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Article *in* Journal of Food Engineering · December 2003

DOI: 10.1016/S0260-8774(03)00054-2

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ELSEVIER

Journal of Food Engineering 60 (2003) 321–325

JOURNAL OF FOOD ENGINEERING

www.elsevier.com/locate/jfoodeng

Effect of composition on the electrical conductance of milk

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Received 2 October 2002; accepted 5 February 2003

Abstract

The contribution of the various components in cow's milk to its electrical conductivity has been studied using the technique of admittance spectroscopy. Measurements at 100 kHz and 8 °C confirm previous observations that the milk conductance is predominantly determined by the salt fraction. Lactose showed very little effect on the conductivity, while the presence of fat resulted in a decrease in the milk conductance with increasing fat content. Sodium caseinate possessed a very low conductance; nevertheless, we suggest that the physical and chemical nature of the casein micelles can influence the overall milk conductivity.

Keywords: Milk; Electrical conductance; Fat globules; Casein

1. Introduction

Electrical conductivity measurements have been used extensively in the food industry; for example to detect contaminates in water, and to monitor microbial growth and metabolic activity (Carcia-Golding, Giallorenzo, Moreno, & Chang, 1995; Curda & Plockova, 1995). The conductivity of milk and dairy products has been studied for more than 40 years to provide values of the fat, water and protein content (Felice, Madrid, Olivera, Rotger, & Valentinuzzi, 1999; Lawton & Pethig, 1993; Mabrook & Petty, 2002; Prentice, 1962) and to detect mastitis (Nielen, Deluyker, Schukken, & Brand, 1992). Milk has conductive properties because of the existence of charged compounds such as salts (Fox & McSweeney, 1998). The distribution of salt fractions between the soluble and colloidal phases has an important effect on the overall milk conductivity. Many factors can affect the conductivity, such as stage of lactation, season of the year and feed. The purpose of this study was to investigate the contribution of the various components of milk to its electrical conductivity by monitoring the admittance over a wide frequency range. It was hoped this simple measurement method would provide some insight into the physical and chemical processes responsible for the electrical behaviour.

2. Electrical admittance

The electrical conduction properties of a material represent its capability to support an electric current. Electrical conductivity, σ, measured in units of Siemen per metre ($S\,m^{-1}$), is a characteristic of all materials, and ranges from about 10^7 $S\,m^{-1}$ for highly conductive materials like metals to approximately 10^{-18} $S\,m^{-1}$ for a good insulator such as quartz. The conductivity of aqueous solutions lies between these two extremes.

Electrical conductance, G, the reciprocal of resistance, has units of Siemens and is related to σ via the specimen dimensions. The conductance of an electrolyte can be measured simply by immersing two electrodes into the solution and applying a voltage. A current will be produced in the external circuit that connects the two electrodes. However, measurements using dc voltages may lead to electrolysis and polarisation of the electrodes, reducing the current passing through the circuit to zero over time. The use of an alternating current circumvents this difficulty. Generally an ac voltage is applied to the sample and both the in-phase current (related to the conductance) and the out-of-phase current (related to the capacitance C) are monitored over a range of frequencies using an impedance analyser. The experiment is referred to as admittance (or impedance) spectroscopy.

Measured conductance G_m and susceptance B_m ($= \omega C_m$ where ω is the angular frequency) values of a salt solution can show the effect of electrode polarisation, as revealed in Fig. 1(a) for 1000 $mg\,l^{-1}$ NaCl. The

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doi:10.1016/S0260-8774(03)00054-2

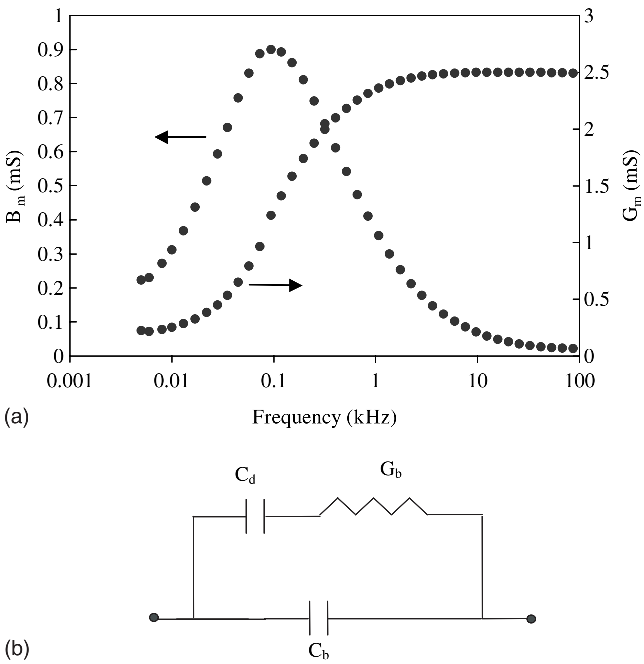

Fig. 1. (a) The frequency dependence of the measured conductance G_m and susceptance B_m of 1000 mg l^{-1} of NaCl at 8 °C. (b) Equivalent circuit for a two-electrode conductivity network.

