25}$ ):

$$\sigma_T = \sigma_{25} + \alpha \cdot (\theta - 25) \quad (4)$$

where  $\theta$  is the temperature in °C and  $\sigma_{25}$  is in S m<sup>-1</sup> and  $\alpha$  is in S m<sup>-1</sup> c<sup>-1</sup>. Several authors have empirically modelled the electrical conductivity of liquid and solid foods (Wang and Sastry, 1997; Fryer and Li, 1993; Palaniappan and Sastry, 1991a,b; Marcotte, 1999). Table 1 summarizes the results of the regression analyses ( $r^2$  is the coefficient of determination).

The values for the aqueous  $\beta$ -lactoglobulin-xanthan mixture regression compared well with those reported for hydrocolloid solutions by Marcotte (1997). The electrical conductivity of the whey protein deposit compared well with those reported for solid foods (Wang and Sastry, 1997).

### CONCLUDING REMARKS

This study reports the effect of temperature on the electrical conductivity of two fouling model fluids formulated with  $\beta$ -lactoglobulin. Continuous ohmic heating of these fouling fluids generates deposit on the electrode surfaces. The temperature dependency of the deposits' electrical conductivity was measured successfully. The role of the xanthan gum in the temperature-electrical conductivity relationship has been highlighted, both for the fluid and for the deposit. Empirical relations for electrical conductivity as a function of temperature have been obtained which will be useful for quantifying and modelling the evolution of the deposit layers when processing a liquid more prone to fouling using continuous ohmic heating.

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