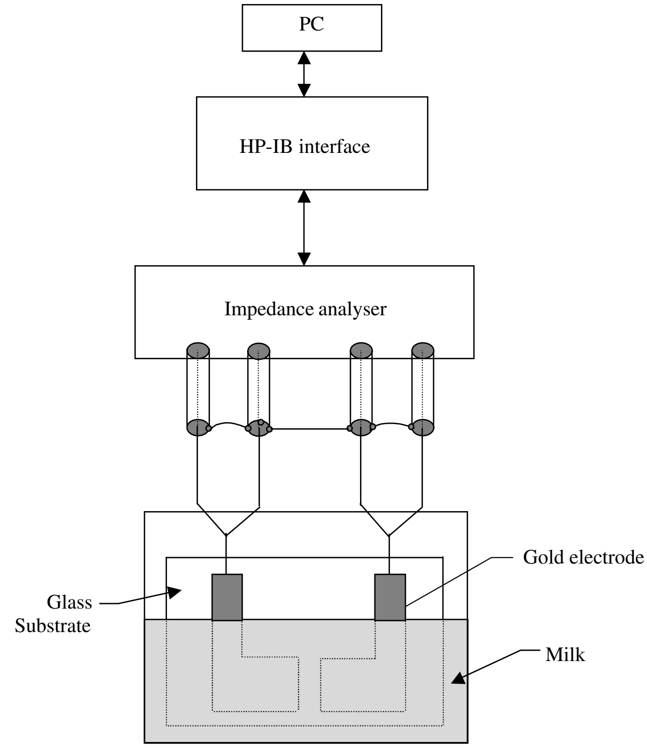

Fig. 2. Schematic diagram of the impedance analyser system.

low frequency region (<1 kHz) represents the electrical characteristic of the interface between the electrodes and the solution, while the high frequency region provides information about the bulk solution. The frequency at which the susceptance reaches a maximum represents the relaxation frequency of the electrode polarisation (Lawton & Pethig, 1993).

The measured conductance and susceptance values do not necessarily directly represent the particular physical components making up the electrode/solution/electrode system (solution conductance, interface capacitance etc.). The electrical admittance between two electrodes immersed in an electrolyte can be modelled using series and parallel combinations of capacitors and resistors as shown in Fig. 1(b) (Mabrook & Petty, 2002). The capacitance C_d represents the double layer capacitance of the electrode/electrolyte interface, while the conductance G_b represents the bulk electrolyte conductance. In parallel with G_b is a capacitor C_b associated with the geometrical capacitance of the two electrodes separated by the measured electrolyte. The values of G_b, C_d and C_b can be related to G_m and B_m using simple circuit theory. For example, as already noted above, at high frequencies, where C_d is effectively a short circuit, $G_m = G_b$.

3. Experimental details

The measurement devices consisted of two gold electrodes (L shaped) 15 mm × 6 mm with a separation of 1 mm. The electrodes (thickness approximately 100 nm) were deposited by thermal evaporation under high vacuum conditions (10^{-6} mbar) onto clean glass microscope slides. Complex admittance measurements, in the frequency range of 5 Hz to 13 MHz, were performed using a HP 4192A impedance analyser. A schematic diagram of the measurement system is shown in Fig. 2. A four terminal configuration was used to connect the device electrodes to the impedance analyser. Calibration measurements on the leads connecting the device to the impedance analyser were also made to take into account the effect of any parasitic elements in the measurement system. Values of the conductance and capacitance of the leads were automatically eliminated from those values measured with the device connected. The r.m.s. amplitude of the ac voltage was 700 mV; no significant changes in the sensing properties of the device were observed at lower voltages.

The conductivity of milk as a function of fat and lactose content was determined using full fat, skimmed, semi-skimmed and lactose-reduced (0% lactose) samples of cow's milk, obtained from the same local supermarket. Untreated cow's milk (raw milk) was obtained from a local farm and supplied on daily basis. The fat content in the full fat milk, lactose reduced milk and untreated milk were given as 3.6%, while the fat content in semi-skimmed and skimmed milk were 1.6% and 0.1%, respectively. Conductivity measurements were also undertaken using solutions containing some of the individual constituents of milk. For this study, separate solutions of concentration 1000 mg l^{-1} of NaCl, KCl, MgCl (Fisher Chemicals) were prepared using ultra-pure water obtained by reverse osmosis, deionisation and UV sterilisation. Sodium caseinate was provided by Guinness UDV and was dissolved in ultra pure water to provide a solution of concentration 3.5% (w/v).

Samples of 25 ml were introduced into the measurement system, which was then placed in a refrigerator to keep the temperature between 2 and 8 °C, measured by a Fluke 2170A digital thermometer. Careful control was very important as the conductivity of milk was found to change significantly with temperature. Before each experiment, the sensor was washed in a diluted detergent, rinsed with ultra pure water for at least 5 min and finally dried by exposure to a flow of dry nitrogen gas. Experiments repeated with 'identical' samples revealed an experimental error in the conductance measurements of ±0.03 mS.

4. Results and discussion

The admittance measurements were obtained from the instrumentation in the form of a capacitance C_m in parallel with a conductance G_m. The electrical conductance of the milk samples, measured at 100 kHz, showed a linear increase with increasing sample temperature at a rate of approximately 5% per degree Celsius (Mabrook & Petty, 2002). This change in conductance for a single degree temperature rise was similar to the difference between the conductance of full fat milk and skimmed milk (5–10% depending on the percentage of fat), emphasising the need for accurate temperature control. The measured conductance and susceptance versus frequency for full fat milk at 8 °C are shown in Fig. 3 (open data points). These data are qualitatively similar to those shown in Fig. 1(a) for the salt solution. The conductance exhibits a rapid variation with frequency below 10 kHz, but remains constant above this value. From Fig. 3 it can be seen that gold electrodes exhibit polarisation at around 250 Hz. The high frequency saturation value of G_m was found to decrease approximately linearly as the concentration of water in the milk increased (Mabrook & Petty, 2002). These results indicate that the high frequency saturation value is a property of the bulk milk solution and not related to the electrodes. The low frequency region represents the properties of the interface between the electrodes and the milk. The geometrical capacitance C_b can be obtained from the value of the measured susceptance B_m at high frequencies, i.e. $C_b = 20$ pF, while the value of G_b was identical to the saturation value of conductance of full fat milk in Fig. 3.

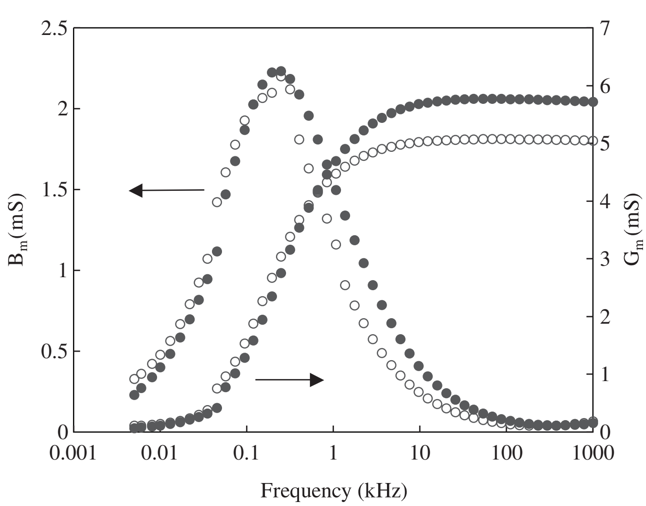

Fig. 3. The frequency dependence of the measured conductance G_m and susceptance B_m of fresh full fat milk (○) and after leaving for 48 h at room temperature (●). Measurements all performed at 8 °C.

It should be noted however that the circuit shown in Fig. 1(b) provides only an approximate electrical equivalent network. In previous work, we have shown that the double layer capacitance C_d, which describes the capacitance of the diffuse layer of charge at an electrode/electrolyte interface, cannot be modelled accurately as an ideal capacitor (Howarth & Petty, 1996). Instead C_d should be treated as a frequency dependent 'universal' capacitor (Jonscher, 1983). This results from the power-law frequency response (universal response) of dielectric relaxation found in a wide range of materials.

Milk is a complex mixture of water, lactose, fat, protein (mostly casein), minerals and vitamins distributed throughout colloidal and soluble phases. The composition of typical fresh full fat cow's milk is shown in Table 1 (Fox & McSweeney, 1998). To understand better the electrical properties of milk conductance, it is important to determine the conductance of each individual component. We therefore undertook a series of conductance measurements using solutions with solid concentrations similar to those listed in Table 1. The results can be summarised in Table 2; the conductance of each component was measured at 100 kHz and 8 °C. It is evident that the conductance of milk is mainly determined by the charged compounds, like the mineral salts. There is a very little contribution from the lactose as the conductance values of full fat milk and full fat

Table 1
Composition of a typical full fat cow's milk (Fox & McSweeney, 1998)

Component	Content
Fat	3.4–5.1% [w/v]
Protein	3.3–3.9% [w/v]
Lactose	4.9–5.1% [w/v]
Water	86–88%
Sodium	350–900 mg l^{-1}
Potassium	1100–1700 mg l^{-1}
Chloride	900–1100 mg l^{-1}
Magnesium	90–140 mg l^{-1}

Table 2
Conductance (at 100 kHz) of milk and its components

Sample	Fat content [wt.%]	Lactose content [wt.%]	Conductance [mS]
Full fat milk	3.6	4.9	5.05 ± 0.03
Semi-skimmed milk	1.6	4.9	5.23 ± 0.03
Skimmed milk	0.1	4.9	5.4 ± 0.03
Untreated milk	3.6	Unknown	4.85 ± 0.03
Lactose reduced milk	3.6	0	5 ± 0.03
NaCl (1000 mg l^{-1})			2.5 ± 0.03
KCl (1000 mg l^{-1})			2.26 ± 0.03
MgCl (1000 mg l^{-1})			1.8 ± 0.03
Sodium caseinate (3.5% w/v)			0.1 ± 0.03
Ultra pure water			<0.001

Temperature = 8 °C. The fat and lactose content of the milk samples (manufacturer's data) are also provided.

milk with reduced lactose content are identical within experimental error.

The salts in milk consist mainly of chlorides, phosphates, citrates, carbonates and bicarbonates of potassium, sodium, calcium, and magnesium. Although the salt content of milk remains constant at about 0.7% w/v, the relative concentrations of the various ions can vary and are influenced by factors such as animal breed, season of the year, feed, and stage of lactation (Fox & McSweeney, 1998). These factors also affect the distribution of calcium, magnesium, and phosphate between soluble and colloidal phases and thus the number of free conducting ions in the milk.

Although casein, the main milk protein, shows a very low conductance compared to the milk salts, Table 2, it can still influence the milk conductivity. Most, but not all, of the casein proteins exist in the colloidal phase. The insoluble salts in milk, especially calcium phosphate, are mainly associated with the casein micelles in this phase. A small percentage of the sodium and potassium ions are linked to the casein as counter-ions to the negatively charged organic phosphate groups of the protein (Fox & McSweeney, 1998). These salts act like bridges between the subunits of the casein micelles and keep the milk in a stable condition. Under certain conditions, these salts can be released into solution thereby increasing the conductivity. An example is provided in Fig. 3 (full data points) where the conductance of full fat milk increases by approximately 15% when the milk is left at room temperature for 48 h. It should be noted that the change in conductance between full fat and skimmed milk is only 5–10% (Table 2). This suggests that the conductivity increase observed as the milk 'goes-off' is not due solely to the deformation of the fat globules. Over time, the links between the subunits in the casein micelles break down and release free ions, mainly calcium; consequently the milk conductance increases.

The changes described above evidently do not have any effect on the characteristics of the interface between the electrodes and the milk solutions as the relaxation frequency of the electrode polarisation remain unchanged, Fig. 3. Furthermore, it was also found that the conductance of milk increased with acidification. In an experiment, freshly squeezed lemon juice was added slowly to full fat milk while both the conductance and pH were monitored. The conductance increased, reaching a saturation value of 5.8 mS at a pH of 4.9–5.0. This conductance figure is similar to that of milk when it has 'gone off' and indicates that, at this point, all the colloidal salts connected to the casein micelles are in a soluble phase and free to contribute to the measured conductance. The addition of acid decreases the pH of the milk and results in gradual solubilisation of the colloidal salts connected to the casein micelles. When the pH of milk reaches a value of about 5.0, all the colloidal calcium and phosphorus are in the soluble phase and the conductance saturates.

Another factor that has an influence on the electrical conductance of milk is the presence of fat (Lawton & Pethig, 1993; Prentice, 1962). The conductance of milk decreases as the percentage of fat increases, as evidenced by the comparison between conductance of full fat milk, semi-skimmed milk, and skimmed milk in Table 2. Our (limited) data are in good agreement with the empirical relationship given by Lawton and Pethig (1993) for volume fractions of fat v up to 0.07

$$G = G_S(1 - v)^n \qquad (1)$$

where G is the electrical conductance of the milk, G_S is the electrical conductance of the fat-free (skimmed) milk, and $n \approx 1.7$. Taking $G_S = 5.4$ mS (Table 2), Eq. (1) predicts that the conductance of semi-skimmed milk (1.6% fat) is 5.25 mS while that for full fat milk (3.6% fat) is 5.07 mS. These compare with experimental data (Table 1) of 5.23 and 5.05 mS, respectively. The reason for this decrease in conductance with increasing fat content is that more than 97% of the total milk fat is in the form of large globules covered by a thin nonconductive membrane. These globules hinder the conductance by occupying volume of the conducting medium and impeding the mobility of the conducting ions. Furthermore, most of these globules vary in diameter from 2 to 10 μm, depend on the breed and the season of the year, changing the conductance of the milk accordingly. The higher

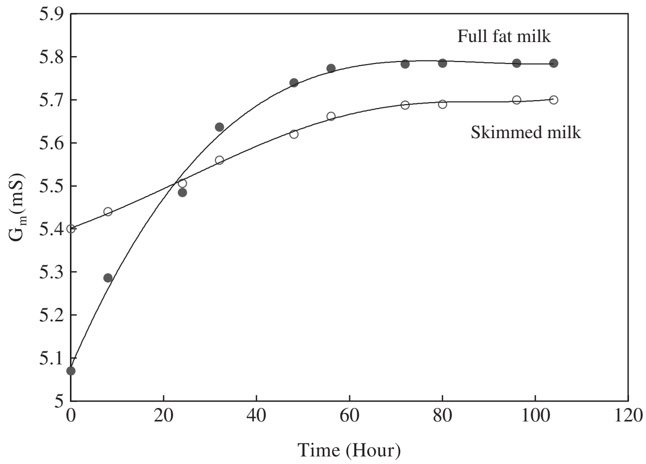

Fig. 4. The variation of the conductance G_m as a function of the time for full fat milk and skimmed milk at 8 °C.

conductance of fresh full fat milk compared to the conductance of untreated milk, with the same fat content, Table 2, is attributed to a reduction in the size of the fat globules, less than 2 μm in diameter, during milk processing (pasteurisation and homogenisation) (Yamada, Mizota, Toko, & Doi, 1997).

Leaving milk at room temperature shows an increase in its conductance for the first 48 h followed by saturation, as shown in Fig. 4. Full fat milk shows a more rapid increase in conductance over the first 24 h and higher saturation value compared to the skimmed milk. This behaviour can be attributed to the clumping of fat globules resulting from the disruption of the thin fat globule membrane, releasing free fatty acids. Approximately 50% of the phospholipids occur in the globule membrane and are released into the milk solution producing free phosphate ions (Swaisgood, 1985). At the same time, the acidity of the milk starts to increase releasing calcium ions to contribute to the conductivity. For the skimmed milk, the effect of the fat globules is very limited as the percentage of fat is less than 0.1%. Therefore, the conductance of skimmed milk shows smaller increase than the conductance of full fat milk.

In summary, ionic conduction due to the presence of Na^+, K^+, and Cl^- is responsible for most of the electrical conductance of milk. However, the variation in of the fat globule size and the structure of the casein, which control the solubilisation of the colloidal salts, also contribute to the overall conductivity.

5. Conclusions

The electrical conductance of milk and milk components has been studied using admittance spectroscopy. Measurements over the frequency range 5 Hz–1 MHz show that the electrode polarisation effect can be avoided by performing the measurements at high frequencies. The conductance of the milk is attributed mainly to its salt content. The variation of the conductance over time was attributed to the breaking of chemical bonds between the casein micelles and the colloidal salts. When the full fat milk 'goes off', the conductance increased by approximately 15%. Fresh full fat milk possessed a higher conductance than untreated milk because of the reduction in size of the milk fat globules. These results could prove useful in the development of sensors for the quality control of milk.

Acknowledgements

This work was supported by the European community under Measurement and Testing Programme of the Research Directorate-General with the contract no. G6RD-CT-2000-00420. We would like to thank the Community College Dairy Unit in Durham for supplying the raw milk and Guinness UDV for supplying the sodium caseinate.

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